CHEMISTRY OF WATER TREATMENT

2ND EDITION

SAMUEL D. FAUST
OSMAN M. ALY

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CRC Press
Taylor & Francis Group
Boca Raton London New York

CRC Press is an imprint of the
Taylor & Francis Group, an informa business

CRC Press
Taylor & Francis Group
6000 Broken Sound Parkway NW, Suite 300
Boca Raton, FL 33487-2742

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CRC Press is an imprint of Taylor & Francis Group

Transferred to Digital Printing 2010

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International Standard Book Number-13: 978-1-57504-011-0 (Hardcover)

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Library of Congress Cataloging-in-Publication Data

Faust, Samuel Denton, 1929-1997
Chemistry of water treatment / Samuel D. Faust, Osman M. Aly.—2nd ed.
p. cm.
Includes bibliographical references and index.
ISBN 1-57504-011-5 (alk. paper)
1. Water—Purification. 2. Water quality. I. Aly, Osman M. II. Title.
TD433.F38 1998
628.1'66—dc20 96-13773

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Publisher's Note
The publisher has gone to great lengths to ensure the quality of this reprint but points out that some imperfections in the original may be apparent.

In memory of Dr. Samuel D. Faust

It is with great sorrow, and pride, that this project is brought to fruition. Dr. Samuel D. Faust, who passed away on February 7, 1997, gave a vote of confidence when he decided that the second edition of *Chemistry of Water Treatment* would be published by our company. His book, written with co-author Dr. Osman Aly, became an important addition to our company.

I regret that Sam never saw the printed book. I have tried to publish it in a manner becoming of his dedication to the manuscript, and his commitment to the field.

Robert (Skip) A. DeWall, Jr.

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ACKNOWLEDGMENTS

Once again, the authors wish to acknowledge the patience of our families who were neglected during the long hours of preparation. We are indebted also to Mrs. Brenda Ciallello whose superb mastery of word processors produced the typed manuscript. We are grateful to our professional colleagues whose works are cited in this text. The authors are appreciative of the vision of Mr. Robert A. "Skip" DeWall, Jr.; we thank the publishers for their excellent efforts and cooperation in the production of this second edition.

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DEDICATION

The senior author dedicates this text to the hundreds of undergraduates and graduate environmental science students with whom he has been associated at Cook College, Rutgers, The State University of New Jersey for over forty years. Their dedication to their studies contributed to an academic career that was beyond gratification.

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Dr. Faust was Professor of Environmental Sciences at Rutgers University. He received his Ph.D. in Environmental Sciences and Chemistry from Rutgers University and was a Research Fellow in Applied Chemistry at Harvard University during the term 1966–67.

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PREFACE

The qualities of natural and treated water are areas of immense concern in our environment. One of the highest priority uses of water is, of course, its ingestion to sustain life. It is well established that water is a medium for transmission of enteric diseases and, in recent years, for transmission of alleged carcinogenic compounds. Consequently, we demand our water to be absolutely "safe" to drink, i.e., potable. On the other hand, the potability of water is not the only concern since water has other uses in the home and industry. As water is drawn from many ground and surface sources, it has diverse qualities which, in turn, dictate the types of treatment, the degree of treatment, and, to a large extent, the quality of the finished product.

In these days of widespread concern about environmental pollution, we are even more conscious of our drinking water quality. We expect it to be free form pathogenic organisms, free from scale-forming substances free from toxic chemicals, free from corrosion and corrosion products, and free from aesthetically offensive substances. Thus, we speak of the six freedoms of water quality. This book intends to serve as a reference for professionals and others concerned with water quality and treatment.

The chemical and, to a lesser extent, microbiological aspects of water quality and treatment are emphasized. It is an application of these two sciences to these two interrelated parts of our immediate environment. This volume does not and is not intended to discuss the design of water treatment, per se. Rather it is intended to demonstrate how chemistry influences the design of water treatment plant, or, mor appropriately, how it *should* influence the design. Historically, water treatment plants have been designed from hydraulic considerations with little regard to chemical aspects. The many chemical reactions used for removal of pollutants from water simply cannot be forced to occur within present designs. This traditional approach must be reexamined in view of today's water quality and treatment.

These three paragraphs appeared in the first edition of "Chemistry of Water Treatment" that was published in 1983. These comments are still valid in the 1990s as we approach the twenty first century. The Safe Drinking Water Act of 1986 and its subsequent amendments have had profound effects on the treatment of drinking water and its finished product. The six freedoms of water quality are still appropriate. In the future, more contaminants will be regulated and more treatments will be needed of which some will be physical and chemical in nature. Current water treatment processes are being challenged for their abilities to meet the current drinking water standards. Will they be sufficient to meet future demands or will new processes have to be devised? This second edition attempts to assess the chemical and physical efficacies of current processes to meet the demands of the Safe Drinking Water Act. Hopefully, this edition will provide the information to those persons responsible, whatever level of the involvement may be, for production of potable water in the 1990s. All chapters from the first edition have been revised significantly and a new chapter, Aeration Technology, has been added. Treatment processes of the future are discussed where appropriate.

Samuel D. Faust
Osman M. Aly

CONTENTS

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ACRONYMS

AA	activated alumina
ADI	accepted daily intake
ANPRM	Advanced Notice for Proposed Rule Making
ASTM	American Society for Testing and Materials
BAC	biological activated carbon
BAT	best available technology
BOM	background organic matter
BP	3,4-benzpyrene
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act
CRW	Colorado River water
CUR	carbon usage rate
DBP	disinfectants/disinfection by-product
DDW	distilled-deionized water
DE	diatomaceous earth
DOC	dissolved organic carbon
DOM	dissolved organic matter
DWEL	drinking water equivalent level
EBCT	empty bed contact time
EDB	ethylenedibromide
EEC	European Economic Community
EPA	Environmental Protection Agency
EPM	electrophoretic mobility
ES	effective size
ESWTR	enhanced surface water treatment rule
FA	fulvic acid
FIFRA	Federal Insecticide, Fungicide, and Rodenticide Act
FTN	flavor threshold number
GWSS	Ground Water Supply Survey
GAC	granular activated carbon
GS-MS	gas-liquid chromatography/mass spectrometry
HA	Health Advisory
HAAs	haloacetic acids
HC	hydrocarbon
HF	hollow fiber
HMW	high molecular weight
IARC	International Agency for Research on Cancer
ICR	Information Collection Rule
iep	isoelectric point
LHH	light halogenated hydrocarbons
LMM	linearized multistate dose-response model
LOAEL	lowest observed adverse effect level
MCL	maximum contaminant level
MCLGs	maximum contaminant level goals
MWDSC	Metropolitan Water District of Southern California
MF	membrane filter
mgad	million gallons per acre per day
MIB	2-methylisoborneol
MTF	multiple tube fermentation
NAS	National Academy of Sciences
NDWR	National Drinking Water Regulations
NOAEL	no observed adverse effect level

NORS	National Organics Reconnaissance Survey
NSF	National Sanitation Foundation
ntu	nephelometric turbidity units
ODW	Office of Drinking Water
OMB	Office of Management and Budget
PAC	powdered activated carbon
PAH	polynuclear aromatic hydrocarbons
PCBs	polychlorinated biphenyls
PD	pore diffusion
PGAC	pulverized granular activated carbon
PTA	packed tower aeration
PVMPI	poly-r-vinyl-N-methyl pyridonium iodide
PWS	public water system
RfD	reference dose
RSSCT	rapid small-scale column test
SCSRC	solids contact slurry recirculating clarifier
SDS	simulated distribution system
SDWA	Safe Drinking Water Act
SMCLs	secondary maximum contaminant levels
SOC	synthetic organic chemicals
SPW	[California] State Project water
SWTR	Surface Water Treatment Rule
TFP	trihalomethane formation potential
THM	trihalomethane
THMFP	trihalomethane formation potential
TOC	total organic carbon
TOX	total organic halide
TTHM	total trihalomethanes
UC	uniformity coefficient
UF	ultrafiltration
USPHS	United States Public Health Service
VOC	volatile organic chemical
WHO	World Health Organization

CHEMISTRY OF WATER TREATMENT

Second Edition

Chapter 1

Criteria and Standards for Drinking Water Quality

1

Criteria and Standards for Drinking Water Quality

HISTORY OF DRINKING WATER STANDARDS

Man's quest for pure water is neither a recent nor a modern development. A compilation of medical lore in Sanskrit (circa 2000 BC) reads: "Impure water should be purified by being boiled over a fire, or being heated in the sun, or by dipping a heated iron into it, or it may be purified by filtration through sand and coarse gravel and then allowed to cool."[1] This statement included the essentials of modern water treatment; namely, disinfection and sand filtration. It also implies that water is a vector for transmission of impurities and diseases. Hippocrates, the father of medicine (460–377 BC), expressed concern about water quality when he said that "water contributed much to health," and asserted that rainwater should be boiled and strained, for otherwise it would have a bad smell and cause hoarseness. Herodotus, an early Greek historian, reports that when warring, Cyrus the Great, King of Persia, took boiled water in silver flagons loaded on four-wheeled carts drawn by mules.[1] This too implies the ancients' concern for water quality, and suggests that the silver flagons were used for their disinfective property.

History also records some early epidemics of waterborne diseases; then, the infamous 1854 cholera outbreak in London, England, and later, typhoid epidemics in the United States reported at Butler, Plymouth, New Haven, Nanticoke, and Reading, that involved 39,029 cases with 361 deaths.[2] By the early 1900s, it was fairly obvious that drinking water contained physical, chemical, and biological impurities that impaired its quality. "Modern" water treatment probably started with the filtration of municipal supplies in Scotland in 1804 and in England in 1829 for the Chelsea Water Company of London.[3] By 1900, there were approximately 10 slow sand water filtration plants in the United States.[1] It was not until 1914 that any expression of water quality standards was noted, with the introduction of testing for *Bacterium coli* as an indicator organism.[4] There was, however, previous concern about the levels of contaminants in drinking water with the 1899 publication[5] of the precursor to the present version of *Standard Methods for the Examination of Water and Wastewater.* Quality criteria and standards initially were confined to drinking water. Recently, however, attempts have been made to apply these concepts to other uses of water such as its recreational and esthetic uses, its use as a medium for fish and other aquatic life, its agricultural uses, and its value as an industrial resource. These additional water quality criteria were reported first in 1968 in the so-called "Green Book" entitled *Water Quality Criteria.*[6]

EVOLUTION OF FEDERAL STANDARDS

In 1893, the U.S. Congress enacted the Interstate Quarantine Act, which authorized the United States Public Health Service (USPHS) Director[7] "to make and enforce such regulations as in his judgment are necessary to prevent the introduction, transmission, or spread of communicable disease from foreign countries into the states or possessions, or from one state or possession to any other state or possession."

This act provided the basis for interstate quarantine regulations in 1894. However, the first water-related regulation was not adopted until 1912, when use of the common drinking cup was prohibited on interstate carriers. This led later to a consideration of the quality of drinking water on interstate carriers.

Early Standards

1914

On October 14, 1914, the Department of the Treasury promulgated a basis for federal, state, and local monitoring of drinking water on interstate carriers. Two bacterial standards were established: (a) a total bacterial count on agar plate was not to exceed 100/mL; and (b) not more than one of five 10-mL portions shall show the presence of *B. coli.* The latter was less than 2.2/100 mL by the dilution technique. Thus, the concept of a maximum contaminant level (MCL) was born.

1925

In order to reflect those water treatment systems with excellent records of preventing waterborne diseases, the coliform standard was revised to: (a) not more than 10% of all 10-mL portions shall show the presence of *B. coli* (i.e., less than 1/100 mL) and (b) not more than 5% of all samples shall show the presence of *B. coli* in three or more of the five 10-mL portions. The latter did not specify the total number of samples, and the frequency of sampling within a given system (Table 1.1) was established also in 1925 with recommended and tolerance limits. It is interesting to note that the 0.3 mg/L standard for iron is still in effect in the 1900s!

1942

The USPHS established an advisory committee in 1941 to revise the 1925 standards. Deliberations of this group led to several significant revisions in the bacteriological and chemical standards. First, bacteriological samples were to be obtained from several locations within a distribution system, and the frequency of sampling was to be specified by the "certifying authority," i.e., a minimum number, dependent on population served, to be examined per month. The coliform count remained at 1/100 mL. Second, tolerance limits (MCL in the 1900s) were established for arsenic, fluoride, lead, and selenium (Table 1.1). The health hazards of metals were recognized, with the expressed omission of barium and hexavalent chromium from distribution systems. Third, recommended limits were established for chloride, copper, iron plus manganese, magnesium, phenols, sulfate, zinc and total solids. These limits should not be exceeded "when more suitable water supplies are available."

1946

Drinking water standards published in 1946 were essentially the same as the 1942 standards, with the exception that a tolerance limit was added for hexavalent chromium. Also, utilization of salts of barium, Cr^{+6}, heavy metal glucosides, and other substances were prohibited in water treatment processes. Later, use of the membrane filter procedure for the bacteriological examination of water samples was authorized by an amendment of the 1946 standards (*Federal Register,* March 1, 1957).

1962

An advisory committee was appointed in the early 1960s that included persons from the USPHS, Food and Drug Administration, U.S. Geological Survey, and 12 national transportation, technical, professional, and trade associations. The 1962 standards recommended maximum limiting concentrations for alkyl benzene sulfonates (synthetic detergents), barium, cadmium, carbon-chloroform extract (an approximate organic content), cyanide, nitrate, and silver. Radioactivity standards were added (Table 1.1). The 1962 standards were very important precursors for the interim drinking water standards of the 1974 Safe Drinking Water Act (SDWA) (Public Law 93-523).

Safe Drinking Water Act

This act regulating drinking water quality was established in a three-step process. First, the U.S. Environmental Protection Agency (EPA) promulgated interim regulations based on the 1962 Public Health Service standards.[8–10] Also included were MCL and minimum monitoring frequencies. These regulations became effective on June 24, 1977,[11] and included limits for 10 inorganic and 6 organic chemicals, turbidity, coliform bacteria and radionuclides. The second step consisted of a two-year study conducted by the National Academy of Sciences (NAS) intended to gather basic information on all contaminants in drinking water that may have an adverse impact on mankind.[11] In the third step, the EPA promulgated more comprehensive regulations, and, in addition, revised primary drinking water regulations following the results of the NAS study and other research activities.

Definitions

Public Law 93-523 provided some relevant definitions, some of which are:[9,10]

1. "Contaminant" means any physical, chemical, biological, or radiological substances or matter in water.
2. "Maximum contaminant level" means the maximum permissible level of a contaminant in water that is delivered to the free-flowing outlet of the ultimate user of a public water system, except in the case of turbidity, where the maximum permissible level is measured at the point of entry to the distribution system. Contaminants added to the water under circumstances controlled by the user, except those resulting from corrosion of piping and plumbing caused by water quality, are excluded from this definition.
3. "Person" means an individual, corporation, company, association, partnership, state, municipal, or federal agency.
4. "Public water system" means a system for the provision to the public of piped water for human consumption, if such system has at least 15 service connections or regularly serves an average of at

Table 1.1. Development of the U.S. Public Health Service Drinking Water Standards.

A. Bacteriological Constituents

Criterion	1914	1925	1942	1946	1962
Frequency of sampling	Not specified	Not specified	Specified by certifying authority	Regulated jointly by reporting agency and certifying authority	Same as 1946
Minimum number of samples to be examined in specified period	Not specified	Not specified	A minimum number, dependent on population served, shall be examined each month	Same as 1942	Same as 1942 except for an increased number per population served
Laboratory procedures	1912 *Standard Methods*	1923 *Standard Methods*	1936 *Standard Methods*	Current edition of *Standard Methods*	Current edition of *Standard Methods*
Inspection of laboratories	Not specified	Not specified	Subject to inspection by certifying authority	Subject to inspection by certifying and reporting agencies	Same as 1946

B. Physical Constituents

	Recommended Limit (Concentration which should not be exceeded when more suitable water supplies can be made available)					Tolerance Limit (Concentration in excess of those listed shall constitute grounds for rejection of the supply)				
Criterion	1914	1925	1942	1946	1962	1914	1925	1942	1946	1962
Color, units	—	20, preferably 10	—	20	15	—	—	20	20[a]	—
Odor, threshold number	—	Generally acceptable	—	Not objectionable	3, inoffensive	—	—	Not objectionable	—	—
Residue:										
Filterable, mg/L	—	—	—	—	500	—	—	—	—	—
Total, mg/L	—	—	500	500	—	—	—	1000	1000	—
Taste	—	Generally acceptable	—	Not objectionable	Inoffensive	—	—	Not objectionable	—	—
Turbidity, units	—	—	—	10	5	—	—	10	10[a]	—
Frequency of sampling	—	Not specified	Not specified	Not specified	At least once each week	—	—	—	—	—
Minimum number of samples to be examined in specified period	—	Not specified	Not specified	Not specified	Not specified	—	—	—	—	—

Table 1.1. Development of the U.S. Public Health Service Drinking Water Standards (Continued).

C. Chemical Constituents

	Recommended limit, mg/L (Concentration which should not be exceeded when more suitable water supplies are available)					Tolerance limit, mg/L (Concentration in excess of those listed shall constitute grounds for rejection of the supply)				
Substance	**1914**	**1925**	**1942**	**1946**	**1962**	**1914**	**1925**	**1942**	**1946**	**1962**
Alkyl benzene sulfonate (ABS)	—	—	—	—	0.5	—	—	—	—	—
Arsenic (AS)	—	—	—	—	0.01	—	—	0.05	0.05	0.05
Barium (Ba)	—	—	—	—	—	—	—	[b]	[b]	1.0
Cadmium (Cd)	—	—	—	—	—	—	—	—	—	0.01
Carbon chloroform extract (CCE)	—	—	—	—	0.2	—	—	—	—	—
Chloride (Cl)	—	250	250	250	250	—	—	—	—	—
Chromium, hexavalent (Cr^{+6})	—	—	—	—	—	—	—	[b]	0.05	0.05
Copper (Cu)	—	—	3.0	3.0	1.0	—	0.2	—	—	—
Cyanide (CN)	—	—	—	—	0.01	—	—	—	—	0.2
Fluoride (F)[d]	—	—	—	—	0.8–1.7[c]	—	—	1.0	1.5	1.4–2.4[c]
Iron (Fe)	—	0.3	[e]	[e]	0.3	—	—	—	—	—
Lead (Pb)	—	—	—	—	—	—	0.1	0.1	0.1	0.05
Manganese (Mn)	—	—	[e]	[e]	0.05	—	—	—	—	—
Magnesium (Mg)	—	100	125	125	—	—	—	—	—	—
Nitrate (NO_3)	—	—	—	—	45[f]	—	—	—	—	—
Phenols	—	—	0.001	0.001	0.001	—	—	—	—	—
Selenium (Se)	—	—	—	—	—	—	—	0.05	0.05	0.01
Silver (Ag)	—	—	—	—	—	—	—	—	—	0.05
Sulfate (SO_4)	—	250	250	250	250	—	—	—	—	—
Zinc (Zn)	—	—	15	15	5	—	5.0	—	—	—

D. Radioactivity, μc/L (Recommended limit[g])

Substance	**1914**	**1925**	**1942**	**1946**	**1962**
Radium 226 (Ra^{226})	—	—	—	—	3
Strontium 90 (Sr^{90})	—	—	—	—	10
Cross beta activity	—	—	—	—	1000[h]
Alpha emitters	—	—	—	—	—

[a] Filtered water only.

[b] Not to be allowed in water in distribution system.

[c] Dependent on annual average maximum daily air temperature over not less than a 5-year period.

[d] Where fluoridation is practiced, minimum recommended limits are also specified.

[e] Iron plus manganese should not exceed 0.3 mg/L.

[f] If NO_3 concentration exceeds 45 mg/L public should be warned against use of water for infant feeding.

[g] Water supplies containing concentrations in excess of these limits will be approved if surveillance of total intakes of radioactivity from all sources indicates that such intakes are within the limits recommended by the Federal Radiation Council for control action.

[h] In absence of strontium 90 and alpha emitters.

least 25 individuals daily at least 60 days out of the year. Such term includes (1) any collection, treatment, storage, and distribution facilities under control of the operator of such system and used primarily in connection with such system; and (2) any collection or pretreatment storage facilities not under such control that are used primarily in connection with such system. A public water system is either a community water system or a noncommunity water system.

The statement, "a system for the provision... regularly serves an average of at least 25 individuals daily at least 60 days out of the year" was used in the definition of a public water system to include campgrounds, service areas, and other public accommodations that are open for slightly less than three months each year.

5. "Community water system" means a public water system that serves at least 15 service connections used by year-round residents or regularly serves at least 25 year-round residents.
6. "Noncommunity water system" means a public water system that is not a community water system.

Public water systems were subdivided into community and noncommunity systems in order to relax the requirements of noncommunity systems in meeting the regulations. The possible health effects of a contaminant in drinking water consumed regularly over a long period of time are often quite different from those in water that is consumed occasionally. Thus, it is not imperative that the water consumed by transients from noncommunity systems be of the same quality as the water consumed by residents; that is, precautions should be taken to prevent the occurrence of contaminants (e.g., nitrate) which may pose a potential health hazard from short-term exposure.

Noncommunity systems include: hotels, motels, schools, service stations, highway rest areas, campgrounds, and other public accommodations that have their own water systems with at least 15 service connections, or that serve water to a daily average of at least 25 people. There are an estimated 200,000 noncommunity systems in the United States, but they are not the principal source of drinking water for their customers.

Interim Primary Standards

Interim standards (Table 1.2) were established in 1975[10] and amended in 1976,[12] 1979,[13] and 1980.[14] These interim standards were essentially identical to the 1962 USPHS standards, for which the USEPA was criticized severely.

Secondary Standards

Nonenforceable guidelines for contaminants that may adversely affect the aesthetic quality of drinking water were also established by the USEPA under the 1974 SDWA.[15] These standards are seen in Table 1.3, they represent reasonable goals for drinking water quality. States were encouraged to establish regulations based on these guidelines.

Safe Drinking Water Act Amendments of 1986

General Comments

The SDWA of 1974 and the major amendments of 1986[16] required the USEPA to establish primary drinking water regulations that: (a) apply to public water systems (defined above); (b) "specify contaminants which, in the judgment of the administrator, may have any adverse effect on the health of persons;" and (c) specify maximum contaminant levels for each substance and treatment techniques for their removal and control. In addition, the 1986 amendments added six new sections to the SDWA and mandated the establishment of a variety of new drinking water regulations according to specific timetables.

Significant revisions were made to the National Drinking Water Regulations (NDWR) (Section 1412 of PL 99-339). Maximum contaminant level goals (MCLGs—nonenforceable health goals) and MCLs must be established for 83 contaminants (Table 1.4). In addition, MCLGs and MCLs must be established for 25 contaminants selected from a priority list to be prepared by the USEPA and updated every 3 years (Table 1.5a). Criteria must be established under which filtration is required for public systems using surface water sources. Also, disinfection is required of all public water supplies.

Drinking Water Priority List (DWPL)

Under Section 1412(b)(3), the USEPA is required to develop a list of contaminants that are known or anticipated to occur in public water systems. Hazardous substances are defined in the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA), and pesticides registered under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) must be considered. Also, the DWPL must include any contaminant removed from the original list of 83 (Table 1.4). The 1991 DWPL is seen in Table 1.5a from which MCLGs and MCLs must be promulgated by January 22, 1993 for a minimum of 25 contaminants. Table 1.5b gives an updated (1995) list of this 1993 mandate for these 25 contaminants.[36a]

MCLGs and MCLs

Section 1412(b)(3) authorized the USEPA administrator to publish MCLGs and promulgated MCLs for each contaminant that "may have any adverse effect on human health and that is known or anticipated to occur in public water systems." The adverse health effect of a contaminant does

Table 1.2. National Interim Primary Drinking Water Regulations.

Contaminant	MCL (enforceable)[a]
Organics	
Endrin	0.0002 mg/L
Lindane	0.0004 mg/L
Methoxychlor	0.1 mg/L
Toxaphene	0.005 mg/L
2,4-D	0.1 mg/L
2,4,5-TP silvex	0.01 mg/L
Trihalomethanes (chloroform, bromoform, bromodichloromethane, dibromochloromethane)	0.10 mg/L
Inorganics	
Arsenic	0.05 mg/L
Barium	1.0 mg/L
Cadmium	0.010 mg/L
Chromium	0.05 mg/L
Fluoride	1.4–2.4 mg/L[b] (ambient temp)
Lead	0.05 mg/L
Mercury	0.002 mg/L
Nitrate (as N)	10 mg/L
Selenium	0.01 mg/L
Silver	0.05 mg/L
Sodium and corrosion	No MCL, monitoring and reporting only
Radionuclides	
Radium 226 and radium 228	5 pCi/L[c]
Gross alpha particle activity	15 pCi/L[d]
Beta particle and photon radioactivity	4 mrem[e] (annual dose equivalent)
Microbials	
Coliforms	<1/100 mL
Turbidity	1 Tu[f] (up to 5 TU)

[a] Monitoring and reporting for each contaminant also required.
[b] Revised MCL and MCLG for fluoride are 4 mg/L.
[c] 5 pCi/L = ~0.19 Bq/L.
[d] 15 pCi/L = ~0.56 Bq/L.
[e] 4 mrem = 4 μSv.
[f] TU = turbidity unit.

not have to be proven conclusively prior to regulation. MCLGs are nonenforceable, health-based goals. They must be set at a level at which there is no known or anticipated adverse effect on human health, and that allows for an adequate margin of safety regardless of cost to reach these goals. On the other hand, MCLs are enforceable standards and must be set as close to the MCLGs as feasible. Cost of treatment techniques is a consideration in setting MCLs.

Regulatory Basis of MCLGs

Noncarcinogens

The process of setting MCLGs for noncarcinogenic compounds differs from the process employed for carcinogens. For noncarcinogens, MCLGs are based on "no effect" levels for chronic lifetime periods of exposure. A safety factor is included. For noncarcinogenic toxicity, an organism is assumed to tolerate and detoxify some amount of a toxic agent without an ill effect up to a certain threshold amount. Threshold is defined as that dose of a contaminant required to elicit a measurable biologic response. As the threshold is

Table 1.3. National Secondary Drinking Water Regulations.

Contaminant	SMCL (nonenforceable)
Chloride	250 mg/L
Color	15 color units
Copper	1 mg/L
Corrosivity	Noncorrosive
Fluoride	2 mg/L
Foaming agent	0.5 mg/L
Iron	0.3 mg/L
Manganese	0.05 mg/L
Odor	3 (threshold odor number)
pH	6.5–8.5
Sulfate	250 mg/L
Total dissolved solids	500 mg/L
Zinc	5 mg/L

Table 1.4. Contaminants Regulated in USEPA Rules.[18]

Rulemaking	Contaminants Regulated	Note
VOCs (Phase I)	Benzene[a]	MCLGs and MCLs have been established for eight VOCs.
	Carbon tetrachloride[a]	
	para-Dichlorobenzene[a]	
	1,2-Dichloroethane[a]	
	1,1-Dichloroethylene[a]	
	1,1,1-Trichloroethane[a]	
	Trichloroethylene[a]	
	Vinyl chloride[a]	
	Monitoring Only	
	List 1	The 34 compounds in List 1 must be monitored by all systems.
	Bromobenzene	
	Bromodichloromethane	
	Bromoform	
	Bromomethane	
	Chlorobenzene	
	Chlorodibromomethane	
	Chlorethane	
	Chloroform	
	Chloromethane	
	o-Chlorotoluene	
	p-Chlorotoluene	
	Dibromomethane	
	m-Dichlorobenzene	
	o-Dichlorobenzene	
	trans-1,2-Dichloroethylene	
	cis-1,2-Dichloroethylene	
	Dichloromethane	
	1,1-Dichloroethane	
	1,2-Dichloropropane	
	1,3-Dichloropropane	
	2,2-Dichloropropane	
	1,1-Dichloropropene	
	1,3-Dichloropropene	
	Ethylbenzene	
	Styrene	
	1,1,1,2-Tetrachloroethane	
	1,1,2,2-Tetrachloroethane	
	Tetrachloroethylene	
	1,1,2-Trichloroethane	
	1,2,3-Trichloropropane	
	Toluene	
	p-Xylene	
	o-Xylene	
	m-Xylene	
	List 2	The two compounds in List 2 must be monitored by systems vulnerable to possible contamination.
	Ethylene dibromide (EDB)	
	1,2-Dibromo-3-chloropropane (DBCP)	
	List 3	The 15 compounds in List 3 may be monitored by systems at state's discretion.
	Bromochloromethane	
	n-Butylbenzene	
	Dichlorodifluoromethane	
	Fluorotrichloromethane	
	Hexachlorobutadiene	
	Isopropylbenzene	
	p-Isopropylbenzene	
	Naphthalene	
	n-Propylbenzene	
	sec-Butylbenzene	

	tert-Butylbenzene	
	1,2,3-Trichlorobenzene	
	1,2,4-Trichlorobenzene	
	1,2,4-Trimethylbenzene	
	1,3,5-Trimethylbenzene	
Fluoride	Fluoride[a]	MCLG and MCL have been revised.
Surface Water Treatment Rule	Turbidity[a]	Treatment technique requirements have been established for surface waters and groundwaters determined to be under the direct influence of surface water.
	Heterotrophic plate count[a]	
	Viruses[a]	
	Giardia lamblia[a]	
	Legionella[a]	
Total Coliform Rule	Total coliform bacteria[a]	Total coliform MCL revised based on presence–absence test.
	Fecal coliform bacteria	
	E. coli	
Lead and Copper	Lead[a]	Treatment technique requirements have been set in place of MCLs.
	Copper[a]	
SOCs and IOCs (Phase II)	**Inorganics**	MCLGs and MCLs have been set for 36 contaminants.
	Asbestos[a]	
	Barium[a]	
	Cadmium[a]	
	Chromium[a]	
	Mercury[a]	
	Nitrate[a]	
	Nitrite[a]	
	Selenium[a]	
	Volatiles	
	cis-1,2-Dichloroethylene[a]	
	1,2-Dichloropropane[a]	
	Ethylbenzene	
	Monochlorobenzene[a]	
	o-Dichlorobenzene[a]	
	Styrene[a]	
	Tetrachloroethylene[a]	
	Toluene[a]	
	trans-1,2-Dichloroethylene[a]	
	Xylenes (total)[a]	
	Pesticides, herbicides, PCBs	
	Alachlor[a]	
	Aldicarb[a]	
	Aldicarb sulfone[a]	
	Aldicarb sulfoxide[a]	
	Atrazine[a]	
	Carbofuran[a]	
	Chlordane[a]	
	Dibromochloropropane (DBCP)[a]	
	2,4-D	
	Ethylene dibromide (EDB)[a]	
	Heptachlor[a]	
	Heptachlor epoxide[a]	
	Lindane[a]	
	Methoxychlor[a]	
	PCBs[a]	
	Pentachlorophenol[a]	
	Toxaphene[a]	
	2,4,5-TP (Silvex)[a]	
	Treatment chemicals	Treatment technique has been set in lieu of MCLs.
	Acrylamide[a]	
	Epichlorophydrin[a]	
	Monitoring Only	
	Organics	All systems must monitor unless a vulnerability assessment determines the system is not vulnerable.
	Aldrin	

	Benzo(a)pyrene Butachlor Carbaryl Dalapon Di-2(ethylhexyl) adipate Di-2(ethylhexyl) phthalates Dicamba Dieldrin Dinoseb Diquat Endothal Glyphosate Hexachlorobenzene Hexachlorocyclopentadiene 3-Hydroxycarbofuran Methomyl Metolachlor Metribuzin Oxamyl (vydate) Picloram Propachlor Simazine 2,3,7,8-TCDD (dioxin) **Inorganics** Antimony[a] Beryllium[a] Cyanide[a] Nickel[a] Sulfate[a] Thallium[a]	
SOCs and IOC (Phase V)	**Inorganics** Antimony[a] Beryllium[a] Cyanide[a] Nickel[a] Thallium[a] **Organics** Benzo(a)pyrene[a] Dalapon[a] Di-2(ethylhexyl) adipate[a] Di-2(ethylhexyl) phthalate[a] Dichloromethane (methylene chloride)[a] Dinoseb[a] Diquat[a] Endothal[a] Endrin[a] Glyphosate[a] Hexachlorobenzene Hexachlorocyclopentadiene[a] Oxamyl (vydate)[a] Picloram[a] Simazine[a] 1,2,4-Trichlorobenzene[a] 1,1,2-Trichloroethane[a] 2,3,7,8-TCDD (Dioxin)[a]	MCLGs and MCLs have been set for 23 contaminants.
Radionuclides	Radon[a] Radium-226[a] Radium-228[a] Uranium[a] Alpha emitters[a] Beta and photon emitters[a]	

Arsenic	Arsenic (total)[a]	
Sulfate	Sulfate	
Groundwater disinfection	Viruses[a]	Treatment technique is required by SDWA.
	Heterotrophic plate count[a]	
D/DBP	**Disinfectants**	List of contaminants to be regulated has not yet been finalized, but these are the most likely to be regulated.
	Chlorine	
	Chloramine	
	Chlorine dioxide	
	Inorganic By-Products	
	Chlorate	
	Chlorite	
	Bromate	
	Organic By-Products	
	Total trihalomethanes	
	Chloroform	
	Bromoform	
	Bromodichloromethane	
	Dibromochloromethane	
	Trichloroacetic acid	
	Dichloroacetic acid	
	Total haloacetic acids	
	Chloral hydrate	
Balance of the DWPL.25 (Phase VIb)		List of contaminants to be regulated has not yet been finalized.
	Inorganics	MCLs are expected for at least 13 contaminants.
	Boron	
	Manganese	
	Molybdenum	
	Zinc	
	Organics	
	Acifluorfen	
	Acrylonitrile	
	Bromomethane	
	Cyanazine	
	Total mixture of 2,4- and 2,6-dinitrotoluene	
	Ethylene thiourea (ETU)	
	Hexachlorobutadiene	
	1,3-Dichloropropene	
	1,3-Trichloropropene	

[a] Included in the 1986 SDWA list of 83 contaminants.

exceeded, the extent of the response will be a function of the dose applied and the length of time exposed.

For noncarcinogenic contaminants, the "no effect" level is known as the reference dose (RfD) (previously referred to as acceptable daily intakes (ADIs). The RfD represents the exposure level that is thought to have no significant risk to humans when a contaminant is ingested daily over a lifetime. Available human and animal toxicity data are revised for a given substance that identifies the highest no-observed-adverse-effect level (NOAEL) or the lowest-observed-adverse-effect level (LOAEL). In turn, the RfD is calculated from:

$$\text{RfD} = \frac{\text{NOEL or LOAEL}}{\text{Uncertainty Factors'}}, \text{ mg / kg body weight / day}$$

These uncertainty factors are used to account for differences in toxicity response within humans and between humans and animals. Compensation is made for such factors as intra- and interspecies variability, the existence of weak or insufficient data, possible synergistic effects, and other factors. The NAS guidelines[19] for the uncertainty factors are:

- An uncertainty factor of 10 should be used when good acute or chronic human exposure data are available and supported by acute or chronic data in other species.
- An uncertainty factor of 100 should be used when good acute or chronic data are available for one species but not for humans.
- An uncertainty factor of 1000 should be used when acute or chronic data in all species are limited or

Table 1.5a. 1991 Drinking Water Priority List.[18]

Inorganics
- Aluminum
- Boron
- Chloramines
- Chlorate
- Chlorine
- Chlorine dioxide
- Chlorite
- Cyanogen chloride
- Hypochlorite ion
- Manganese
- Molybdenum
- Strontium
- Vanadium
- Zinc

Pesticides
- Asulam
- Bentazon
- Bromacil
- Cyanazine
- Cyromazine
- DCPA (and its acid metabolites)
- Dicamba
- Ethylenethiourea
- Fomesafen
- Lactofen/acifluorfen
- Metalaxyl
- Methomyl
- Metolachlor
- Metribuzin
- Parathion degradation product (4-nitrophenol)
- Prometon
- 2,4,5-T
- Thiodicarb
- Trifluralin

SOCs
- Acrylonitrile
- Bromobenzene
- Bromochloroacetonitrile
- Bromodichloromethane
- Bromoform
- Bromomethane

SOCs, continued
- Chlorination–chloramination by-products (misc.), e.g., haloacetic acids, haloketones, chloral hydrate, MX-2 [3-chloro-4-(dichloromethyl)-5-hydroxy-2 (5H)-furanone], *N*-organochloramines
- Chloroethane
- Chloroform
- Chloromethane
- Chloropicrin
- *o*-Chlorotoluene
- *p*-Chlorotoluene
- Dibromoacetonitrile
- Dibromochloromethane
- Dibromomethane
- Dichloroacetonitrile
- 1,3-Dichlorobenzene
- Dichlorodifluoromethane
- 1,1-Dichloroethane
- 2,2-Dichloropropane
- 1,3-Dichloropropane
- 1,1-Dichloropropene
- 1,3-Dichloropropene
- 2,4-Dinitrophenol
- 2,4-Dinitrotoluene
- 2,6-Dinitrotoluene
- 1,2-Diphenylhydrazine
- Fluorotrichloromethane
- Hexachlorobutadiene
- Hexachloroethane
- Isophorone
- Methyl ethyl ketone
- Methyl isobutyl ketone
- Methyl-*t*-butyl ether
- Naphthalene
- Nitrobenzene
- Ozone by-products, e.g., aldehydes, epoxides, peroxides, nitrosamines, bromate, iodate
- 1,1,1,2-Tetrachloroethane
- 1,1,2,2-Tetrachloroethane
- Tetrahydrofuran
- Trichloroacetonitrile
- 1,2,3-Trichloropropane

Microbials
- *Cryptosporidium*

incomplete. Other uncertainty factors can be used to account for other variations in the available data.

A drinking water equivalent level (DWEL) is calculated using the RfD. A DWEL represents a lifetime exposure at which adverse health effects are not anticipated to occur. This assumes 100% exposure from drinking water:

$$\frac{\text{DWEL}}{\text{mg/L}} = \frac{\text{RfD, mg/kg day} \times \text{body weight (70 kg)}}{\text{UF} \times 2\ \text{L/day (daily consumption of water)}}$$

When an MCLG for a noncarcinogen is determined, contributions from other sources of exposure, including air and food, are considered also. When sufficient data are available from other sources, the MCLG is calculated from:

$$\text{MCLG} = \text{RfD} - \text{food contribution} - \text{air contribution}$$

In cases where exposure data are not readily available from other sources, the MCLG is determined from:

$$\text{MCLG} =$$

$$\text{DWEL} \times \text{percentage drinking water contribution}$$

Table 1.5b. Preliminary List of Contaminants Included in Phase VIb.[36a]

Contaminant	Expected mg/L	Expected mg/L	Expected BAT[a]
Inorganics			
Boron	0.6 to 1	0.6 to 1	LS, IE, RO, NF
Manganese	0.2	0.2	IE, LS, OF
Molybdenum	0.04	0.04	IE, RO, NF
Zinc	2	2	LS, RO, NF
Pesticides			
Acifluorfen	Zero	0.002	GAC
Bromomethane	0.01	0.01	PTA
Cyanazine	0.001	0.001	GAC
Dicamba	0.2	0.2	GAC
1,3-Dichloropropene	Zero	0.0006	GAC, PTA
Ethylene thiourea (ETA)	Zero	0.025	GAC
Methomyl	10.2	0.2	GAC
Metolachlor	0.1	0.1	GAC
Metribuzin	0.2	0.2	GAC
Trifluralin	0.005	0.005	GAC
Other SOCs			
Acrylonitrile 2,4- and	Zero	0.003	PTA
2,6-Dinitrotoluene (total mixture)	Zero	0.003	GAC
Hexachlorobutadiene (HCBD)	0.001	0.001	GAC, PTA
1,1,1,2-Tetrachloroethane	0.07	0.07	PTA
1,2,3-Trichloropropane (TCP)	Zero	0.0008	GAC, PTA
Unregulated monitoring			
Bromacil	NA	NA	NA
Prometon	NA	NA	NA
Methyl-*t*-butyl-ether	NA	NA	NA

[a] LS—lime-softening; IE—ion exchange; RO—reverse osmosis; NF—nanofiltration; OF—oxidation and filtration; GAC—granular activated carbon; PTA—packed-tower aeration; NA—not applicable (monitoring only).

A conservative value of 20% is usually used in these situations. This provides an additional safety factor of 5 that covers most of the regulated contaminants.

Carcinogens

A two-phase process determines the MCLG no-effect levels for contaminants that may have cancer-causing potential (carginogenicity). First, the toxicological database for noncarcinogenic toxicity is assessed for factors that affect absorption of the contaminant when ingested (pharamacokinetics-metabolic changes), mutagenicity (capacity to cause or induce permanent changes in genetic material), and reproductive and developmental effects. Secondly, the carcinogenic potential is assessed directly by either long-term bioassay studies with animals (e.g., rodents) or indirectly by mutagenicity and other short-term tests. The onset of cancer in humans is difficult to evaluate because it is a multistage event. Consequently, a threshold effect for carcinogens has not been demonstrated experimentally, according to the 1977 report of the NAS Safe Drinking Water Committee.[19] This led to a policy *assumption* that, indeed, a zero-effect exposure dose has been demonstrated for carcinogens. Consequently, the exposure of humans to any amount of a potential carcinogen represents some finite level of risk. However, such a risk could be extremely small at very low doses.

Since human epidemiology data usually cannot define cause and effect relationships and human health effects data are not known for many contaminants, the potential risk to humans is estimated from the response of laboratory animals to the contaminant.[20] The underlying assumption is that effects observed in animals may also occur in humans. Needless to say, this is extremely controversial. Nonetheless, the USEPA has been guided by the following principles recommended in 1977 by the NAS:[19]

Principle 1: Effects in animals, properly qualified, are applicable to humans.

Principle 2: Methods do not now exist to establish a threshold for long-term effects of toxic agents.

Principle 3: The exposure of experimental animals to toxic agents in high doses is a necessary and valid method of discovering possible carcinogenic hazards in humans.

Principle 4: Material should be assessed in terms of human risk, rather than "safe" or "unsafe."

These principles serve as a basis for an assessment of such irreversible human health effects as carcinogenicity, for regulatory purposes.

In 1986, the USEPA established guidelines for classification of contaminants based on the weight of evidence of carcinogenicity:[21]

Group A:	Human carcinogen (sufficient from epidemiological studies)
Group B:	Probable human carcinogen
Group B1:	At least limited evidence of carcinogenicity to humans
Group B2:	Usually a combination of sufficient evidence in animals and inadequate data in humans
Group C:	Possible human carcinogen (limited evidence of carcinogenicity in animals in the absence of human data)
Group D:	Not classified (inadequate animal evidence of carcinogenicity)
Group E:	No evidence of carcinogenicity for humans (no evidence of carcinogenicity in at least two adequate animal tests in different species or in both epidemiological and animal studies)

These guidelines are used internally by the USEPA to classify contaminants of regulatory concern. In turn, a contaminant's carcinogenicity determines how the USEPA establishes an MCLG for that compound. A three-category approach is used to set MCLGs based on the weight of evidence of carcinogenicity via consumption of drinking water. These three categories are:

Category	Evidence of Carcinogenicity via Ingestion	Setting MCLG
I	Strong	Set at zero
II	Limited or equivocal	Calculate based on RfD plus added safety margin or set within cancer risk range of 10^{-5} to 10^{-6}
III	Inadequate or none	Calculate RfD

The cancer classification listed above does not necessarily determine the regulatory category, since the USEPA's Office of Drinking Water considers results of carcinogenicity evaluations by its own researchers as well as those from the International Agency for Research on Cancer (IARC) and the NAS. All of this unnecessarily confuses the issue.

Nonetheless, MCLGs must be established for those contaminants with a potential human health risk. For Category I (group A or B) substances, the MCLG is set at zero (zero is not a number, but a concept, as in "none"). This MCLG is based upon strong evidence of carcinogenicity from the appropriate toxicological database and upon the scientific consensus that safe threshold levels for carcinogens have not been demonstrated. Interestingly, this initiative comes from congressional guidance and not from any language in the SDWA.[20]

Category II contaminants, possible human carcinogens, are not regulated as human carcinogens, but are treated more conservatively than Category III noncarcinogens. Two options are available for Category II substances because the method of establishing MCLGs is much more complex than the other two categories. These options are: first the MCLG is based on the RfD plus an additional uncertainty factor of 1 to 10 to account for evidence of possible carcinogenicity: 1–10; other considerations (such as significance of the adverse health effect, pharmacokinetic factors, or quality of available data) may necessitate use of an additional uncertainty factor.

The second option for calculation of an MCLG is based on a lifetime risk from 10^{-5} (1 in 10^5 persons) to 10^{-6} (1 in 10^6 persons) that an individual would get cancer.

When sufficient chronic toxicity data are available, the first option is used. An MCLG is based on an RfD and DWEL following the method described above for Category III contaminants. An additional uncertainty factor is added. If there are insufficient data to use option 1, then the MCLG is based on a risk calculation, provided sufficient data are available from lifetime exposure studies in animals that are, in turn, manipulated using a linearized multistate dose-response model (LMM).[20-22] This model uses dose-response data to calculate a human carcinogenic potency factor (q_1^*), which is used to determine the drinking water concentration associated with theoretical upperbound excess cancer risks of 10^{-4}, 10^{-5}, and 10^{-6}. The equation is:

$$\begin{array}{c}\text{Drinking water concentration}\\ \text{mg / L}\end{array} = \frac{(10^{-x})\,(70\text{ kg})}{(q_1^*)\,(2\text{L / D})} \qquad (1)$$

where 10^{-x} = risk level (x = 4, 5, or 6); 70 kg = assumed adult body weight; $q_1^* = (\mu\text{g/kg/day})^{-1}$; and 2L/D = assumed adult water consumption rate. It should be noted that there are a large number of uncertainties in establishing MCLGs for Category II contaminants, the possible human carcinogens. For example, the potency factors (q_1^*) have limited availability.

Regulatory Basis of MCLs

MCLs are enforceable standards by the USEPA and the appropriate state regulatory agencies. Section 1412(b)(4) and (5) of the SDWA requires the establishment of MCLs "as close to the MCLGs as feasible, with the use of the best available technology (BAT) treatment techniques, and other means that are available, taking cost into consideration."[23] Also, Section 1412(a)(3) mandates that an MCLG be proposed and promulgated simultaneously with the corresponding MCL. The USEPA accomplishes this for each contaminant by preparing separate support documents on the occurrence and human exposure, health effects and toxicology, analytical methods and monitoring, and treatment technologies and costs.

An example of this process is the volatile organic chemicals (VOC) rule that became effective on January 9, 1989 (originally published on July 8, 1987).[24] MCLs were established for eight VOCs that included designation of GAC adsorption and packed-tower stripping as BATs for seven of the compounds. Packed-tower stripping was selected as the BAT for vinyl chloride. These determinations were based upon the demonstrated cost and efficiency of the treatment methods. VOCs are regulated as known or probable carcinogens (Category I) for which the MCLGs are zero. MCLs for these compounds, are, of course, not zero, but are based upon a "reference risk range" of 10^{-4} to 10^{-6}. The USEPA considers that MCLs set within this range are "safe" levels and protective of human health. "Safe" generally means that adverse effects on human health are unlikely.

Compliance Monitoring Requirements

Drinking water utilities are required to monitor raw and finished water supplies for each contaminant regulated by the USEPA under the SDWA for compliance to their MCLs. Monitoring requirements vary according to type of contaminant, system size, vulnerability to contamination, and other factors. Consequently, the USEPA standardized monitoring in the promulgated Phase II (SOCs and IOCs) regulations.[26] In turn, this was synchronized with the Phase I VOCs requirements, which are known as the standardized monitoring framework.[27] This framework was developed for source-related contaminants associated with chronic human health effects: VOCs, pesticides, radionuclides, and most inorganic chemicals. Nitrate, nitrite, and microbial contaminants are not included because they are associated with acute health effects. Also, monitoring for contaminants that are regulated by a treatment technique instead of by an MCL (lead, copper, turbidity, acrylamide, and epichlorohydrin), disinfectants, and disinfection by-products is not included.

All public water systems are subject to a nine-year compliance cycle, which is, in turn, divided into three three-year compliance periods. The first nine-year compliance cycle begins on January 1, 1993 and ends on December 31, 2001. Within the first cycle, the first compliance period begins January 1, 1993 and ends December 31, 1995; the second begins January 1, 1996 and ends December 31, 1988; the third begins January 1, 1999 and ends December 31, 2001.[25] Each state may establish its own monitoring plan and priorities according to its own criteria, subject, of course, to USEPA approval. Details of these considerations are found in References 25, 26, and 27. Compliance monitoring requirements for contaminants regulated on January 1, 1993 are summarized in Figure 1.1.[25] Whenever a new regulation is established, the USEPA will require the initial round of monitoring to begin the first full three-year compliance period 18 months after the effective date of promulgation.

Monitoring requirements may be reduced and even waived in certain situations and for specific contaminants. This is accomplished through each of the states monitoring plans, and with the approval of the USEPA. Details of these exceptions may be found in References 25 to 28.

USEPA Process for Establishing Standards

A flow diagram for the bureaucratic development of regulations established by the USEPA is seen in Figure 1.2. All of this involves interpretation of the various mandates and directives of the SDWA, technical and scientific assessments to meet the SDWA requirements, preparation of regulations that blend the technical and scientific aspects with policy considerations, review of draft regulations within the agency, and review by the public draft and proposed regulations.

Technical and scientific assessments (Figure 1.2) require support documents for each contaminant that, in turn, is prepared on: occurrence and human exposure, health effects and toxicology, analytical methods and monitoring, and treatment technologies and costs. Also, a regulatory impact assessment is prepared for each assessment.

The USEPA has conducted several national surveys of public water systems, of which several have been completed:

Community Water Supply Survey (1969 USPHS)[29]
National Organics Reconnaissance Survey (1975)[30]
National Organics Monitoring Survey (1976–1977)[31]
National Screening Program for Organics (1977–1981)[32]
Community Water Supply Survey (1978)[29]
National Rural Water Survey (1978)[32]
Ground Water Supply Survey (1980–1981)[33]
National Inorganics and Radionuclides Survey (1986)[34]
National Pesticides Survey (initiated in 1987)[32]

These surveys provide the national, statistically based evaluation of the various contaminants found in raw and finished drinking waters. Unfortunately, some are outdated and in "unpublished" reports. Nonetheless, these data are employed as part of the decision process on which contami-

<table>
<tr><th></th><th>1993</th><th>1994</th><th>1995</th><th>1996</th><th>1997</th><th>1998</th><th>1999</th><th>2000</th><th>2001</th></tr>
<tr><td>Asbestos
Base requirement</td><td colspan="3">One sample at each sampling point</td><td colspan="3">No requirements</td><td colspan="3">No requirements</td></tr>
<tr><td>Waiver*</td><td colspan="3">No samples required</td><td colspan="3">Not applicable</td><td colspan="3">Not applicable</td></tr>
<tr><td>Inorganics
Surface water base requirement</td><td colspan="3">One sample at each sampling point each year</td><td colspan="3">One sample at each sampling point each year</td><td colspan="3">One sample at each sampling point each year</td></tr>
<tr><td>Groundwater base requirement</td><td colspan="3">One sample at each sampling point each year</td><td colspan="3">One sample at each sampling point each year</td><td colspan="3">One sample at each sampling point each year</td></tr>
<tr><td>Waiver†</td><td colspan="9">One sample at each sampling point</td></tr>
<tr><td>VOCs
Base requirement</td><td colspan="9">Four quarterly samples at each sampling point</td></tr>
<tr><td>Reduced monitoring*</td><td colspan="3">One sample at each sampling point each year</td><td colspan="3">One sample at each sampling point each year§</td><td colspan="3">One sample at each sampling point each year§</td></tr>
<tr><td>Waiver**
Surface water</td><td colspan="3">State discretion</td><td colspan="3">State discretion</td><td colspan="3">State discretion</td></tr>
<tr><td>Groundwater</td><td colspan="6">One sample at each sampling point</td><td colspan="3">One sample at each sampling point</td></tr>
<tr><td>Pesticides
Base requirement</td><td colspan="3">Four quarterly samples at each sampling point</td><td colspan="3">Four quarterly samples at each sampling point</td><td colspan="3">Four quarterly samples at each sampling point</td></tr>
<tr><td>Reduced monitoring‡
Systems >3,300 people</td><td colspan="3">Not applicable</td><td colspan="3">Two samples at each sampling point</td><td colspan="3">two samples at each sampling point</td></tr>
<tr><td>Systems <3,300 people</td><td colspan="3">Not applicable</td><td colspan="3">One sample at each sampling point</td><td colspan="3">One sample at each sampling point</td></tr>
<tr><td>Waiver††</td><td colspan="3">No samples required</td><td colspan="3">No samples required</td><td colspan="3">No samples required</td></tr>
<tr><td>Unregulated contaminants
Organics</td><td colspan="3">Four quarterly samples at each sampling point</td><td colspan="3">Not applicable</td><td colspan="3">Not applicable</td></tr>
<tr><td>Inorganics</td><td colspan="3">One sample at each sampling point</td><td colspan="3">Not applicable</td><td colspan="3">Not applicable</td></tr>
<tr><td>Waiver††</td><td colspan="3">No samples required</td><td colspan="3">Not applicable</td><td colspan="3">Not applicable</td></tr>
</table>

Figure 1.1. Compliance monitoring requirements for contaminants regulated as of January 1, 1993. (^{a} Waivers from asbestos monitoring are available for all systems based on vulnerability assessment. ^{b} For all systems, states may waive the base monitoring requirements after three samples lower than the MCL are taken. ^{c} For all systems, reduced monitoring is allowed, provided initial monitoring is completed by December 31, 1992, and no contamination was detected. ^{d} Groundwater systems may be allowed to reduce monitoring to one sample at each sampling point per three-year compliance period after no detection in three years of annual monitoring. ^{e} Waivers are allowed, provided initial monitoring is completed by December 31, 1992, and no contamination was detected. ^{f} Reduced monitoring is allowed for systems in which contamination has not been detected.[25])

nants should be regulated, and on the potential impact of their regulation. Obviously, monitoring requirements for these contaminants can be determined by the states, for those systems that may be affected. The occurrence documents include estimates of human exposure to various substances by such exposures from air and food.

The health effects documents provide a comprehensive review of available literature on the potential adverse human health effects of the various contaminants in drinking water. Some of these documents were published by the NAS in the series "Drinking Water and Health."[19] Data from human epidemiology studies, animal studies, and sometimes human clinical studies were evaluated. The health effects assessment attempts to determine toxicology endpoints. The following subjects are considered: carcinogenicity, mutagenicity, teratology, pharmacokinetics, absorption factors, and metabolism. Hopefully, all of these evaluations lead to cancer risk estimates for carcinogens, and RfDs for noncarcinogens.

Analytical methods and monitoring techniques are especially important in the regulation of contaminants in raw and

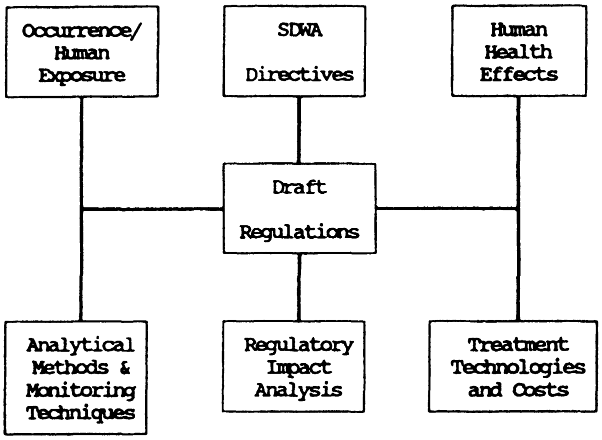

Figure 1.2. Development of draft USEPA regulations. Adapted from *Federal Register.*

finished drinking waters. Many factors are considered in selecting the appropriate analytical methods:

- reliability (precision and accuracy) of the analytical results
- specificity in the presence of interferences
- availability and performance of laboratories
- rapidity of analysis for routine use.
- cost of analysis

Many documents are available that provide the requisite guidance.

The treatment and costs document summarizes the availability and performance of the various treatment technologies that reduce contaminants in raw waters. Treatment costs have been determined for each best available technology (BAT) for many sizes of water systems. The BATs are based upon a number of factors, some of which are:

- have the highest efficiencies of removal
- are compatible with other types of water treatment processes
- are available as manufactured items or components
- are not limited to application in a particular geographic region
- have integrity for a reasonable service life as a public work
- are reasonably affordable by large metropolitan or regional systems
- can be mass-produced and put into operation in time for implementation of regulations.

The regulatory impact assessment is required under Presidential Executive Order 12291 (Figure 1.2). This document is submitted to the Office of Management and Budget (OMB) for review. It contains an evaluation of the potential national costs, other impacts, and benefits of proposed and final regulations.

The reader is directed to Reference 35 for details of the intra-agency (USEPA) review process and public participation in regulation development. These are important in the regulatory process of contaminants in drinking water.

Federal (U.S.) Drinking Water Regulations

Contaminants to be regulated by the 1986 SDWA amendments are given in Table 1.4. A schedule of development for all current and anticipated regulations is summarized in Table 1.6[36] that lists *Federal Register* citations for Advanced Notice for Proposed Rule Making (ANPRM) notices, as well as for proposed and final rules. The dates given in Table 1.6 are based upon the USEPA's regulatory agenda.[18] These dates can change at any time, since priorities change within the agency.

USEPA National Primary Drinking Water Regulations

Table 1.2 shows the interim primary drinking water (NIPDW) regulations that were enforceable MCLs until revised. Final MCLGs and MCLs have been established and revised for a number of contaminants. Table 1.7 gives the USEPA primary drinking water regulations that existed in 1996 and those that are proposed. Secondary maximum contaminant levels (SMCLs) are seen in Table 1.8.

Surface Water Treatment Regulations

Regulations for filtration, disinfection, turbidity, *Giardia lamblia*, viruses, *Legionella*, and heterotrophic bacteria (all are subject to primary drinking water regulations) were promulgated June 29, 1989.[37] These regulations, known as the Surface Water Treatment Rule (SWTR), apply to all public community and noncommunity water systems that employ surface water sources or groundwater sources under the direct influence of surface water. It is assumed that all surface waters and groundwaters may be at risk from contamination by *Giardia lamblia*, viruses, and *Legionella* (Table 1.7). The USEPA recommends levels of turbidity and heterotrophic plate count (HPC) to be as close to zero as possible. To date, MCLGs have not been formally established for these two constituents.

Instead of MCLs, treatment requirements have been established for *Giardia*, viruses, HPC bacteria, *Legionella*, and turbidity. Disinfection with or without filtration must achieve at least 99.9% (3-log) removal or inactivation of *Giardia lamblia* cysts and 99.99% (4-log) removal or inactivation of viruses.

Operating criteria have been established for those systems that have filtration currently or must install filtration

Table 1.6. Status of USEPA Drinking Water Regulations.[36a]

Status of Promulgated USEPA Drinking Water Regulations.[36a]				
Rule	**Final Rule Published**	**Legal Status**	**Activity**	**Possible Congressional Activity**
Analytical Methods	Dec. 5, 1994 (59 *FR* 62466)	Rule effective Jan. 6, 1995		
Drinking Water Priority List	Jan. 14, 1991 (59 *FR* 1470)	Revised list was due January 1994; USEPA decided not to revise the list pending SDWA reauthorization.		New process for selecting contaminants for regulation expected to replace current SDWA requirement to regulate 25 contaminants every 3 years
Fluoride	Apr. 2, 1986	Request for new information published Jan. 3, 1990 (55 *FR* 160); USEPA decided not to revise existing MCL: public comment on this decision was requested Dec. 29, 1993: final action delayed pending resources		
Lead and Copper	June 7, 1991 (56 *FR* 26460); correction notices published July 15, 1991 (56 *FR* 32112), June 29, 1992 (57 FR 28785), and June 30, 1994 (59 *FR* 33860)	USEPA is considering technical changes for proposal and promulgation in 1995.	U.S. District Court ruled Dec. 6, 1994, on lawsuits filed by the Natural Resources Defense Council and AWWA; court upheld treatment technique approach, ruled in favor of AWWA.	Provisions limiting lead in certain materials and submersible pumps may be added to SDWA.
Phase I VOCs	July 8, 1987 (52 *FR* 23690); correction notices published July 1, 1988 (53 *FR* 25108), and July 1, 1994 (59 *FR* 34320)	Analytical methods and monitoring revised in Phase II; additional changes under consideration		
Phase II SOCs and IOCs	Final rule for 33 contaminants published Jan. 30, 1991 (56 *FR* 3600); final rule for five contaminants published July 1, 1991 (56 *FR* 30266); correction notice	Changes regarding monitoring triggers and MDLs are under consideration.	Petitions for review were filed on four contaminants: U.S. Court of Appeals ruling Aug. 21, 1992 upheld USEPA's rule in its entirety.	Monitoring relief expected for small systems

	published July 1, 1994 (59 *FR* 34320)	
Phase V SOCs and IOCs	July 17, 1992 (57 FR 31776); correction notice published July 1, 1994 (59 *FR* 34320)	Changes regarding monitoring triggers and MDLs are under consideration.
Surface Water Treatment Rule	June 29, 1989 (54 *FR* 27488)	Enhanced Surface Water Treatment Rule has been proposed; separate guidance for *Cryptosporidium* to be developed
Total Coliform Rule	June 29, 1989 (54 *FR* 27547); partial stay published Jan. 15, 1991 (56 *FR* 1556)	USEPA considering changes to the rule
Trihalomethanes	Nov. 29 1979 (44 *FR* 68624); BAT established Feb. 28, 1983 (48 *FR* 8406); analytical methods revised Aug. 3, 1993 (58 *FR* 41344)	Proposed D/DBP Rule to revise regulations for trihalomethanes

Status of Proposed USEPA Drinking Water Regulations.[36a]

Rule	Proposal Published	Status	Legal Activity	Possible Congressional Activity
Disinfectants/ Disinfection By-products	July 29, 1994 (59 *FR* 38668)	USEPA evaluating public comments		Regulation deadlines may be included in the reauthorized SDWA.
Enhanced Surface Water Treatment Rule	July 29, 1994 (59 *FR* 38832)	Public comments being accepted until May 30, 1996		Regulation deadlines may be included in the reauthorized SDWA.
Information Collection Rule	Feb. 10, 1994 (59 *FR* 6332)	USEPA evaluating public comments; final rule expected June 1995; monitoring to begin October 1995		Regulation deadlines may be included in the reauthorized SDWA.
Primacy withdrawal process	Aug. 8, 1994 (59 *FR* 40458)	USEPA evaluating public comments; final rule due June 1995		

Table 1.6. Status of USEPA Drinking Water Regulations[36a] (Continued).

Radionuclides	July 18, 1991 (56 *FR* 33056)	USEPA preparing final rule to meet court-ordered deadline of Apr. 30, 1995; radon to be delayed and regulated separately		Congress prohibited USEPA from spending FY 1995 money to promulgate a radon standard.
Sulfate	Dec. 20, 1994 (59 *FR* 65578)	Final rule due May 31, 1996		Congress may allow regulation of another contaminant of greater health concern in place of sulfate.

Status of Anticipated USEPA Drinking Water Regulations.[36a]

Anticipated Rule	Schedule	Status	Legal Activity	Possible Congressional Activity
Aldicarb, aldicarb sulfone, and aldicarb sulfoxide	Reconsideration proposal expected early 1995	Final rules set July 1, 1991 (56 *FR* 30266); MCLs postponed May 27, 1991 (57 *FR* 22178); USEPA will revise MCLs upward.		
Arsenic	Proposal due Nov. 30, 1995; final rule due Nov. 30, 1997	USEPA considering new MCL between 0.002 and 0.020 mg/L; rule may be delayed because of uncertainty over health effects.		Delay of rule pending National Academy of Sciences study of arsenic health effects is possible.
Groundwater Disinfection Rule (GWDR)	Proposal due Aug. 30, 1995; final rule due Aug. 30, 1997	USEPA released draft rule July 31, 1992 (57 *FR* 33960); agency reforming workgroup and further delay expected; new approaches to draft rule to be considered		
Monitoring triggers and MDLs	To be determined	USEPA workgroup being formed to resolve issues regarding monitoring triggers and MDLs		
Phase VIb SOCs and IOCs	Proposal due Feb. 28, 1995; final rule due Feb. 28, 1997	USEPA informally released draft rule in summer 1994.		New process for selecting contaminants for regulation and for setting standards is expected.

Table 1.7. USEPA Drinking Water Standards and BAT for Regulated Contaminants.[36a]

Contaminant	Regulation	Status	MCLG mg/L	MCL mg/L	BAT[a]
Organics					
Acrylamide	Phase II	Final	Zero	TT	PAP
Alachlor	Phase II	Final	Zero	0.002	GAC
Aldicarb	Phase II	Delayed	0.001	0.003	GAC
Aldicarb sulfone	Phase II	Delayed	0.001	0.002	GAC
Aldicarb sulfoxide	Phase II	Delayed	0.001	0.004	GAC
Atrazine	Phase II	Final	0.003	0.003	GAC
Benzene	Phase I	Final	Zero	0.005	GAC, PTA
Benzo(a)pyrene	Phase V	Final	Zero	0.0002	GAC
Bromodichloromethane	D/DBP	Proposed	Zero	NA	EC
Bromoform	D/DBP	Proposed	Zero	NA	EC
Carbofuran	Phase II	Final	0.04	0.04	GAC
Carbon tetrachloride	Phase I	Final	Zero	0.005	GAC, PTA
Chloral hydrate	D/DBP	Proposed	0.04	TT	EC
Chlordane	Phase II	Final	Zero	0.002	GAC
Chloroform	D/DBP	Proposed	Zero	NA	EC
2,4-D	Phase II	Final	0.07	0.07	GAC
Dalapon	Phase V	Final	0.2	0.2	GAC
Di(2-ethylhexyl) adipate	Phase V	Final	0.5	0.5	GAC, PTA
Di(2-ethylhexyl) phthalate	Phase V	Final	Zero	0.006	GAC
Dibromochloromethane	D/DBP	Proposed	0.06	NA	EC
Dibromochloro-propane (DBCP)	Phase II	Final	Zero	0.0002	GAC, PTA
Dichloroacetic acid	D/DBP	Proposed	Zero	NA	EC
p-Dichlorobenzene	Phase I	Final	0.075	0.075	GAC, PTA
o-Dichlorobenzene	Phase II	Final	0.6	0.6	GAC, PTA
1,2-Dichloroethane	Phase I	Final	Zero	0.005	GAC, PTA
1,1-Dichloroethylene	Phase I	Final	0.007	0.007	GAC, PTA
cis-1,2-Dichloroethylene	Phase II	Final	0.07	0.07	GAC, PTA
trans-1,2-Dichloroethylene	Phase II	Final	0.1	0.1	GAC, PTA
Dichloromethane (methylene chloride)	Phase V	Final	Zero	0.005	PTA
1,2-Dichloropropane	Phase II	Final	Zero	0.005	GAC, PTA
Dinoseb	Phase V	Final	0.007	0.007	GAC
Diquat	Phase V	Final	0.02	0.02	GAC
Endothal	Phase V	Final	0.1	0.1	GAC
Endrin	Phase V	Final	0.002	0002	GAC
Epichlorohydrin	Phase II	Final	Zero	TT	PAP
Ethylbenzene	Phase II	Final	0.7	0.7	GAC, PTA
Ethylene dibromide (EDB)	Phase II	Final	Zero	0.00005	GAC, PTA
Glyphosate	Phase V	Final	0.7	0.7	OX
Haloacetic acids	D/DBP				
(sum of 5: HAA5)[b]	Stage 1	Proposed		0.060	EC
	Stage 2	Proposed		0.030	EC + GAC
Heptachlor	Phase II	Final	Zero	0.0004	GAC

Table 1.7. USEPA Drinking Water Standards and BAT for Regulated Contaminants[36a] (Continued).

Contaminant	Regulation	Status	MCLG mg/L	MCL mg/L	BAT[a]
Heptachlor epoxide	Phase II	Final	Zero	0.0002	GAC
Hexachlorobenzene	Phase V	Final	Zero	0.001	GAC
Hexachlorocyclopentadiene	Phase V	Final	0.05	0.05	GAC, PTA
Lindane	Phase II	Final	0.0002	0.0002	GAC
Methoxychlor	Phase II	Final	0.04	0.04	GAC
Monochlorobenzene	Phase II	Final	0.1	0.1	GAC, PTA
Oxamyl (vydate)	Phase V	Final	0.2	0.2	GAC
Pentachlorophenol	Phase II	Final	Zero	0.001	GAC
Picloram	Phase V	Final	0.5	0.5	GAC
Polychlorinated biphenyls (PCBs)	Phase II	Final	Zero	0.0005	GAC
Simazine	Phase V	Final	0.004	0.004	GAC
Styrene	Phase II	Final	0.1	0.1	GAC, PTA
2,3,7,8-TCDD (dioxin)	Phase V	Final	Zero	5×10^{-6}	GAC
Tetrachloroethylene	Phase II	Final	Zero	0.005	GAC, PTA
Toluene	Phase II	Final	1	1	GAC, PTA
Toxaphene	Phase II	Final	Zero	0.005	GAC
2,4,5-TP (silvex)	Phase II	Final	0.05	0.05	GAC
Trichloroacetic acid	D/DBP	Proposed	0.3	NA	EC
1,2,4-Trichlorobenzene	Phase V	Final	0.07	0.07	GAC, PTA
1,1,1-Trichloroethane	Phase I	Final	0.2	0.2	GAC, PTA
1,1,2-Trichloroethane	Phase V	Final	0.003	0.005	GAC, PTA
Trichloroethylene	Phase I	Final	Zero	0.005	GAC, PTA
Trihalomethanes	Interim	Final	NA	0.10	AD, PR, SPC
(sum of 4: TTHMs)[c]	D/DBP				
	Stage 1	Proposed	NA	0.080	EC
	Stage 2	Proposed	NA	0.040	EC + GAC
Vinyl chloride	Phase I	Final	Zero	0.002	PTA
Xylenes (total)	Phase II	Final	10	10	GAC, PTA
Inorganics					
Antimony	Phase V	Final	0.005	0.006	C-F,[d] RO
Arsenic	Interim	Final	NA	0.05	NA[d]
Asbestos (fibers/L > 10 μm)	Phase II	Final	7 million fibers/L	7 million fibers/L	C-F,[d] DF, DEF, CC
Barium	Phase II	Final	2	2	IX, RO, LS[d]
Beryllium	Phase V	Final	Zero	0.001	IX, RO, C-F,[d] LS,[d] AA, IX
Bromate	D/DBP	Proposed	Zero	0.010	DC
Cadmium	Phase II	Final	0.005	0.005	C-F,[d] LS,[d] IX, RO
Chlorite	D/DBP	Proposed	0.08	1.0	DC
Chromium (total)	Phase II	Final	0.1	0.1	C-F,[d] LS, (Cr III),[d] IX, RO
Copper	LCR	Final	1.3	TT	CC, SWT
Cyanide	Phase V	Final	0.2	0.2	IX, RO, Cl_2
Fluoride	Fluoride	Final	4	4	AA, RO
Lead	LCR	Final	Zero	TT	CC, PE, SWT, LSLR

Mercury	Phase II	Final	0.02	0.002	C-F (influent ≤ 10 μg/L),[d] LS,[d] GAC, RO (influent ≤ 10 μg/L)
Nickel	Phase V	Final	0.1	0.1	LS,[d] IX, RO
Nitrate (as N)	Phase II	Final	10	10	IX, RO, ED
Nitrite (as N)	Phase II	Final		1	IX, RO
Nitrate + nitrite (both as N)	Phase II	Final	10	10	IX, RO
Selenium	Phase II	Final	0.05	0.05	C-F (Se IV),[d] LS,[d] AA, RO, ED
Sulfate	Sulfate	Proposed	500	500	RO, IX, ED
Thallium	Phase V	Final	0.0005	0.002	IX, AA
Radionuclides					
Beta-particle and photon emitters	Interim	Final		4 mrem	
	Radionuclides	Proposed	Zero	4 mrem	C-F, IX, RO
Alpha emitters	Interim	Final		15 pCI/L	
	Radionuclides	Proposed	Zero	15 pCI/L	C-F, RO
Radium-226 + Radium-228	Interim	Final		5 pCI/L	
Radium-226	Radionuclides	Proposed	Zero	20 pCI/L	LS,[d] IX, RO
Radium-228	Radionuclides	Proposed	Zero	20 pCI/L	LS,[d] IX, RO
Radon	Radionuclides	Proposed	Zero	300 pCI/L	AR
Uranium	Radionuclides	Proposed	Zero	20 μg/L	C-F,[d] LS,[d] AX
Microbials					
Cryptosporidium	ESWTR	Proposed	Zero	TT	C-F, SSF, DEF, DF, D
E. coli	TCR	Final	Zero	[g]	D
Fecal coliforms	TCR	Final	Zero	[g]	D
Giardia lamblia	SWTR	Final	Zero	TT	C-F, SSF, DEF, DF, D
Heterotrophic bacteria	SWTR	Final[e]		TT	C-F, SSF, DEF, DF, D
Legionella	SWTR	Final[e]	Zero	TT	C-F, SSF, DEF, DF, D
Total coliforms	TCR	Final	Zero	[f]	D
Turbidity	SWTR	Final		PS	C-F, SSF, DEF, DF, D
Viruses	SWTR	Final[e]	Zero	TT	C-F, SSF, DEF, DF, D

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[a] AA—activated alumina; AD—alternative disinfectants; AR—aeration; AX—anion exchange; CC—corrosion control; C-F—coagulation and filtration; Cl_2—chlorination; D—disinfection; DC—disinfection system control; DEF—diatomaceous earth filtration; DF—direct filtration; EC—enhanced coagulation; ED—electrodialysis; GAC—granular activated carbon; IX—ion exchange; LS—lime softening; LSLR—lead service line replacement; NA—not applicable; OX—oxidation; PAP—polymer addition practices; PE—public education; PR—precursor removal; PS—performance standard; PTA—packed-tower aeration; RO—reverse osmosis; SPC—stop prechlorination; SSF—slow sand filtration; SWT—source water treatment; TT—treatment technique.

[b] Sum of the concentrations of mono-, di-, and trichloroacetic acids and mono- and dibromoacetic acids.

[c] Sum of the concentrations of bromodichloromethane, dibromochloromethane, bromoform, and chloroform.

[d] Coagulation-filtration and lime softening are not BAT for small systems for variances unless treatment is already installed.

[e] Final for systems using surface water: also being considered for groundwater systems.

[f] No more than 5% of the samples per month may be positive. For systems collecting fewer than 40 samples per month, no more than 1 sample per month may be positive.

[g] If a repeat total coliform sample is fecal coliform- or *E. coli*-positive, the system is in violation of the MCL for total coliforms. The system is also in violation of the MCL for total coiforms if a routine sample is fecal coliform- or *E. coli*-positive and is followed by a total coliform-positive repeat sample.

Table 1.8. USEPA Secondary Standards.

Contaminant	Regulation	Status	SMCLs[a]
Aluminum	Phase II	Final	0.05 to 0.2
Chloride	Interim	Final	250
Color	Interim	Final	155 color units
Copper	Interim	Final	1
Corrosivity	Interim	Final	Noncorrosive
Fluoride	Fluoride	Final	2
Foaming agents	Interim	Final	0.5
Hexachlorocyclopentadiene	Phase V	Proposed	0.008
Iron	Interim	Final	0.3
Manganese	Interim	Final	0.05
Odor	Interim	Final	3 TON
pH	Interim	Final	6.5-8.5
Silver	Phase II	Final	0.10
Sulfate	Interim	Final	250
Total dissolved solids (TD)	Interim	Final	500
Zinc	Interim	Final	5

[a] Units of measure are milligrams per liter unless noted otherwise.

because of the SWTR. Turbidity of filtered water must, at no time, exceed 5 ntu (nephelometric turbidity units) and must meet the following turbidity limits in 95% of the measurements from: conventional treatment or direct treatment, 0.5 ntu; slow sand filtration, 1 ntu; diatomaceous earth filtration, 1 ntu; and other state approved technologies, 1 ntu. Turbidity measurements must be made every 4 hours by grab sampling or continuous monitoring.

A residual disinfectant, usually chlorine, in finished water entering the distribution system cannot be less than 0.2 mg/L for more than four hours; furthermore, the residual disinfectant in the finished water anywhere in the distribution system cannot be undetectable in more than 5% taken in a month and for any two consecutive months. HPC may be measured instead of a disinfectant residual. If the HPC measurement is less than 500 colonies/mL, then the site has a "detectable" residual for compliance purposes.

Requirements to Avoid Filtration (SWTR)

All public water systems are required to filter their surface and groundwaters (under the influence of surface water) unless they can meet certain criteria related to source water quality and site-specific conditions. These criteria are divided into eight areas:[23]

1. Coliform limits—to avoid filtration, the fecal coliform level prior to disinfection must be less than or equal to 20/100 mL in at least 90% of samples taken, or the total coliform level prior to disinfection must be less than or equal to 100/100 mL in at least 90% of samples taken. Sampling frequency is based on system size. The calculation is based on the previous 6 months of monitoring results.
2. Turbidity limits—to avoid filtration, the turbidity level prior to disinfection must not exceed 5 ntu, based on measurements taken every 4 hours. A system may occasionally exceed 5 ntu and still avoid filtration if the state determines that this turbidity level occurred because of unusual circumstances, and not more than two such violations have occurred in the past 12-month period or more than five violations in the past 120 months.
3. Disinfection—to avoid filtration, a system must practice disinfection and achieve 99.9 and 99.99% inactivation of *Giardia* cysts and viruses, respectively. This must be demonstrated by the system each day it delivers water to consumers by meeting minimum CT values in the rule. CT is the product of disinfectant residual C (mg/L) times contact time T (minutes), measured at peak hourly flow determined at or prior to the first customer tap. As stated previously, the disinfectant residual in water entering the distribution system must not be less than 0.2 mg/L. The disinfectant residual in the distribution system cannot be undetectable in more than 5% of the samples in a month, for any two consecutive months. A system may measure for HPC in lieu of disinfectant residual in the distribution system. See Chapter 11 for additional information and details about disinfection and calculation of CT values.
4. Watershed control—to avoid filtration, systems must establish and maintain an effective watershed control program.
5. On-site inspection requirements—to avoid filtration, a system must have an annual on-site inspection conducted by the state (or third party approved by the state) to demonstrate that the system is maintaining an adequate watershed

control program and reliable disinfection treatment.

6. Absence of waterborne disease outbreaks—to avoid filtration, a system cannot have been identified as a source of waterborne disease outbreak, or, if it has been, the system must have been modified sufficiently to prevent another outbreak.
7. Compliance with the total coliform MCL—to avoid filtration, a system must comply with the total coliform rule requirements.
8. Compliance with the total trihalomethane (TTHM) MCL—to avoid filtration, a system must comply with the TTHM regulation.

Compliance Requirements for the SWTR

Surface Water Systems. Unfiltered systems must meet monitoring requirements beginning 18 months (December 29, 1990) following promulgation (June 29, 1989), unless the state has determined that filtration is required. Also, unfiltered systems must meet the criteria to avoid filtration beginning 30 months after promulgation (December 29, 1991), unless the state has determined that filtration is required or that they are in violation of a required treatment technique. Unfiltered systems must install filtration within 18 months following the failure to meet any one of the criteria (cited above) to avoid filtration, or within 48 months (June 29, 1993) following promulgation.

The interim turbidity monitoring and MCL requirements have remained in effect for unfiltered systems until 30 months (December 30, 1991) and for filtered systems (June 29, 1993) until 48 months following promulgation. If a state determined before December 30, 1991, that an unfiltered system must filter, the systems must comply with the interim standard for turbidity (Table 1.2) by June 29, 1993, or until filtration is installed, whichever is later.

Groundwater Systems. All systems that use groundwater under direct influence of surface water must meet the treatment techniques under the surface water treatment rule. States must determine which community and noncommunity groundwater systems are under the direct influence of surface water within 5 years (1994) and 10 years (1999), respectively, following promulgation. Unfiltered systems under the direct influence of surface water must begin monitoring within 6 months following the determination of direct influence unless the state has determined that filtration is required. Another provision is that systems under direct influence of surface water must begin meeting the criteria to avoid filtration 18 months after determination of direct influence, unless the state has determined that filtration is required. Unfiltered systems must install filtration within 18 months following the failure to meet any of the criteria to avoid filtration.

No variances from the filtration and disinfection requirements of the SWTR are allowed. However, exemptions are allowed for all requirements except disinfection residual requirements at the point of entry to the distribution system.

The reader is directed to References 23, 35, 38, 39 and the appropriate *Federal Register* Reference 37 for detailed information on the extremely complex SWTR.

Information Collection Rule (ICR)

Circa September 1992, a "Reg Neg" committee was established by the USEPA to develop, through the process of negotiation, a revised standard for trihalomethanes (TTHMs) (see below), as well as possible standards for additional disinfection by-products (DBPs) (see below). It was the intent of this committee to develop regulations that would balance the risks from DBPs with microbial risks. Subsequently, three draft rules were developed: information collection rule, disinfectants/disinfection by-products (D/DBP) rule, and enhanced surface water treatment rule (ESWTR). The ICR (Information Collection Rule) is designed to gather the data needed to help establish the requirements for Stage 2 of the D/DBP rule (see below) and the "interim" ESWTR. The D/DBP rule essentially addresses the DBP concerns for both surface and groundwaters, whereas the ESWTR addresses the microbial concerns for surface water only.

The initial draft of the ICR (July 2, 1993) is presented in great detail in Reference 39a. Originally, the ICR was scheduled for promulgation in December 1993, but there have been several delays in this process (see below). In any event, the ICR has three major components: (a) microbial monitoring requirements, (b) DBP monitoring requirements, and (c) testing requirements at bench-scale, pilot-scale, or both.

The major purpose of microbial monitoring is to provide data that can be used to:

- assess pathogen occurrence (*Giardia, Cryptosporidium, E. coli* or fecal coliform, and enteroviruses)
- improve understanding of microbial health risks and the effectiveness of treatment for pathogen removal
- evaluate the adequacy of the Surface Water Treatment Rule for microbial removal
- evaluate the adequacy of the Total Coliform Rule for ensuring microbial quality
- determine whether relationships exist between the occurrence, removal, or both of protozoan pathogens and viruses
- evaluate whether different levels of treatment should be required, based on source-water quality[39a]

Systems that utilize surface water or groundwater under the direct influence of surface water and serve 10,000 to 100,000 persons will conduct microbial monitoring (total coliforms, *E. coli* or fecal coliforms, *Giardia*, and *Cryptosporidium*). Systems that serve >100,000 must monitor for viruses in addition to the aforementioned list. Small systems (<10,000 persons) will not be required to monitor because of resource limitations. Data from medium and large systems will be extrapolated to estimate pathogen occurrence in small systems. Large systems will be required to monitor finished water if *Giardia, Cryptosporidium*, or viruses are detected in the source water.

The major DBP monitoring requirements are designed to:

- determine source water characteristics that influence DBP formation
- determine the concentrations of DBPs in drinking water
- refine existing methods for predicting DBP formation based on treatment and water quality
- help define cost-effective monitoring requirements that protect public health.

The reader is directed to Reference 39a for the myriad basic monitoring requirements for DBPs (five tables!) that are based upon Cl_2 as the primary disinfectant. Systems that utilize such alternative disinfectants as hypochlorite solutions, chloramines, ozone, and ClO_2 must monitor for DBPs of concern for the particular disinfectant.

The third component of the ICR requires bench- or pilot-scale testing, or both, with the intent to control DBP precursors. Total organic carbon (TOC) will be utilized as a surrogate for these precursors. TOC removal requirements will be on enhanced coagulation (see Chapter 6) or softening (see Chapter 8) in Stage 1 of the D/DBP rule. Large systems (>100,000) may be required to evaluate granular activated carbon (GAC) (see Chapter 4) or membranes (see Chapter 7) as part of the ICR if "low" TOC limits are established.

Here again, the reader is directed to Reference 39a for details of the testing requirements, which are based on type of disinfectant, TTHM content, haloacetic acid (HAA5) content, and the TOC content of the source water. For example, if Cl_2 is used, TTHMs >40 mg/L, HAA5 >30 mg/L, and TOC ≥40 mg/L, then bench- and/or pilot-scale testing will be required, the extent of which is dependent upon population (>50,000 or >100,000).

The proposed ICR was published in the *Federal Register* on February 10, 1994.[39b] The Reg-Neg committee had agreed, initially, to propose the ICR in December 1993 and to promulgate it in June 1994 so that monitoring could begin in October 1994.[39c] However, the USEPA decided in May 1994 to delay promulgation of the final ICR until September 1994, and to delay implementation to allow more time for training. This delay affected the initiation of microbial and DBP monitoring and precursor removal studies.

The deadlines described in the previous paragraph were not met, and the promulgation was anticipated in June 1995, with monitoring scheduled in October 1995.[39d] This reference describes the preparatory work needed for the ICR.

Another delay in the promulgation of the ICR was announced in August, 1995.[39e] Several technical and developmental issues have not been resolved fully. Some of the key issues are: (a) which PWS (public water system) will monitor?, (b) data flow and computer software are under development and testing, (c) the adequacy of some microbial monitoring methods is still questionable (this is especially true of the analytical methods for *Giardia* and *Cryptosporidium*), and (d) implementation and enforcement questions remain. ICR was promulgated in May 1996. Monitoring began in July 1997 for 18 months and data are expected in mid 1999.

Enhanced Surface Water Treatment Rule

The proposed ESWTR was published in the *Federal Register* on July 29, 1994 as an "interim" rule.[39f] The "final" rule will be developed at a later date. The "interim" ESWTR applies to all public water systems using surface water or groundwater under the direct influence of surface water that serve over 10,000 persons. This proposed ESWTR was developed by the USEPA and the Reg-Neg Committee, with the conviction that the current SWTR needs revision to provide additional protection from pathogenic organisms. This is essentially applicable to *Cryptosporidium,* which was not addressed by the SWTR.

Some of the significant provisions of the ESWTR are:

- All systems would be required to conduct a sanitary survey of the entire system within 5 years of promulgation and to conduct this survey every 5 years thereafter. This applies to those systems who wish to avoid filtration.
- An MCLG of zero is proposed for *Cryptosporidium.*
- A watershed protection program must be maintained to minimize the levels of *Cryptosporidium.*
- It amends the SWTR definition of groundwater under the direct influence of surface water to include *Cryptosporidium.*

The proposed "interim" ESWTR may include treatment requirements for viruses, *Giardia*, and *Cryptosporidium.* As microbial data from the ICR become available, the USEPA intends to develop risk reduction and cost estimates for the various treatment alternatives listed below in tabular form.

Alternative A: Enhanced Treatment for Giardia. This is based on source levels of *Giardia*. Utilities that serve more than 10,000 persons would be required to achieve greater reductions than the 3-log *Giardia* reduction currently required.

Option 1.

No. of *Giardia*/100L	Required treatment level (%)
<1	99.9 (3-log).
1–9	99.99 (4-log).
10–99	99.999 (5-log).
>99	99.9999 (6-log).

Option 2.

No. *Giardia*/100L	Required treatment level (%)
10–99	99.99 (4-log).
100–999	99.999 (5-log).
>1000	99.9999 (6-log).

Alternative B: Specific Treatment for Cryptosporidium. All community and noncommunity public water systems using any surface water source or groundwater under the direct influence of surface water that serve over 10,000 persons would be required to reduce *Cryptosporidium* densities.

Option 1.

No. *Cryptosporidium*/100L	Required treatment level (%)
<1	99.9 (3-log).
1–9	99.99 (4-log).
10–99	99.999 (5-log).
>99	99.9999 (6-log).

Option 2.

No. *Cryptosporidium*/100L	Required treatment level (%)
<1	99 (2-log).
1–9	99.9 (3-log).
10–99	99.99 (4-log).
>99	99.999 (5-log).

Option 3.

No. *Cryptosporidium*/100L	Required treatment level (%)
<10	99 (2-log).
10–99	99.9 (3-log).
>99	99.99 (4-log).

Alternative C: 2-log (99%) Removal of Cryptosporidium. Systems that filter must achieve at least 2-log removal of *Cryptosporidium* between the source water and the first customer.

Alternative D: Specific Disinfection Treatment for Viruses. Option 1. Surface water (or groundwater under the direct influence) systems that serve 10,000 or more people must achieve, through disinfection alone, at least 0.5-log inactivation of *Giardia.*

Option 2. Surface water (or groundwater under the direct influence) systems that serve 10,000 or more people must achieve, through disinfection alone, a 4-log (99.99%) inactivation of viruses.

Alternative E: No Change in Existing SWTR. Under this alternative the existing SWTR requirements for *Giardia* and viruses would not change. This alternative would give EPA additional time to fully develop and evaluate the microbial data collected under the Information Collection Rule, while accumulating additional data on pathogen occurrence, treatment performance, and health effects, since the current SWTR has not been in effect long enough to evaluate projected improvements in drinking water quality and public health benefits.

The reader is directed to Reference 39f for the rationale of the ESWTR.

Ground Water Disinfection Rule (GWDR)

The 1986 amendments to the SDWA require the USEPA to promulgate disinfection requirements for all public water supplies. These requirements were discussed above for surface water supplies and for those groundwater supplies under the direct influence of surface water. A draft rule for the disinfection of groundwaters was published in 1992.[39g] The GWDR will apply to community and noncommunity systems. Major provisions of the draft rule were summarized previously.[39h] Several delays have postponed the proposed rule until August of 1995, with the final rule due August 30, 1997 (Table 1.6). The GWDR will include requirements for disinfection of source water, distribution system disinfection, qualified operators, treatment techniques, MCLGs, natural disinfection requirements, monitoring and analysis, reporting, and provisions for variances and exemptions.

The USEPA has chosen viruses as the target organism for the GWDR. This is "because viruses are generally considered to be more mobile in groundwater and more resistant to disinfection than bacteria." An MCLG of zero would be established for viruses with no MCLG for heterotrophic plate count (HPC) bacteria. The USEPA is considering inclusion of *Legionella* in this rule. Since such protozoan pathogens as *Giardia* and *Cryptosporidium* are not normally found in groundwater, they are not included in this rule.

Criteria are given for chemical disinfection of source water and for "natural disinfection," details of which are given in References 39g and 39h. There are prequalifying conditions for avoidance of chemical disinfection of source water via natural disinfection.[39i] An apparent contradiction to the latter is that each community water system would be required to maintain a disinfectant residual of at least 0.2 mg/L at the entry point to the distribution system at all times. A detectable disinfectant residual or an HPC concentration of less than 500/mL in the water within the distribution would be required. Other requirements are summarized in Reference 39h.

Total Coliform Rule

The 1986 SDWA amendments included a revised total coliform rule that was promulgated finally in 1989.[40] This revised rule established an MCLG for total coliforms (including fecal coliforms and *E. Coli*) at zero and an MCL based on the presence–absence (P–A) of total coliforms. The latter represents a major change from the 1974 interim standards, which estimate a coliform density.

The MCL for water distribution systems testing at least 40 samples per month permits no more than 5% of the monthly samples to be positive for total coliforms. Those distribution systems analyzing less than 40 samples per month may have no more than one positive sample per month. Also, the new rule does not allow substitution of chlorine residual monitoring as did the 1974 rule. All state primary agencies were required to adopt rules at least as stringent as the federal rule no later than December 31, 1990. In recognition of limited financial and human resources, the USEPA allowed states to negotiate an extension of up to 2 years (until December 1992) to adopt new coliform rules under the revised primary rule.[41]

Monitoring Requirements

All public water systems must sample according to a written sample-siting plan that is subject to review and revision by the state. The population served determines the monthly routine monitoring requirements (Table 1.9). Noncommunity water systems using groundwater and serving less than 1,000 persons may sample less frequently than once a month (quarterly) until a sanitary survey is conducted. After June 29, 1994, this category of noncommunity water systems must monitor at least once a year. In another category, noncommunity water systems using surface water or groundwater under the direct influence of surface water must monitor at the same frequency as a same-sized community water system.

Repeat sample monitoring requirements under the new rule are quite extensive and detailed (Table 1.10). Example: for each routine sample that tests positive for total coliforms, a set of three or four repeat samples must be analyzed, one of which must come from the same tap as the original sample. Two repeat samples in the set must be collected from within five service connections of the original sample, with one upstream and one downstream. Repeat samples must be collected within 24 hours of notification of the original result, except, of course, when the state waives this requirement. There are contingencies for positive results in the repeat samples and for utilities that routinely collect less than five routine samples per month. Details of repeat sampling requirements are found in References 23, 35, and 40.

Analytical Requirements

A 100-mL standard sample volume must be used for total coliforms, regardless of the analytical method. Analyses for these organisms may utilize the 10-tube multiple tube fermentation (MTF) technique, the membrane filter (MF) technique, the P-A coliform test, or the minimal media ONPG-MUG test (the Colilert test).[40,42] The 5-tube MTF technique (20-mL sample portions) or a single culture bottle containing MTF medium may be used if a 100-mL water sample is employed.

At the time the total coliform rule was promulgated,[40] no methods had been approved by the USEPA for *E. Coli*. Testing for this microorganism is allowed by the rule in lieu of fecal coliforms. This has distinct advantages over the fecal coliform test. Subsequently, the USEPA approved two *E. Coli* tests. One of these is a test protocol whereby *E. Coli* can be transferred successfully from ONPG-positive cultures to EC-MUG medium. This transferability protocol was approved for compliance monitoring in 1992.[43] Simply, this means that the MMO-MUG test for total coliforms can be used in combination with EC-MUG medium for *E. Coli*. A second test protocol was developed by the USEPA that evaluated the performance of the MMO-MUG test when low densities of stressed *E. Coli* are present. Acceptance of this test was announced by the USEPA in early 1992.[18]

Volatile Organic Chemicals (VOCs) Rule—Phase I

The VOC regulation established MCLGs and MCLs for eight compounds (Tables 1.4 and 1.7): benzene, carbon tetrachloride, *p*-dichlorobenzene, 1,2-dichloroethane, 1,1-dichloroethylene, 1,1,1-trichloroethane, trichloroethylene, and vinyl chloride. After proposals, reproposals, amendments, etc., the final VOC rule was published in 1987[44] and corrections to the final rule were published in 1988.[45] The VOC requirements pertain to both community water systems and nontransient, noncommunity water systems, and have been in effect since early 1989. Monitoring (Figure 1.1) is a significant aspect of this VOC rule. Deadlines for all system sizes have expired for initial VOC monitoring. However, all states should have adopted VOC regulations by 1994.

Synthetic Organic (SOCs) and Inorganic (IOCs) Chemicals Rule—Phase II

New drinking water regulations for 38 SOCs and IOCs (Table 1.4) were finalized by the USEPA for 33 of these contaminants in 1991.[46] Rules for the remaining five compounds (barium, pentachlorophenol, aldicarb, aldicarb sul-

Table 1.9. Routine Sampling Requirements Under the Total Coliform Rule.[23]

Population Served	Minimum Number of Routine Samples per Month	Population Served	Minimum Number of Routine Samples per Month
25–1,000[a]	1	59,001–70,000	70
1,001–2,500	2	70,000–83,000	80
2,501–3,300	3	83,001–96,000	90
3,301–4,100	4	96,001–130,000	100
4,101–4,900	5	130,001–220,000	120
4,901–5,800	6	220,001–320,000	150
5,801–6,700	7	320,001–450,000	180
6,701–7,600	8	450,001–600,000	210
7,601–8,500	9	600,001–780,000	240
8,501–12,900	10	780,001–970,000	270
12,901–17,200	15	970,001–1,230,000	300
17,201–21,500	20	1,230,001–1,520,000	330
21,501–25,000	25	1,520,001–1,850,000	360
25,001–33,000	30	1,850,001–2,270,000	390
33,001–41,000	40	2,270,001–3,020,000	420
41,001–50,000	50	3,020,001–3,960,000	450
50,001–59,000	60	3,960,001 or more	480

[a] Includes public water systems that have at least 15 service connections but serve fewer than 25 people.

Table 1.10. Monitoring and Repeat-Sample Frequency After a Total-Coliform-Positive Routine Sample.[23]

Number of Routine Samples per Month	Number of Repeat Samples[a]	Number of Routine Samples Next Month[b]
1 or less	4	5/month
2	3	5/month
3	3	5/month
4	3	5/month
5 or more	3	See Table 1.13

[a] Number of repeat samples in the same month for each total-coloform-positive routine sample.

[b] Except when the state invalidates the original routine sample, substitutes an on-site evaluation of the problem, or waives the requirement on a case-by-case basis.

foxide, and aldicarb sulfone) were reproposed[28] and finalized, also in 1991.[27] MCLGs and MCLs are found in Table 1.7 for these 38 SOCs and IOCs. MCLs for all Phase II contaminants took effect on July 30, 1992, except the five compounds that became effective on January 1, 1993.[47] Monitoring requirements are established according to the standardized framework seen in Figure 1.1.

Secondary MCLs, related to aesthetic effects, were set for two substances under Phase II (Table 1.8). An SMCL was established for aluminum at 0.05 to 0.2 mg/L to prevent post-precipitation of $Al(OH)_3$ and discoloration of drinking water in distribution systems. An SMCL of 0.1 mg/L for silver was set for prevention of skin discoloration (argyria). Also, the USEPA considered setting SMCLs for seven organic chemicals under the Phase II rule.[48] However, they deferred to the odor SMCL of TON 3, rather than set individual SMCLs over and above their MCLs for health reasons.[36]

Synthetic Organic and Inorganic Chemicals Rule—Phase V

The Phase V rule will set regulations for 6 IOCs and 18 SOCs (Table 1.4). A proposed rule was published in 1990[49] and finalized in 1992 (*FR*, **57**, 31776, July 17, 1992), with implementation in early 1994. The MCLGs, MCLs, and an SMCL are seen in Tables 1.7 and 1.8. The standardized monitoring framework[36] will be used for the Phase V compounds, whose effective date is anticipated to be January 1993 to December 1995.

Disinfectants/Disinfection By-Products (D/DBP)—Phase VIa

The D/DBP rule has been rewritten by the Reg-Neg Committee[39f,50a] that differs significantly from its original version that was published in 1991.[50] This revised D/DBP rule was developed concurrently with the ICR and the ESWTR (see above), and will be implemented in two stages.

The D/DBP rule addresses complex and interrelated issues. The risk of microbial disease outbreaks must be balanced against the risks associated with disinfectants and their by-products. Stage 1 will be promulgated and implemented over a time frame that was started in March 1994 and, hopefully, will be completed in January 2002.[50a] Stage 2 occurs over the same period of time as Stage 1, but will be renegotiated following collection of additional occurrence and treatment data under the ICR. The D/DBP rule will apply to all community and nontransient, noncommunity water systems that add a chemical disinfectant during any part of the drinking water treatment process.

The advisory committee that negotiated the revised D/DBP rule will set MCLGs for nine DBPs (Table 1.7) in Stage 1 and revise in Stage 2 if necessary. Also, Stage 1 will establish the MCL for TTHMs at 0.080 mg/L (Table 1.7), which will be lowered to 0.040 mg/L in Stage 2 for PWSs that serve more than 10,000 persons using surface water or groundwater under the direct influence of surface water. Stage 1 also will set an MCL for the total HAA5 at 0.060 mg/L (Table 1.7), which will be lowered to 0.030 mg/L in Stage 2. In addition, MCLs will be set in Stage 1 for bromate, 0.010 mg/L, and for chlorite, 1.0 mg/L (Table 1.7).

Other provisions of the revised D/DBP rule are: (a) compliance monitoring for TTHMs and HAA5 based on system size; (b) compliance monitoring for bromate (ozone) and chlorite (ClO_2) for certain systems using these disinfectants; (c) analytical methods for DBPs, (d) BATs for meeting the MCLs for DBPs (Stage 1 BAT is enhanced coagulation or GAC, whereas Stage 2 is enhanced coagulation or softening and GAC); (e) goals and limits will be established for disinfectant residuals of chlorine, chloramine, and chlorine dioxide:

Disinfectant Residual	MRDLG[a] mg/L	MRDL[b] mg/L
Chlorine (free chlorine)	4	4.0
Chloramines (as total chlorine)	4	4.0
Chlorine dioxide	0.08	0.8

[a] MRDLG = maximum residual disinfectant goal
[b] MRDL = maximum residual disinfectant limit)

(f) treatment technique requirements for removal of DBP precursors (DBPPs) will be established (either enhanced coagulation or enhanced softening for TOC removal that can be avoided if certain criteria are met); and (g) compliance monitoring for DBPP removal will be calculated quarterly. The reader is directed to References 39f and 50a for details of these and other provisions of the revised D/DBP rule.

Disinfectants/Disinfection By-Products—Phase VIb

The USEPA must regulate at least 25 contaminants under the D/DBP rule and Phase VIb [36] from the DWPL that was published in 1991[18,51] (Table 1.5a). The preliminary list of these 25 contaminants is seen in Table 1.5b, a final list is expected to be published in mid 1998.

Radionuclide Rule—Phase III

The radionuclide rule will establish MCLGs and MCLs for radon-222, radium-226, radium-228, natural uranium, and beta particles and photon emitters. Since all of the radionuclides are classified as known human carcinogens, MCLGs will be set at zero. Interim regulations for some of these substances are seen in Table 1.2. Proposed MCLGs and MCLs are given in Table 1.7. A formal proposal was published in July 1991,[52] with a final rule expected in April 1993. The proposed rule will apply to all community water systems and nontransient noncommunity water systems.

The U.S. Congress has delayed promulgation of a final radon standard through the fiscal year 1995 because of the controversy over the proposed radon standard.[36a] The USEPA is expected to proceed with regulation of all radionuclides except radon; that was removed from the "package" for various reasons. This means that the final MCLs for Ra^{226} and Ra^{228} could be lower than those seen in Table 1.7. A proposed MCL of 300 pCi/L for radon is seen in Table 1.7 also.

Lead and Copper Rule

The revised lead and copper rule is, perhaps, the most controversial of the 1986 SDWA amendments. The new rules were the subject of intense discussions. They were hailed by many water utilities as a positive step forward, criticized by many as deficient or illegal, and defended by the USEPA as the best approach for minimizing exposure to lead and copper in drinking water. After several proposals, the final rule was published July 7, 1991,[53] and corrections were issued on July 15, 1991.[54]

The new rule applies to all community water systems and to nontransient, noncommunity systems. The interim MCL for lead (Table 1.2) was replaced by a treatment technique requirement (Table 1.7) consisting of corrosion control, public education, and lead service line removal.[55] Human health effects of lead and copper are documented in References 53 and 55.

Table 1.11. Lead and Copper Monitoring Schedule.[55]

Monitoring Period	Location	Frequency
Initial monitoring	Targeted high-risk interior taps	Every six months[a,b]
After installation of corrosion control	Targeted high-risk interior taps	Two consecutive six-month monitoring periods
After state specifies water quality limits for optimal corrosion control	Targeted high-risk interior taps	Two consecutive six-month monitoring periods[b]
Reduced monitoring	Targeted high-risk interior taps	Once a year[c]
	Targeted high-risk interior taps	Once every three years[d]

[a] Large systems collect water samples from taps for two six-month monitoring periods before conducting comparative corrosion control treatment studies.

[b] Small and medium-size systems collect water samples from taps until the samples exceed the lead or copper action level, triggering the treatment technique requirement.

[c] Systems meeting the lead and copper action level or maintaining optimal corrosion control treatment specified by the state for two consecutive six-month monitoring periods may reduce tap water sampling to once a year and collect the reduced number of samples indicated in Table 1.12.

[d] Systems meeting the lead and copper action level or maintaining optimal corrosion control treatment specified by the state for three consecutive years may reduce the frequency of collecting tap water samples to once every three years and collect the reduced number of samples indicated in Table 1.12.

An extremely significant portion of the revised lead and copper rule is the monitoring requirement of every 6 months. Two 6-month monitoring periods are required per calendar year (Table 1.11),[55] organized according to system size (Table 1.12).[55] Samples of tap water are required at high risk locations, that is, homes in which lead solder has been installed since 1982, or that have lead pipes or lead service lines. Samples (1 L) of first-drawn tap water must be taken (usually by residents) from a cold water tap in the kitchen or the bathroom. Water must have been allowed to lie motionless in the distribution pipes for at least six hours before collection.

Treatment technique requirements are initiated when action levels for lead (0.015 mg/L) or copper (1.3 mg/L) are exceeded and measured in the 90th percentile at the customer's tap. Treatment consists of optimal corrosion control, source water treatment, public education, and lead service line replacement. An action level is not an MCL, but represents a concentration above which the utilities must reduce lead and copper and inform consumers about actions they can take to lower exposure to these metals in water.

Additional water quality monitoring is required for those water systems that exceed the lead or copper action levels. The constituents are given in Table 1.13 that are used to identify optimal treatment, and, if treatment is installed, to determine whether or not a system remains in compliance. This water quality monitoring is, of course, related to system size and population (Table 1.14), and is implemented in accordance with the schedule in Table 1.11. States must specify the levels of these water quality constituents that reflect optimal corrosion control and, if maintained for three consecutive years, the monitoring schedule may be modified.

There is a significant public education requirement in the revised lead and copper rule. All public water systems that exceed the lead action level must deliver the USEPA-developed public education program (Table 1.15) to their customers within 60 days. The public education program informs the public about adverse health effects of lead and explains the procedures people can adopt to reduce exposure to lead in their drinking water. This includes flushing the tap, cooking with cold water rather than hot, checking for lead solder in new plumbing, and having their water tested for lead. This program must remain in effect by the water system for as long as the lead action level is exceeded.

The reader is directed to References 53 to 55 for details of the new lead and copper rule. Chapter 8 documents the treatment techniques for optimal corrosion control.

Arsenic

Currently, arsenic has an interim primary drinking water quality standard of 0.05 mg/L. The promulgation of an MCLG and an MCL has been delayed because the USEPA sought additional technical information about adverse human health effects.[36a,55] Subsequently, the USEPA is under a court-ordered deadline to propose revised regulations for arsenic no later than November 30, 1995, with the final rule due two years later (Table 1.6).

The USEPA, however, has completed its human health assessment for noncancer effects and has determined a reference dose (RfD) of 0.0003 mg/kg/d.[56] The drinking water equivalent level (DWEL) is calculated to be 10.5 mg/L (see above). If based on noncancer effects, the anticipated MCLG would be 0.002 mg/L (assuming a 20% exposure from drinking water).

The carcinogenicity of arsenic is under review by the USEPA. Initial indications are that arsenic will be classified as a group A human carcinogen (see above), with an

Table 1.12. Tap Sampling Requirements for Lead and Copper.[55]

System Size Population	Number of Sampling Sites Initial Base Monitoring	Number of Sampling Sites Reduced Monitoring
>100,000	100	50
10,001 to 100,000	60	30
3,301 to 10,000	40	20
501 to 3,300	20	10
101 to 500	10	5
100	5	5

Table 1.13. Water Quality Monitoring Schedule (Other than Lead and Copper).[55]

Monitoring Period	Constituents	Location	Frequency
Initial monitoring	pH, alkalinity, orthophosphate or silica,[b] calcium, conductivity, temperature	Taps and at entry point(s) to the distribution system	Every six months
After installation of corrosion control	pH, alkalinity, orthophosphate or silica,[b] calcium[c]	Taps	Every six months
	pH, alkalinity dosage rate and concentration (if alkalinity is adjusted as part of corrosion control), inhibitor dosage rate and inhibitor residual	Entry point(s) to the distribution system	Biweekly
After state specifies water quality limits for optimal corrosion control	pH, alkalinity, orthophosphate or silica,[b] and calcium[c]	Taps	Every six months
	pH, alkalinity, dosage rate and concentration (if alkalinity is adjusted as part of corrosion control), inhibitor dosage rate and inhibitor residual[d]	Entry point(s) to the distribution system	Biweekly
Reduced monitoring	pH, alkalinity, orthophosphate or silica,[b] and calcium	Taps[e,f]	Every six months
	pH, alkalinity dosage rate and concentration (if alkalinity is adjusted as part of corrosion control), inhibitor dosage rate and inhibitor residual[d]	Entry point(s) to the distribution system	

[a] Small and medium-size systems have to monitor water quality only during monitoring periods in which the system exceeds the lead or copper action level. Large systems must monitor water quality during each monitoring period.

[b] Orthophosphate must be measured only when an inhibitor containing a phosphate compound is used. Silica must be measured only when an inhibitor containing silicate compound is used.

[c] Calcium must be measured only when calcium carbonate stabilization is used as part of corrosion control.

[d] Inhibitor dosage rates and inhibitor residual concentrations (orthophosphate or silica) must be measured only when an inhibitor is used.

[e] Systems maintaining optimal corrosion control treatment specified by the state for two consecutive six-month monitoring periods may reduce tap water quality monitoring to once a year and collect the reduced number of samples indicated in Table 1.14.

[f] Systems maintaining optimal corrosion control treatment specified by the state for three consecutive years may reduce tap water quality monitoring to once every three years and collect the reduced number of samples indicated in Table 1.14.

Table 1.14. Tap Sampling Requirements for Water Quality (Other than Lead and Copper).[55]

System Size Population	Number of Sampling Sites Initial Base Monitoring	Sampling Sites Reduced Monitoring
>100,000	25	10
10,001 to 100,000	10	7
3,301 to 10,000	3	3
501 to 3,300	2	2
101 to 500	1	1
100	1	1

Table 1.15. Public Education Program Requirements.[55]

		Actions Required	
System	**Condition**	**Within 60 Days**	**Repeat Frequency**
Community water	Fails to meet lead action level[a]	1. Insert notices containing all of the mandatory written language and mandatory alert language	Every 12 months as long as lead action level is exceeded
		2. Submit all of the mandatory written language to major daily and weekly newspapers.	Every 12 months as long as lead action level is exceeded
		3. Delivery pamphlets and/or brochures containing the mandatory written language on the health effects of lead and steps that can be taken in the home to reduce exposure to lead in drinking water to the following: • public schools and/or local school boards • city or county health department • women, infants, and children and/or Head Start program(s) whenever available • public and private hospitals and/or clinics • pediatricians • family planning clinics • local welfare agencies	Every 12 months as long as lead action level is exceeded
		4. Submit the mandatory public service announcement to at least five of the radio and television stations that reach the largest audiences in the community served.	Every six months as long as lead action level is exceeded
	Meets the lead action level during the most recent six-month monitoring period	No actions required	No actions required
Nontransient, noncommunity systems	Fails to meet lead action level[a]	Deliver educational materials containing the mandatory written language on background information, health effects of lead, and steps that can be taken in the home to reduce exposure to lead in drinking water by: • placing informational posters in a public place or common area in each of the buildings served by the system • distributing informational pamphlets and/or brochures on lead in drinking water to each person served by the system	At least once each calendar year that the system exceeds the action level
	Meets the lead action level during the most recent six-month monitoring period	No actions required	No actions required

[a] A water system failing to meet the lead action level must offer to sample the tap water of any customer who requests it. The system is not required to pay for collecting or analyzing the sample, nor is the system required to collect and analyze the sample itself.

MCLG of zero.[57] Epidemiologic studies indicate a significant health risk of 10^{-4} cancer risk at about 0.002 mg/L.[57] In any event, the MCL must be set as close to the MCLG as feasible, using best available technology and taking cost into consideration. Several scenarios for setting the MCL are possible. If BATs can lower arsenic contents (see Chapter 9) to below the practical quantitation level (PQL), then the MCL will be set at the PQL of 0.002 mg/L.[55] However, if the individual cancer risk greatly exceeds 1 in 10,000 at the PQL, then the USEPA would have to specify a treatment technique to lower concentration to be within the agency's range of acceptable risk. The SDWA amendment mandates the proposal of arsenic MCL by January 1, 2000, which must be promulgated by January 1, 2001.

USEPA Secondary Drinking Water Regulations

Table 1.8 lists those contaminants that may adversely affect the aesthetic quality (taste, odor, and appearance) of drinking water. Secondary maximum contaminant levels (SMCLs) are given for each constituent. These are not enforceable by the federal government, but states are encouraged to adopt and enforce them. Apparently there is some latitude in these standards, since states may establish higher or lower levels that depend on "local conditions," provided that public health and welfare are not affected adversely. It should be noted that hexachlorocyclopentadiene has a proposed SMCL of 0.008 mg/L, which is, presumably, due to a taste or odor in drinking water. This compound also has an MCL of 0.05 mg/L (Table 1.7).

INTERNATIONAL DRINKING WATER QUALITY REGULATIONS

Canadian Drinking Water Guidelines

A shared federal-provincial responsibility for drinking water quality occurs in Canada. Generally, provincial governments are responsible for adequacy and safety of water supplies, whereas the Federal Department of National Health and Welfare develops quality guidelines and conducts research. Guidelines for Canadian drinking water quality are developed jointly through a federal-provincial mechanism. These guidelines are not legally enforceable unless promulgated as regulations by the appropriate provincial agency. The current guidelines were revised in 1989[58] and are listed in Table 1.16.

World Health Organization (WHO) Guidelines

The WHO's Guidelines for Drinking Water Quality is concerned mostly with the protection of public health throughout the world.[59] Hopefully, this will eliminate or reduce to a minimum those constituents in drinking water that are known to be hazardous to the health and well-being of a community and/or country. Tables 1.17 to 1.21 present a summary of these guideline values. WHO's intent is that individual values should not be used directly from these tables. Rather, these values should be used and interpreted from the information contained in Chapters 2 to 5 in Reference 59 and, of course, within national policies and authorities of the various countries.

European Economic Community (EEC) Drinking Water Directives

The EEC issued a council directive in 1980 that related to water quality intended for human consumption.[60] The EEC directive provided for the establishment of standards for toxic chemicals and bacteria that present a human health hazard, as well as the definition of physical, chemical, and biological parameters for various uses of water, including human consumption. Member states of the EEC were directed to initiate laws, regulations, and administrative provisions for compliance with the directives on water standards (Table 1.22) by July 1985.[61]

CONTAMINANT REMOVAL EFFECTIVENESS

A list of contaminants, water treatment processes, and a range of removal efficiencies is given in Table 1.23.[62] Contaminants are grouped as primary, secondary, and proposed regulations. Subjectively, the removal efficiencies are rated on a percentage basis. This table of information is offered as a general guideline for, perhaps, selection of a water treatment process for a specific and/or a group of contaminants. There are a number of factors that influence removal efficiencies. A particular treatment process may not be effective in and of itself for removal of a contaminant. However, many of the processes are employed together in a sequence in a treatment plant that may achieve effective removal. Nonetheless, the reader will have a general idea of the capabilities of various processes. More detailed information is given in subsequent chapters through case studies of various treatment scenarios.

Table 1.16. Canadian Drinking Water Quality Guidelines.[a]

Microbiological Characteristics

1. No sample should contain more than 10 total coliform organisms per 100 mL, none of which should be fecal coliforms; and
2. No consecutive samples from the same site should show the presence of coliform organisms; and
3. For community drinking water supplies:
   (a) not more than 10 percent of the samples based on a minimum of 10 samples should show the presence of coliform organisms; and
   (b) not more than one sample from a set of samples taken from the community on a given day should show the presence of coliform organisms.

Turbidity

The maximum acceptable concentration for turbidity is 1 ntu for water entering a distribution system. A maximum of 5 ntu may be permitted if it can be demonstrated that disinfection is not compromised by the use of this less stringent value. An aesthetic objective of 5 ntu has been set for the point of consumption.

Chemical and Physical Characteristics[b]

Parameter	MAC[c]	IMAC[c]	AO[c]	Status
Aldicarb	0.009			
Aldrin + dieldrin	0.0007			Under review
Ammonia[d]				Proposed
Arsenic[e]	0.025			
Asbestos[d]				
Atrazine		0.06		
Azinphos-methyl	0.02			
Barium		1.0		Proposed
Bendiocarb	0.04			
Benzene	0.005			
Benzo(a)pyrene	0.00001			Under review
Boron	5.0			
Bromoynil		0.005		
Cadmium	0.005			
Calcium[d]				Proposed
Carbaryl	0.09			
Carbofuran	0.09			
Carbon tetrachloride	0.005			
Chlordane	0.007			Under review
Chloride			≤250	Proposed
Chlorpyrifos	0.09			
Chromium	0.05			
Color			≤15 tcu[f]	
Copper			≤1.0	
Cyanazine		0.1		
Cyanide	0.2			Under review
Diazinon	0.2			
Dicamba	0.12			
1,2-Dichlorobenzene	0.2		≤0.003	
1,4-Dichlorobenzene	0.005		≤0.001	
Dichlorodiphenyltrichloroethane (DDT) + metabolites	0.03			Under review
1,2-Dichloroethane		0.005		Proposed
Dichloromethane	0.05			
2,4-Dichlorophenol	0.9		≤0.0003	
Dichlorophenoxyacetic acid, 2,4-(2,4-D)	0.1			Under review
Diclofop-methyl	0.009			
Dimethoate		0.02		
Diquat	0.07			
Diuron	0.15			
Ethylbenzene			≤0.0024	
Fluoride	1.5			Under review

Table 1.16. Canadian Drinking Water Quality Guidelines[a] (Continued).

Chemical and Physical Characteristics[b]

Parameter	MAC[c]	IMAC[c]	AO[c]	Status
Gasoline[d]				
Glyphosate		0.28		
Heptachlor + heptachlorepoxide	0.003			Under review
Iron			≤0.3	Proposed
Lead	0.01			Proposed
Lindane	0.004			Under review
Magnesium[d]				Proposed
Malathion	0.19			
Manganese			≤0.05	Proposed
Mercury	0.001			
Methoxychlor	0.9			
Metolachlor		0.05		
Metribuzin	0.08			
Monochlorobenzene	0.08		≤0.03	Proposed
Nitrate	45.0			Proposed
Nitrilotriacetic acid (NTA)[e]	0.40			
Odor			Inoffensive	
Paraquat		0.01		
Parathion	0.05			
Pentachlorophenol	0.06		≤0.03	
pH			6.5–8.5	
Phorate		0.002		
Picloram		0.19		Proposed
Selenium	0.01			
Simazine		0.01		
Sodium			≤200	Proposed
Sulfate			≤500	Proposed
Sulfide (as H_2S)			<0.05	Proposed
Taste			Inoffensive	
Temephos		0.28		
Temperature			≤15°C	
Terbufos		0.001		
2,3,4,6-Tetrachlorophenol	0.1		≤0.001	
Toluene			≤0.024	
Total dissolved solids			≤500	Under review
Triallate	0.23			
Trichloroethylene	0.05			Proposed
2,4,6-Trichlorophenol	0.005		≤0.002	
2,4,5-(2,4,5-T)-Trichlorophenoxyacetic acid	0.28		≤0.02	
Trifluralin		0.045		Proposed
Trihalomethanes	0.35			Under review
Turbidity	1 ntu		≤5 ntu	
Uranium	0.1			
Xylenes			≤0.3	
Zinc			≤5.0	Proposed

[a] *Guidelines for Canadian Drinking Water Quality.* Health and Welfare Canada, Ottawa (4th ed., 1989).

[b] Units are given in milligrams per litre unless otherwise noted.

[c] MAC = maximum acceptable concentration, IMAC = interim maximum acceptable concentration, AO = aesthetic objective.

[d] Data indicate no need to set numerical guideline.

[e] New limit approved since publication of 1989 guidelines.

[f] tcu = true color unit.

Table 1.17. World Health Organization Guidelines for Microbiological and Biological Quality.[59]

Organism	Unit	Guideline Value	Remarks
I. Microbiological Quality			
A. Piped Water Supplies			
A.1. Treated water entering the distribution system			
Fecal coliforms	number/100 mL	0	Turbidity <1 ntu; for disinfection with chlorine, pH preferably <8.0; free chlorine residual 0.2–0.5 mg/L following 30 min (minimum) contact
Coliform organisms	number/100 mL	0	
A.2. Untreated water entering the distribution system			
Fecal coliforms	number/100 mL	0	
Coliform organisms	number/100 mL	0	In 98% of samples examined throughout the year—in the case of large supplies when sufficient samples are examined
Coliform organisms	number/100 mL	3	In an occasional sample, but not in consecutive samples
A.3. Water in the distribution system			
Fecal coliforms	number/100 mL	0	
Coliform organisms	number/100 mL	0	In 95% of samples examined throughout the year—in the case of large supplies when sufficient samples are examined
Coliform organisms	number/100 mL	3	In an occasional sample, but not in consecutive samples
B. Unpiped Water Supplies			
Fecal coliforms	number/100 mL	0	
Coliform organisms	number/100 mL	10	Should not occur repeatedly; if occurrence is frequent and if sanitary protection cannot be improved, an alternative source must be found if possible
C. Bottled Drinking Water			
Fecal coliforms	number/100 mL	0	Source should be free from fecal contamination
Coliform organisms	number/100 mL	0	
D. Emergency Water Supplies			
Fecal coliforms	number/100 mL	0	Advise public to boil water in case of failure to meet guideline value
Coliform organisms	number/100 mL	0	
Enteroviruses		NGV[a]	
II. Biological Quality			
A. Protozoa (pathogenic)		NGV[a]	
B. Helminths (pathogenic)		NGV[a]	
C. Free-living organisms (algae, others)		NGV[a]	

[a] NGV = no guideline value set.

Table 1.18. World Health Organization Guidelines for Inorganic Constituents of Health Significance.[59]

Constituent	Guideline Value[a]	Remarks
Arsenic	0.05	
Asbestos	NGV[b]	
Barium	NGV	
Beryllium	NGV	
Cadmium	0.005	
Chromium	0.05	
Cyanide	0.1	
Fluoride	1.5	Includes both natural fluoride and deliberately added fluoride. Local or climatic conditions may necessitate adaptation.
Hardness	NGV	
Lead	0.05	
Mercury	0.001	
Nickel	NGV	
Nitrate	10	
Nitrite	NGV	
Selenium	0.01	
Silver	NGV	
Sodium	NGV	

[a] All values are in mg/L.

[b] NGV = No guideline value set.

Table 1.19. World Health Organization Guidelines for Organic Constituents of Health Significance.[59]

Constituent	Guideline Value[a]	Remarks
Aldrin and dieldrin	0.03	
Benzene	10[b]	
Benzo(a)pyrene	0.01[b]	
Carbon tetrachloride	3[b]	Tentative guideline value[c]
Chlordane	0.3	
Chlorobenzenes	NGV[d]	Odor threshold concentration between 0.1 and 3 μg/L
Chloroform	30[b]	Disinfection efficiency must not be compromised when controlling chloroform content
Chlorophenols	NGV	Odor threshold concentration 0.1 μg/L
2,4-D	100[e]	
DDT	1	
1,2-Dichloroethane	10[b]	
1,1-Dichloroethene	0.3[b]	
Heptachlor and heptachlor epoxide	0.1	
Hexachlorobenzene	0.01[b]	
Gamma-HCH (lindane)	3	
Methoxychlor	30	
Pentachlorophenol	10	
Tetrachloroethane[f]	10[b]	Tentative guideline value[c]
Trichloroethane[f]	30[b]	Tentative guideline value[c]
2,4,6-Trichlorophenol	10[b,e]	Odor threshold concentration, 0.1 μg/L
Trihalomethanes	NGV	

[a] All values are in μg/L.

[b] These guideline values were computed from a conservative hypothetical mathematical model which cannot be experimentally verified, and values should therefore be interpreted differently. Uncertainties involved may amount to two orders of magnitude (i.e., from 0.1 to 10 times the number).

[c] When the available carcinogenicity data did not support a guideline value, but the compounds were judged to be of importance in drinking water and guidance was considered essential, a tentative guideline value was set on the basis of the available health-related data.

[d] NGV = No guideline value set.

[e] May be detectable by taste and odor at lower concentrations.

[f] These compounds were previously known as 1,1-dichloroethylene, tetrachloroethylene, and trichloroethylene, respectively.

Table 1.20. World Health Organization Guidelines for Aesthetic Quality.[59]

Constituent	Guidelines Value[a]	Remarks
Aluminum	0.2	
Chloride	250	
Chlorobenzenes and chlorophenols	NGV[b]	These compounds may affect taste and odor
Color	15 tcu[c]	
Copper	1.0	
Detergents	NGV	There should not be any foaming, taste, or odor problem
Hardness	500 (as $CaCO_3$)	
Hydrogen sulfide	Not detectable by consumers	
Iron	0.3	
Manganese	0.1	
Oxygen, dissolved	NGV	
pH	6.5–8.5	
Sodium	200	
Solids, total dissolved	1000	
Sulfate	400	
Taste and odor	Inoffensive to most consumers	
Temperature	NGV	
Turbidity	5 ntu[d]	Preferable <1 for disinfection efficiency
Zinc	5.0	

[a] Unless otherwise specified, all units are mg/L.
[b] NGV = No guideline value set.
[c] ntu = nephelometric turbidity unit.
[d] tcu = true color unit.

Table 1.21. World Health Organization Guidelines for Radioactive Constituents.[59]

Constituents	Guideline Value[a]	Remarks
Gross alpha activity	0.1	If the levels are exceeded, more detailed radionuclide analysis may be necessary.
Gross beta activity	1	Higher levels do not necessarily imply that the water is unsuitable for human consumption.

[a] Units are Bq/L.

Table 1.22. EC Drinking Water Directive—List of Parameters.[61]

Parameter	Unit of Measurement	Guide Level (GL)	Maximum Admissible Concentration (MAC)	Comments
Organoleptic				
Color	mg/L, Pt-Co scale	1	20	
Turbidity	mg SiO_2/L	1	10	
Odor	Dilution number	0	2 at 12°C 3 at 25°C	To be related to the taste tests
Taste	Dilution number	0	3 at 12°C 3 at 25°C	To be related to the odor tests
Physicochemical				
Temperature	°C	12	25	
Hydrogen ion	pH unit	6.5–8.5		Maximum admissible value 9.5
Conductivity	μS/cm at 20°C	400		
Chlorides	mg Cl/L	25		
Sulfates	mg SO_4/L	25	250	
Silica	mg SiO_2			
Calcium	mg Ca/L	100		
Magnesium	mg Mg/L	30	50	
Sodium	mg Na/L	20		
Potassium	mg K/L	10	12	
Aluminum	mg Al/L	0.05	0.2	
Total hardness				See lower portion of table
Dry residue	mg/L after drying at 180°C		1,500	
Dissolved oxygen	Percent O_2 saturation			
Free carbon dioxide	mg CO_2/L			
Substances undesirable in excessive amounts				
Nitrates	mg NO_3/L	25	50	
Nitrites	mg NO_2/L		0.1	
Ammonium	mg NH_4	0.05	0.5	
Kjeldahl nitrogen	mg N/L		1	Excluding N in NO_2 and NO_3
Potassium permanganate oxidizability	mg O_2/L	2	5	Measured when heated in acid medium
Total organic carbon (TOC)	mg C/L			The reason for any increase in the usual concentration must be investigated.
Hydrogen sulfide	μg S/L		Undetectable organoleptically	
Substances extractable in chloroform	mg/L dry residue	0.1		
Dissolved or emulsified hydrocarbons, mineral oils	μg/L		10	After extraction by petroleum ether
Phenols (phenol index)	μg C_6H_5OH/L		0.5	Excluding natural phenols that do not react with chlorine

Boron	µg B/L	1,000		
Surfactants (reacting with methylene blue)	µg/L (lauryl sulfate)		200	
Organochlorine compounds not covered by pesticides and related products				Haloform concentrations must be as low as possible.
Iron	µg Fe/L	50	200	
Manganese	µg Mn/L	20	50	
Copper	µg Cu/L	100	At plant	Above 3,000 µg/L, astringent taste, discoloration, and corrosion may occur.
		3,000	At supply point	
Zinc	µg Zn/L	100	At plant	Above 5,000 µg/L, astringent taste, discoloration, and corrosion may occur.
		5,000	At supply point	
Phosphorus	µg P_2O_5/L	400	5,000	
Fluoride	µg F/L			
	8–12°C		1,500	MAC varies according to average temperature in geographical area concerned.
	25–30°C		700	
Cobalt	µg Co/L			
Suspended solids		None		
Residual chlorine	µg Cl/L			
Barium	µg Ba/L	100		
Silver	µg Ag/L	10		If silver is used nonsystematically to process the water, a MAC value of 80 µg/L may be authorized.
Toxic substances				
Arsenic	µg As/L		50	
Beryllium	µg Be/L			
Cadmium	µg Cd/L		5	
Cyanides	µg CN/L		50	
Chromium	µg Cr/L		50	
Mercury	µg Hg/L		1	
Nickel	µg Ni/L		50	
Lead	µg Pb/L		50 (in running water)	
Antimony	µg Sb/L		10	
Selenium	µg Se/L		10	
Vanadium	µg V/L			
Pesticides and related products	µg/L			Pesticides and related products means insecticides, herbicides, fungicides, PCBs, and PCTs,
Separate			0.1	
Total			0.5	
Polycyclic aromatic hydrocarbons	µg/L		0.2	

Table 1.22. EC Drinking Water Directive—List of Parameters[61] (Continued).

Parameter	Volume of Sample mL	Guide Level (GL)	Maximum Admissible Concentration (MAC) Membrane Filter Method	Maximum Admissible Concentration (MAC) Multiple Tube Method (MPN)
Microbiological				
Total coliforms[a]	100		0	MPN <1
Fecal coliforms	100		0	MPN <1
Fecal streptococci	100		0	MPN <1
Sulfite-reducing *Clostridia*	20			MPN ≤1
Total bacteria counts for water supplied for human consumption				
37°C	1		10	
22°C	1		10	
Total bacteria counts for water in closed containers				
37°C	1		5	
22°C	1		20	

Parameter	Unit of Measurement	Minimum Required Concentration	Comments
Softened water intended for human consumption[b]			
Total hardness	mg Ca/L	60	Calcium or equivalent cations
Hydrogen ion	pH		The water should not be aggressive.
Alkalinity	mg HCO_3/L	30	The water should not be aggressive.
Dissolved oxygen			The water should not be aggressive.

[a] Provided a sufficient number of samples is examined (95% consistent results)

[b] If, owing to its excessive natural hardness, the water is softened before being supplied for consumption, its sodium content may, in exceptional cases, be higher than the values given in the MAC column. An effort must be made to keep the sodium content as low as possible, and the essential requirements for the protection of public health may not be disregarded.

Table 1.23. General Effectiveness of Water Treatment Processes for Contaminant Removal.[62]

Contamination Categories	Aeration and Stripping	Coagulation Processes, Sedimentation, Filtration	Lime Softening	Ion Exchange		Membrane Processes			Chemical Oxidation Disinfection	Adsorption		
				Anion	Cation	Reverse Osmosis	Ultra Filtration	Electro-dialysis		GAC	PAC	Activated Alumina
A. Primary contaminants												
1. Microbial and turbidity												
Total coliforms	P	G–E	G–E	P	P	E	E	—	E	F	P	P–F
Giardia lamblia	P	G–E	G–E	P	P	E	E	—	E	F	P	P–F
Viruses	P	G–E	G–E	P	P	E	E	—	E	F	P	P–F
Legionella	P	G–E	G–E	P	P	E	E	—	E	P	P	P–F
Turbidity	P	E	G	F	F	E	E	—	P	F	P	P–F
2. Inorganics												
Arsenic (+3)	P	F–G	F–G	G–E	P	F–G	—	F–G	P	F–G	P–F	G–E
Arsenic (+5)	P	G–E	G–E	G–E	P	G–E	—	G–E	P	F–G	P–F	E
Asbestos	P	G–E	—	—	—	—	—	—	P	—	—	—
Barium	P	P–F	G–E	P	E	E	—	G–E	P	P	P	P
Cadmium	P	G–E	E	P	E	E	—	E	P	P–F	P	P
Chromium (+3)	P	G–E	G–E	P	E	E	—	E	F	F–G	F	P
Chromium (+6)	P	P	P	E	P	G–E	—	G–E	P	F–G	F	P
Cyanide	P	—	—	—	—	G	—	G	E	—	—	—
Fluoride	P	F–G	P–F	P–F	P	E	—	E	P	G–E	P	E
Lead	P	E	E	P	F–G	E	—	E	P	F–G	P–F	P
Mercury (inorganic)	P	F–G	F–G	P	F–G	F–G	—	F–G	P	F–G	F	P
Nickel	P	F–G	E	P	E	E	—	E	P	F–G	P–F	P
Nitrate	P	P	P	G–E	P	G	—	G	P	P	P	P
Nitrite	F	P	P	G–E	P	G	—	G	G–E	P	P	P
Radium (226 and 228)	P	P–F	G–E	P	E	E	—	G–E	P	P–F	P	P–F
Selenium (+6)	P	P	P	G–E	P	E	—	E	P	P	P	G–E
Selenium (+4)	P	F–G	F	G–E	P	E	—	E	P	P	P	G–E
3. Organics												
VOCs	G–E	P	P–F	P	P	F–E	F–E	F–E	P–G	F–E	P–G	P
SOCs	P–F	P–G	P–F	P	P	F–E	F–E	F–E	P–G	F–E	P–E	P–G
Pesticides	P–F	P–G	P–F	P	P	F–E	F–E	F–E	P–G	G–E	G–E	P–G
THMs	G–E	P	P	P	P	F–G	F–G	F–G	P–G	F–E	P–F	P
THM precursors	P	F–G	P–F	F–G	—	G–E	F–E	G–E	F–G	F–E	P–F	P–F

Table 1.23. General Effectiveness of Water Treatment Processes for Contaminant Removal[62] (Continued).

				Ion Exchange		Membrane Processes				Adsorption		
Contamination Categories	Aeration and Stripping	Coagulation Processes, Sedimentation, Filtration	Lime Softening	Anion	Cation	Reverse Osmosis	Ultra Filtration	Electro-dialysis	Chemical Oxidation Disinfection	GAC	PAC	Activated Alumina
B. Secondary contaminants												
Hardness	P	P	E	P	E	E	G–E	E	P	P	P	P
Iron F–G	F–E	E	P	G–E	G–E	G	G–E	G–E	P	P	P	
Manganese	P–F	F–E	E	P	G–E	G–E	G	G–E	F–E	P	P	P
Color P	F–G	F–G	P–G	—	—	—	—	F–E	E	G–E	G	
Taste and odor	F–E	P–F	P–F	P–G	—	—	—	—	F–E	G–E	G–E	P–F
Total dissolved solids	P	P	P–F	P	P	G–E	P–F	G–E	P	P	P	P
Chloride	P	P	P	F–G	P	G–E	P	G–E	P	P	P	—
Copper	P	G	G–E	P	F–G	E	—	E	P–F	F–G	P	—
Sulfate	P	P	P	G–E	P	E	P	E	P	P	P	G–E
Zinc P	F–G	G–E	P	G–E	E	—	E	P	—	—	—	
TOC F	P–F	G	—	G–E	G	G–E	P–G	G–E	F	F–G	—	
Carbon dioxide	G–E	P–F	E	P	P	P	P	P	P	P	P	P
Hydrogen sulfide	F–E	P	F–G	P	P	P	P	P	F–E	F–G	P	P
Methane	G–E	P–E	P	P	P	P	P	P	P	P	P	P
C. Proposed contaminants												
VOCsG–E	P	P–F	P	P	F–E	F–E	F–E	P–G	F–E	P–G	P	
SOCsP–F	P–G	P–F	P	P	F–E	F–E	F–E	P–G	F–E	P–E	P–G	
Disinfection by-products	—	P–E	P–F	P–F	—	P	F–G	F–G	F–G	F–E	F–G	—
Radon	G–E	P	P	P	P	P	P	P	P	E	P–F	P
Uranium	P	G–E	G–E	E	G–E	E	—	E	P	F	P–F	G–E
Aluminum	P	F	F–G	P	G–E	E	—	E	P	—	—	—
Silver F–G	G–E	P	G	—	—	—	P	F–G	P–F	—	—	

P—poor (0 to 20% removal); F—fair (20 to 60% removal); G—good (60 to 90% removal); E—excellent (90 to 100% removal); "—"—not applicable/insufficient data.
Note: Costs and local conditions may alter a process's applicability.

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Chapter 2

Organic Compounds in Raw and Finished Waters

2

Organic Compounds in Raw and Finished Waters

THE NATURE AND TYPES OF ORGANIC POLLUTANTS

Much concern has been expressed about the introduction and subsequent distribution of organic compounds throughout the environment, especially those from anthropogenic sources. This chapter examines the nature and types of organic pollutants in raw and finished waters. Some insight may be derived into the occurrence and distribution of organic compounds throughout various natural aquatic systems to determine whether they are hazardous or damaging to the environment, as well as whether they need to be removed.

The synthetic organic compound and/or its derivative probably enters natural aquatic environments concurrently with the development of its initial manufacturing process. Waste disposal problems undoubtedly lead to its discharge into a river or some other body of water. There is some evidence in the scientific literature that potable, recreational, irrigational, fish, and shellfish waters are contaminated with foreign organic compounds. Much of the early evidence was largely circumstantial, as observed from physiological responses of various aquatic organisms. The advent of chromatographic separation procedures and of the confirmatory procedures—nuclear magnetic resonance and mass spectrometry—has led to positive identification of organic compounds in aquatic environments and in the attendant solid phases of bottom sediments.

Many newspaper headlines and television programs have featured the "discovery" of low-molecular-weight halogenated hydrocarbons in drinking water.[1] It was charged that these organic compounds, especially trichloromethane (chloroform), were formed in the chlorination process for disinfection. Furthermore, it was suggested that some of these organic compounds may be physiologically harmful to humans because chloroform, for example, may be carcinogenic to laboratory animals—in this case, mice.

Numerous publications have documented, to some extent, the occurrence of organic compounds in aquatic environments.[2] These include the naturally occurring organics of color bodies,[3] polynuclear aromatic hydrocarbons (PAH),[3] and synthetic compounds such as pesticides,[4] detergents, polychlorinated biphenyls,[5] petrochemicals, and halogenated hydrocarbons.[6] In addition to these reports, the USEPA has conducted several national surveys of public water systems for organic compounds: National Organics Reconnaissance Survey (1975),[7] National Organics Monitoring Survey (1976–1977),[8] National Screening Program for Organics (1977–1981),[9] the National Pesticides Survey,[10] and the Ground Water Supply Survey (1980–1981).[11] These surveys provide data for regulation of organic compounds for the Safe Drinking Water Acts of 1974 and 1986 (see Chapter 1). The sources and origins of these compounds are many, diverse, and reasonably well known. Consideration is given here to some of the more significant compounds and their occurrences in potable water supplies.

OCCURRENCES

Volatile Organic Chemicals—Phase I

The SDWA amendments of 1986 have regulated and have established MCLGs and MCLs for eight volatile organic chemicals (Tables 1.4 and 1.7). In addition, all systems must monitor for 34 VOCs (Table 1.4, list 1), for two compounds, ethylene dibromide (EDB) and 1,2-dibromo-3-chloropropane (DBCP) (Table 1.4, list 2), if systems are vulnerable to possible contamination, and for 15 other VOCs (Table 1.4, list 3) at the state's discretion. Most of these compounds have, of course, been isolated and identified in raw and finished drinking waters throughout the United States.

Evidence for the occurrence of VOCs in water supplies was accumulated in the late 1960s and early 1970s. For example, Table 2.1 shows several low-molecular-weight and volatile organic compounds that were isolated and identi-

Table 2.1. Compounds Identified from Finished Water.[12,13]

Acetone
Acetophenone
Acetylenedichloride
Benzene
Benzothialzole
Bromobenzene
Bromochlorobenzene
Bromodichloromethane
Bromoform
Bromophenylphenylether
Butylbenzene
Camphanol
Camphor
Caprolactam
Carbon tetrachloride
Chlorobenzene
Chlorodibromomethane
Chloroethoxyether
Chloroethylether
Chloroform
Chlorohydroxybenzophenone
bis-(2-Chloroisopropyl) ether
Choromethylether
Chloronitrobenzene
Chloropyridine
Chloromethylethylether
Dibromobenzene
Dichloroethane
Dichloroethylether
Dimethoxybenzene
Dimethylnaphthalene
Dimethylsulfoxide
Dinitrotoluene
Ethylbenzene
Ethylenedichloride
Exo-2-camphanol
Hexachlorobenzene
Hexachloroethane
Hydroxyadiponitrile
Isoborneol
Isocyanic acid
Isopropanyl-isopropylbenzene
Isopropylbenzene
p-Menth-1-en-8-ol
o-Methoxyphenol
2-Methoxybiphenyl
Methylbenzothiazole
Methylbiphenyl
Methylchloride
Nitroanisole
Nitrobenzene
Octane
Pentane
Propylbenzene
Styrene
Tetrachloroethylene
Toluene
Trichloroethane
Triglycodichloride
Thiomethylbenzothiazole
Vinylbenzene
Xylene

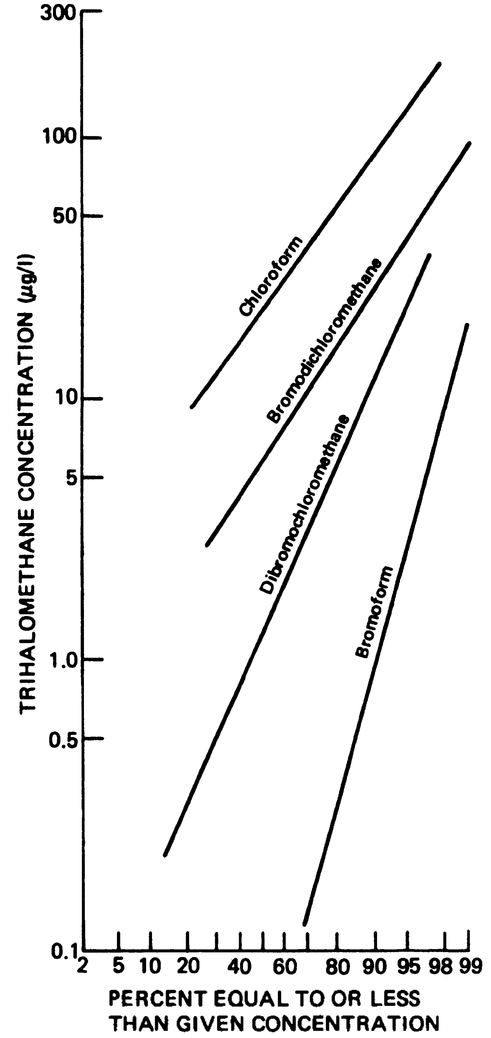

Figure 2.1. Frequency distribution of halogenated methane concentrations found in the NORS study of drinking water in 80 U.S. cities.[7]

fied from a finished municipal water supply on the Ohio River prior to 1974.[12,13] In another survey, chloroform (94.0 µg/L), bromodichloromethane (20.8 µg/L), dibromochloromethane (2.0 µg/L), and ethyl alcohol were recovered and identified in a finished drinking water by gas-liquid chromatographic/mass spectrometric techniques.[14] Also, chloroform was found in the raw water source at a rather constant value (with time), 0.9 ± 0.2 µg/L. Similar results and compounds were reported for the drinking water of New Orleans, Louisiana.[15,16] In addition, five halogenated hydrocarbons were isolated from blood plasma pooled from eight humans: l-chloropropene, chloroform, carbon tetrachloride, dichloroethane, trichloroethylene, dichloropropane, bromodichloromethane, tetrachloroethylene, and dibromochloromethane. Three isomers of dichlorobenzene were found also in the blood plasma. Speculation was offered that drinking water was the source of the halogenated hydrocarbons.

The reports cited above undoubtedly prompted the U.S. Environmental Protection Agency to conduct a nationwide survey of "the concentration and potential effects of certain organic chemicals in drinking water."[7] This resulted in a National Organics Reconnaissance Survey (NORS) for chloroform, dibromochloromethane, bromodichloromethane, and bromoform (the trihalomethane (THM) and carbon tetrachloride in 80 surface and groundwater supplies throughout the United States. (See Figure 2.1.) In general, these five compounds were not detected in all of the raw waters. However, many finished waters contained one or more of the four THMs. Consequently, it was concluded that their occurrence was caused by chlorination practices, and their concentrations were related to the organic content of the raw water. When detected, the THMs were present at less than 4.0 µg/L in the raw water.

Results of the NORS study for finished waters are summarized in Table 2.2,[7] where the frequency distributions are given for the four THMs. Generally, the following con-

Table 2.2. Results of NORS Study for Finished Waters.

Compound (μg/L)	Number of Cities with Positive Results	Concentration Minimum	 Median	 Maximum
Chloroform	<0.1	21.0	311	
Bromodichloromethane	78	0.3	6.0	116
Dibromochloromethane	72	<0.4	1.2	110
Bromoform	<0.8	[a]	92	
Carbon Tetrachloride	10	<2.0		3

[a] 93.8% of 80 cities had ≤5 μg/L bromoform.

ditions produce the highest concentrations of THM: surface water as the source, prechlorination and the presence of more than 0.4 μg/L of free chlorine. Obviously, this study focused on the relevant water treatment practices producing the THMs.

As part of the NORS of drinking water supplies, there was also a detailed study of the occurrence of volatile organics in drinking waters of five cities: Miami, Seattle, Ottumwa (Iowa), Philadelphia, and Cincinnati.[18,19] Altogether, there were 72 volatile compounds found in the finished water, with the following common to five cities:[19]

acetaldehyde
bromodichloromethane
2-butanone
chlorodibromomethane
chloromethane
dichloromethane
ethanol
3-methylbutanal
3-methyl-2-butanone
2-methylpropanal
propanal
2-propanone (acetone)
trichloromethane

Their concentrations and the standard deviations of the organics are seen Table 2.3.[18] It is doubtful that these compounds resulted from chlorination practices; rather, they may have originated from anthropogenic sources and were not removed by treatment.

On November 29, 1979, the THM MCL of 0.1 mg/L was promulgated by the USEPA (Reference 13, Chapter 1). This MCL was retained in the 1986 amendments to the SDWA on an interim basis (Table 1.7). In the mid-1980s, a national survey was conducted by the Metropolitan Water District of Southern California and Decision Research under partial funding by the AWWA Research Foundation (AWWARF). This was a survey of THMs in drinking water, and determined the extent and costs of compliance with the existing THM regulation.[19a] A questionnaire was prepared and mailed to 1,255 water utilities that served more than 10,000 customers. The essential results of the AWWARF survey, seen in Table 2.4, are compared to two previous surveys by the USEPA: the NORS of 1975[7] and the NOMS of 1976–1977.[8] A comparison of the AWWARF's overall THM average of 42 μg/L with the averages of the NORS and NOMS (all phases) shows a 40–50% reduction in national THM concentrations as a result of compliance with the THM regulation. One of the issues here is the cost of compliance to a THM standard. This survey revealed that compliance with the 0.10 mg/L MCL was not particularly costly for water utilities, but lowering the MCL significantly below 50 μg/L would cause large numbers of utilities to exceed the MCL, and would require billions of dollars of capital expenditures to bring those utilities into compliance.[19a]

Additional evidence for the occurrences and distribution of VOCs in drinking water supplies came from the 1982 Ground Water Supply Survey (GWSS).[11] In this survey, 500 water supplies were selected at random throughout the United States, and another 500 supplies having a high potential for contamination by organics were selected by states on a nonrandom basis. Concentrations of 29 VOCs in addition to five trihalomethanes and TOC were measured. The five most frequently found compounds other than the THMs were: trichloroethylene, 1,1,1-trichloroethane, tetrachloroethylene, *cis*- and/or *trans*-1,2-dichloroethylene, and 1,1-dichloroethane. Tables 2.5 and 2.6 show the results of the nonrandom samples, where nearly 25% of the large systems and 7% of the small systems were contaminated with trichloroethylene. Noteworthy is the observation that the THMs occurred with more frequency in the smaller systems (Table 2.5) than in the larger systems. On the other hand, the highest THM contents were found in the larger systems (Table 2.6). All of this does, indeed, indicate that VOC contamination of groundwater supplies in the United States is widespread, and that significant numbers of people were exposed to VOC contents greater than their individual MCLs.

Synthetic Organic Chemicals—Phases II, V, and VIb

There are 19 synthetic organic chemicals on the Phase II list (Table 1.4) that received their final MCLGs and MCLs in early 1991 and that became effective in mid-1992 (Table 1.7). Also, there are 25 additional SOCs that must be monitored (unless the system is not vulnerable) under Phase II. Most of these 34 SOCs are organic pesticides and herbicides. PCBs, benzo(a)pyrene, and dioxin are in Phase II also.

Table 2.3. Concentrations and Standard Deviations of Selected Organics from Five-City Survey.[a]

	Cincinnati, OH		Miami, FL		Ottumwa, IA		Philadelphia, PA		Seattle, WA
Compound	Concentration by GCMS (μg/L)	Standard Deviation (μg/L)	Concentration by GCMS (μg/L)	Standard Deviation (μg/L)	Concentration by GCMS (μg/L)	Standard Deviation (μg/L)	Concentration by GCMS (μg/L)	Standard Deviation (μg/L)	Concentration by GCMS (μg/L)
Benzene	0.3	0.1	<0.1	—	<0.1	—	0.2	0.1	[b]
Chlorobenzene	0.1	0.04	1	0.5	[b]		<0.1	—	[b]
Chloroethene (vinyl chloride)	[b]	—	[c]	—	[b]	—	[c]	—	[b]
1,1-Dichloroethene (vinyl chloride)	[b]	—	0.1	0.2	[b]	—	<0.1	—	[b]
cis-1,2-Dichloroethene	<0.1	—	12	2	[b]	—	0.1	0.1	[b]
trans-1,2-Dichloroethene	[b]	—	1	0.2	[b]	—	[b]	—	[b]
Nitrotrichloromethane (chloropicrin)	3	2.3	0.4	0.1	[b]	—	2	2	[b]
Tetrachloroethane	0.3	0.2	<0.1	—	0.2	0.2	0.4	0.3	[b]
Toluene	<0.1		[b]	—	[b]	—	0.7	0.4	[b]
Trichloroethene	0.1	0.1	0.3	0.1	<0.1	—	0.5	0.2	[b]

[a] Reproduced from Lingg et al.,[18] courtesy of the American Water Works Association.

[b] Not detected.

[c] Not quantified by GCMS.

Table 2.4. Comparison of Results of National THM Surveys.[19a]

Survey	Number of Cities	THMs—µg/L Mean	Median	Range
NORS[a,b]	80	68	41	ND[c]-482
NOMS—phase 1[b,d]	111	68	45	ND-457
NOMS—phase 2[e]	113	117	87	ND-784
NOMS—phase 3D[f]	106	53	37	ND-295
NOMS—phase 3T[e]	105	10	74	ND-695
NOMS—all phases	105/113	84	55	ND-784
AWWARF[f,g]	727	42	39	ND-360

[a] NORS—National Organics Reconnaissance Survey.

[b] Samples shipped and stored at 35–47°F (2–8°C) for one to two weeks prior to analysis.

[c] ND—none detected (detection levels differed significantly among the three surveys).

[d] NOMS—National Organic Monitoring Survey.

[e] Samples stored at 68–77°F (20–25°C) for three to six weeks prior to analysis.

[f] Sodium thiosulfate added.

[g] Samples collected and analyzed in compliance with THM monitoring and analysis regulations.

Table 2.5. Summary of Occurrences from 321 Nonrandom Sample Sites Serving Fewer than 10,000 Persons.[11]

Parameter	Quantitation Limit (µg/L)	Occurrences Number	Percent	Median of Positives (µg/L)	Maximum Value (µg/L)
Vinyl chloride	1.0	0	0		
1,1-Dichloroethylene	0.2	5	1.6	0.35	3.0
1,1-Dichloroethane	0.2	6	1.9	0.62	1.2
cis- and/or *trans*-1,2-Dichloroethylene	0.2	11	3.4	1.3	17
1,2-Dichloroethane	0.5	3	0.9	2.9	3.4
1,1,1-Trichloroethane	0.2	25	7.8	1.2	8.2
Carbon tetrachloride	0.2	9	2.8	0.44	15
1,2-Dichloropropane	0.2	3	0.9	1.2	1.4
Trichloroethylene	0.2	23	7.2	1.2	29
Tetrachloroethylene	0.2	27	8.4	0.79	21
Benzene	0.5	5	1.6	1.6	12
Toluene	0.5	4	1.2	0.67	0.79
Ethylbenzene	0.5	3	0.9	0.87	0.95
Bromobenzene	0.5	2	0.6	0.97	1.2
m-Xylene	0.2	8	2.5	0.38	0.83
o + *p*-Xylene	0.2	10	3.1	0.44	2.5
p-Dichlorobenzene	0.5	4	1.2	0.74	0.90
1,1,2-Trichloroethane	0.5	0	0		
1,1,1,2-Tetrachloroethane	0.2	0	0		
1,1,2,2-Tetrachloroethane	0.5	0	0		
Chlorobenzene	0.5	1	0.3	2.7	2.7
1,2-Dibromo-3-chloropropane	5.0	0	0		
n-Propylbenzene	0.5	1	0.3	0.98	0.98
o-Chlorotoluene	0.5	0	0		
p-Chlorotoluene	0.5	0	0		
m-Dichlorobenzene	0.5	0	0		
o-Dichlorobenzene	0.5	1	0.3	2.2	2.2
Styrene	0.5	0	0		
Isopropylbenzene	0.5	0	0		
Chloroform	0.2	155	48.3	1.6	100
Bromodichloromethane	0.2	144	44.9	2.0	49
Dibromochloromethane	0.5	135	42.1	3.5	63
Dichloroiodomethane	1.0	5	1.6	1.4	4.2
Bromoform	1.0	88	27.4	3.7	110

Table 2.6. Summary of Occurrences from 158 Nonrandom Sample Sites Serving More than 10,000 Persons.[11]

Parameter	Quantitation Limit (µg/L)	Occurrences		Median of Positives (µg/L)	Maximum Value (µg/L)
		Number	Percent		
Vinyl chloride	1.0	6	3.8	2.7	8.4
1,1-Dichloroethylene	0.2	10	6.3	0.34	0.64
1,1-Dichloroethane	0.2	17	10.8	0.87	4.2
cis- and/or *trans*-1,2-Dichloroethylene	0.2	27	17.1	2.7	120
1,2-Dichloroethane	0.5	4	2.5	1.8	9.8
1,1,1-Trichloroethane	0.2	26	16.5	0.93	21
Carbon tetrachloride	0.2	6	3.8	0.70	9.4
1,2-Dichloropropane	0.2	4	2.5	0.70	18
Trichloroethylene	0.2	38	24.1	1.5	130
Tetrachloroethylene	0.2	18	11.4	0.66	69
Benzene	0.5	3	1.9	2.7	12
Toluene	0.5	1	0.6	1.5	1.5
Ethylbenzene	0.5	0	0		
Bromobenzene	0.5	0	0		
m-Xylene	0.2	0	0		
o + *p*-Xylene	0.2	0	0		
p-Dichlorobenzene	0.5	0	0		
1,1,2-Trichloroethane	0.5	0	0		
1,1,1,2-Tetrachloroethane	0.2	0	0		
1,1,2,2-Tetrachloroethane	0.5	0	0		
Chlorobenzene	0.5	0	0		
1,2-Dibromo-3-chloropropane	5.0	0	0		
n-Propylbenzene	0.5	0	0		
o-Chlorotoluene	0.5	1	0.6	2.4	2.4
p-Chlorotoluene	0.5	0	0		
m-Dichlorobenzene	0.5	0	0		
o-Dichlorobenzene	0.5	1	0.6	2.7	2.7
Styrene	0.5	0	0		
Isopropylbenzene	0.5	0	0		
Chloroform	0.2	100	63.3	2.1	430
Bromodichloromethane	0.2	100	63.3	2.2	110
Dibromochloromethane	0.5	87	55.1	4.6	51
Dichloroiodomethane	1.0	8	5.1	1.2	4.1
Bromoform	1.0	60	38.0	5.1	68

Eighteen organic chemicals are scheduled for regulation under Phase V of the 1986 SDWA (Table 1.4). These include several pesticides as well as methylene chloride, PAHs, and dioxin. Under Phase VIb, 10 organic pesticides and 5 SOCs should have had their MCLGs and MCLs finalized in 1995 (Table 1.5b).

Pesticides—Surface Waters

A National Pesticide Monitoring Program was initiated in the late 1960s to establish a network to survey major rivers in the United States.[20] Initially, 39 rivers were selected for monthly sampling. In the early 1970s, the program was revised to quarterly samples of water, as well as bed sediments of 161 sites in the conterminous United States, Alaska, Hawaii, and Puerto Rico.[21] These pesticides were sought: 11 chlorinated hydrocarbons, 2 organophosphates, and 3 phenoxy herbicides.

A 5-year (1964–1968) summary of the pesticidal monitoring represents, perhaps, the "peak" contents in major U.S. rivers.[22] Several chlorinated hydrocarbons were found (in order of decreasing frequency): dieldrin, endrin, DDT, DDE, DDD, aldrin, heptachlor, heptachlor epoxide, lindane and BHC, and chlordane. The highest concentration was 0.47 µg/L of dieldrin in the Tombighee River at Columbia, Mississippi. Six organophosphorus pesticides were sought, but only two were found in one sample in the Snake River at Wawawai, Washington: parathion, 0.050 µg/L, and ethion, 0.380 µg/L. Table 2.7 shows a comparison of the maximum pesticide concentrations found in this five-year survey with the 1986 MCL values. It is noteworthy that all of the pesticide concentrations found in this early survey are below these MCL values.

Later, local and national surveys of surface waters for pesticides and herbicides reported concentrations that exceeded the 1986 MCL values. For example, two rivers in

Table 2.7. Maximum Pesticide Concentration Found vs. Primary Drinking Water Standards.[a]

Pesticide	MCLs (μg/L)	Max. Conc. Found (μg/L)
Dieldrin	[b]	0.407
Endrin	2.0[c]	0.133
DDT	[b]	0.316
DDE	[b]	0.050
DDD	[b]	0.840
Heptachlor	0.4	0.048
Heptachlor epoxide	0.2	0.067
Aldrin	[b]	0.085
Lindane (BHC)	0.2	0.112
Chlordane	2.0	0.169
Methoxychlor	40.0	[d]
Toxaphene	5.0	[e]
Organophosphates + carbamates	[b]	0.380
Herbicides		
2,4-D	70.0	[d]
2,4,5-TP	50.0	[d]

[a] Table 1.7, Chapter 1.
[b] None recommended.
[c] Proposed—Phase V.
[d] Not determined.
[e] Not detected.

Ohio were monitored for atrazine, alachlor, metolachlor, cyanazine, metribuzin, carbofuran, linuron, and simazine in a study to examine their fate during drinking water treatment.[23] In May–July 1984, the mean and maximum concentrations of alachlor and atrazine in the Maumee and Sandusky Rivers exceeded their MCLs (Table 2.8). The MCLs for carbofuran and simazine were not exceeded in this brief 20-day survey. Similar results were observed in a 1987–1989 survey of the lower Mississippi River and its tributaries for triazine and chloroacetanilide herbicides and their degradation products.[24] The effects of spring flush on the occurrence of 11 triazine herbicides in several surface waters of the midwestern United States that drain the "corn belt" were also evaluated.[25] In this study, water samples were collected from 149 sites in 122 basins during March and April (preplanting, 1989–1990), May and June (postplanting, 1989–1990), and October and November (harvest, 1989) at U.S. Geological Survey stream flow-gauging stations. "Large" concentrations of herbicides were flushed from cropland and were transported through the surface-water system as pulses in response to late spring and early summer rainfall. In this 1989–1990 survey, several herbicides exceeded the MCL values for drinking water. For example, 52% of the sites exceeded the MCL for atrazine (3.0 μg/L), 32% for alachlor (2.0 μg/L), and 7% for simazine (1 μg/L proposed at time of study).

The distribution of organonitrogen herbicides in surface water in 15,300 square miles of the lower Kansas basin, March 1989 to February 1990, was surveyed.[25a] About 85% of this area is agricultural land that is typical of raw crop production in the midcontinental United States. Atrazine was the most extensively applied herbicide in the area; it was detected most frequently, 95%, and in the highest concentrations. Two Phase VIb compounds, metolachlor and cyanazine, were detected at 58% and 40% frequency, respectively. Simazine and alachlor were detected also, but at lower frequencies of 38% and 24%, respectively. The concentrations of these organonitrogen herbicides varied seasonally, as expected, with the higher median concentrations occurring in the spring and summer and lower concentrations in the fall and winter (Table 2.9). Note that the health advisory levels (HAL) in Table 2.9 have become the expected MCLs for metolachlor and cyanazine (Table 1.5b).

Pesticides—Ground Waters

The USEPA conducted a survey of approximately 1,300 community water system (CWS) wells and rural domestic wells for the presence of 101 pesticides, 25 pesticide degradates, and nitrate.[26] The following pesticides and degradation products were detected above the minimum reporting limits of the survey: DCPA (dimethyl tetrachloroterephthalate) acid metabolites (0.10 μg/L), atrazine (0.12 μg/L), simazine (0.38 μg/L), prometron (0.15 μg/L), hexachlorobenzene (0.06 μg/L), DBCP (dibromochloropropane) (0.10 μg/L), dinoseb (1.3 μg/L), ethylene dibromide (0.10 μg/L), lindane (0.43 μg/L), ethylene thiourea (4.5 μg/L), bentazon (0.25 μg/L), and alachlor (0.50 μg/L). Results of this groundwater survey are given in Tables 2.10 and 2.11.[26] DCPA acid metabolites were the most frequently detected pesticide and/or degradation products with 6.4% (CWS wells) and 2.5% (rural wells). Atrazine was the second most commonly detected pesticide in this groundwater survey. It was estimated that atrazine was present at or above the detection limit of 0.12 μg/L in about 1.7% of the CWS wells and 0.7% of the rural wells. Occurrences of the other pesticides are seen in Tables 2.10 and 2.11, where their estimated percentages are 1.0 and less. These numbers appear to be "low" or even insignificant, but they do indicate widespread distribution of pesticides in the groundwater supplies of the United States.

In another national well water survey, the frequency of occurrence of alachlor and several other agrochemicals in water from private, rural domestic wells was determined for all counties in the United States where alachlor is sold.[27] Of the estimated 6 million private domestic wells in the target area, less than 1% have detectable levels of alachlor. Similar occurrence frequencies were found for metolachlor and simazine. However, atrazine was the most commonly detected pesticide in the alachlor use area, with an occurrence frequency near 12%. Concentrations of all detected pesticides in rural well water were very low and are rarely

Table 2.8. Pesticides in the Maumee and Sandusky Rivers.

Maumee River[a,b] Pesticides at Bowling Green—May–July 1984			
	Concentration (μg/L)		
Pesticide	Mean[c]	Maximum	MCL (μg/L)
Alachlor	3.58	12.3	2.0
Metolachlor	2.55	7.03	—
Atrazine	4.69	8.63	3.0
Cyanazine	1.96	6.12	—
Metribuzin	1.25	4.90	—
Carbofuran	1.06	2.05	40.0
Simazine	0.29	0.53	4.0 (Proposed)
Sandusky River[c,d] Pesticides at Tiffin—May–July 1984			
Alachlor	4.89	13.7	
Metolachlor	8.17	22.3	
Atrazine	5.92	11.3	
Cyanazine	1.81	3.63	
Metribuzin	1.82	6.03	
Carbofuran	0.58	1.20	
Simazine	0.44	1.15	

[a] 6,313-sq-mi watershed.
[b] Twenty sample days.
[c] Mean concentration for number of days detected.
[d] 1,251-sq-mi watershed.
[e] Nineteen sample days.

Table 2.9. Frequency of Detection that Exceeded the MCL or HAL for Selected Herbicides in the Lower Kansas River Basin, March 1989 Through February 1990.[25a]

Herbicide	Frequency of Detection[a] (percent)	Samples That Exceeded MCL or HAL[b] (percent)
Atrazine	95	17
Metolachlor	58	0
Cyanazine	40	2.3
Simazine	38	0
Alachlor	24	3.5

[a] Based on 173 samples.
[b] MCL for atrazine—3.0 μg/L; HAL for metolachlor—100 μg/L; HAL for cyanazine—1.0 μg/L; MCL for simazine—4.0 μg/L; MCL for alachlor—2.0 μg/L.

expected to exceed any health-based standard, as seen in Table 2.12.

Polychlorinated Biphenyls

Polychlorinated biphenyls (PCBs) are a class of colorless and stable compounds, each containing a biphenyl nucleus with two or more substituent chlorine atoms. Technical PCBs are a mixture that often contain between 40 and 60 different chlorinated biphenyls (arochlors). They are quite insoluble in water.

Surprisingly few reports are in the scientific literature, to date, about the occurrence of PCBs in aquatic environments. The distribution of Aroclor® 1254 was investigated for the water, sediment, and biota of Escambia Bay, Florida.[28] Most of this PCB resided in some sort of a solid phase (i.e., fish crustacean or sediment), since the contents in water were less than 0.1 μg/L. It was not detected at some sampling stations in the water phase. However, sediment samples taken near a wastewater outfall reached a high content of 486 ppm. In an effort to develop analytical methodology for PCBs in

Table 2.10. Estimated Number and Percent of Community Water System Wells Containing NPS Analytes.[26]

Analyte	Estimated Number	95% C.I. (lower–upper)	Estimated Percent	95% C.I. (lower–upper)[a]	NPS Reporting Limit[b] (μg/L)
DCPA acid metabolites	6,010	(3,170–8,840)	6.4	(3.4–9.3)	0.10
Atrazine	1,570	(420–2,710)	1.7	(0.5–2.9)	0.12
Simazine	1,080	(350–2,540)	1.1	(0.4–2.7)	0.38
Prometon	520	(78–1,710)	0.5	(0.1–1.8)	0.15
Hexachlorobenzene	470	(61–1,630)	0.5	(0.1–1.7)	0.060
Dibromochloropropane (DBCP)	370	(33–1,480)	0.4	(<0.1–1.6)	0.010
Dinoseb	25	(1–870)	<0.1	(<0.1–0.9)	1.3

[a] Numbers between zero and 0.05 are reported as less than 0.1 (<0.1).

[b] The EPA established specific reporting limits for each analyte.

Table 2.11. Estimated Number and Percent of Rural Domestic Wells Containing NPS Analytes.[26]

Analyte	Estimated Number	95% C.I. (lower–upper)	Estimated Percent	95% C.I. (lower–upper)[a]	NPS Reporting Limit[b] (μg/L)
DCPA acid metabolites	264,000	(129,000–477,000)	2.5	(1.2–4.5)	0.10
Atrazine	70,800	(13,300–214,000)	0.7	(0.1–2.0)	0.12
Dibromochloropropane (DBCP)	38,400	(2,740–164,000)	0.4	(<0.1–1.6)	0.010
Prometon	25,600	(640–142,000)	0.2	(<0.1–1.4)	0.15
Simazine	25,100	(590–141,000)	0.2	(<0.1–1.3)	0.38
Ethylene dibromide	19,200	(160–131,000)	0.2	(<0.1–1.2)	0.010
Gamma-HCH (Lindane)	13,100	(14–120,000)	0.1	(<0.1–1.1)	0.043
Ethylene thiourea	8,470	(1–111,000)	0.1	(<0.1–1.1)	4.5
Bentazon	7,160	(1–109,000)	0.1	(<0.1–1.0)	0.25
Alachlor	3,140	(1–101,000)	<0.1	(<0.1–1.0)	0.50

[a] Numbers between zero and 0.05 are reported as less than 0.1 (<0.1).

[b] EPA established specific reporting limits for each analyte.

Table 2.12. Estimated Percent Occurrence of the Five Herbicides in the Alachlor Use Area.[27]

	Estimated % of Wells At or Above[a]				
Chemical	Detection	0.1 μg/L	0.2 μg/L	0.5 μg/L	1 μg/L
Alachlor	0.78 (0.29)	0.36 (0.22)	0.32 (0.20)	0.06 (0.03)	0.03 (0.02)
Atrazine	11.68 (5.13)	2.32 (0.75)	1.11 (0.40)	0.23 (0.11)	0.16 (0.11)
Cyanazine	0.28 (0.20)	0.08 (0.06)	[b]	[b]	[b]
Metolachlor	1.02 (0.38)	0.40 (0.21)	0.40 (0.22)	0.29 (0.20)	0.22 (0.20)
Simazine	1.60 (0.87)	0.10 (0.08)	0.01 (0.01)	0.01 (0.01)	<0.01 (<0.01)

[a] Standard errors are given in parentheses.

[b] No occurrences of cyanazine at or above this level were found in the sample.

water, contents in untreated and treated tap water were reported as: 0.50 and 0.33 ppt, respectively.[29]

In the 1971–1972 National Pesticides Monitoring Program for the distribution of PCBs in various aquatic environments of the United States, residues were detected in water samples from 19 states.[20] PCB concentrations ranged from 0.1 to 4.0 μg/L in unfiltered water samples and from 5.0 to 3200 μg/kg in bottom sediments. Residues were found also in fish and aquatic plants. This report provides strong evidence for the ubiquitous occurrence and distribution of PCBs. In addition, PCBs were found in eight sampling stations on Lake Ontario. Concentrations in water ranged from 35 to 97 μg/L.[30]

The NOMS (Natural Organic Monitoring Survey) (1976–1977) found PCBs in 6% of finished groundwater supplies at levels of 0.1 μg/L and in approximately 2% of finished surface waters at less than or equal to 1.4 µg/L.[8] One state reported 32 of 163 groundwater supplies had up to 1.27 µg/L in finished water in 1978.[31]

Polynuclear Aromatic Hydrocarbons (PAH)

Polynuclear aromatic hydrocarbons are a diverse class of compounds that consist of substituted and unsubstituted polycyclic and heterocyclic aromatic rings. These compounds are considered as naturally occurring because their origin is usually in petroleum. However, they are released into the environment through a pyrolytic industrial operation of some sort. Examples are the preparation of acetylene from natural gas; the hydrolysis of kerosene to benzene, toluene, and other organic solvents; the pyrolysis of wood, etc. There is a legitimate concern about the occurrence of these compounds in our environment and drinking water because of the carcinogenic properties exhibited in laboratory animals by some PAHs; especially benzo(a)pyrene (B[a]Py). PAHs are extremely insoluble in water; e.g., the solubility of benzo(a)-pyrene is about 10 µg/L.

There is evidence that PAHs are found in almost all aquatic environments. This is especially true in fresh surface waters receiving wastewaters that are known sources of PAH, and downstream from petroleum refineries. Some typical concentrations of 3,4-BP and PAH are reported in Table 2.13 from various Russian, German, and American rivers.[32] These contents result from a special effort to sample the rivers below known sources of PAH. Basu and Saxena[33] reported "total" PAH concentrations of 0.6636 and 0.3518 µg/L for the raw drinking water supplies of Pittsburgh and Philadelphia, respectively. The finished drinking waters contained "total" PAH values of 0.0028 and 0.0149 µg/L, respectively. Herbes[34] investigated the partitioning of PAH between dissolved and particulate phases in natural waters. A "significant" fraction, 15–65% of anthracene, for example, would be associated with detrital and living organic matter in natural waters. Borneff and Kunte[35] have found PAH concentrations up to 0.10 µg/L in drinking water. These researchers have concluded that PAH contents between 0.15 and 0.20 µg/L in drinking water constitute questionable safety. In 1980, the European Community (EC) adopted a 0.20 µg/L concentration as a drinking water standard (Table 1.22). Chlorinated PAHs have been isolated from tap water in Japan.[36]

Disinfectants/Disinfection By-Products—Phase VIa

Several by-products of the chlorination-disinfection process are organic compounds: total trihalomethanes, haloacetonitriles, haloketones, haloacetic acids, chlorophenols, aldehydes, chloropicrin, and chloral hydrate (Figure 2.2).[37] Most of these compounds will be regulated with their own MCLGs and MCLs sometime in the mid to late 1990s (Table 1.4).

In September 1987, the USEPA's Office of Drinking Water entered into a cooperative agreement with the Association of Metropolitan Water Agencies (AMWA) to perform a study of the occurrence and control of DBPs.[37] The State of California's Department of Health Services (CDHS) initiated a similar study, also in 1987. The USEPA study included 25 water utilities across the United States, whereas the CDHS study involved 10 water utilities in California. Table 2.14 shows the baseline data for the four sampling quarters in 1988. For the 35 utilities, chloroform is the THM with the highest median value, whereas the more brominated THMs had the lowest medians. Seasonal temperature differences were observed for the THMs, as expected. The highest THM levels were recorded in the summer and fall quarters.

Further examination of the USEPA and CDHS study for the third sampling quarter (Figure 2.3) shows that, on a weight basis, THMs were the largest class of DBPs detected.[37] The second largest fraction was the haloacetic acids (HAAs). The median level of THMs was approximately twice that of HAAs. These latter DBPs may result from the

Table 2.13. Typical Concentration Ranges of 3,4-BP and PAH in Fresh Surface Waters.[32]

Source	3,4-BP (µg/L)	PAH[a] (µg/L)	Total PAH (µg/L)
Rhine River	0.05–0.11	0.01–0.73	0.73–1.50
German Rivers	0.001–0.04	0.04–1.3	0.12–3.1
A U.S. River	0.078–0.150	—	—
Rivers[b]	0.0001–12	—	—
Moscow Reservoirs	4–13	—	—
Volga River	0.0001	—	—
Sunzha River	0.05–3.5	—	—
Oyster River, Connecticut	0.078–0.150	—	—

[a] May be carcinogenic.

[b] Receiving wastewaters that are sources of PAH.

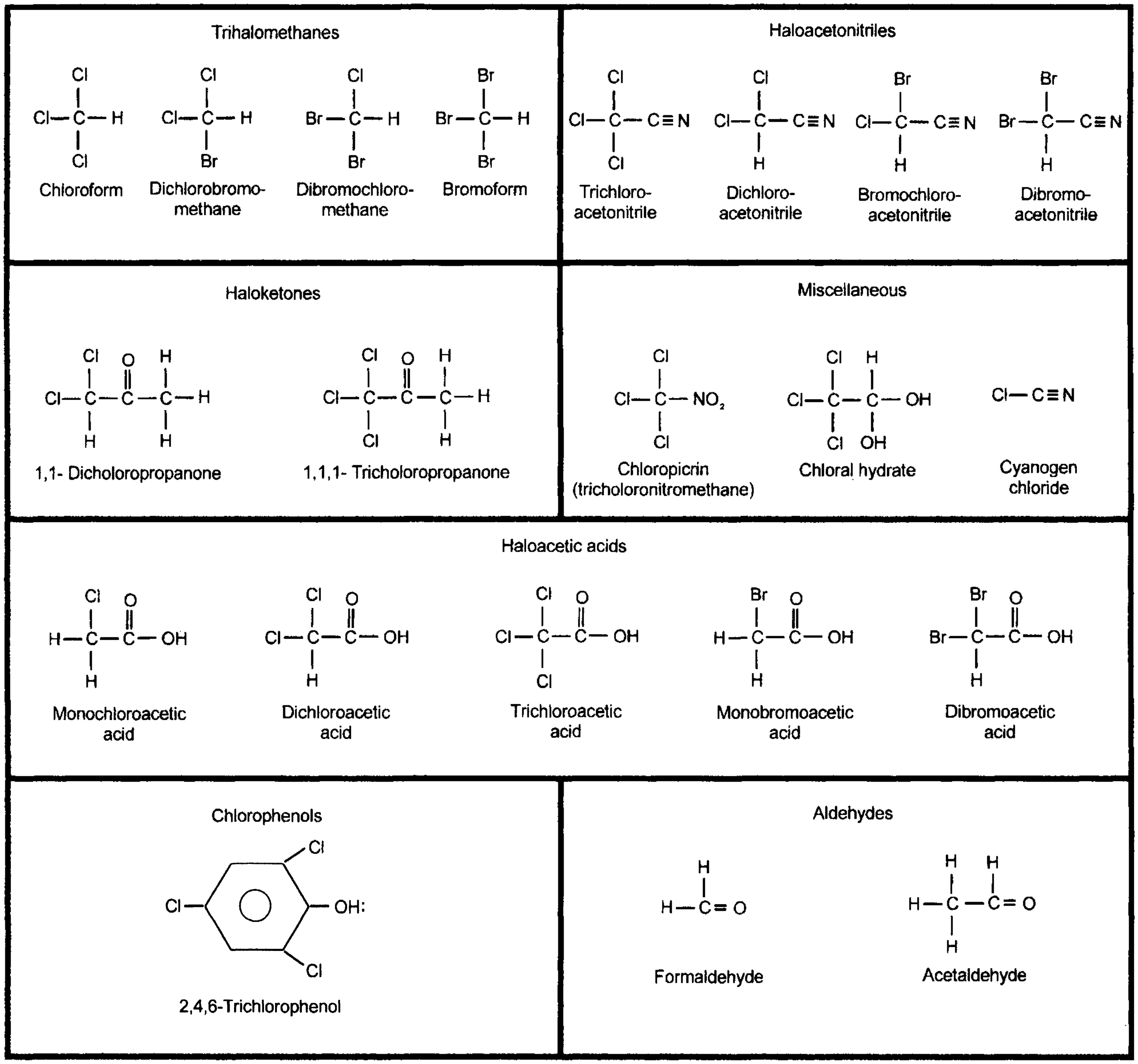

Figure 2.2. Structural formulas for DBPs.[37]

chlorination of humic and fulvic acids, where dichloro- and trichloroacetic acids have been determined.[38–40] Other apparent products of chlorination observed in this quarter were the haloacetonitriles, haloketones, aldehydes, chloropicrin, chloral hydrate, and cyanogen chloride.

Dihaloacetonitriles have been found in nine Dutch drinking waters that were disinfected by chlorine.[41] All of these waters were found to contain DHANs in the range 0.04 to 1.05 µg/L and THMs in the range 3.1 to 49.5 µg/L. In general, the brominated DHANs and THMs were higher in concentration than the chlorinated compounds.

Formation Potential for Disinfection By-Products

Disinfection by-products, obviously, are formed from a variety of organic precursors. Consequently, there is a need to estimate as quantitatively as possible, the potential of a raw water to form DBPs upon chlorination. *Standard Methods* has a proposed procedure called the "trihalomethane formation potential" (TFP).[42] The TFP definition is "the concentration of THMs formed in water buffered at pH 7.0, containing an excess of free chlorine with a chlorine residual of 1 to 5 mg/L after being held 7 days at 25°C." This test

Table 2.14. Quarterly Median Values of DBPs in Drinking Water.[37]

	Concentration[a] (μg/L)			
Disinfection By-Product	1st Quarter (Spring 1988)	2nd Quarter (Summer 1988)	3rd Quarter (Fall 1988)	4th Quarter (Winter 1989)
Trihalomethanes				
Chloroform	15	15	13	9.6
Bromodichloromethane	6.9	10	5.5	4.1
Dibromochloromethane	2.6	4.5	3.8	2.7
Bromoform	0.33	0.57	0.88	0.51
Total trihalomethanes[b]	34	44	40	30
Haloacetonitriles				
Trichloroacetonitrile	<0.012	<0.012	<0.029	<0.029
Dichloroacetonitrile	1.2	1.1	1.1	1.2
Bromochloroacetonitrile	0.50	0.58	0.70	0.59
Dibromoacetonitrile	0.54	0.48	0.51	0.46
Total haloacetonitriles	2.8	2.5	3.5	4.0
Haloketones				
1,1-Dichloropropanone	0.52	0.46	0.52	0.55
1,1,1-Trichloropropanone	0.80	0.35	0.60	0.66
Total haloketones	1.4	0.94	1.0	1.8
Haloacids				
Monochloroacetic acid	<1.0	1.2	<1.0	1.2
Dichloroacetic acid	7.3	6.8	6.4	5.0
Trichloroacetic acid	5.8	5.8	6.0	4.0
Monobromoacetic acid	<0.5	<0.5	<0.5	<0.5
Dibromoacetic acid	0.9	1.5	1.4	1.0
Total haloacids	18	20	21	13
Aldehydes				
Formaldehyde	NA[c]	5.1	3.5	2.0
Acetaldehyde	NA	2.7	2.6	1.8
Total aldehydes	NA	6.9	5.5	4.2
Miscellaneous				
Chloropicrin	0.16	0.12	0.10	0.10
Chloral hydrate	1.8	3.0	2.2	1.7
Cyanogen chloride	0.45	0.60	0.65	0.80
2,4,6-Trichlorophenol	<0.3	<0.4	<0.4	<0.4
Halogenated DBP$_{sum}$[d]	64	82	72	58
Total organic halide	150	180	170	175
Plant influent characteristics				
Total organic carbon (mg/L)	NA	2.9	2.9	3.2
Ultraviolet absorbance (cm^{-1})	NA	0.11	0.11	0.13
Chloride (mg/L)	NA	28	32	23
Bromide (mg/L)	NA	0.07	0.10	0.07

[a] Except where otherwise indicated (plant influent characteristics).

[b] Total class median values are not the sums of the medians of the individual compounds but rather the medians of the sums of the compounds within that class.

[c] NA—not analyzed.

[d] The halogenated DBP$_{sum}$ median values are not the sum of the class medians for all utilities but rather the medians of the halogenated DBP$_{sum}$ values for all utilities. This value is only the sum of XDBPs measured in this study.

does not simulate drinking water treatment processes, but is useful in estimating THM precursors. It is a surrogate test that attempts to determine a maximum potential yield of THMs in a raw water supply. The TFP is simply the sum of the individual concentrations (usually μg/L) of the four trihalomethanes.

Much research has been conducted on the TFP since their discovery in finished drinking water by Rook[43] and the early work by the USEPA.[44] Model compounds, the total organic content (TOC), etc., have been employed and correlated with the formation of THMs. Typical results are seen in Table 2.15 for TFPs from the chlorination of raw drinking waters

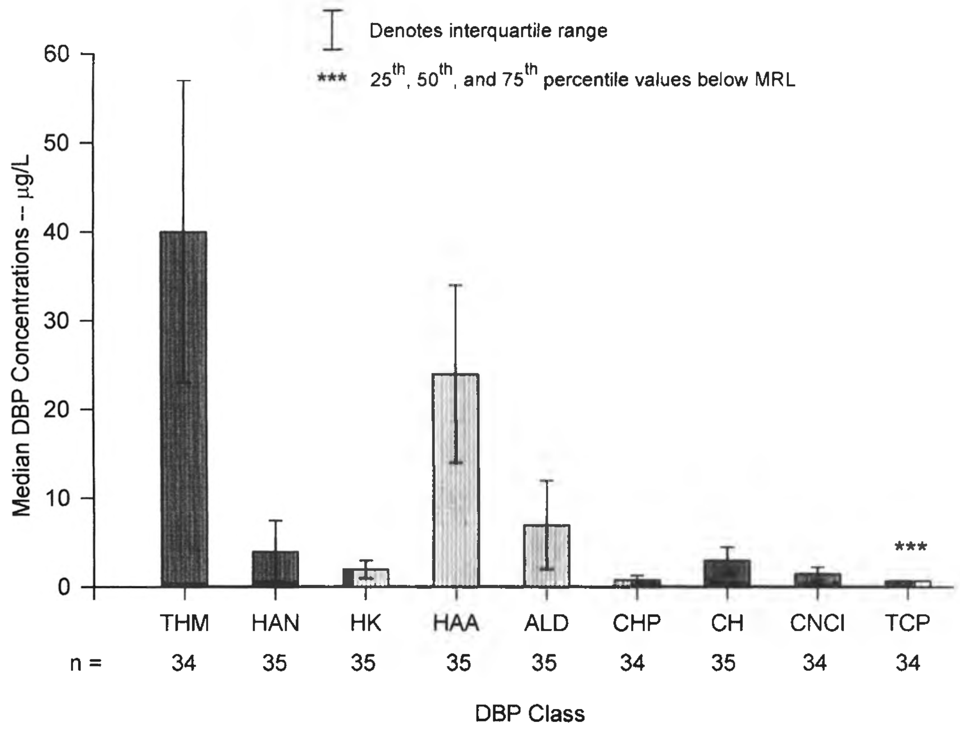

Figure 2.3. DBP concentration by class for third quarter (THM—trihalomethanes; HAN—haloacetonitriles; HK—haloketones; HAA—haloacetic acids; ALD—aldehydes; CHP—chloropicrin; CH—chloral hydrate; CNCl—cyanogen chloride; TCP—2,4,6-trichlorophenol).[37]

at pH 7.0.[45] Here the TOC, mg/L, represents the organic content of the raw waters. Considerable quantities of DBP were formed, as seen by the quantities of TOX (total organic halides), TTHM (total trihalomethanes), TCAA (trichloroacetic acid), DCAA (dichloroacetic acid), TCAC (1,1,1-trichloroacetone), and DCAN (dichloroacetonitrile). These data indicate that the TFP as defined by *Standard Methods* inadequately accounts for all DBPs. Certainly there is a good correlation between TOC and THMFP (or TFP) for a single water subject to day-to-day source variations or various degrees of treatment.[46] However, waters from different sources tend to have different specific THM yields, as seen in Table 2.15.

In order to account for the differences in reactivity of raw waters (Table 2.15), the various formation potentials were divided by their TOC concentrations to obtain specific formation potentials. [The data in Table 2.16 indicate that the normalized formation potentials show a small degree of variability among the eight waters for TOXFP, THMFP, TCAAFP, and TCACFP (CV=14–22%), whereas DCAAFP and DCANFP were much more variable (CV=29 and 40%)]. The average specific THMFP was 51 µg/mg C; that is, apparently, a consistent number from many studies of raw waters.[45] Certainly, raw water supplies with naturally occurring organic matter do form DBPs in a reasonably stoichiometric manner.

THM formation potential was determined for 50 groundwater supplies in Kansas.[47] The mean TOC and THMFP concentrations were 1.03 ± 0.76 mg/L and 46.7 ± 39.5 µg/L, respectively. THMFP was strongly correlated with TOC (r=0.953). Only 8% of the THMFP concentrations exceeded 100 µg/L, but 56% exceeded 25 µg/L and 90% exceeded 10 µg/L. Here again, the issue of a THM MCL lower than 100 µg/L is highlighted. It may be extremely difficult for water utilities in Kansas and elsewhere in the United States to meet a substantially lower THM standard.

Precursors for Disinfection By-Products

Early Research

One of the first reports on formation of THMs in natural surface waters came from chlorination practices in the Rotterdam Waterworks.[43] Gas-liquid chromatographic and mass spectrometric techniques were employed to identify $CHCl_3$, CCl_4, $CHCl_2Br$, $CHClBr_2$, and $CHBr_3$ (Figure 2.2). The observation of these compounds led to two perplexing questions: (1) What is/are the precursor(s)? and (2) What is the source of the bromine? Considerable research has been conducted since the early 1970s to answer these questions.

Table 2.15. Results (Raw Data) of Chlorination of Raw Drinking Waters at pH 7.[45]

		Chlorine			Formation Potentials (µg/L)					
City	Date	TOC (mg/L)	Dose (mg/L)	Consumed (mg/L)	TOX	TTHM	TCAA	DCAA	TCAC	DCAN
1	02/23/83	NA[a]	20[b]	4.77	843	191	60	51	6.3	6.5
1	01/16/84	6.8	20	11.2	1,350	302	394	165	6.1	8.5
1	01/27/84	4.8	20	9.65	1,100	260	311	128	4.9	7.3
2	12/15/83	14.1	40	25.0	3,440	959	635	594	18.3	9.4
3	12/15/83	7.6	20	14.2	1,300	325	384	163	5.1	11.5
4	12/15/83	6.9	20	12.2	1,170	283	312	129	4.8	9.1
5	01/06/84	6.7	20	13.5	1,450	342	388	162	8.1	11.9
6	01/17/84	8.0	40	19.25	2,380	539	697	313	9.0	5.3
7	01/18/84	26.6	60	42.2	5,140	1,280	1,630	616	25.3	12.0
8	02/23/83	NA	20[b]	4.03	948	201	69	49	8.8	8.5
9	10/14/83	NA	60	24.6	2,650	581	365	211	25.2	3.0
10	10/27/83	NA	20	8.75	808	257	197	113	7.1	5.4

[a] NA—not analyzed.

[b] 24-h chlorine contact time; all others 72 h.

Table 2.16. Results of Chlorination of Raw Drinking Waters at pH 7 (data normalized to 1 mg TOC/L).[45]

City	Chlorine Consumed (mg/mg TOC)	Specific Formation Potential (mg/mg TOC)					
		TOX	TTHM	TCAA	DCAA	TCAC	DCAN
1	2.01	229	54.3	64.8	26.6	1.0	1.5
1	1.66	200	44.8	58.4	24.4	0.91	1.3
2	1.77	244	68.0	45.0	42.1	1.3	0.67
3	1.87	172	42.8	50.6	21.5	0.67	1.5
4	1.77	170	41.0	45.1	18.7	0.70	1.3
5	2.01	216	51.2	58.0	24.1	1.2	1.8
6	2.41	298	67.4	87.0	39.1	1.1	0.66
7	1.58	193	48.2	61.2	23.4	0.95	0.45
Average	1.89	215	52.2	58.8	27.5	0.98	1.1
CV[a]—percent	(14)	(18)	(19)	(22)	(29)	(22)	(40)

[a] Coefficient of variation.

Early studies, 1974–1980, were summarized in the first edition of this tome that sought precursors yielding the above THMs.[48] This early research looked at such model compounds as: acetone, polyhydric phenols, and natural organic color compounds (humic and fulvic acids) by Rook.[43,49] For example, such degradation products of humic and fulvic acids as: resorcinol, phloroglucinol, pyrogallol, catechol, orcinol, 2,6-dihydroxytoluene, *o*- and *m*-phthalic acids, and 3,5-dihydroxybenzoic acids have been researched as precursors for THMs.[50] On the basis of these compounds and proposed structures for humic and fulvic acids, "hydroxylated aromatic rings with two free meta-positioned OH groups are available active sites for haloform formation."[50]

Other early studies indicated that algae are also apparent precursors in the formation of THMs.[51,52] Various amounts of $CHCl_3$ were produced from the chlorination of algal biomass of two species of green and two species of blue-green algae.[51] Similar results were observed from the chlorination of seven species of green, blue-green, and diatom algae.[52]

Most of the above early research focused upon naturally occurring precursors that produced the above five THMs. Such factors as time, temperature, and [H^+] were reported to affect the yield of $CHCl_3$ from various precursors.[48] Generally, the yield of $CHCl_3$ is increased significantly as the [H^+] decreases up to pH values of 11.

Late Research

Such DBPs as: the dihaloacetonitriles (DHANs) haloacetic acids, etc., appeared in the literature in the early 1980s. Apparently, these compounds were not observed in the earlier studies because they decompose on such commonly used gas chromatographic phases as OV101, and hydrolyze at elevated temperatures and pH values.[53] The pressure of DHANs in chlorinated water supplies was reported in 1980. This, of course, initiated research for precursors of these acetonitriles, for example, dichloroacetonitrile, $CHCl_2CN$ (0.3 to 8.1 µg/L), and some contained CHBrClCN (ND-1.8 µg/L). The average DHAN concentration was about 10% of the average THM concentration on a molar basis. Subsequently, aqueous chlorination experiments conducted on aquatic fulvic acid and two species of aquatic algae (a blue-green and a green) yielded DHANs under conditions similar to those used for water treatment. $CHCl_2CN$ was found in all experimental samples, whereas CHBrClCN was found only in samples containing high concentrations of brominated THMs (Table 2.17). These brominated DBPs are found in waters that contain inorganic bromide.[56,57]

Chlorination of fulvic acid isolated from a natural water produced a variety of C_1 to C_4 aliphatic acids in addition to $CHCl_3$.[58] Yields of the four principal reaction products—trichloroacetic acid, $CHCl_3$, dichloroacetic acid, and dichlorosuccinic acid—are approximately 14 wt % of starting organic material and account for 53% of the total organic halogen (Table 2.18). No halogenated aromatic products were identified. Similar results were observed when terrestrial humic acid was chlorinated at pH 7.2.[59] The principal products were $CHCl_3$, di- and trichloroacetic acid, and chlorinated C-4 diacids. At a "high" chlorine dose (3.35 Cl_2:C molar ratio), many new chlorination products were detected; among them were some chlorinated aromatic acids.

The search for DBP precursors continued with the chlorination of three naturally occurring amino acids: aspartic acid, tyrosine, and tryptophan.[60] These compounds were found to form chloroform, dichloroacetonitrile, and chloral hydrate as the major DBPs. The appearance of $CCl_3CH(OH)_2$ was confirmed positively where its presence was speculated in previous studies.

In order to investigate the formation of dichloroacetonitrile and chloral hydrate in environmental samples, two different lake water samples were chlorinated and the chlorinated effluents from two domestic wastewater treat-

Table 2.17. Yields (ppb) of DHANs and THMs from the Reaction of Chlorine (10 ppm) with Fulvic Acid and Algae (1 ppm TOC).[55]

Sample	Reaction Time, h	$CHCl_2CN$	CHBrClCN	$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$
Fulvic acid (pH 7)	4	3.4	ND[a]	16	0.6	ND	ND
	24	6.5	ND	33	1.4	ND	ND
	48	5.8	ND	57	1.7	ND	ND
	120	4.1	ND	80	2.0	ND	ND
Blue-green algae (pH 6)	4	0.5	0.3	0.5	0.1	ND	ND
	24	1.4	0.6	3.4	0.4	ND	ND
	48	2.3	0.5	7.6	0.6	ND	ND
	120	3.5	0.4	16	0.8	ND	ND
Blue-green algae (pH 7)	4	0.6	ND	3.7	0.2	ND	ND
	24	1.9	ND	16	0.6	ND	ND
	48	2.5	ND	27	0.9	ND	ND
	120	2.3	ND	48	1.7	ND	ND
Blue-green algae (pH 8)	4	0.9	ND	9.8	0.3	ND	ND
	24	1.9	ND	28	0.9	ND	ND
	48	1.5	ND	39	1.5	ND	ND
	120	0.9	ND	59	1.8	ND	ND
Green algae (pH 7)	4	0.5	ND	2.5	0.2	ND	ND
	24	1.0	0.1	8.8	0.7	ND	ND
	48	0.8	0.2	15	0.8	ND	ND
	120	0.5	0.5	28	1.1	ND	ND
Green algae (pH 7, 0.3 ppm Br^-)	4	0.5	0.3	1.3	1.5	1.9	ND
	24	1.0	1.0	3.9	6.9	5.9	0.7
	48	0.7	1.1	5.9	11	8.3	1.4
	120	0.5	0.9	10	20	13	2.8
Green algae (pH 7, 1.5 ppm Br^-)	4	0.6	0.8	0.7	1.7	4.3	2.2
	24	0.6	0.9	1.3	5.0	10	6.5
	48	0.3	0.9	2.0	6.9	14	9.8
	120	0.3	0.9	2.3	13	39	22

[a] Not detected.

Table 2.18. Yields of Chlorination Products from Extracted Fulvic Acid (Black Lake).[56]

Product	mg/g of FA	mg of C/g of FA	Original TOC (%)	Final TOX (%)
Trichloroacetic acid[a]	90.3	13.3	3.0	32.1
$CHCl_3$[b]	38.2	3.8	0.8	17.3
Dichloroacetic acid[c]	10.2	1.9	0.4	3.6[d]
Dichlorosuccinic acid[c]	3.4	0.9	0.2	
Total	142.1	19.1	4.4	53.0

[a] As determined by isotope dilution GC/MS.

[b] As determined by the method of Bellar and Lichtenburg (16 in Reference 59).

[c] Amounts recovered in the ether extract.

[d] Sum of dichloroacetic and dichlorosuccinic acids.

ment plants were collected and analyzed for chlorination by-products.[60] For the latter, samples were found to contain 32–80 μg/L of chloral hydrate. A sample of lake water was chlorinated at pH 7.2 for 70 minutes with 12 mg/L chlorine that produced 239 μg/L of $CHCl_3$, 19 μg/L of $CHCl_2CN$, and 30 μg/L of $CCl_3CH(OH)_2$. Similar results were observed from the chlorination (20 mg/L Cl_2) of another lake water at a pH of 7.6. The rates of formation of these DBPs were extremely rapid, with the above concentrations appearing in 30 minutes or less.

Drainage waters from agricultural soils contain significant quantities of dissolved organic carbon (DOC) that, in turn, serve as precursors for DBPs. A concerted study of these waters was conducted in the Sacramento River Delta of California where the THMFP ranged from 208 to 3580 μg/L, the DHANs ranged from 0.8 to 130 μg/L, the DCAA ranged from 34 to 1650 μg/L, and the TCAA ranged from 24 to 1990 μg/L.[61] An excellent correlation of the THMFP was observed with DOC, a surrogate parameter for organic matter:

$$\text{THMFP} = -5.00 + 1.07\,(\text{DOC}),\ r^2 = 0.98 \qquad (1)$$

Significantly, the DOC associated with drainage waters exhibited much higher levels of THMFP than a series of related river and lake waters. This would be expected inasmuch as agricultural lands produce more organic matter than watersheds for lakes and rivers.

The research for precursors for DBPs has been focused mainly on naturally occurring sources. These include: the humic and fulvic acid fractions from dissolved organic matter (DOM), amino acids, algae, degradation products of humic and fulvic acids, lake, river and agricultural drainage waters, etc. The full range of DBPs shown in Figure 2.2 was observed in the many studies cited above. Undoubtedly, these DBPs are in finished waters that are chlorinated for disinfection. Many of these DBPs can be eliminated by simply removing the precursors before Cl_2 is added (See Chapters 6 and 11). Nonetheless, it may be necessary to promulgate MCLGs and MCLs for these many DBPs because of their possible effects on human health (See Chapter 1 and text below).

Kinetics of Disinfection By-Product Formation

Early research indicated that "the THM reaction is one of the slowest reactions of interest to the water utility practitioner."[62] The formation reaction occurs over several hours (Figure 2.4) and some systems (Figure 2.4a) exhibited significant increases after 24 hours of reaction. The kinetics of THM formation is dependent on many factors such as $[H^+]$, $[Cl_2]$, [precursor], and temperature. On the other hand, there is evidence that THM formation occurs within 2 h.[63,64] However, it is difficult to follow kinetics with precision because there are competing reactions for the chlorine.

A kinetic equation for the THM reaction is:

$$\frac{d[Cl_2]}{dt} = -k_1\,[Cl_2]\,[TOC] \qquad (2)$$

where it is assumed that the rate of chlorine consumption is dependent on its content and precursor content is expressed as TOC.[62] Furthermore, if it is assumed that the [TOC] is not significantly reduced, then:

$$\ln\frac{[Cl_2]_t}{[Cl_2]_o} = -k_1\,[TOC]\,t \qquad (3)$$

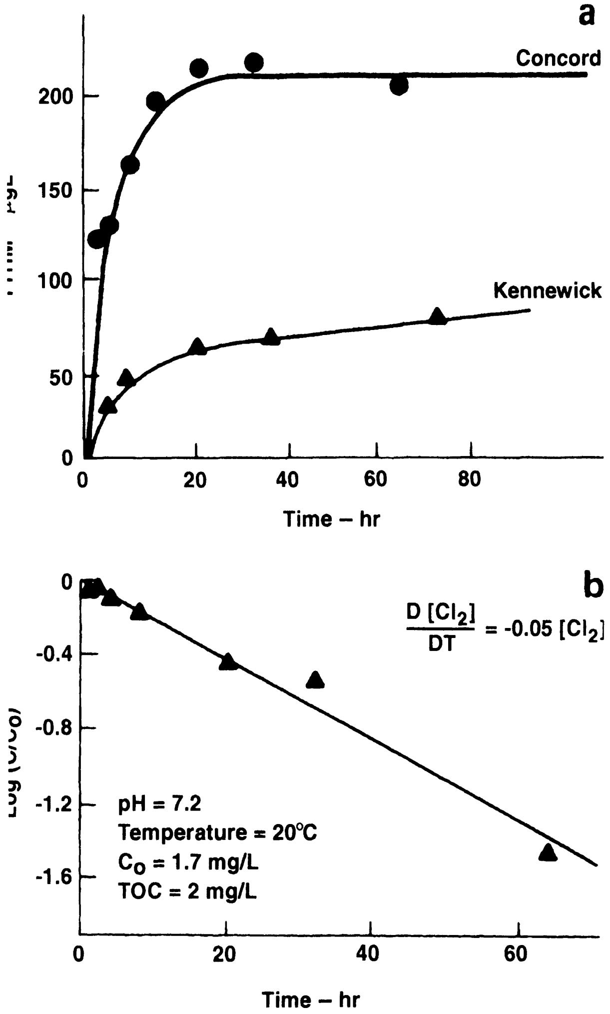

Figure 2.4. (a) THM formation. (b) First-order plot of chlorine consumption. Reproduced from Trussell and Umphres,[62] courtesy of the American Water Works Association.

This equation represents a first-order reaction with respect to chlorine residual (Figure 2.4b). Another approach assumes that the rate of THM formation is related to residual chlorine to the first power:

$$\frac{d[THM]}{dt} = -\frac{dC}{dt} = k_2\,[Cl_2]\,[C]^m \qquad (4)$$

where m is the order of reaction with respect to [C], the precursor concentration. When m is 3, a third-order reaction gives "a good fit."[62]

One intent of kinetic studies is to develop predictive models for the formation of DBPs from various precursors. For example, several mathematical equations were used to formulate an overall model for predicting chloroform from humic acid in terms of time, initial total organic carbon (TOC), initial chlorine to TOC ratio, reaction temperature, and reaction pH.[65] All of these reaction components of the model are especially relevant in the operation of a water treatment plant and enforcement of the THM MCL. A generalized reaction is:

$$\text{Precursor (as TOC)} + Cl_2 \rightarrow CHCl_3 \qquad (5)$$

This is a simple $CHCl_3$ formation reaction based upon the absence of both bromide as a reactant and brominated haloforms as products. Kinetically, three mathematical models describe the role of each component of the reaction:

$$[CHCl_3] = k_a t^z \qquad (6)$$

$$[CHCl_3] = k_b \left(\frac{[Cl_2]}{[TOC]}\right)^y t^z \qquad (7)$$

$$[CHCl_3] = k_c\,[TOC]^x\, t^z \qquad (8)$$

where $[CHCl_3]$ is the chloroform concentration, µg/L; t is the reaction time, hours; [TOC] is the initial TOC concentration, mg/L; $[Cl_2]/[TOC]$ is the initial Cl_2 to TOC ratio; x, y, and z are empirically derived constants; and k_a, k_b, and k_c are empirical reaction rate constants. In turn, these three submodels were incorporated into an overall model:

$$[CHCl_3] = K[TOC]^x \left(\frac{CL_2}{TOC}\right)^y t^z \qquad (9)$$

where K is an overall reaction constant that includes reaction constants for effects of pH and temperature. In this empirical study, a multiple linear regression technique was employed to obtain the reaction constants and the exponents x, y, and z in the above equations.[65] This resulted in:

$$\ln[CHCl_3] = \ln K + x\ln[TOC] + y\ln\left(\frac{CL_2}{TOC}\right) + z\ln t \qquad (10)$$

Regression of the appropriate experimental data yielded these values of K, x, y, and z of 16.8, 0.95, 0.28, and 0.22, respectively, with a correlation coefficient of 0.99. Figure 2.5 shows the natural log-log plot of measured versus predicted $CHCl_3$ concentrations based on Equation 10 and the above values of K, x, y, and z obtained from the regression.[65] Undoubtedly, this approach can be used for other precursors and DBPs that would be unique to a given water supply system.

An empirical rate equation was developed for the formation of THMs from chlorination of synthetic humic acid solutions and several river and lake waters in Japan.[66] This equation was obtained:

$$[THM] = K(pH - a)\,[TOC]\,[Cl_2]_o^m\, t^n \qquad (11)$$

where [THM] is the concentration of total THM after t hours; [TOC] and $[Cl_2]_o$ are the concentrations of total organic carbon and chlorine dosage; K is the overall reaction rate constant; and a, m, and n are parameters. The latter values, obtained empirically for humic acid, were 8.2×10^{-4} ($l^m mg^{-m} h^{-n}$), 2.8, 0.25, and 0.36, respectively. In this study, THM formation was followed over a reaction period of 50 hours wherein [THM] peaked at about 10 h, but slowly continued to increase afterward. This observation is consistent with Figure 2.4.[62] The same investigators in Reference 66 developed empirical rate equations for formation of total organic halogen (TOX) formation from humic acid and extracts of leaf mold.[67] In this study, reaction times up to 175 hours were utilized wherein TOX formation peaked within 10–50 h, after which the [TOX] continued to increase slowly.

Additional empirical models for predicting THMFP and kinetics of formation are found in Reference 68. Linear and nonlinear multiple regression models were employed for THM formation during the chlorination of natural waters. These models, according to the authors, can serve as an accurate predictor of 96-h and 2-h THMFP levels in waters subjected to alum coagulation, activation carbon adsorption, or ozone oxidation.

Most of the kinetic studies cited above have employed the relatively high-molecular-weight model compounds of humic and fulvic acids. The rate of appearance of $CHCl_3$ and other DBPs is "slow," with reaction times of 50 to 175 hours. On the other hand, there is some experimental evidence that dichloroacetonitrile (DCAN) and chloral are formed rather quickly from the chlorination of aspartic acid.[60] Approximately 300 µg/L of DCAN and 200 µg/L chloral were formed within 30 minutes at pH 6.4. Apparently, low-molecular-weight and structurally less complex precursors can produce their DBPs at relatively rapid rates and within hydraulic detention times of water treatment plants.

Ozone Disinfection By-Products

Ozone is an alternative disinfectant to chlorine for drinking water and, of course, does not form chlorinated by-products. As used in drinking water, ozone is not expected to survive to the point of consumption. Therefore, concerns about its safety are confined to by-products that result from its utilization. These products include a variety of aldehydes, ketones, carboxylic acids, unstable peroxides, and bromate.[69] The last compound, bromate, is scheduled for regu-

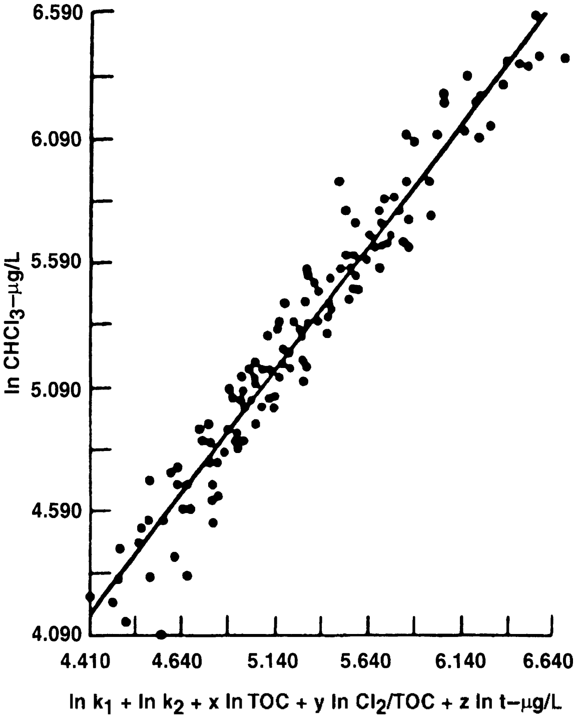

Figure 2.5. Natural log-log plot of measured vs. predicted chloroform concentration.[65]

lation in the mid 1990s (Table 1.4), whereas the other compounds are on the 1991 Drinking Water Priority List (Table 1.5).

Ozone reacts with double bonds in organic compounds to yield carbonyl-containing products, and will form the bromate ion if the Br^- ion is present (see below). One of the earliest reports came from the Lengg drinking water treatment plant in Zurich, Switzerland, where the formation of alkanals (aldehydes) in ozonated water was observed.[70] Some aldehydes were detected in the raw water; however, concentrations increased after ozonation up to 0.92 µg/L of decanal (decyl aldehyde).

The occurrence of (C_6 – C_{15}) aldehydes was reported in State Project water and Los Angeles Aqueduct water that was tested at the Los Angeles Aqueduct Filtration Plant.[71-73] The aqueduct water had a TOC content of 1.1 to 1.9 mg/L and was predosed with an ozone concentration of 1.0 mg/L and post-dosed with 1.0 to 1.5 mg/L Cl_2. The aldehydes that were identified and quantified in the raw and finished waters are shown in Table 2.19[71] and summarized in Table 2.20.[72] Raw water concentrations averaged 0.2 µg/L; that increased to 0.5 to 3.0 µg/L following ozonation. The higher levels of aldehydes seemed to be inversely proportional to the ozone dose. This concurs with a similar observation at the Lengg plant in Switzerland. The aldehydes are oxidized, perhaps, to organic acids.

Table 2.14 gives the formaldehyde and acetaldehyde contents in finished drinking waters of 25 utilities across the United States and 10 utilities in California.[37] However, it was not possible to assess the levels of these two aldehydes that were formed by disinfection. The highest concentrations were reported as 36 and 16 µg/L, respectively, for formaldehyde and acetaldehyde in a plant using ozone and chlorine. Also, the highest concentrations in finished water from a plant using chlorine alone were 17 and 7.1 µg/L, respectively.

Aldehyde and other by-products are, indeed, formed in µg/L quantities when water containing natural organics is ozonated and/or chlorinated. What, then, is the potential human health significance of these by-products? To date (1996), none of these compounds has been shown to have caused health problems, although little information is available on this subject. Compared to chlorine and chlorine dioxide, ozone appears to yield the smallest quantities of mutagenic by-products and, in some cases, may even decrease the mutagenicity of water.[74,75]

Brominated Disinfection By-Products

Ozonation of natural waters containing the Br^- ion leads to the formation of inorganic hypobromite and bromate and many brominated organic by-products. A few of the latter have been identified: bromoform, dibromoacetonitrile, dibromoacetic acid, cyanogen bromide, bromopicrin, 1,1-dibromoacetone, other bromoacetic acids, and bromohydrins.[76,77] Consequently, it is important to document the conditions under which these compounds would form at a water treatment plant.

Early studies were concerned with the formation of bromoform ($CHBr_3$) in ozonated groundwater samples containing natural organic matter and Br^-.[78] $CHBr_3$ concentrations increased with increasing $[Br^-]$ and decreased as pH value was increased from 5 to 9. Similar results were observed with ozonations of two source waters: California State Project Water and Colorado River Water.[79] In this study, bromate (BrO_3^-), cyanogen bromide, bromoform, dibromoacetic acid, and other brominated organic DBPs were observed at "low" levels (Figure 2.6).[79] Here again, the pH value was an important factor in the formation of the BrO_3^- ion, whose concentration was increased over the range of 7.4 to 9.1. Also, higher concentrations of ozone (usually applied for taste and odor control) have the potential to increase the $[BrO_3^-]$.

The operational variables of $[Br^-]$, $[O_3]$, pH, alkalinity, and ammonia were researched for their effects on brominated by-products in deionized, distilled water (DDW), and a natural lake water.[76] First, a systematic study was conducted of the by-products obtained from a natural lake water, to which various amounts of Br^- had been added, and it was oxidized with O_3. Table 2.21 and Figure 2.7a show the effect of $[Br^-]$ and the formation of dissolved organic bro-

Table 2.19. Aldehydes Identified in Ozonated Finished Water at Los Angeles Aqueduct Filtration Plant.[71]

Aldehyde	Concentration (μg/L) Raw	Concentration (μg/L) Finished
Hexanal	0.008	0.401
Heptanal	0.008	2.000
Octanal	0.047	0.209
Nonanal	0.139	0.464
Decanal	0.615	1.080
Undecanal	0.075	0.401
Dodecanal	0.014	0.107
Tridecanal	0.004	0.098
Tetradecanal	0.016	0.108

Table 2.20. Summary of Aldehyde Data for Ozonated State Project Water.[72]

Aldehyde	Concentration (μg/L) Range (Raw)	Median (Raw)	Range (Finished)	Median (Finished)
Hexanal	ND	ND	0.100–0.401	0.149
Heptanal	ND	ND	0.125–2.000	1.344
Octanal	ND	ND	ND–0.209	ND[a]
Nonanal	nd–0.55	0.030	0.4–0.107	0.095
Decanal	0.130–0.25	0.190	0.184–0.395	0.270

[a] nd = not detected.

mide (DOBr). The data show that as [Br^-] was increased, the formation of DOBr was increased. Moreover, Figure 2.7a shows that DOBr formation was enhanced at the lower pH values where HOBr is the predominant species. Table 2.21 also shows that BrO_3^- yields were not increased at higher pH values (runs 011-015). These results are at variance with those of other researchers.[79]

The data in Table 2.21 and Figure 2.7b show that as alkalinity was increased, the formation of DOBr was inhibited greatly, and that no BrO_3^- was detected in the runs (016–018) with added alkalinity. Apparently HCO_3^- scavenges OH radicals, which may play a role in the formation of a brominated by-product by affecting the level of HOBr, the most active species for DOBr formation. The added levels of alkalinity (runs 016–108) also suppressed the formation of BrO_3^-.

Substantial effects of ammonia were expected because of the formation of bromamines, which renders HOBr unavailable for reaction with natural organics.[80] The effect of ammonia was less than expected (Figure 2.7c and Table 2.21, runs 019–021), but some lesser amounts of DOBr were observed.[76] However, the BrO_3^- levels were affected. For example, no BrO_3^- was detected in runs 020 and 021 at the higher ammonia levels. In this study of the effect of operational variables on the formation of DOBr, the yield was less than 10% in most runs in Table 2.21. All of this should be viewed in the context of what effects these trace quantities of DOBr may have on human health.

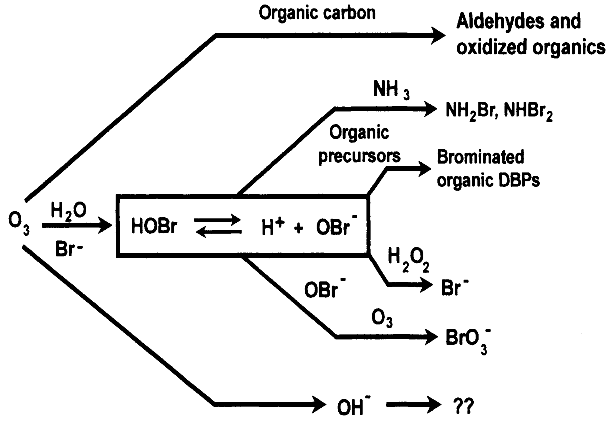

Figure 2.6. Possible reactions of ozone in water.[79]

In order to comply with the new and more stringent regulations of disinfection, drinking water utilities have studied alternative treatments. Starting in 1989, pilot-plant and full-scale studies of O_3 treatment were supported by the AWWA Research Foundation (AWWARF) and were performed in association with the Metropolitan Water District of Southern California (MWD) and other utilities.[81] Ozonation facilities were surveyed for the occurrence and control of DBPs and for unknown ozone DBPs. At the same time, a pilot-scale study evaluated ozone and PEROXONE (the addition

Table 2.21. The Role of the Matrix Variable on the Yield of Bromated By-Products upon Ozonation of University Lake Water[a].[76]

Run	$[Br^-]$ Before O_3 µM	$[Br^-]$ After O_3 µM	DOBr µM as Br	Bromate µM[b]	MBA µg/L	$CHBr_3$ µg/L	DBAN µg/L	MBAA µg/L	DBAA µg/L	TBAA µg/L	Organic Bromide Identified[c] percent	Bromide Recovered percent
001	A[d] (0.4)	0.4	ND[d]	BDL[d]	BDL	BDL	BDL	BDL	BDL	BDL	ND	100
002	A + 5	0.3	0.6	BDL	3.1	BDL	BDL	BDL	2.9	BDL	5.0	2
003	A + 10	6.5	3.7	0.2	6.4	2.3	0.5	BDL	11.2	BDL	5.0	04
004	A + 50	38	8.0	0.5	36	48	3.8	6.7	34	14	18	93
005	A + 100	84	11	0.4	41	76	6.0	7.7	48	25	18	95
006	A (0.4)	0.4	ND	BDL	BDL	BDL	BDL	BDL	BDL	BDL	ND	100
007	A + 5	2.1	2.7	0.1	7.1	0.9	BDL	BDL	10	BDL	6	98
008	A + 10	5.2	5.4	0.2	12	2.7	BDL	BDL	15	BDL	5	99
009	A + 50	31	15	0.2	38	36.5	3.6	4.3	28	18	8.2	92
010	A + 100	58	21	0.2	46	42	5.1	5.4	44	35.5	8	79
011	A (0.4)	0.4	ND	BDL	BDL	BDL	BDL	BDL	BDL	BDL	ND	100
012	A + 5	5	ND	BDL	BDL	BDL	BDL	BDL	BDL	BDL	ND	100
013	A + 10	10	ND	BDL	BDL	BDL	BDL	BDL	BDL	BDL	ND	100
014	A + 50	48	0.3	0.1	2.1	0.5	BDL	BDL	5.2	BDL	25	97
015	A + 100	96	1.8	0.2	10.5	7.1	BDL	BDL	17.5	BDL	18	98
016	A + 10	7.4	2.4	BDL	4.3	1.1	BDL	BDL	7.5	BDL	5	98
017	A + 10	8.9	0.7	BDL	1.9	BDL	BDL	BDL	4.3	BDL	7	96
018	A + 10	9.9	ND	BDL	BDL	BDL	BDL	BDL	BDL	BDL	ND	99
019	A + 10	6.7	3.4	0.1	5.2	1.7	BDL	BDL	9.3	BDL	4.4	102
020	A + 10	7.0	2.9	BDL	3.8	0.9	BDL	BDL	6.0	BDL	3.4	99
021	A + 10	7.7	1.6	BDL	1.2	BDL	BDL	BDL	2.1	BDL	1.8	93

[a] Ozone dose—1 mg O_3:1 mg DOC (DOC = 5 mg as C/L). Quenching agent for neutral and acidic extraction of brominated organics was $(NH_4)_2SO_4$.

[b] For bromate analyses, 0.1 µM = 13 µg BrO_3^-/L.

[c] Organic bromide identified = sum of targeted compounds/DOBr.

[d] A—ambient Br^- concentration (0.4 µM); BDL—below detection limit; ND—not detected.

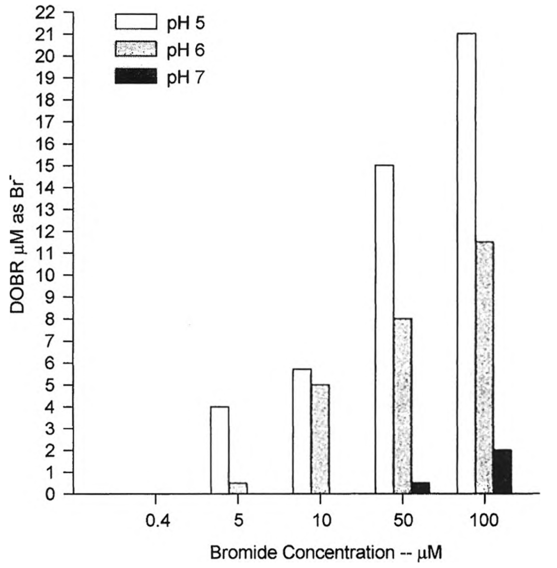

Figure 2.7a. Formation of dissolved organic bromide as a function of bromide concentration and pH.[76]

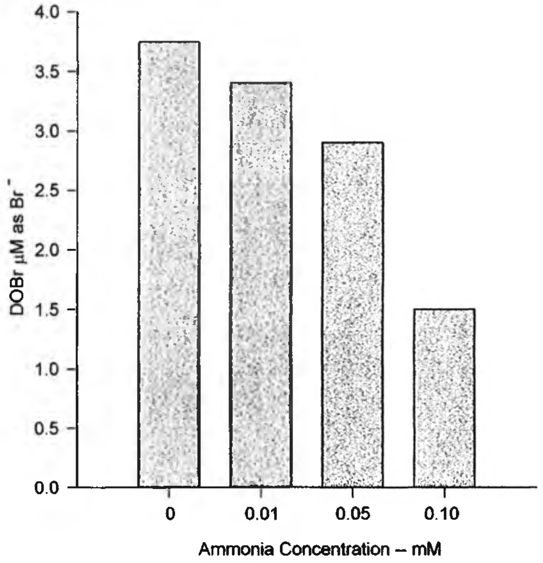

Figure 2.7c. Formation of dissolved organic bromide as a function of ammonia concentration.[76]

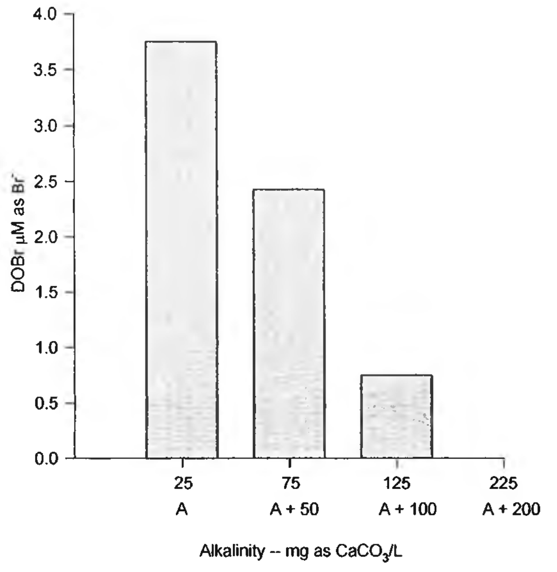

Figure 2.7b. Formation of dissolved organic bromide as a function of alkalinity (A—ambient alkalinity = 25 mg as $CaCO_3$/L).[76]

of hydrogen peroxide) for the control of microorganisms, taste- and odor-causing chemicals, and DBPs. The primary concern was the formation of BrO_3^- under plant conditions.

Table 2.22 summarizes the bromate occurrence for the ozone tests at ambient pH, Br^-, and NH_3-N levels for several utilities in the MWD studies.[81] Several observations were reported: (a) when the $[Br^-]$ was less than 0.06 mg/L, bromate was not detected with current minimum reporting levels (MRL, see footnotes in Table 2.21) at the indicated ozone dosages, (b) when the $[Br^-]$ was in the 0.18 to 0.33 mg/L range, BrO_3^- was detected at levels of 9–60 μg/L, and (c) Br^- spiking up to 0.8 mg/L at utility F increased the bromates formation from 10 to 20 μg/L. All of this research led to a conclusion that there is a minimum $[Br^-]$; i.e., a threshold value above which BrO_3^- formation is observed.

This threshold level was identified to be ~0.2 mg/L Br^- when an MRL level of 5.0 μg/L is employed for BrO_3^- formation.[81,82] This MRL level is significant because it may represent the eventual regulatory level. Consequently, the analytical methodology must be improved for detection of BrO_3^- in drinking water.

Many of the above observations and conclusions concerning the formation of brominated DBPs during O_3 and Br^- reactions were reported for several surface waters in California and groundwaters in California and Florida.[83] The major thrust of this study was the effect of water source, i.e., various organic precursors, on the formation of such DBPs as bromoform, bromoacetic acids (BAAs), bromoacetones (BACs), and bromoacetonitriles (BANs). Such environmental factors as pH, $[O_3]$, temperature, and alkalinity were examined. Both organic and inorganic by-products were increased when $[Br^-]$ was increased, but decreased with an increase in alkalinity. When the pH value was lowered, organic DBPs generally were increased, whereas BrO_3^- formation was favored by a high pH. Both ozonation and incubation temperatures had a positive effect on the formation of CH_3Br and BrO_3^-. PEROXONE apparently favored BrO_3^- formation over organic BP formation, whereas the ad-

Table 2.22. Bromate Occurrence for Ozone Tests at Ambient pH, Br$^-$, and NH$_3$–N[a].[81]

Utility Code	Br$^-$ mg/L	O_3 Dose mg/L	O_3 Residual mg/L	HRT[b] min	pH	Temperature °C	BrO$_3^-$ mg/L[c]
A1	0.03	1.0;0.5[d]	0.95;1.4[d]	5;5[d]	7.4	13	ND(<10)[e]
A2	0.02	3.0	0	51	7.4	20	5
B	0.04	4.0	0	3.5	5.6	21	ND(<10)
C	<0.01	1.6	0.50	10	6.6	1	ND(<5)[f]
D1	0.28	1.0;0.46[d]	0.05	7	8.0	17	<10–10
D2	0.22	1.4	0.12	7.4	7.9	19	9–18
E[g]	0.24	3;3[h]	NA[i]	5.6;16.25[h]	7.8;9.9[h]	30	ND(<10)
F1	0.19	9.3	0	12	9.3	25	10
F2	0.65	9.3	NA	12	9.4	28	10
F3	0.80	9.3	0	12	9.4	26	20
G	<0.01	0.94	0.40	5	6.8	17	ND(<5)
H	0.06	1.8	0	20	7.4	26	ND(<5)
I1	0.05	2.0;0.42[h]	0;0[h]	19;29[h]	7.6;7.2[h]	22	<5–8
I2	0.04	1.5;0.6[h]	0;0.12[h]	31;23[h]	8	10	ND–5
I3	0.04	2.5;0.6[h]	0.1;0.1[h]	15.5;11.5[h]	8	10	ND–7
J	0.33	2;2[d]	0.35[f]	3.5;3.5[d]	~8	17	10
MWD[j]							
CRW	0.06	2.0	1.05	12	8.4	15	ND(<10)
CRW-SPW[l]	0.18	2.0	1.00	12	8.3	15	10–20
SPW	0.28	2.0	0.71	6	8.0	17	40–60

[a] These data do not include the PEROXONE studies but do include bromide spiking at utility F.

[b] Contact times may include detection times in downstream basins.

[c] These data represent a range of values from ozone contactor effluent through plant effluent.

[d] This utility ozonated the water in a two-stage contactor.

[e] ND (<10)—not detected at or above MRL of 10 μg/L.

[f] ND (<5)—not detected at or above MRL of 10 μg/L.

[g] This utility chloraminated first-stage ozone contactor effluent.

[h] This utility ozonated the water at two locations in the plant.

[i] NA—not analyzed.

[j] Residual out of the second stage of the contactor.

[k] MWD—Metropolitan Water District of Southern California pilot-plant testing.

[l] Ozonated 50:50 blend of CRW and SPW.

dition of NH$_3$ reduced both BrO$_3^-$ and organic BPs. These studies certainly have identified those treatment plant conditions under which brominated BPs form from ozonation disinfection processes.

A laboratory study investigated the effects of [Br$^-$], pH, reaction time, and [Cl$_2$] on the formation of chlorinated and brominated DBPs from the chlorination of commercial humic acid (HA).[84] Experimental conditions were somewhat elevated from plant operation in an effort to produce the by-products. For example, Cl$_2$ dosages of 11.5 and 25 mg/L were employed in a statistical evaluation of the study. Typical results are seen in Figures 2.8a, b, and c, where acidic pH values and reaction times greater than 48 hours favored the formation of bromochloroacetic acid (BCAA), dichlorobromoacetic acid (DCBAA), and dibromochloroacetic acid (DBCAA), respectively. Bromide concentrations ranged from 0.0 to 4.5 mg/L. This is certainly evidence for the formation of brominated DBPs from HA under conditions that may not be represented in actual treatment plant situations.

Four separation processes were investigated in another laboratory study in an effort to control the formation of DBPs in finished waters from natural sources.[85] These processes (GAC, PAC, anion exchange, and membrane filtration) were designed to remove the NOM before a disinfectant was applied. The essential results were that: (a) as the DOC was decreased, with chlorination of these systems where the [Br$^-$] was held constant there was a shift to brominated THMs; (b) "at low DOC concentrations, the percentage of brominated THMs was higher in treated effluents than in influent water;" and (c) those processes that were most effective for controlling the formation of CHCl$_3$ were, in turn, the least effective for control of CHBr$_3$. The latter observation is extremely significant in the event that brominated DBPs are, indeed, hazardous to human health at the μg/L level.

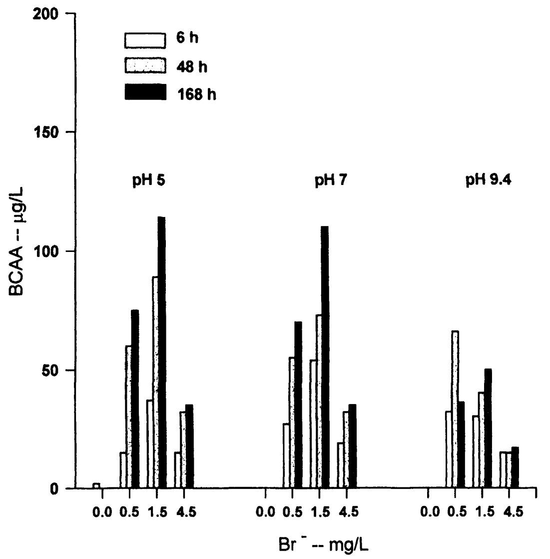

Figure 2.8a. Effect of bromide ion, pH, reaction time, and low chlorine dosage on formation of BCAA (block 2, chlorine dose—11.5 mg/L; HA—2.83 mg as NVTOC/L).[84]

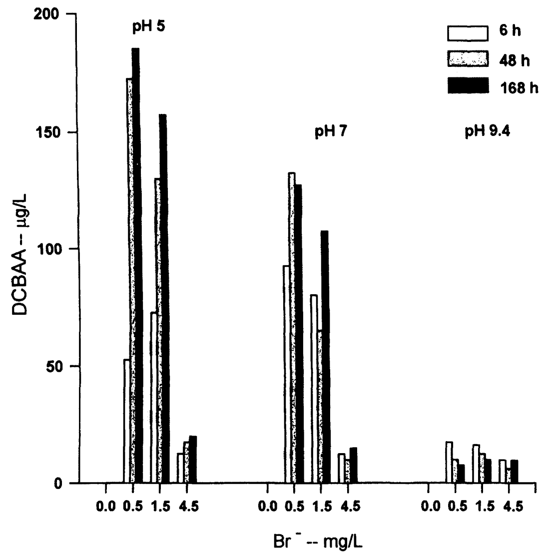

Figure 2.8b. Effect of bromide ion, pH, reaction time, and low chlorine dosage on formation of DCBAA (block 2, chlorine dose—11.5 mg/L; HA—2.83 mg as NVTOC/L).[84]

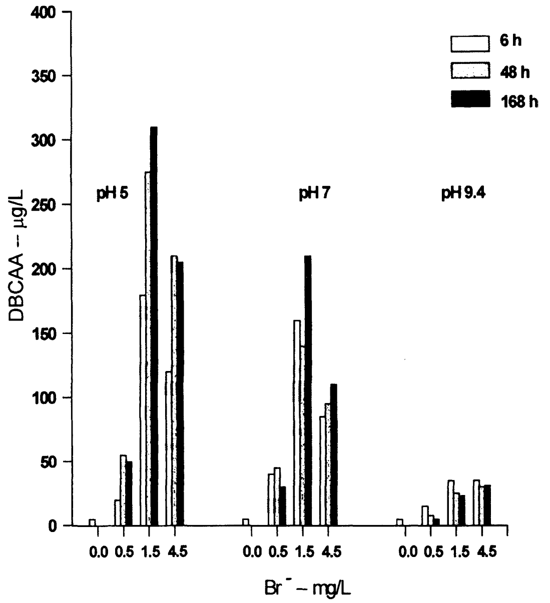

Figure 2.8c. Effect of bromide ion, pH, reaction time, and low chlorine dosage on formation of DBCAA (block 2, chlorine dose—11.5 mg/L; HA—2.83 mg as NVTOC/L).[84]

Prevention of Disinfection By-Product Formation

A simplistic approach for the elimination or reduction in the DBP content in drinking waters is to employ a disinfectant other than chlorine. Obviously, the alternative technique would have to be as effective as chlorine. The use of chloramine (NH_2Cl and/or $NHCl_2$, see Chapter 11) was proposed for the drinking water of Huron, South Dakota.[86] According to the NORS study,[7] their water supply contained THM in excess of the proposed (at that time) MCL of 100 µg/L. Disinfection had been achieved by a combination of chlorine, $KMnO_4$, and lime-soda softening (i.e., pH>11.0). The alternative disinfectant was chloramine treatment through addition of ammonium sulfate and chlorine. This was a reasonably good choice inasmuch as the softening process reduced the total coliform count some 68–100%. The appropriate laboratory and field studies were conducted to demonstrate the assurance of disinfection in the distribution system during and after the transition to the chloramine treatment. Figure 2.9 shows the [THM] during this period of time, where percentage reductions ranged from 72 to 79%, and the average of 37 µg/L satisfied the EPA's maximum contaminant level. There was a subsequent discussion about the effectiveness of chloramine disinfection.[87] An extremely strong argument was presented for use of chloramines as a primary disinfectant from 30 years of experience: "when properly applied at effective dosages (1.5 to 1.8 mg/L, in their case), chloramine produces 100% kills of pathogenic bacteria species and also effectively reduces total bacterial populations to an acceptable range."[88]

Several options are available to control THM and achieve disinfection at the same time:[89]

1. Use a disinfectant that does not produce THM.
2. Reduce the precursor concentration prior to chlorination.
3. Remove the THMs after their formation.

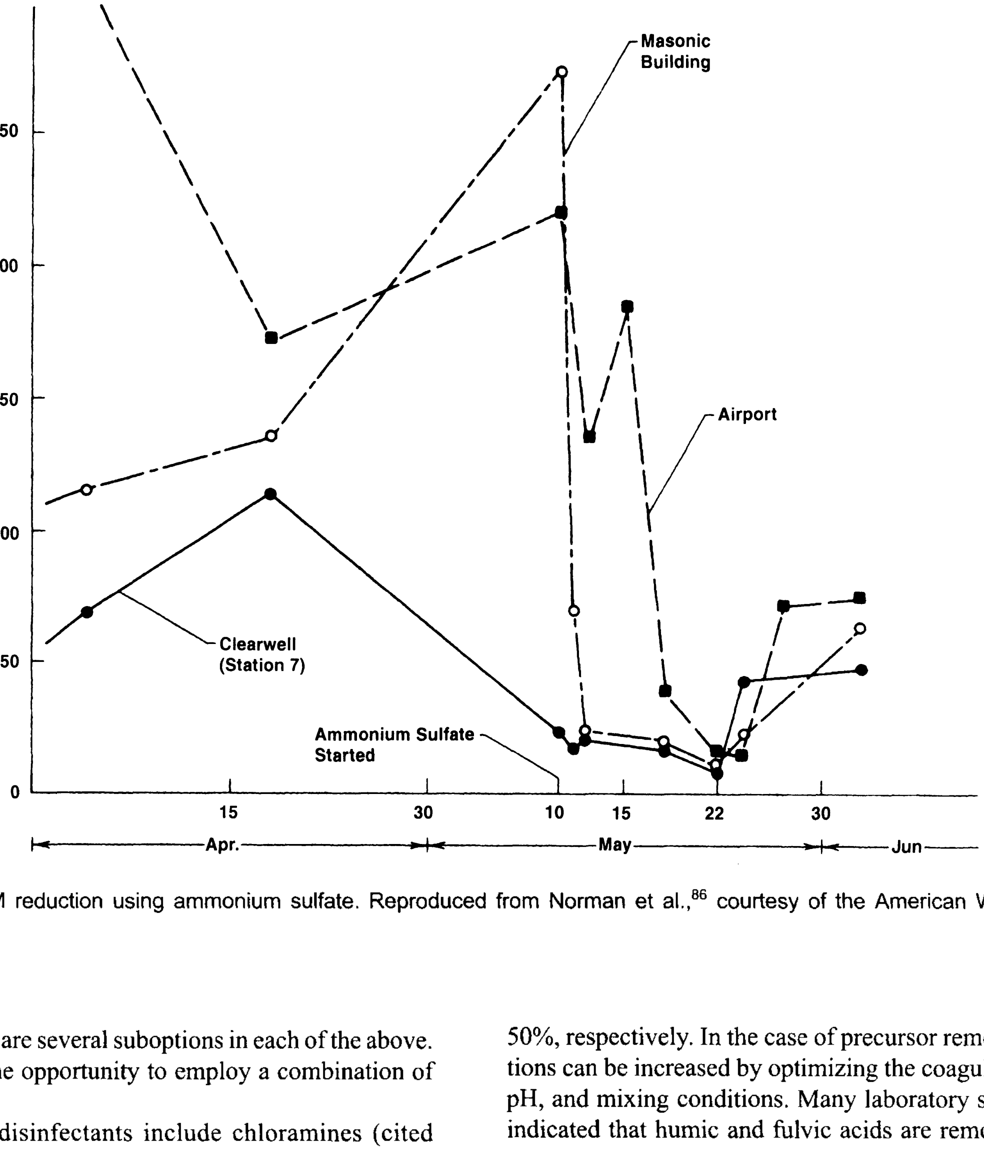

Figure 2.9. THM reduction using ammonium sulfate. Reproduced from Norman et al.,[86] courtesy of the American Water Works Association.

In turn, there are several suboptions in each of the above. Also, there is the opportunity to employ a combination of all three.

Alternative disinfectants include chloramines (cited above), chlorine dioxide (ClO_2), and ozone (O_3). The last two oxidants can be used also to reduce precursor concentrations prior to disinfection. An argument against use of chloramine disinfection is the "100-fold increase in contact time to inactivate coliform bacteria and enteric pathogens as compared to free available chlorine."[89] This is an "old" argument that has been rebutted many times. The experience of Brodtmann and Russo[88] has been repeated throughout the water treatment industry. Commonly used water treatment alternatives are given in Figure 2.10,[89] where the logic of "the least costly approach" was used. Any treatment modifications generally involve maximizing the efficiency of precursor removal during coagulation, flocculation, sedimentation, and filtration, as well as changing the chlorination point or dosage. The last recommendation has been successful at Cincinnati, Ohio[89] and Louisville, Kentucky,[90] where reductions of THM were 75% and 40–50%, respectively. In the case of precursor removal, reductions can be increased by optimizing the coagulant dosage, pH, and mixing conditions. Many laboratory studies have indicated that humic and fulvic acids are removed by coagulation to approximately 90% and 60%, respectively.[91] However, higher-than-normal coagulant dosages are required. Another modification is the installation of a second chlorination point in the distribution system. This was successful at the East Bay Municipal Utility District, California, where the initial chlorine dosage was decreased from 2.0 to 0.5 mg/L and an increase of the chlorine residual in the distribution system to 0.5 mg/L was effected. The [THM] was reduced by 50% at the consumer's tap.[92] More information on precursor removal and control of THM is given in Chapters 6 and 11.

Some operational experience has been obtained with the use of ClO_2 as an alternative to Cl_2 for disinfection and preventing the formation of DBPs. For example, the Evansville (Indiana) Water and Sewer Utility conducted a comparative study of a pilot plant using ClO_2 and a full-scale plant that used Cl_2.[93] The major intent of this case study was

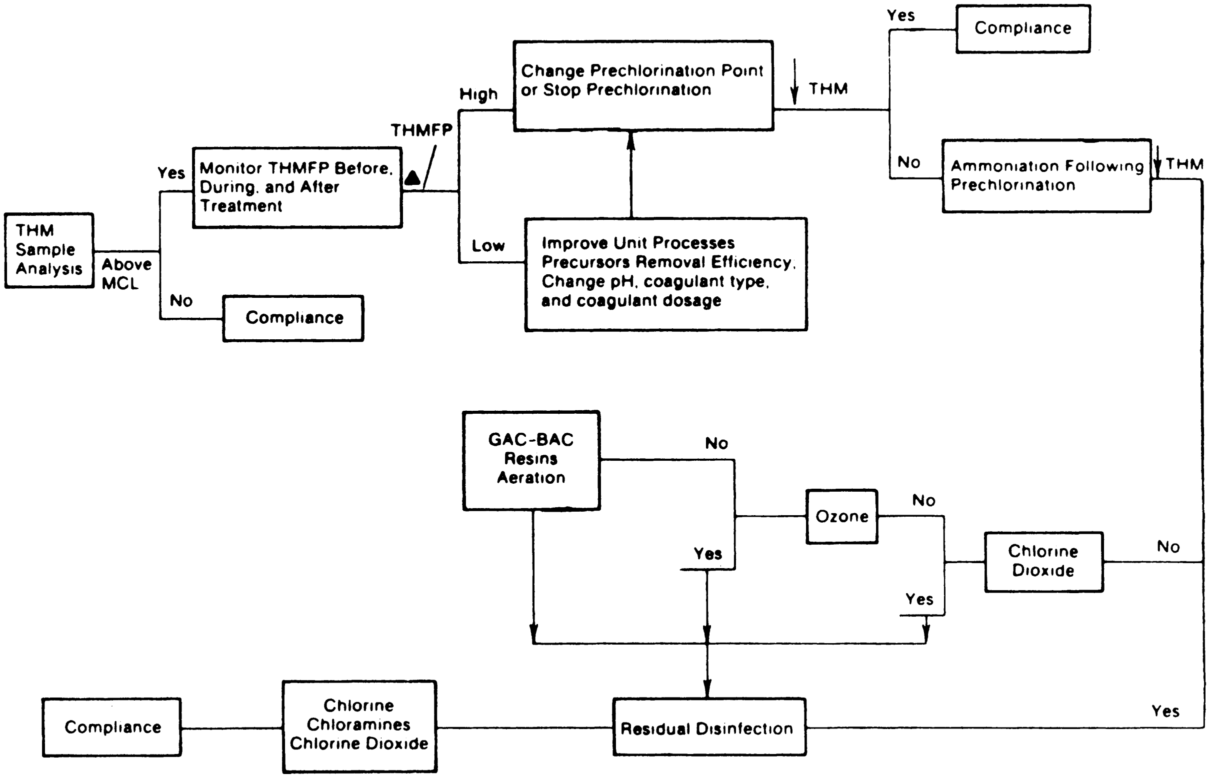

Figure 2.10. General approach to THM control. Reproduced from Vogt and Regli,[89] courtesy of the American Water Works Association.

prevention of DBP formation. Chlorine dioxide was so effective in the reduction of THMs that it was incorporated in Evansville's full-scale plant in 1983. With the use of ClO_2 as a predisinfectant, this utility was able to maintain annual average TTHM levels between 50 to 80 μg/L in their distribution systems.

Chlorine dioxide is not without problems, however. Chlorite ions (ClO_2^-), a reduction product, have a deleterious effect on the red blood cell survival rate when its concentration exceeds 10 mg/L.[94] Consequently, the USEPA intends to promulgate MCLG and MCL values for chlorite sometime in the 1990s (see Table 1.4). Also, see Chapter 11 for additional information on the possible human health effects of chlorite.

An EPA Publication (EPA 600/2-81-156), "Treatment Techniques for Controlling Trihalomethanes in Drinking Water," appeared in late 1981.[44] It addresses the Groups 1 and 2 technologies for THM control that were cited in Chapter 1. In this publication, which is a compilation of several studies, three approaches were investigated for THM control: removal of THM, removal of THM precursors, and the use of alternative disinfectants to chlorine. Of these three technologies, the applications of alternative disinfectants are the most effective and the least costly. ClO_2, O_3, and chloramines produce no significant concentrations of THM when used as disinfectants (see Chapter 11). However, the major disadvantage of this approach is that it does not remove precursors of the THM. Instead, ClO_2 and the chloramines may produce some other types of halogenated products from the organic matter in the water (see above). Also, there are some other disadvantages of these three disinfectants (summarized below).

For removal of the THM and their precursors, nine approaches are available: oxidation, aeration, adsorption, clarification, ion exchange, biodegradation, pH adjustment, source control, and intense mixing during disinfection. Within the nine treatments, 19 techniques were researched. Table 2.23 summarizes the effectiveness of these techniques for control of THM. Estimated costs are available also in this EPA publication.

Phenolic Compounds

Hydroxy derivatives of benzene (i.e., phenol, C_6H_5OH) require special mention because of their possible effects on the taste and odor quality of potable water, potential toxicity to aquatic life in natural waters,[95] and possible human health effects.[94] Two phenols, 4-nitrophenol and 2,4-dinitrophenol, are on the 1991 drinking water priority list

(Table 1.5). Also, an MCLG of zero and an MCL of 0.001 mg/L have been proposed for pentachlorophenol (Table 1.7). The role of phenol in these three effects on water quality is somewhat controversial, largely because of the analytical difficulties of quantitatively detecting and identifying these compounds in natural waters.

Naturally Occurring Sources

Many phenolic compounds may be derived from natural products. For example, seven hydroxy derivatives of benzene were found from degradative studies of the "color macromolecules."[96] These compounds were: catechol, resorcinol, vanillin, vanillic acid, syringic acid, protocatechuic acid, and 3,5-dihydroxybenzoic acid. In natural waters, there is the possibility that these compounds may arise from the microbially catalyzed degradation of color molecules. Many of these phenols have been recovered and identified in two rivers in Japan.[97]

A rather unique source of naturally occurring phenolic compounds was reported.[98] The phenolic acids *m*-hydroxybenzoic acid, *m*-hydroxyphenylacetic acid, and *m*-hydroxyphenylpropinoic acid were isolated from liquid manure (defined as urine from domestic animals). Average amounts of these three compounds were 35.8, 27.4, and 40.0 mg/L, respectively. In view of the rather substantial population of domestic farm animals in the world, liquid manure may represent a significant source of naturally occurring phenolic compounds.

Anthropogenic Sources

Many sources may be cited for industrially sponsored phenolic compounds: petroleum refineries, manufacturers of synthetic organic chemicals, ammoniacal liquors from coke ovens, domestic wastewater, fungicides and pesticides, hydrolysis and photochemical oxidation of organophosphorus and carbamate pesticides, and microbial degradation of phenoxyalkyl acid herbicides. The first four sources may be, perhaps, the most significant, and provide the greatest contents to the aquatic environments. Typical phenols and their contents in petroleum refinery effluents are given in Table 2.24.[99] The phenolic content of a typical domestic wastewater is in the 108–128 µg/L range.[100]

Contents of Surface and Groundwaters

Surprisingly, few data are available in the literature that document phenolic contents of surface waters of the United States. It would appear from the many sources of phenols cited above that they should have ubiquitous occurrence. Some indication may be obtained from surveys of the Delaware Estuary and several of its estuaries.[101] Table 2.25 shows these data were produced from the wet, colorimetric 4-aminoantipyrine [4-AAP] method for phenolic compounds.[102,103] This method does not yield a "total" phenol content largely because 4-AAP does not react with many para-substituted phenols. As such, the concentrations given in Table 2.25 should be viewed as minimum values. How much greater the actual phenol content isn't known with any degree of certainty. The Delaware Estuary receives many industrial and several petroleum refinery effluents. These phenol contents reflect many, many sources.

Phenolic compounds are quite persistent under the "proper conditions." These conditions are usually found in groundwater aquifers. For example, in 1962 the contamination of groundwaters by phenols after the end of World War II was observed at Alma, Michigan.[104] An accidental spill of commercial carbolic acid (95–100% phenol, C_6H_5OH) occurred in southeastern Wisconsin in July 1974.[105] After 19 months of monitoring, the groundwater in the area surrounding the spill remained contaminated. Phenol contents ranged from 0.036 to 1130 mg/L, whereupon 200 mg/L remained at the conclusion of the monitoring period in the well nearest the spill (120 m).

Several specific phenolic compounds were identified in a Delaware Estuary survey:[101] *o*-chlorophenol, *o*-cresol, 6-chloro-*o*-cresol, *o*-nitrophenol and 3,5-xylenol were identified by gas-liquid chromatography. Such identification techniques can provide much information about sources of the phenols.

Halogenated Phenols

Halogenated phenolic compounds frequently occur from the chlorination of waters, such as natural waters or wastewaters, that contain precursors or a parent molecule. Several examples are given here and in Chapter 3.

Hypochlorous acid (HOCl) was added to aqueous solutions of 2,6-dichloro-, 2,4-dichloro-, 2,4,5-trichloro-, 2,4,6-trichloro-, 2,3,4,6-tetrachloro-, penta-, and *o*-nitrophenol at pH values of 3.5 and 6.0.[106–108] Several products were identified: chlorinated phenols, chloro-*p*-benzoquinones, chlorinated 2,5-cyclohexadienes, and derivatives of cyclohexenone. Reaction periods of 20–24 hours were employed. These chlorinated products may very well occur in drinking waters in the process of superchlorination.

That chlorophenols occur in contaminated surface waters in substantial quantities and frequency was reported for several rivers in the Netherlands. Typical data are seen in Table 2.26 for the Rhine River.[109] 2,6-Dichlorophenol, 2,4,5-trichlorophenol, 2,4,6-trichlorophenol, 2,3,4,6-tetrachlorophenol, and pentachlorophenol occur with the greatest frequencies and have the highest concentrations. Industrial and/or municipal wastewater discharges were undoubtedly the sources of these chlorophenols. Pentachlorophenol is used extensively as a wood preservative. Its occurrence in natural aquatic environments is almost ubiquitous.[110]

Table 2.23. Effectiveness of THM-Removal Techniques.[44]

Treatment	Precursor	Trihalomethanes	Other By-Products	Disinfection	Remarks
Ozone Oxidation	Good to very good destruction is technically feasible. The apparent concentration may increase at low doses. High doses and long contact times are required for good destruction, and complete destruction is difficult.	No effect by ozone, some incidental gas stripping.	Some are formed, but they will not contain chlorine unless free chlorination or chlorine dioxide is employed. Bromine-containing THM may not be formed on later chlorination.	Excellent, but no residual is created. Organisms may regrow in the distribution system.	Slightly better at high pH.
Chlorine Dioxide Oxidation	Good destruction is technically feasible, but complete destruction was not achieved.	No effect.	Some are formed by the process and some will contain halogen.	Good and provides a residual. Slightly more effective at high pH.	Residual oxidant should be limited to 0.5 mg/L because of health effects.
Potassium Permanganate Oxidation	Fair destruction is technically feasible, but complete destruction was not achieved.	No effect.	Some are formed by the process and some will contain halogen, if free chlorine or chlorine dioxide is used.	Poor; a disinfectant must be used.	Pink water with overdose. Better at high pH.
Lowering pH	Fair decline of Term THM concentration is technically feasible. Affects the rate of reaction between free chlorine and precursor, thereby lowering resulting THM concentration.	No effect.	None formed by the process, but some formed during final disinfection.	Free chlorine is more effective at lower pH.	May cause some corrosion problems.
Diffused-Air Aeration	No effect and THM will form if free chlorine is used.	Good to very good removal is technically feasible, but bromine-containing THMs are harder to remove than chloroform. High air-to-water ratios are difficult to achieve.	None are known to be formed by the process but some are still formed during disinfection. By-products will contain halogen if free chlorine or chlorine dioxide is used.	Disinfection is required.	Influent air can be cleaned. Possible air pollution problems. Removes regulated contaminant. Some removal of SOC[a] and T&O#[b] compounds.

Tower Aeration	No effect and THM will form if free chlorine is used.	Good to very good removal is feasible, but bromine-containing THMs are harder to remove. High air-to-water ratios can be achieved.	None known to be formed by the process, but some are still formed during disinfection. By-products will contain halogen if free chlorine or chlorine dioxide is used.	A disinfectant is required.	Difficult to clean air, may entrain particulates. Possible air pollution problems. Removes regulated contaminant. May have to protect from freezing. Some removal of SOC and T&O# compounds.
Powdered Activated Carbon Adsorption	Good to very good removal is feasible. Removal is influenced by influent concentration and the loading is proportional to the influent concentration.	Good to very good removal is feasible. Bromine-containing THMs are better adsorbed than chloroform. Removal is influenced by influent concentration and the loading is proportional to the influent concentration.	None are formed by the process. Some removal of those coming to the process and less reformation as related to TOC removal. Will contain halogen if chlorine or chlorine dioxide is used.	Removes chlorine so must post-disinfect. Some reduction in disinfectant demand.	Some removal of SOC and T&O# compounds. No desorption with decreasing concentration because PAC only used once. Sludge disposal a problem.
Granular Activated Carbon Adsorption	Good to very good removal technically feasible. Removal is nearly complete when adsorbent is fresh, then breakthrough toward exhaustion begins. Complete exhaustion generally does not occur, however. Loading is proportional to influent concentration and desorption may occur when the influent concentration declines.	Good to very good removal is technically feasible. Removal is nearly complete when adsorbent is fresh but then breakthrough to exhaustion occurs. Bromine-containing THM adsorbed better than chloroform. Loading is proportional to influent concentration and desorption will occur if the influent concentration drops.	None formed by the process and some can be removed. Because of good TOC removal, fewer are formed during disinfection.	Chlorine removed, so postdisinfection required. Disinfectant demand is lower than when TOC is removed.	SOC & T&O# compounds also removed. Requires reactivation or replacement. Complete removal does not last long. Possible Corrosion problems if effluent TOC[c] concentration near zero.
Clarification by Coagulation, Sedimentation, Filtration	Good removal is feasible. If reaction with free chlorine is fast, delaying chlorination until after clarification will permit more removal. More removal will occur at lower pH but the reaction between free chlorine and precursor will be slower.	No effect.	None formed by the process and some may be removed. Because of TOC removal, fewer are formed later during disinfection. Some will contain halogen if free chlorine or chlorine dioxide is used.	Disinfectant demand lower if disinfection is delayed.	Sludge disposal problem. Iron salts may be somewhat better than alum.

Table 2.23. Effectiveness of THM-Removal Techniques[44] (Continued).

By Precipitative Softening	Good removal is technically feasible. The faster reaction rate between free chlorine and precursor at higher pH should result in additional benefit by delaying chlorination.	No removal by process. High pH accelerates reaction to form THMs.	None formed by the process. Because of TOC removal, fewer are formed during disinfection. Some will contain halogen if free chlorine or chlorine dioxide is used.	Effectiveness of free chlorine reduced at higher pH. Disinfectant demand will be lower if disinfection is delayed.	Sludge disposal a problem.
By Direct Filtration	Good removal is technically feasible. THM concentrations will be lower if chlorination is delayed until after the process.	No effect.	None formed by the process. Because of TOC removal, fewer are formed during disinfection. Some will contain halogen if free chlorine or chlorine dioxide is used.	Disinfectant demand lower if disinfection follows clarification.	Little sludge produced. May require polymers.

[a] SOC = Synthetic Organic Compound.

[b] T&O# = Taste and Odor Number.

[c] TOC = Total Organic Carbon.

Table 2.24. Determination of Phenols in Refinery and Petrochemical Plant Effluents.[a]

	Concentration of Phenols Found in Various Streams by Chromatographic Method (ppm)		
Type of Phenol	Biologically Treated Refinery Wastewater[b]	Once-Through Refinery Cooling Water[c]	Petrochemical Plant Process Wastewater[d]
Phenol	0.01	0.02	0.36
Cresols	0.22	0.22	0.04
Dimethyl Phenols	2.59	0.02	0.40
Trimethyl Phenols	0.71	0.03	0.17
Other Phenolics	0.31	0.07	0.21
Total Phenols	3.83	0.36	1.18
Total Phenols by Colorimetric Method	2.3	0.39	1.03

[a] Reproduced from Chriswell et al.,[99] courtesy of the American Chemical Society.
[b] Major components: 2,5-dimethyl phenol (0.87 ppm), 3,5-dimethyl phenol (0.82 ppm).
[c] Major components: *m*- and *p*-cresol (0.20 ppm).
[d] Major components: phenol (0.36 ppm), 3,4-dimethyl phenol (0.32 ppm).

Table 2.25. Summary of the Phenolics Reconnaissance Survey of the Delaware Estuary, July 1974–June 1976.[101]

			Phenolic Concentration (μg/L)	
Sites	No. Sites	No. Samples	Average	Range
Delaware				
Water, All sampling	73	189	11	1–142
Water, Shore sampling[a]	27	64	17	1–142
Water, Boat sampling[46]	125	8	1–32	
Upper estuary[a]	24	85	10	1–32
Lower estuary[b]	22	40	5	1–29
Muds	58	64	227[c]	<10–917[c]
Tributaries, Water, Shore	14	17	16	1–36
Delaware, Above Trenton, Water	7	13	3	1–8
Storm Runoff, Pennypack Sewer[d]	1	25	16	1–32
Refinery Effluent, Arco	2	8	15	1–40

[a] Trenton to Artificial Island.
[b] Below Artificial Island.
[c] mg/kg, dry wt.
[d] Two storm events.

Chlorophenols are formed also from the chlorination of naturally occurring organic compounds.[111] Hypochlorous acid was reacted with two natural compounds—*p*-hydroxybenzoic acid and vanillic acid—under a variety of conditions. A mixture of 4-chlorophenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol was produced when *p*-hydroxybenzoic acid was chlorinated. These kinds of chlorination reactions presumably account for the occurrence of chlorophenols in such natural waters as the Rhine River, Delaware Estuary, and Weser Estuary.[112]

Bromophenols may be formed during chlorination of phenol (C_6H_5OH) in the presence of bromide ions. The formation of 2,4,6-tribromophenol was reported under these conditions.[113] A brominated phenol was observed also in the process of chlorinating humic acid with Br^- in the system.[114]

A special notation should be given to the distribution of pentachlorophenol (PCP) in aquatic environments. Many of the reports[106–114] cite the occurrence of this chlorinated phenol in natural waters and, frequently, in the attendant bottom sediments. In addition, significant quantities of PCP were detected in sewage influent and effluent, Willamette River water and subsequently the finished drinking water of Corvallis, Oregon.[115] "Potentially dangerous levels" of PCP were found in a tributary of the Delaware River.[116] An industrial wastewater discharge was responsible for PCP concentrations as high as 10.5 ppm. Likewise, significant quantities of PCP were found

Table 2.26. Concentrations (in $\mu g/L$ = ppb) of Chlorophenols in the River Rhine at Kilometer 865 (Lobith) in 1976 and 1977.[a]

	1976			1977		
Phenol	**Frequency (%)**	**Max.**	**Med.**	**Frequency (%)**	**Max.**	**Med.**
2-Chlorophenol	2	2.3	—[b]	0	—	—
3-Chlorophenol	4	6.0	—	0	—	—
4-Chlorophenol	16	3.9	—	0	—	—
2,3-Dichlorophenol	10	0.72	—	25	0.86	—
2,4-Dichlorophenol	47	0.59	—	48	0.35	—
2,5-Dichlorophenol	37	0.29	—	35	0.26	—
2,6-Dichlorophenol	75	0.45	0.15	64	0.43	0.10
3,4-Dichlorophenol	0	—	—	2	0.23	—
3,5-Dichlorophenol	37	0.52	—	12	0.77	—
2,3,4-Trichlorophenol	0	—	—	4	0.21	—
2,3,5-Trichlorophenol	0	—	—	1	0.18	—
2,3,6-Trichlorophenol	4	0.05	—	23	0.11	—
2,4,5-Trichlorophenol	80	0.61	0.15	46	0.66	—
2,4,6-Trichlorophenol	94	2.5	0.19	87	0.51	0.18
3,4,5-Trichlorophenol	6	0.07	—	29	0.37	—
2,3,4,5-Tetrachlorophenol	0	—	—	4	0.37	—
2,3,4,6-Tetrachlorophenol	88	0.38	0.14	90	0.56	0.08
2,3,5,6-Tetrachlorophenol	12	0.06	—	65	0.17	0.03
Pentachlorophenol	100	2.4	0.73	100	11	1.1

[a] Reproduced from Wegman and Hofster,[109] courtesy of the International Association on Water Pollution Research.
[b] — = Nondetectable.

in stormwater runoff into the Delaware Estuary[103] and from industrial discharges into two urban rivers near Tokyo, Japan.[97] Additional sources of chlorinated phenols, in general, are human urine[117] and PCP, in particular.[118]

HUMAN HEALTH EFFECTS OF ORGANIC CONTAMINANTS

Chapter 1 presents and discusses the regulatory basis for MCLGs and MCLs for the various organic contaminants that may occur in drinking water supplies. Their effect on human health is, of course, the primary concern. Rationale for each contaminant is presented in numerous *Federal Register* references (see Chapter 1) and in Reference 94. A variety of adverse health effects are possible:

- *Toxic:* Causing a deleterious response in a biological system, seriously injuring function, or producing death. These effects may result from acute conditions (short high-dose exposure), chronic (long-term, low-dose) exposure, or subchronic (intermediate-term and dose) exposure.
- *Neurotoxic:* Exerting a destructive or poisonous effect on nerve tissue.
- *Carcinogenic:* Causing or inducing uncontrolled growth of aberrant cells into malignant tumors.
- *Mutagenic:* Causing heritable alteration of the genetic material within living cells.
- *Teratogenic:* Causing nonhereditary congenital malformations (birth defects) in offspring.

Many tests and protocols are available to evaluate the above health effects from which data are compiled by the USEPA as a basis for drinking water regulations. The agency uses a number of sources of data and several peer review systems, which include the NAS and the IARC. The assessment framework is reported in Chapter 1. The SDWA requires that the USEPA make conservative judgments to assure protection of public health. Lack of data and discrepancies among the various peer and advisory groups lead to different conclusions. This is frequently apparent in the assignment of cancer risks, where the use of different models and assumptions can lead to significantly different figures. However, the USEPA values for cancer risks are most frequently cited.[94] Table 2.27 gives the USEPA drinking water regulations and health advisories for several organic contaminants.[94]

The Health Advisory (HA) program is sponsored by the Office of Drinking Water (ODW) of the USEPA.[119] HAs describe nonregulatory concentrations of drinking water contaminants at which adverse health effects would not be anticipated to occur over specific exposure durations. These advisories are developed for one-day, ten-day, longer-term (approximately 7 years or 10% of an individual's lifetime), and lifetime exposure based on data describing noncarcinogenic endpoints of toxicity. HAs do

Table 2.27. USEPA Drinking Water Regulations and Health Advisories for Organic Contaminants.[94]

						Health Advisories								
	Regulations					10-kg Child			70-kg Adult					
Chemical	Status reg.[a]	NIPDWR, mg/L	MCLG, mg/L	MCL, mg/L	Status HA[a]	1-day, mg/L	10-day, mg/L	Longer-term, mg/L	Longer-term, mg/L	RfD, mg/(kg•day)	DWEL, mg/L	Life-time, mg/L	10^{-4} Cancer risk, mg/L	USEPA Cancer Group
Acenaphthylene	—	—	—	—	—	—	—	—	—	0.06	—	—	—	—
Acifluorfen	—	—	—	—	F	2	2	0.1	0.4	0.013	0.4	—	0.1	B2
Acrylamide	F	—	zero	TT[b]	F	1.5	0.3	0.02	0.07	2×10^{-4}	0.007	—	0.001	B2
Acrylonitrile	L	—	—	—	—	0.02	0.02	0.001	0.004	1×10^{-4}	0.004	—	0.007	B1
Adipatos (diethylhexyl)	F	—	0.4	0.4	—	—	—	—	—	0.7	20	0.5	—	C
Alachlor	F	—	zero	0.002	F	0.1	0.1	—	—	0.01	0.4	—	0.04	B2
Aldicarb	F	—	0.001	0.003	F	0.01	0.01	0.01	0.01	0.0013	0.04	0.01	—	D
Aldicarb sulfone	F	—	0.001	0.002	F	0.06	0.06	0.06	0.2	0.006	0.2	0.04	—	D
Aldicarb sulfoxide	F	—	0.001	0.004	F	0.01	0.01	0.01	0.04	0.0013	0.04	0.01	—	D
Aldrin	—	—	—	—	—	3×10^{-4}	3×10^{-4}	3×10^{-4}	9×10^{-4}	3×10^{-5}	9×10^{-4}	—	2×10^{-4}	B2
Ametryn	—	—	—	—	F	9	9	0.9	3	0.009	0.3	0.06	—	D
Ammonium sulfamate	—	—	—	—	F	20	20	20	80	0.25	8	2	—	D
Anthracene (PAH)	L	—	—	—	—	—	—	—	—	0.3	—	—	—	D
Atrazine	F	—	0.003	0.003	F	0.1	0.1	0.05	0.2	0.005	0.2	0.003	—	C
Baygon	—	—	—	—	F	0.04	0.04	0.04	0.1	0.004	0.1	0.003	—	C
Bentazon	—	—	—	—	F	0.3	0.3	0.3	0.9	0.0025	0.9	0.02	—	D
Benz(a)anthracene (PAH)	T	—	zero	1×10^{-4}	—	—	—	—	—	—	—	—	—	B2
Benzene	F	—	zero	0.005	F	0.2	0.2	—	—	—	—	—	0.1	A
Benzo(a)pyrene (PAH)	F	—	zero	2×10^{-4}	—	—	—	—	—	—	—	—	—	B2
Benzo(b)fluoranthene (PAH)	T	—	zero	2×10^{-4}	—	—	—	—	—	—	—	—	—	B2
Benzo(g,h,i)perylene (PAH)	T	—	—	—	—	—	—	—	—	—	—	—	—	
Benzo(k)fluoranthene (PAH)	T	—	zero	2×10^{-4}	—	—	—	—	—	—	—	—	—	B2
bis-2-Chloroisopropyl ether	—	—	—	—	F	4	4	4	13	0.04	1	0.3	—	—
Bromacil	—	—	—	—	F	5	5	3	9	0.13	5	0.09	—	C
Bromobenzene	—	—	—	—	D	—	—	—	—	—	—	—	—	—
Bromochloroacetonitrile	L	—	—	—	D	—	—	—	—	—	—	—	—	—
Bromochloromethane	—	—	—	—	D	—	—	—	—	—	—	—	—	—
Bromodichloromethane (THM)	L	0.1	—	—	D	7	7	0.1	0.7	0.02	0.7	—	0.03	B2

Table 2.27. USEPA Drinking Water Regulations and Health Advisories for Organic Contaminants[94] (Continued).

						Health Advisories								
	Regulations					10-kg Child			70-kg Adult					
Chemical	Status reg.[a]	NIPDWR, mg/L	MCLG, mg/L	MCL, mg/L	Status HA[a]	1-day, mg/L	10-day, mg/L	Longer-term, mg/L	Longer-term, mg/L	RfD, mg/(kg•day)	DWEL, mg/L	Life-time, mg/L	10^{-4} Cancer risk, mg/L	USEPA Cancer Group
Bromoform (THM)	L	0.1	—	—	D	15	15	0.1	0.7	0.02	0.7	—	—	B2
Bromomethane	—	—	—	—	F	0.1	0.1	0.1	0.5	0.001	0.05	0.01	—	D
Butylate	—	—	—	—	F	2	2	1	4	0.05	2	0.35	—	D
Butylbenzene (*n*-)	—	—	—	—	D	—	—	—	—	—	—	—	—	—
Butylbenzene (*sec*-)	—	—	—	—	D	—	—	—	—	—	—	—	—	—
Butylbenzene (*tert*-)	—	—	—	—	D	—	—	—	—	—	—	—	—	—
Butylbenzylphthalate (BBP)	T	—	—	—	—	—	—	—	—	0.2	—	—	—	C
Carbaryl	—	—	—	—	F	1	1	1	1	0.1	4	0.7	—	D
Carbofuran	F	—	0.04	0.04	F	0.05	0.05	0.05	0.2	0.005	0.2	0.04	—	E
Carbon tetrachloride	F	—	zero	0.005	F	4	0.2	0.07	0.3	7×10^{-4}	0.03	—	0.03	B2
Carboxin	—	—	—	—	F	1	1	1	4	0.1	4	0.7	—	D
Chloral hydrate	L	—	—	—	D	7	1	0.2	0.6	0.002	0.06	0.06	—	D
Chloramden	—	—	—	—	F	3	3	0.2	0.5	0.015	0.5	0.1	—	D
Chlordane	F	—	zero	0.002	F	0.06	0.06	5×10^{-4}	5×10^{-4}	4.5×10^{-3}	0.002	—	0.003	B2
Chlorodibromomethane (THM)	L	0.1	—	—	D	7	7	0.1	0.7	0.02	0.7	0.1	—	C
Chloroethane	L	—	—	—	D	—	—	—	—	—	—	—	—	—
Chloroform (THM)	L	0.1	—	—	D	—	—	—	—	0.01	—	—	0.6	B2
Chloromethane	L	—	—	—	D	—	—	—	—	—	—	—	—	—
Chlorophenol (2,4,6-)	L	—	—	—	D	—	—	—	—	—	—	—	0.3	B2
Chlorophenol (2,4-)	L	—	—	—	D	0.03	0.03	0.03	0.1	0.003	0.1	0.02	—	D
Chlorophenol (2-)	L	—	—	—	D	0.05	0.05	0.05	0.2	0.005	0.2	0.04	—	D
Chloropicrin	L	—	—	—	—	—	—	—	—	—	—	—	—	—
Chlorothalonil	—	—	—	—	F	0.2	0.2	0.2	0.5	0.015	0.5	—	0.15	B2
Chlorotoluene (*o*-)	L	—	—	—	F	2	2	2	7	0.02	0.7	0.1	—	D
Chlorotoluene (*p*-)	L	—	—	—	F	2	2	2	7	0.02	0.7	0.1	—	D
Chrysene (PAH)	—	—	zero	2×10^{-4}	—	—	—	—	—	—	—	—	—	B2
Cyanazine	L	—	—	—	F	0.1	0.1	0.02	0.07	0.002	0.07	0.01	—	D
Cyanogen chloride	L	—	—	—	D	—	—	—	—	—	—	—	—	—
Cymene (*p*-)	—	—	—	—	D	—	—	—	—	—	—	—	—	—
2,4-D	F	0.1	0.07	0.07	F	1	0.3	0.1	0.4	0.01	0.4	0.07	—	D

Dacthal (DCPA)	—	—	—	—	F	80	80	5	20	0.5	20	4	—	D
Dalapon	F	—	0.2	0.2	F	3	3	0.3	0.9	0.026	0.9	0.2	—	D
Diazinon	—	—	—	—	F	0.02	0.02	0.005	0.2	9×10^{-5}	0.003	6×10^{-4}	—	D
Dibenz(a,h)-anthracene (PAH)	T	—	zero	3×10^{-4}	—	—	—	—	—	—	—	—	—	B2
Dibromoacetonitrile	L	—	—	—	D	—	—	—	—	—	—	—	—	—
Dibromochloropropane (DBCP)	F	—	zero	2×10^{-4}	F	0.2	0.05	—	—	—	—	—	0.03	B2
Dibromomethane	L	—	—	—	D	—	—	—	—	—	—	—	—	D
Dibutyl phthalate (DBP)	T	—	—	—	—	—	—	—	—	0.1	—	—	—	D
Dicamba	L	—	—	—	F	0.3	0.3	0.3	1	0.03	1	0.2	—	D
Dichloroacetaldehyde	L	—	—	—	D	—	—	—	—	—	—	—	—	—
Dichloroacetic acid	L	—	—	—	D	50	50	0.5	2	0.005	0.2	0.003	—	C
Dichloroacetonitrile	L	—	—	—	D	—	—	—	—	0.008	—	—	—	C
Dichlorobenzene (*p*-)	F	—	0.075	0.075	F	10	10	10	40	0.1	4	0.075	—	C
Dichlorobenzene (*o*-,*m*)	F	—	0.6	0.6	F	9	9	9	30	0.089	3	0.6	—	D
Dichlorodifluoromethane	—	—	—	—	F	40	40	9	30	0.2	5	1	—	D
Dichloroethane (1,1-)	L	—	—	—	D	—	—	—	—	—	—	—	—	—
Dichloroethane (1,2-)	F	—	zero	0.005	F	0.7	0.7	0.7	2.6	—	—	—	0.04	B2
Dichloroethylene (1,1-)	F	—	0.007	0.007	F	2	1	1	4	0.009	0.4	7	—	C
Dichloroethylene (*cis*-1,2-)	F	—	0.07	0.07	F	4	1	3.5	1	0.01	0.4	0.07	—	D
Dichloroethylene (*trans*-1,2-)	F	—	0.1	0.1	F	20	2	2	6	0.02	0.6	0.1	—	D
Dichloromethane	F	—	zero	0.005	F	10	2	—	—	0.06	2	—	0.5	B2
Dichloropropane (1,1-)	—	—	—	—	D	—	—	—	—	—	—	—	—	—
Dichloropropane (1,2-)	F	—	zero	0.005	F	—	0.09	—	—	—	—	—	0.06	B2
Dichloropropane (1,3-)	L	—	—	—	D	—	—	—	—	—	—	—	—	—
Dichloropropane (2,2-)	L	—	—	—	D	—	—	—	—	—	—	—	—	—
Dichloropropene (1,1-)	L	—	—	—	D	—	—	—	—	—	—	—	—	—
Dichloropropene (1,3-)	L	—	—	—	F	0.03	0.03	0.03	0.100	3×10^{-4}	0.01	—	0.02	B2
Dieldrin	L	—	—	—	F	5×10^{-4}	5×10^{-4}	5×10^{-4}	0.002	5×10^{-5}	0.002	—	2×10^{-4}	B2
Diethylphthalate (DEP)	T	—	—	—	D	—	—	—	—	0.8	—	—	—	D
Diethylhexylphthalate (DEHP)	F	—	zero	0.006	D	—	—	—	—	0.02	—	—	0.3	B2
Dimethrin	—	—	—	—	F	10	10	10	40	0.3	10	2	—	D
Dimethylphthalate (DMP)	L	—	—	—	—	—	—	—	—	—	—	—	—	D
Dinitrotoluene (2,4-)	L	—	—	—	D	—	—	—	—	—	—	—	—	—
Dinoseb	F	—	0.007	0.007	F	0.3	0.3	0.01	0.04	0.001	0.04	0.007	—	D
Dioxane (*p*-)	—	—	—	—	F	4	0.4	—	—	—	—	—	0.7	B2
Diphenamid	—	—	—	—	F	0.3	0.3	0.3	1	0.03	1	0.2	—	D
Diquat[b]	F	—	0.02	0.02	—	—	—	—	—	0.0022	—	—	—	D
Disulfoton	—	—	—	—	F	0.01	0.01	0.003	0.009	4×10^{-4}	0.001	3×10^{-4}	—	E

Table 2.27. USEPA Drinking Water Regulations and Health Advisories for Organic Contaminants[94] (Continued).

						Health Advisories								
	Regulations					10-kg Child			70-kg Adult					
Chemical	Status reg.[a]	NIPDWR, mg/L	MCLG, mg/L	MCL, mg/L	Status HA[a]	1-day, mg/L	10-day, mg/L	Longer-term, mg/L	Longer-term, mg/L	RfD, mg/(kg•day)	DWEL, mg/L	Life-time, mg/L	10^{-4} Cancer risk, mg/L	USEPA Cancer Group
Diuron	—	—	—	—	F	1	1	0.3	0.9	0.002	0.07	0.01	—	D
Endothall	F	—	0.1	0.1	F	0.8	0.8	0.2	0.2	0.02	0.7	0.1	—	D
Endrin	F	2×10^{-4}	0.002	0.002	F	0.02	0.02	0.003	0.01	0.003	0.009	0.002	—	D
Epichlorohydrin	F	—	zero	TT[b]	F	0.1	0.1	0.07	0.07	0.002	0.07	—	0.4	B2
Ethylbenzene	F	—	0.7	0.7	F	30	3	1	3	0.1	3	0.7	—	D
Ethylene dibromide (EDB)	F	—	zero	5×10^{-5}	F	0.008	0.008	—	—	—	—	—	4×10^{-5}	B2
Ethylene glycol	—	—	—	—	F	20	6	6	20	2	40	7	—	D
ETU	L	—	—	—	F	0.3	0.3	0.1	0.4	3×10^{-5}	0.001	—	0.02	B2
Fenamiphos	—	—	—	—	F	0.009	0.009	0.005	0.02	25×10^{-5}	0.09	0.002	—	D
Fluometuron	—	—	—	—	F	2	2	2	5	0.013	0.4	0.09	—	D
Fluorene (PAH)	T	—	—	—	—	—	—	—	—	0.04	—	—	—	D
Fluorotrichloromethane	—	—	—	—	F	7	73	12	0.3	10	2	—	D	
Fonofos	—	—	—	—	F	0.02	0.02	0.02	0.07	0.002	0.07	0.01	—	D
Formaldehyde	—	—	—	—	D	10	5	5	29	0.15	5	1	—	B1-Inhal
Gasoline	—	—	—	—	D	—	—	—	—	—	—	5(benzene)	—	—
Glyphosphate	F	—	0.7	0.7	F	20	20	1	1	0.1	4	0.7	—	D
Heptachlor	F	—	zero	4×10^{-4}	F	0.01	0.01	0.005	0.005	5×10^{-4}	0.02	—	8×10^{-4}	B2
Heptachlor epoxide	F	—	zero	2×10^{-4}	F	0.01	—	1×10^{-4}	1×10^{-4}	13×10^{-6}	4×10^{-4}	—	4×10^{-4}	B2
Hexachlorobenzene	F	—	zero	0.001	F	0.05	0.05	0.05	0.2	8×10^{-4}	0.03	—	0.002	B2
Hexachlorobutadiene	—	—	—	—	F	0.3	0.3	0.1	0.4	0.002	0.07	0.001	0.05	C
Hexachlorocyclopentadiene	F	—	0.05	0.05	—	—	—	—	—	0.007	0.2	—	—	D
Hexane (*n*-)	—	—	—	—	F	10	4	4	10	—	—	—	—	D
Hexazinone	—	—	—	—	F	3	3	3	9	0.03	1	0.2	—	D
HMX	—	—	—	—	F	5	5	5	20	0.05	2	0.4	—	D
Hypochlorous acid	L	—	—	—	—	—	—	—	—	—	—	—	—	—
Indeno(1,2,3-c,d)-pyrene (PAH)	T	—	zero	4×10^{-4}	D	—	—	—	—	—	—	—	—	B2
Isophorone	L	—	—	—	D	15	15	15	15	0.2	7	0.1	0.9	C
Isopropylbenzene	—	—	—	—	D	—	—	—	—	—	—	—	—	—
Lindane	F	0.004	2×10^{-4}	2×10^{-4}	F	1	1	0.03	0.1	3×10^{-4}	0.01	2×10^{-4}	0.003	C
Malathion	—	—	—	—	D	0.2	0.2	0.2	0.8	0.02	0.8	0.2	—	D
Maleic hydrazide	—	—	—	—	F	10	10	5	20	0.5	20	4	—	D
MCPA	—	—	—	—	F	0.1	0.1	0.1	0.4	0.0015	0.053	0.011	—	E
Methomyl	—	—	—	—	F	0.3	0.3	0.3	0.3	0.025	0.9	0.2	—	D
Methoxychlor	F	0.1	0.04	0.04	F	6	2	0.5	2	0.05	2	0.4	—	D

Methyl ethyl ketone	—	—	—	—	F	80	8	3	9	0.025	0.9	0.2	—	D
Methyl parathion	—	—	—	—	F	0.3	0.3	0.03	0.1	25×10^{-5}	0.009	0.002	—	D
Methyl tert butyl ether	L	—	—	—	D	3	3	0.5	2	0.005	0.2	0.04	—	D
Metolachlor	L	—	—	—	F	2	2	2	5	0.15	5	0.1	—	C
Metribuzin	L	—	—	—	F	5	5	0.3	0.9	0.025	0.9	0.2	—	D
Monochloroacetic acid	L	—	—	—	D	—	—	—	—	—	—	—	—	—
Monochlorobenzene	F	—	0.1	0.1	F	2	2	2	7	0.02	0.7	0.1	—	D
Naphthalene	—	—	—	—	D	0.5	0.5	0.5	2	0.04	1	0.3	—	D
Nitroguanidine	—	—	—	—	D	10	10	10	40	0.1	4	0.7	—	D
Nitrocellulose (non-toxic)	—	—	—	—	F	—	—	—	—	—	—	—	—	—
Oxamyl (Vydate)	F	—	0.2	0.2	F	0.2	0.2	0.2	0.9	0.025	0.9	0.2	—	E
Ozone by-products	L	—	—	—	—	—	—	—	—	—	—	—	—	—
Paraquat	—	—	—	—	F	0.1	0.1	0.05	0.2	0.0045	0.2	0.03	—	E
Pentachloroethane	—	—	—	—	D	—	—	—	—	—	—	—	—	—
Pentachlorophenol	F	—	zero	0.001	F	1	0.3	0.3	1	0.03	1	0.2	—	D
Phenanthrene (PAH)	T	—	—	—	—	—	—	—	—	—	—	—	—	—
Phenol	—	—	—	—	D	6	6	6	20	0.06	20	4	—	D
Picloram	F	—	0.5	0.5	F	20	20	0.7	2	0.07	2	0.5	—	D
Polychlorinated biphenols (PCBs)	F	—	zero	5×10^{-4}	P	—	—	0.001	0.004	—	—	—	5×10^{-4}	B2
Prometon	—	—	—	—	F	0.2	0.2	0.2	0.5	0.015	0.5	0.1	—	D
Pronamide	—	—	—	—	F	0.8	-.8	0.8	3	0.075	3	0.05	—	C
Propachlor	—	—	—	—	F	0.5	0.5	0.1	0.5	0.013	0.5	0.09	—	D
Propazine	—	—	—	—	F	1	1	0.5	2	0.02	0.7	0.01	—	C
Propham	—	—	—	—	F	5	5	5	20	0.02	0.6	0.1	—	D
Propylbenzene (*n*-)	—	—	—	—	D	—	—	—	—	—	—	—	—	—
Pyrene (PAH)	T	—	—	—	—	—	—	—	—	0.03	—	—	—	D
RDX	—	—	—	—	F	0.1	0.1	0.10.4	0.003	0.1	0.002	0.03	C	
Simazine	F	—	0.004	0.004	F	0.5	0.5	0.05	0.2	0.002	0.06	0.001	—	C
Styrene	F	—	0.1	0.1	F	20	2	2	7	0.2	7	0/0.1	0.001	B2/C
2,4,5-T	L	—	—	—	F	0.8	0.8	0.8	1	0.01	0.35	0.07	—	D
2,3,7,8-TCDD (dioxin)	F	—	zero	$\times 10^{-8}$	F	1×10^{-6}	1×10^{-7}	1×10^{-8}	4×10^{-8}	1×10^{-9}	4×10^{-8}	—	2×10^{-8}	B2
Tebuthiuron	—	—	—	—	F	3	3	0.7	2	0.07	2	0.5	—	D
Terbacil	—	—	—	—	F	0.3	0.3	0.3	0.9	0.013	0.4	0.09	—	E
Terbufos	—	—	—	—	F	0.005	0.005	0.001	0.005	13×10^{-8}	0.005	9×10^{-4}	—	D
Tetrachloroethane (1,1,1,2-)	L	—	—	—	—	F	2	2	0.9	3	0.03	0.07	0.1	C
Tetrachloroethane (1,1,2,2-)	L	—	—	—	D	—	—	—	—	—	—	—	—	—
Tetrachloroethylene	F	—	zero	0.005	F	2	2	1	5	0.01	0.5	—	0.07	B2
Toluene	F	—	1.0	1.0	F	20	3	3	10	0.3	10	2	—	D
Toxaphene	F	0.005	zero	0.005	F	0.5	0.04	—	—	0.1	0.0035	—	0.003	B2
2,4,5-TP	F	0.01	0.05	0.05	F	0.2	0.2	0.07	0.3	0.0075	0.3	0.05	—	D

Table 2.27. USEPA Drinking Water Regulations and Health Advisories for Organic Contaminants[94] (Continued).

						Health Advisories								
	Regulations					10-kg Child			70-kg Adult					
Chemical	Status reg.[a]	NIPDWR, mg/L	MCLG, mg/L	MCL, mg/L	Status HA[a]	1-day, mg/L	10-day, mg/L	Longer-term, mg/L	Longer-term, mg/L	RfD, mg/(kg•day)	DWEL, mg/L	Life-time, mg/L	10^{-4} Cancer risk, mg/L	USEPA Cancer Group
Trichloroacetaldehyde	L	—	—	—	D	—	—	—	—	—	—	—	—	—
Trichloroacetic acid	L	—	—	—	D	30	30	30	100	0.3	10	0.2	—	D
Trichloroacetonitrile	L	—	—	—	D	—	—	—	—	—	—	—	—	—
Trichlorobenzene (1,2,4-)	F	—	0.07	0.07	F	0.1	0.1	0.1	0.5	0.001	0.05	0.009	—	D
Trichlorobenzene (1,3,5-)	—	—	—	—	F	0.6	0.6	0.6	2	0.006	0.2	0.04	—	D
Trichloroethane (1,1,1-)	F	—	0.2	0.2	F	100	40	40	100	0.09	1	0.2	—	D
Trichloroethane (1,1,2-)		—	0.003	0.005	F	0.6	0.4	0.4	1	0.004	0.1	0.003	0.06	C
Trichloroethanol (2,2,2-)	L	—	—	—	—	—	—	—	—	—	—	—	—	—
Trichloroethylene	F	—	zero	0.005		—	—	—	—	0.007	0.3	—	0.3	B2
Trichloropropane (1,1,1-)	—	—	—	—	D	—	—	—	—	—	—	—	—	—
Trichloropropane (1,2,3-)	—	—	—	—	F	0.6	0.6	0.6	2	0.006	0.2	0.04	—	—
Trihalomethanes (total)	F	0.1	zero	0.1	—	—	—	—	—	—	—	—	—	—
Trifluralin	L	—	—	—	F	0.03	0.03	0.03	0.1	0.0075	0.26	0.005	0.5	C
Trimethylbenzene (1,2,4-)	—	—	—	—	D	—	—	—	—	—	—	—	—	—
Trimethylbenzene (1,3,5-)	—	—	—	—	D	—	—	—	—	—	—	—	—	—
Trinitroglycerol	—	—	—	—	F	0.05	0.05	0.05	0.05	—	—	0.05	—	—
Vinyl chloride	F	—	zero	0.002	F	3	3	0.01	0.05	—	—	—	15×10^{-4}	A
Xylenes	F	—	10	10	F	40	40	40	10	2	60	10	—	D

Information based on USEPA, Office of Drinking Water, Criteria and Standards Division, summary of drinking water regulations and health advisories (April 1990).

Definitions for abbreviations in column heads are as follows:

NIPDWR—National interim primary drinking water regulation. Interim enforceable drinking water regulations first established under the Safe Drinking Water Act that are protective of public health to the extent feasible.

MCLG—Maximum contaminant level goal. A nonenforceable concentration of a drinking water contaminant that is protective of adverse human health effects and allows an adequate margin of safety.

MCL—Maximum contaminant level. Maximum permissible level of a contaminant in water that is delivered to any user of a public water system.

RfD—Reference dose. An estimate of a daily exposure to the human population that is likely to be without appreciable risk of deleterious effects over a lifetime.

DWEL—Drinking water equivalent level. A lifetime exposure concentration protective of adverse, noncancer health effects, and assumes that all the exposure to a contaminant is from a drinking water source.

[a] The codes for the Status Regulations and Status Health Advisory columns are as follows: F—final; D—draft; L—listed for regulation; P—proposed; T—tentative (to be proposed).

[b] TT—treatment technique.

Note: Large discrepancies between lifetime and longer-term health advisory values may occur because of the USEPA's conservative policies, especially with regard to carcinogenicity, relative source contribution, and less-than-lifetime exposures in chronic toxicity testing. These factors can result in a cumulative uncertainty factor (UF) of 10 to 1000 when calculating a lifetime health advisory.

not quantitatively incorporate any potential carcinogenic risk from such exposure.

The HAs for noncarcinogenic toxicants are calculated from:

$$\begin{aligned} HA &= \frac{(\text{NOAEL or LOAEL}) \times (\text{BW})}{(\text{UF}) \times (\_\text{L/day})} \\ &= \text{mg/L or } \mu\text{g/L} \end{aligned} \qquad (12)$$

where: NOAEL or LOAEL = No - or Lowest - Observed - Adverse - Effect Level in mg/kgBW/day; BW = assumed body weight of a child (10 kg) or an adult (70 kg); UF = uncertainty factor (10,100, or 1000) in accordance with NAS/ODW guidelines (see Chapter 1); _L/day = assumed daily water consumption of a child (1 L/day) or an adult (2 L/day).

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Chapter 3

Tastes and Odors in Drinking Water

3

Tastes and Odors in Drinking Water

INTRODUCTION

Consumers often judge the potability of drinking water by its organoleptic qualities, i.e., taste and odor. An off-tasting and/or odorous water is thought to be unsafe to drink. This association is fallacious, since odorous water may be free of pathogenic bacteria and/or hazardous chemicals and may meet the appropriate MCL values. Nevertheless, when consumers detect a change in water quality through taste and odor, they frequently will register a complaint with the water utility. Complaints of taste and odor are those most frequently made about water quality.

Sources of tastes and odors are many and varied. They range from such biological sources as algae and actinomycetes to individual organic compounds. Tastes and odors may occur also within the water distribution system through chemical reactions. The formation of such disinfection byproducts from chlorine and phenol is cited frequently. Metallic tastes may arise from corrosion of iron and copper pipes. This chapter attempts to document the sources and measurements of tastes and odors in drinking water. This chapter will not describe the physiological mechanisms involved in olfaction, taste, and other oral sensitivities. The reader is directed to Reference 1 for this information.

MEASUREMENTS OF TASTE AND ODOR

Weber-Fechner "Law"

It is extremely difficult to quantify and systematize the highly complex taste and odor sensations. Of the several attempts made to organize and describe these sensations, the relationship perhaps most often cited is the Weber-Fechner "law":[2]

$$S = K \log R \tag{1}$$

where S = sensation
R = stimulus
K = constant peculiar to the odorous substance and the observer's sensitivity

This "law" states that the stimulus must increase geometrically if the sensation is to increase by an equal amount in an arithmetic proportion. This relationship is seen below in the threshold odor test. However, the Weber-Fechner "law" is subjective at best, and does not have universal application.

Threshold Odor Number and Odor Intensity Index

Odor, like taste, depends on contact of a stimulating substance with appropriate human receptor cell (the nose and/or the tongue). Despite rapid strides in relating sensory qualities to chemical analyses, most odors are too complex and are detectable at concentrations too low to permit their definition by isolating and determining the odor-producing chemicals.[3] The ultimate odor-testing device is the human nose. Odor tests are performed to provide qualitative descriptions and approximate quantitative measurements of odor intensity. The method for intensity measurement presented below is the threshold odor test in *Standard Methods*[3] and the *Annual Book of ASTM Standards*.[4] These sensory tests are useful for quality control of raw and finished water (SMCL of 3 TON, Table 1.8), and for control of odor through the treatment process.

Laboratory measurement of an odorous sensation of water may be reported by either the Threshold Odor Number (TON) or by the Odor Intensity Index (OII).[3,4] The TON is the ratio by which the odorous sample is diluted with odor-free water to be "just detectable" to the observer. Mathematically, the TON is:

$$\text{TON} = \frac{A + B}{A} \tag{2}$$

where A = amount (mL) of original sample
B = amount (mL) of odor-free water

TON is dimensionless. OII is the number of times the original sample must be diluted in half with odor-free water for the odor to be "just detectable." OII is mathematically expressed as:

$$\text{OII} = 3.3 \log \frac{200}{A} + 3D \tag{3}$$

where A = amount (mL) of original sample
D = number of 25:175 primary dilutions required to reach the "just detectable" odor level

The relationship between TON and OII is:

$$\text{TON} = 2^{\text{OII}} \tag{3}$$

In conducting the actual measurement, a panel of five or more testers is selected. The measurements ideally should be taken in an odor-free atmosphere and in a special room ventilated with air that is filtered through activated carbon and maintained at a constant temperature and humidity. The test essentially consists of preparing the sample and dilution water at 40°C. A higher temperature of 60°C may be employed also. A series of dilutions of the sample is prepared in accordance with Column 2 in Table 3.1. Note that the original sample volume is 200 mL and that all subsequent dilutions are made to this volume. The observer may be presented with seven flasks in this order:[3]

mL sample diluted to 200 mL	12	0	17	25	0	35	50
Response	–	–	–	+	–	+	+

The odorous samples are presented to the observer in an increasing order of concentration. At least two blanks are inserted into the series. The appropriate TON value is recorded for each observer. The results are averaged arithmetically if the spread of values is not too great. The OII test is basically the same as the TON test, with the exception that the observer is presented with three clean, coded, and odor-free flasks for each test trial, of which two contain odor-free water. The reader should consult the latest edition of *Standard Methods*[3] for recent innovations in odor testing.

Taste and Flavor Analyses

The gustatory sensations of taste are called bitter, salty, sour, and sweet. They result from chemical stimulation of sensory nerve endings located in the papillae of the tongue and soft palate.[1] Flavor refers to a complex of gustatory, olfactory, and trigeminal sensations that result from chemical stimulation of sensory nerve endings located in the tongue, nasal cavity, and oral cavity. Methods for sensory analysis below require that the sample be taken into the mouth (i.e., tasted), but this requires evaluation of the complex sensation called flavor.

Standard Methods lists three methods for the sensory evaluation of water samples taken orally: the flavor threshold test (FTT), the flavor rating assessment (FRA), and the flavor profile analysis (FPA).[3] There is a note of caution: "Make flavor tests only on samples known to be safe for ingestion. Do not use samples that may be contaminated with bacteria, viruses, parasites, or hazardous chemicals. Do not make flavor tests on wastewaters or similar untreated effluents."[3] These tests are limited, for the most part, to finished waters. Summaries of the three flavor tests are given below.

Flavor Threshold Test (FTT)

This method attempts to measure detectable flavor quantitatively. A flavor threshold number (FTN) is determined from the greatest dilution of sample with a reference water that yields a definitely perceptible difference. It is, essentially, identical to the threshold odor test described above. The FTN is computed as follows:

$$\text{FTN} = \frac{A + B}{A} \tag{5}$$

where A = sample volume, mL
B = reference water (diluent) volume, mL. Table 3.2 shows the FTN values corresponding to various dilutions.

In conducting the flavor measurements, a panel of five or more testers is selected. Precautions with regard to background odors, etc., are identical to the threshold odor test. The test consists essentially of preparing the sample and dilution water at 15 ± 1°C. A series of dilutions is prepared in accord with Column 2 in Table 3.2. Here again, the original sample volume is 200 mL and all subsequent dilutions are made to this volume. The observer is presented with nine flasks in this order:

mL sample diluted to 200 mL	6	8	12	0	17	25	35	0	50
Response	–	–	–	–	–	+	+	–	+

The flavored samples are presented to the observer in an increasing order of concentration. At least two blanks are

Table 3.1. Dilution of Sample and Reporting of Results.[3,4]

	Volume Transferred to Odor Flask (mL)[a]	Threshold Odor Number (Dilution Factor)	Odor Intensity Index
Original Sample	200	1	0
	100	2	1
	50	4	2
	25	8	3
	12.5	16	4
Dilution A (25 mL of original sample diluted to 200 mL)	50	32	5
	25	64	6
	12.5	128	7
Dilution B (25 mL of dilution A diluted to 200 mL)	50	256	8
	25	512	9
	12.5	1,024	10
Dilution C (25 mL of dilution B diluted to 200 mL)	50	2,050	11
	25	4,100	12
	12.5	8,200	13
Dilution D (25 mL of dilution C diluted to 200 mL)	50	16,400	14
	25	32,800	15
	12.5	65,500	16
Dilution E (25 mL of dilution D diluted to 200 mL)	50	131,000	17
	25	262,000	18
	12.5	524,000	19
	6.25	1,050,000	20

[a] Volume in odor flask made up to 200 mL with odor-free water.

Table 3.2. Flavor Threshold Numbers Corresponding to Various Dilutions.[3]

Sample Volume (mL)	Diluent Volume (mL)	Flavor Threshold No. (FTN)
200	0	1
100	100	2
70	130	3
50	150	4
35	165	6
25	175	8
17	183	12
12	188	17
8	192	25
6	194	33
4	196	50
3	197	67
2	198	100
1	199	200

inserted into the series. The appropriate FTN value is recorded for each observer. The results are averaged arithmetically if the spread of values is not too great. Mean and standard deviation of all FTNs are calculated if the distribution is reasonably symmetrical; otherwise, the threshold value of the panel is expressed as the median or geometric mean of individual thresholds.

Flavor Rating Assessment (FRA)

The FRA is employed to estimate the acceptability of finished water for daily consumption.[3] This procedure has been used in laboratory research and consumer surveys in order to recommend standards governing mineral content in drinking water. Each tester is presented with a list of nine statements (see below) about the water ranging on a scale from very favorable to very unfavorable. The person's task is to select the statement that best expresses their opinion. A scale number is assigned to each statement and the panel rating for a given sample is an appropriate measure of a central tendency of the scale numbers for that sample.

A panel of several testers is presented finished water samples undiluted at a recommended temperature of 15°C. Sample order of presentation is random. Each sample is tasted twice by each tester in order to reach a final judgment. The following scale is employed for rating, with each recorded as an integer ranging from one (highest quality) to nine (lowest quality). Here again, mean and standard deviation of all ratings are calculated if the distribution is reasonably symmetrical. Median or geometric mean of individual ratings is used if the ratings are not symmetrical.

Action tendency scale:

1. I would be very happy to accept this water as my everyday drinking water.
2. I would be happy to accept this water as my everyday drinking water.

3. I am sure that I could accept this water as my everyday drinking water.
4. I could accept this water as my everyday drinking water.
5. Maybe I could accept this water as my everyday drinking water.
6. I don't think I could accept this water as my everyday drinking water.
7. I could not accept this water as my everyday drinking water.
8. I could never drink this water.
9. I can't stand this water in my mouth and I could never drink it.

Flavor Profile Analysis (FPA)

The Metropolitan Water District of Southern California (MWDSC) adopted a sensory technique—the flavor-profile analysis method—from the food industry.[6]

Subsequently, the EPA method was evaluated in Philadelphia, Pennsylvania and in France at Lyonnaise des Eaux.[1] The EPA differs from the TON method in that it uses a panel of at least four members to describe the intensities and characteristics of tastes and odors. Intensities are individually recorded and rated on a seven-point scale for every perceivable contributor to the overall perception of a water sample in this method.

The essence of the EPA method is the presentation of a sample to a highly trained panel at the same time. A standardized procedure for smelling and tasting follows, with the resulting descriptor(s) and intensity(ies) noted by each panel member. If a discrepancy exists among the panelists, the panel tries to resolve these differences with reference materials. Descriptors and the intensity scale are given in Table 3.3 and details of the test procedure are given in References 1 and 7.

BIOLOGICAL SOURCES OF TASTES AND ODORS

Surface water supplies, especially those contained in reservoirs, frequently have a taste and odor problem due to such biological sources as actinomycetes and algae. Also, protozoans, fungi, and other aquatic microbiota have been implicated frequently. Descriptors of these tastes and odors range from fishy to earthy, woody, musty, hay-like, manure-like, and geranium-like. The earthy-woody-musty tastes and odors, which are reported most frequently, are products of certain blue-green algae and actinomycetes, and a few fungi. Difficulty has been encountered in the past in removing these natural tastes and odors. Considerable research effort in the 1950s and 1960s was concentrated on the microbiological aspects. However, the emphasis shifted in the mid-1960s to attempts to isolate and identify individual compounds responsible for these natural tastes and odors. This research led to the discovery of such compounds as geosmin and 2-methylisoborneol (MIB) from cultures of actinomycetes. Later in the 1960s and 1970s, taste and odor research shifted from actinomycetes to blue-green algae (the cyanobacteria). Much of this research is presented below. However, the reader is directed to four excellent literature reviews in References 8–11 about taste and odor research from biological sources.

Actinomycetes

Actinomycetes are filamentous bacteria, and not fungi as their name implies. Their filaments branch as they grow, which serves to distinguish them from other bacteria.[12] They are found in a variety of habitats, including the water and sediment of lakes, streams, and rivers, and live in association with algae and higher aquatic plants.

It was found in the early 1950s that tastes and odors in reservoirs of the southwestern United States were attributable to actinomycetes.[13,14] Much of the evidence came from laboratory cultures of various aquatic organisms from different lakes in the Southwest. These organisms, in turn, produced by-products that had tastes and odors similar to those found in the lakes. This early research concentrated on two reservoirs, Lake Overholser and Lake Hefner, that supply Oklahoma City. An important point came from these observations that, at a water temperature of 3°C in February, a TON of 22 was recorded despite low plankton counts.[14] Furthermore, the types of odors produced by actinomycetes were very offensive when the TON reached a value of five.

Numerous reports of actinomycete-induced taste and odor problems in drinking water have been published (see Reference 1, p. 59, for sources). For example, empirical information from Morris's[15] and Erdei's[16] observations of tastes and odors arising from midwestern rivers suggests that this organoleptic quality problem chronically occurs at runoff periods during late winter thaws. These tastes and odors are very intense, but usually persist for only short periods of time and decrease with subsidence of the river flood stage. Furthermore, the taste was intensified by chlorination of the water, which produced bitter "medicinal tastes and odors." Early chemical analysis indicated that the taste-producing compounds were primarily phenolic in nature. In one specific instance, the actinomycetes' density was correlated with TON.[16] In the springs of 1961, 1962, and 1963, a taste and odor of a distinct musty or earthy character developed in the water supply of Cedar Rapids, Iowa,[15] and Omaha, Nebraska.[16] Two genera of actinomycetes were subsequently isolated and identified: *Micromonospora* and *Streptomyces*. The earthy, musty odor rising from the laboratory plates was characteristic of the odor in the Iowa River at Cedar Rapids. An empitical relation between the numbers of acti-

Table 3.3. Intensity Scales at Water Utilities Using the EPA Method.[1]

	Intensity Scale	
Verbal Description	**Original EPA Test and MWDSC[a]**	**PWD, PSWC, LE[b,c]**
Threshold[d]	)(	1
Very slight	1/2	2
Slight	1	4
Slight to moderate	1-1/2	6
Moderate	2	8
Moderate to strong	2-1/2	10
Strong	3	12

[a] MWDSC = Metropolitan Water District of Southern California.

[b] PWD = Philadelphia Water Department; PSWC = Philadelphia Suburban Water Company; and LE = Lyonnaise des Eaux.

[c] These values are simply a multiplication by four of the original scale values, except the threshold value.

[d] The value of intensity that represents an odor or flavor just perceivable by a panelist or that was perceived by 50 percent of the panel. In the)(–3 scale,)(is plotted as 1/4.

nomycetes per milliliter and the TON in the Missouri River at Omaha, Nebraska was established.[16]

Actinomycetes can be a problem in water distribution systems, since these microorganisms, under certain environmental conditions, can produce the typical earthy, moldy, and musty tastes in pipes inside buildings.[17] In England, these tastes and odors have arisen in cold water pipes adjacent to hot water pipes and where there was little use of water at night or on weekends. These citations were made when the temperature was 20°C. This is consistent with the knowledge concerning the effect of temperature on the growth rate of actinomycetes. Growth normally begins at approximately 7–8°C; however, rapid growth does not begin until after 20°C is reached. From this point, the growth rate is very rapid to 33–34°C, whereupon it begins to diminish slightly. When 41°C is reached, growth diminishes abruptly. The other important growth factor, nutrients, may be provided by adsorption of the necessary organic matter on scales and encrustations on the internal side of the pipes. Some support for this contention may be seen in Table 3.4, which shows "typical" data for the occurrence of actinomycetes in a distribution system.[17] Another problem area may be found in the dead ends of distribution systems where the water does not circulate and where there is infrequent flushing. Scale, etc., tends to accumulate in these dead ends, which then provide the necessary nutrients for the growth of microorganisms.

Algae

Many individuals involved in the production of potable and palatable water strongly believe that algae are the most important cause of tastes and odors in raw supplies.[18] Algae are ubiquitous and contribute heavily to the organoleptic quality of drinking water. A few algae are reasonably well known for producing specific distinctive tastes and odors, whereas a greater number of others contribute to the organoleptic quality according to local conditions. Certain of the diatoms, blue-green algae and flagellates are the principal offenders, but certain of the green algae, including desmids, are involved also. Most of the attention, however, has been focused on the blue-green algae. Palmer[18,19] has tabulated many of the algae associated with tastes and odors in drinking water. Several representative species of these various algae are seen in Table 3.5 with their taste and odor descriptors and, in some cases, with their tongue sensation. These descriptors are not "standard" terms, but they do represent an attempt to describe the type of taste and odor associated with algae.

Early descriptions of odors were grouped into four general categories:[19]

1. "aromatic"—includes odors characteristic of fruits, vegetables, and spices, as well as objectionable odors, such as skunk or garlic. These odors are produced by some pigmented flagellates and diatoms.
2. "fishy"—which Palmer stated "...is produced often by the same algae that are responsible for the aromatic odors. The organisms generally are present in much larger numbers when the fishy odor is evident."
3. "grassy"—which is "...the most common odor produced by green algae and is apparent only when the organisms are present in large numbers. It is reported also for certain blue-green algae and occasionally for diatoms and pigmented flagellates."

Table 3.4. Occurrence of Actinomycetes in a Distribution System.[17]

	TON	Actinomycetes (org./mL)	Temperature (°C)
Raw water	1	70	26
Finished water	2	11	27
Clear well	2	12	27
Distance from plant			
2 miles	10	44	27.6
4 miles	16	106	28
8 miles	24	450	28

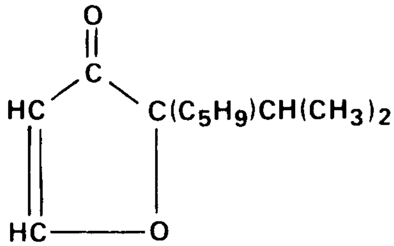
4. "musty" and "earthy"—also described as "potato-bin" and "moldy." Other odors, such as "...weedy, swampy, marshy, peat, strawlike and woody..." were thought to be possible modifications or combinations of the grassy and musty odors.

Other descriptors are "septic" odors, frequently associated with an abundance of blue-green algae, and "chlorophenolic, iodoform, and medicinal," from the chlorination of algae metabolites (see Chapter 2).[18,19]

Some excellent field data have been developed for the relationship between blue-green algae and actinomycetes with the resultant odors.[21,22] This is seen in Figure 3.1, where an annual cycle of blue-green algae and actinomycetes is suggested. It is hypothesized that blue-green algae are a nutrition source for the actinomycetes, whose population peaks after the blue-green population begins to decline. The TON peaks upon decline of both biological organisms. Bacterial decomposition of the algae and actinomycete residues apparently releases odorous material to the water.

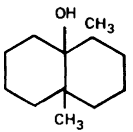
Chemistry of Odors from Biological Sources

Early research attempted to characterize chemically the individual compounds responsible for tastes and odors from biologic sources.[23] Several identification techniques were employed, most of which utilized the classical separation scheme for organic compounds according to solubility. For example, a series of ethyl ether extractions of a steam distillate was used to isolate odorous compounds from laboratory cultures of actinomycetes.[24] After steam distillation of the culture, a "neutral" faction is eventually obtained that has the characteristics of a pale yellow oil. It was felt that this neutral fraction was responsible for the typical mustiness of the actinomycetes. Subsequent work was devoted to chemical characterization of compounds in this faction. Initial tests with 2,4-dinitrophenylhydrazine gave a weak positive test for a carbonyl group. Unsaturation was indicated by the Baeyer's test. Analyses revealed the percentages of C, H, and O to be 74.98, 8.93, and 16.69, respectively, with an apparent mol. wt. of 103. Infrared analysis confirmed the presence of the carboxyl OH and a carbonyl group, but did not yield any additional information about the compound's identity. Later, the mol. wt. was revised to 194 with an empirical formula of $C_{12}H_{18}O_2$.[25] A compound called "mucidone" (from the Latin *mucid* meaning musty, and *one,* denoting a ketone) was proposed to be responsible for the musty odor from actinomycetes. From nuclear magnetic resonance (NMR) techniques and mass spectroscopic measurements, a structure was suggested:

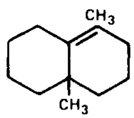


mucidone

Gerber and Lechevalier[26] and Gerber[27–29] may have provided the correct solution to the earthy, musty odor from actinomycetes through their "discovery" of geosmin (from Greek *ge,* meaning earth, and *osme,* meaning odor). This compound is a neutral oil with an approximate boiling point of 270°C. It contains C, H, and O, but no nitrogen. This compound was isolated from a number of cultures of *Streptomyces* by extraction, distillation, and gas-liquid chromatographic techniques. High-resolution mass spectroscopy and NMR techniques[27,28] indicated molecular formulas of $C_{12}H_{22}O$ for geosmin and $C_{12}H_{20}$ for argosmin. Their structural formulas are:



geosmin



argosmin C

Argosmin C is obtained from geosmin by treatment with 10% HCl standing at room temperature for four days. Argosmin has no odor.

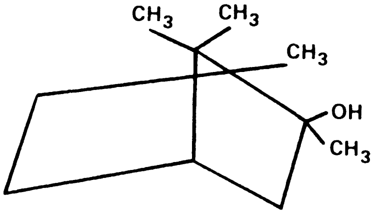
Table 3.5. Algae-Generated Tastes and Odors.[18–20]

	Odor Description			
Algae Class	**Moderate Quantities of Algae**	**Large Quantities of Algae**	**Taste Description**	**Tactile Sensation**
Cyanophycea				
Anabaena	Grassy, musty, nasturtium	Rotten, septic, medicinal	—	—
Anabaenopsis	—	Grassy	—	—
Aphanizomenon	Grassy, musty, nasturtium	Rotten, septic, medicinal	Sweet	Dry
Cylindrospermum	Grassy	Septic	—	—
Gloeotrichia	—	Grassy	—	—
Gomphosphaeria	Grassy	Grassy	Sweet	—
Microcystis or Anacysts	Grassy, musty	Rotten, septic, medicinal	Sweet	—
Nostoc	Musty	Rotten, septic, medicinal	—	—
Oscillatoria	Grassy	Musty, spicy	—	—
Rivularia	Grassy	Musty	—	—
Chlorophyceae				
Actinastrum	—	Grassy, musty	—	—
Ankistrodesmus	—	Grassy, musty	—	—
Chara	Garlic, skunk	Musty, garlic	—	—
Chlamydomonas	Musty, grassy	Fishy, septic, medicinal	Sweet	Sickly sweet, oily
Chlorella	—	Musty	—	—
Cladophora	—	Septic	—	—
Closterium	—	Grassy	—	—
Cosmarium	—	Grassy	—	—
Dictyosphaerium	Grassy, nasturtium	Fishy	—	—
Eudorina	—	Fishy	—	—
Gloeocystis	—	Rotten, medicinal	—	—
Gonium	—	Fishy	—	—
Hydrodictyon	—	Rotten, septic	—	—
Nitella	Grassy	Grassy, rotten	Bitter	—
Pandorina	—	Fishy	—	—
Pediastrum	—	Grassy	—	—
Scenedesmus	—	Grassy	—	—
Spirogyra	—	Grassy	—	—
Staurastrum	—	Grassy	—	—
Tribonema	—	Fishy	—	—
Ulothrix	—	Grassy	—	—
Volvox	Fishy	Fishy	—	—
Diatoms				
Asterionella	Spicy, geranium	Fishy	—	—
Cyclotella	Grassy, spicy, geranium	Fishy	—	—
Diatoma	—	Aromatic	—	—
Fragilaria	Grassy, spicy, geranium	Musty	—	—
Melosira	Grassy, spicy, geranium	Musty	—	Sickly sweet, oily
Meridion	—	Spicy	—	—
Pleurosigma	—	Fishy	—	—
Stephanodiscus	Grassy, spicy, geranium	Fishy	—	Sickly sweet, oily
Synedra	Grassy	Musty, fishy	—	Sickly sweet, oily
Tabellaria	Grassy, spicy, geranium	Fishy	—	—
Chrysophyceae				
Dinobryon	Violets, fishy	Fishy	—	Sickly sweet, oily
Mallomonas	Violets	Fishy	—	—
Synura	Cucumber, rotten, medicinal, muskmelon	Fishy	Bitter	Dry, metallic, sickly sweet, oily
Uroglenopsis	Cucumber	Fishy	—	Sickly sweet, oily
Euglenophyceae				
Euglena	—	Fishy	Sweet	—

Table 3.5. Algae-Generated Tastes and Odors[18-20] (Continued).

Algae Class	Odor Description: Moderate Quantities of Algae	Odor Description: Large Quantities of Algae	Taste Description	Tactile Sensation
Dinophyceae				
Ceratium	Fishy	Rotten, septic, medicinal	Bitter	—
Glenodinium	—	Fishy	—	Sickly sweet, oily
Peridinium	Cucumber	Fishy	—	—
Cryptophyceae				
Cryptotomonas	Violets	Violets, fishy	Sweet	—

Later, a musty-smelling compound was isolated from certain actinomycete cultures.[29] This compound was identified as 2-methylisoborneol (MIB) (also, 2-exo-hydroxy-2-methyl bornane).



2-exo-hydroxy-2-methyl bornane

This compound was isolated and identified from the culture broth of three actinomycetes: *Streptomyces antibioticus*, *S. praecox*, and *S. griseus*.[30] Table 3.6 lists several actinomycete species that can produce either geosmin or MIB, or both of these two chemicals. Most organisms belong to the genus *Streptomyces*, although a few *Nocardia* species and one or two others can produce them also.

The names for geosmin and 2-methylisoborneol by the system of the International Union of Pure and Applied Chemists (IUPAC) are *trans*-1,10-dimethyl-*trans*-9-decalol and 1,2,7,7-tetramethyl-exo-bicyclo (2.2.1) heptan-2-ol, respectively.

The algae producers of the earthy-musty odors apparently are restricted to the blue-green genera, *Anabaena* and *Oscillatoria*. An earthy odor was observed during the routine transfer of a culture of the filamentous blue-green algae *Symploca muscorum* and *Oscillatoria tenuis*.[36] Table 3.7 shows the blue-green algae that have been reported to produce geosmin in laboratory cultures.

Many species of blue-green algae have been reported to produce MIB in laboratory cultures: *Lyngbya cf. cryptovaginata*,[37] *Oscillatoria tenuis* var. *levis* and *O. curviceps*,[38] *O. limosa*,[39] and *Phormidium tenue*.[40] These blue-green algae had been isolated from various lakes and reservoirs in Manitoba, Canada, California, and Japan.

Odorous sulfur compounds from aquatic organisms have been reported.[41,42] Hydrogen sulfide (H_2S) was produced by *S. odorifer*.[41] Several mercaptans and sulfides were extracted from three species of blue-green algae.[42] Tentatively identified were: isopropyl mercaptan, isobutyl mercaptan, n-butyl mercaptan, dimethyl disulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide. The odor of dimethyl sulfide at low concentrations strongly resembles the "fishy" odor associated with such low-molecular-weight amines as methylamine and ethylamine. For example, dimethyl sulfide was isolated from a culture of a *Phormidium* species.[43] The reader is directed to Reference 11 for a literature review of the many odorous compounds other than geosmin and MIB that emanate from aquatic organism sources.

ANTHROPOGENIC SOURCES OF TASTES AND ODORS

Organic Compounds

Many tastes and odors in drinking waters arise from various organic compounds reacting as individual molecules or reacting in an additive, synergistic, or antagonistic manner. Sources of these organics are many and diverse, but the majority originate from a manufacturing wastewater that has been discharged in an improper manner. The practice of chlorination in a water treatment plant frequently will enhance the organoleptic quality. For example, the chlorination of water containing phenol (C_6H_5OH) produces a series of chlorophenols that have OTC at the µg/L level. This reaction is examined below in greater detail. Descriptors for the types of odors originating with organic compounds are many and varied. The American Society for Testing and Materials (ASTM) D-19 Committee on Water classified the odors by chemical types.[4] This classification is seen in Table 3.8, where most of the chemical types are organic compounds.

Odor Threshold Concentrations of Individual Compounds

Several investigators have reported the OTC of many organic compounds that may be present in raw water supplies. Most of these values were determined in the laboratory. Table 3.9 gives the odor characteristics and OTC values for several

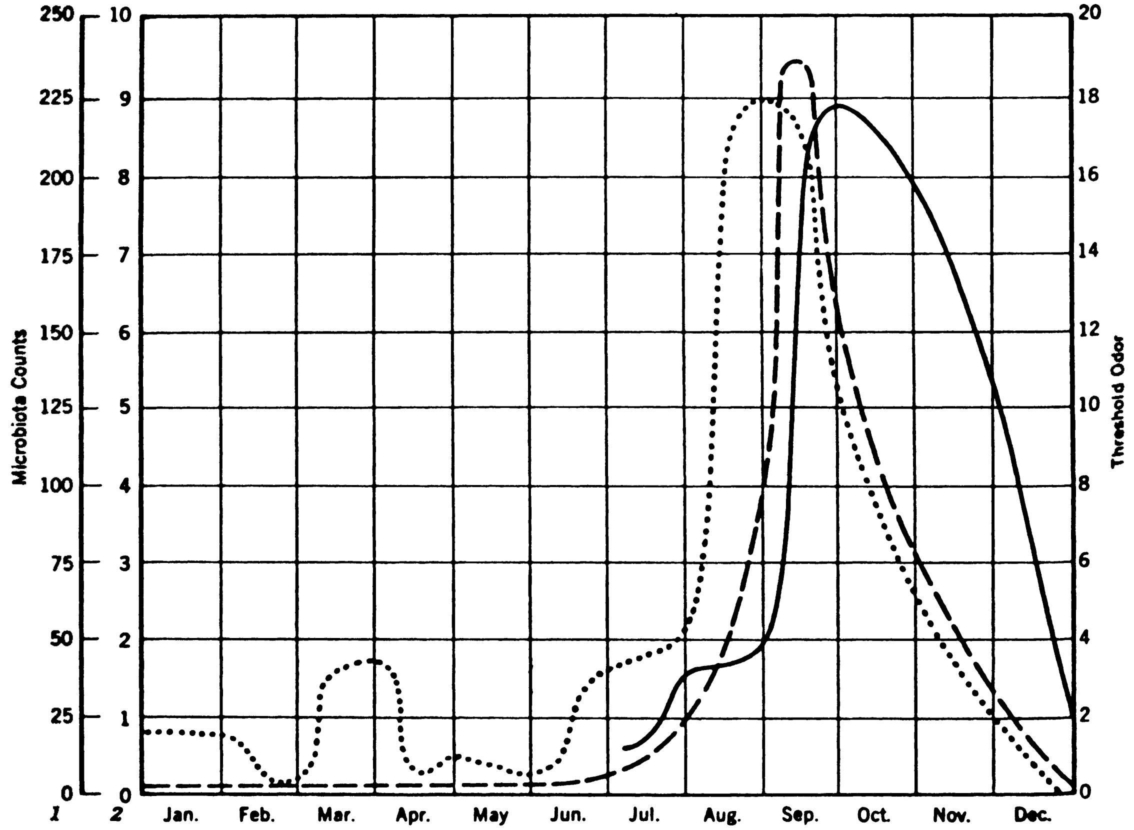


Figure 3.1. Average annual cycle of blue-green algae and actinomycetes with resulting threshold odors. Reproduced from Silvey and Roach,[21] courtesy of the American Water Works Association.

organic sulfur compounds.[44] The OTC values for several industrial chemicals found in the Kanawha River are given in Table 3.10.[48] The OTC values of several organic chemicals (pure substances) have been reported also from laboratory studies.[46] These compounds (Table 3.11) were selected on the basis of frequency of use as an industrial chemical that may eventually find its way into a wastewater.

The direction and occurrence of light halogenated hydrocarbons (LHH) and other organic compounds in drinking water affect the organoleptic qualities as well as the physiological qualities (see also Chapter 2). This initiated a study of the organic compounds that are probably involved in the taste impairment of drinking water in 20 cities of the Netherlands.[47] Data are rare for the taste quality of drinking water. As a result of the 20-city study, some 20 organic compounds from a total of 180 identified by gas-liquid chromatography/mass spectrometry (GC-MS) were identified as impairing the taste of drinking water. These compounds are given in Table 3.12a, along with their OTC. The C:OTC ratio values in Column 4 represent the odor potential for a given compound. All of the compounds had a C:OTC ratio of at least 0.1 (1%), suggesting that these compounds would affect the water's taste at these values. The threshold taste values apparently are less than the odor threshold values.

Table 3.12b lists the most frequently detected organic compounds in the 20 drinking waters of the Netherlands. In turn, these compounds were grouped together into similar families (e.g., total haloforms: chloroform and bromoform) in order to evaluate their effect on taste quality. A multiple regression technique was employed for taste rating and the presence of representative compounds of the haloform group, chlorobenzene group, chlorinated ether group, etc. In turn, multiple regression equations were calculated where "high correlation coefficients" indicated that a particular group of compounds accounted for the variance of the taste rating. Actual taste tests were performed with individual compounds by a national panel of 50 adults. Table 3.12c gives the correlation coefficients for the seven groups of organics. These data indicated that water taste is associated with all parameters except the polycyclic aromatics and phthalates.

Table 3.6. Actinomycetes That Produce Geosmin or MIB in Culture.[1]

Organism		Reference
Geosmin producers		
Actinomyces biwako	B-strain	31
Microbispora rosea	3748	27
Nocardia sp.	SS1/1	27
Nocardia sp.	W-68	27
Nocardia sp.	1-15	27
Streptomyces antibioticus	IMRU 3720	26
S. fradiae	IMRU 3535	26
S. griseus	LP 16	26
S. odorifer	IMRU 3334	26
S. alboniger	12462	27
S. lavendulae	3440 1-Y	27
S. viridochromogenes	94	27
S. griseoluteus		32
S. chibaensis		33
S. fragilis		33
S. griseoflavus		33
S. neyegawaensis		33
S. phaeofaciens		33
S. prunicolor		33
S. versipellis		33
S. werraensis		
S. albidoflavus		8
MIB Producers		
Actinomadura sp.	1-15	29
Nocardiopsis (Actinomadura) dassonvillei	IMRU 1324	29
Streptomyces antibioticus	ATTC 5324	30
S. griseus	ATTC 10137	30
S. praecox	ATTC 3374	30
S. griseoluteus		32
S. lavendulae	IMRU 3440-1Y	29
S. odorifer		34
S. chilbaensis		33
S. fragilis		33
S. neyagawaenis		33
S. phaeofaciens		33
S. prunicolor		33
S. versipellis		33
S. werraensis		33

OTC of Mixtures

Rarely does a natural water contain an individual odorous compound. More likely, a natural water receives a mixture of compounds from a variety of sources. In this case, the odorous compounds may react in one of four ways: (1) independence, (2) subtraction, (3) addition, or (4) synergism. These interactive effects of odor threshold have been examined through laboratory studies and statistical analysis of the data.[48,49]

For example, the odor stimulus of a mixture of odorants, A and B, is represented by R_{A+B} (see Equation 1).[49] For these four cases,

independence: $R_{A+B} = R_A$ or R_B
subtraction: $R_{A+B} < R_A$ or R_B
addition: $R_{A+B} = R_A + R_B$
synergism: $R_{A+B} > R_A + R_B$

The reader is directed to References 48 and 49 for laboratory-produced conditions of suppression and/or enhancement of odors by mixtures of organic compounds. These studies were limited to binary mixtures in order to simulate actual conditions of raw water supplies.

TASTES AND ODORS RESULTING FROM TREATMENT PROCESSES

Contaminants in raw water supplies will be removed or structurally modified by coagulation, adsorption, and oxidation processes. Perhaps the most significant treatments

Table 3.7. Blue-Green Algae Reported To Be Producers of Geosmin[a]

Genus	Species
Anabaena	*circinalis*
	macrospora
	scheremetievi
	species
Aphanizomenon	*gracile*
	species
Lyngbya	*aestuarii*
Oscillatoria	*agardhii*
	amoena
	brevis
	bornetti fa. *tenuis*
	cortiana
	prolifica
	simplicissima
	species
	species
	splendida
	tenuis
	variabilis
Phormidium	*inundatum*
Schizothrix	*mueller*
Symploca	*muscorum*

[a] See Reference 1 for citations of original investigators.

affecting taste and odor problems are the oxidative processes of chlorination and ozonation. So-called disinfection by-products (see Chapter 2) are formed, of which some are well-known taste and odor compounds.

Halogen Compounds

Many consumers object to the tastes and odors imparted to finished waters by the chlorine disinfectants themselves. Several investigators have reported threshold taste and odor values for chlorine, bromine, and iodine. For example, threshold values for chlorine residuals varied significantly with pH: at pH 5.0 the threshold value was 0.075 mg/L; at 7.0, 0.156 mg/L; and at 9.0, 0.450 mg/L.[50] Table 3.13 gives the sensory threshold values for three halogen compounds. In another study, hypochlorous acid and hypochlorite ion have similar chlorinous flavors and odors.[51] Solutions of monochloramine give a chlorine-like odor and flavor, whereas the dichloramine odor and flavor has been described as swimming pool-like, chlorine-like, or bleachy.

Chlorophenols

Perhaps the formation of chlorophenols via the reaction of chlorine and phenol (C_6H_5OH) was one of the first disinfection by-products reported in finished waters.[52] Consumers frequently complained about "iodine" or "medicinal" tastes in their drinking water from municipal systems. Chlorophenols have extremely "low" OTC values (see Table 3.11), whereas phenol (C_6H_5OH) has a relatively "high" OTC value—5.9 mg/L.[46] Consequently, a finished water may leave the treatment plant with acceptable taste and odor qualities. If this water should contain a "trace" concentration (<1.0 mg/L) of phenol, then chlorophenolic compounds may be formed in the distribution system. Development of this condition becomes a kinetic problem; namely, it is essential to know the rate at which the chlorophenols are formed.

The intensity of tastes and odors produced by stepwise chlorination of phenolic compounds was determined.[53,54] Table 3.14 shows the effects of adding chlorine (0.0 to 10.0 mg/L) on the threshold taste number of a 1.0 mg/L solution of phenol (C_6H_5OH). Taste observations were made after reaction times of 2 and 24 hr. These data reveal the extremely significant fact that the "medicinal" taste of chlorophenols develops slowly. This "slow" reaction would permit formation of chlorophenols in a water distribution system, provided the ratios (on a basis of ppm) of Cl_2:phenol were in the 0.5:1 to 3:1 range. These data in Table 3.14 also establish another significant fact about the operational aspects of water treatment. Phenolic compounds may be oxidized completely by chlorine when the reaction conditions are appropriate—namely, when the ratio of Cl_2:phenol exceeds 4:1, and when a sufficient reaction time is provided. Table 3.15 shows some additional chlorination studies of several phenols.

Additional efforts were made to identify the chlorophenolic compounds responsible for the off-taste (see Figure 3.2).[52] Using infrared spectroscopy and paper chromatographic techniques, the products obtained by chlorination of phenol (C_6H_5OH) to maximum taste were as shown in Table 3.16.

There was no trace of these chlorophenols: 3-CP, 2,5-DCP, 3,4-DCP, 2,4,5-TCP, 2,3,4,5-tetra CP and PCP. Apparently, 2,4-DCP and 2,6-DCP were responsible for the maximum taste intensity. That 2,4-DCP, 2,6-DCP, and 2-CP have the greatest tastes and odors may be seen in Table 3.17. The threshold OTCs[52] differ widely from the values reported in Table 3.11.[46] Nevertheless, the above observations have an extremely useful and practical value. For example, two operational parameters were investigated. The effect of the pH value is given in Table 3.18.[52] Maximum taste intensities were observed at a pH value of 8.0, whereas lesser tastes were observed at pH values of 6.0, 9.0, and 10.0. This is due to formation of dichlorophenols at a pH of 8.0. Another operational parameter was the combined effect of ammonia and pH value on the rate of chlorination of phenol. The appearance of 2,6-DCP was employed to fol-

Table 3.8. Odors Classified by Chemical Types.[a]

Odor Characteristic[b]						
Sweetness	**Pungency**	**Smokiness**	**Rottenness**	**Odor Class**	**Chemical Types**	**Examples**
100	50	0–50	50	Estery	Esters, ethers, lower ketones	Lacquer, solvents, most fruits, many flowers
100	50–100	0–100	50	Alcoholic	Phenols, cresols, alcohols	Creosote, tars, smokes, alcohol, liquor, rose and spicy flower, spices and herbs
50	50	0–50	50	Carbonyl	Aldehydes, higher ketones	Rancid fats, butter, stone fruits and nuts, violets, grasses and vegetables
50	100	0–50	50	Acidic	Acid anhydrides, organic acids, sulfur dioxide	Vinegar, perspiration, rancid oils, resins, body odor, garbage
100	50–100	50–100	0–100	Halide	Quinones, oxides, ozone, halides, nitrogen compounds	Insecticides, weed killers, musty and moldy odors, husks, medicinal odors, earth, peat
50	50	100	100	Sulfury	Selenium compounds, arsenicals, mercaptans, sulfides	Skunks, bears, foxes, rotting fish and meat, cabbage, onion, sewage
100	50	50	100	Unsaturated	Acetylene derivatives, butadiene, isoprene	Paint thinners, varnish, kerosene, turpentine, essential oils, cucumber
100	50	0–50	100	Basic	Vinyl monomers, amines, alkaloids, ammonia	Fecal odors, manure, fish and shellfish, stale flowers such as lilac, lily, jasmine, and honeysuckle

[a] Reproduced from *Annual Book of ASTM Standards,*[4] courtesy of the American Society for Testing and Materials.

[b] The degree of odor characteristic perceived is designated as follows: 100 indicates a high level of perception, 50 indicates a medium level of perception, and 0 indicates a low level of perception.

Table 3.9. Odor Characteristics and Threshold Concentration.[a]

Substance	Formula	Threshold Odor (mg/L)	Remarks
Allyl Merceptan	$CH_2:CH \bullet CH_2 \bullet SH$	0.00005	Very disagreeable, garlic-like odor
Ammonia	NH_3	0.037	Sharp, pungent odor
Benzyl Mercaptan	$C_6H_5CH_2 \bullet SH$	0.00019	Unpleasant odor
Chlorine	Cl_2	0.010	Pungent, irritating odor
Chlorophenol	$Cl \bullet C_6H_4 \bullet OH$	0.00018	Medicinal odor
Crotyl Mercaptan	$CH_3 \bullet CH:CH \bullet CH_2 \bullet SH$	0.000029	Skunk odor
Diphenyl Sulfide	$(C_6H_5)_2S$	0.000048	Unpleasant odor
Ethyl Mercaptan	$CH_3CH_2 \bullet SH$	0.00019	Odor of decayed cabbage
Ethyl Sulfide	$(C_2H_5)_2S$	0.00025	Nauseating odor
Hydrogen Sulfide	H_2S	0.0011	Rotten egg odor
Methyl Mercaptan	CH_3SH	0.0011	Odor of decayed cabbage
Methyl Sulfide	$(CH_3)_2S$	0.0011	Odor of decayed vegetables
Pyridine	C_6H_5N	0.0037	Disagreeable, irritating odor
Skatole	C_9H_9N	0.0012	Fecal odor, nauseating
Sulfur Dioxide	SO_2	0.009	Pungent, irritating odor
Thiocresol	$CH_3C_6H_4 \bullet SH$	0.0001	Rancid, skunk-like odor
Thiophenol	C_6H_5SH	0.000062	Putrid, nauseating odor

[a] Reproduced from Dague,[44] courtesy of the Water Pollution Control Federation.

Table 3.10. Threshold Odors of Industrial Chemicals in the Kanawha River.[45]

Chemical	Concentration at Which Odor is Just Detectable (mg/L)
Naphthalene	0.0068
Tetralin	0.018
Styrene	0.037
Acetophenone	0.065
Ethyl Benzene	0.14
Bis-(2-Chloroisopropyl) Ether	0.20
2-Ethyl Hexanol	0.27
Bis-(2-Chloroethyl) Ether	0.36
Diisobutylcarbinol	1.30
Phenyl Methylcarbinol	1.45
2-Methyl-5-ethyl Pyridine	0.019

low this reaction rate. Three appropriately buffered solutions were prepared, each containing 1 ppm phenol, 7 ppm chlorine, and 3 ppm ammonia. Aliquots were withdrawn periodically and checked for 2,6-DCP by paper chromatography. Phenol was present in all cases, but 2,6-DCP formed slowly at pH 9, slightly faster at pH 8, and not at all at pH 6. After five days, residual chlorine was still present in all three solutions.

These results indicate that the course of chlorination (Figure 3.2) resulting in products of intense taste also occurs in the presence of ammonia, but much more slowly. Under suitable conditions, this phenomenon may result in a "medicinal" taste that will be apparent to the water consumer, even if it is not detectable at the water plant.

Chlorine Dioxide–Induced Tastes and Odors

Chlorine dioxide (ClO_2) has been utilized historically for control of odors, disinfection, oxidation of soluble metals, and minimization of THM formation (see Chapter 2). In recent years, however, adverse odors in distribution systems have been associated with this oxidant. The reported odors were sporadic and occurred randomly throughout the distribution system. They were described most commonly as chlorinous, kerosene-like, and cat urine-like. Consequently, a questionnaire survey was conducted of 37 water utilities in the United States that use ClO_2 in their treatment process.[55,56] One focus of this survey was to investigate the causes of adverse odors encountered when ClO_2 is in use. The major purpose of adding ClO_2 by these utilities was to

Table 3.11. Odor Threshold Concentrations for Various Chemicals.[a]

Chemical	No. of Panelists	No. of Observations	Threshold Odor Level (ppm)[b]	
			Average	Range
Acetic Acid	9	9	24.3	5.07–81.2
Acetone	12	17	40.9	1.29–330
Acetophenone	17	154	0.17	0.0039–2.02
Acrylonitrile	16	104	18.6	0.0031–50.4
Allyl Chloride	10	10	14,700	3600–29,300
n-Amyl Acetate	18	139	0.08	0.0017–0.86
Aniline	8	8	70.1	2.0–128
Benzene	13	18	31.3	0.84–53.6
n-Butanol	32	167	2.5	0.012–25.3
n-Butyl Mercaptan	8	94	0.006	0.001–0.06
p-Chlorophenol	16	24	1.24	0.02–20.4
o-Cresol	13	21	0.65	0.016–4.1
m-Cresol	29	147	0.68	0.016–4.0
Dichloroisopropylether	8	8	0.32	0.017–1.1
2,4-Dichlorophenol	10	94	0.21	0.02–1.35
Dimethylamine	12	29	23.2	0.01–42.5
Ethylacrylate	9	9	0.0067	0.0018–0.0141
Formaldehyde	10	11	49.9	0.8–102
2-Mercaptoethanol	9	9	0.64	0.07–1.1
Mesitylene	13	19	0.027	0.00024–0.062
Methylamine	10	10	3.33	0.65–5.23
Methyl Ethyl Pyridine	16	20	0.05	0.0017–0.225
Methyl Vinyl Pyridine	8	8	0.04	0.015–0.12
β-Naphthol	14	20	1.29	0.01–11.4
Octyl Alcohol	10	10	0.13	0.0087–0.56
Phenol	12	20	5.9	0.016–16.7
Pyridine	13	130	0.82	0.007–7.7
Quinoline	11	17	0.71	0.016–4.3
Styrene	16	23	0.73	0.02–2.6
Thiophenol	10	10	13.5	2.05–32.8
Trimethylamine	10	10	1.7	0.04–5.17
Xylene	10	21	2.21	0.26–4.13

[a] Reproduced from Baker,[49] courtesy of the American Water Works Association.

[b] Temperature = 40 ± 1°C.

provide preoxidation and predisinfection, while avoiding THM formation at the same time.

Descriptive responses to the questionnaire survey are seen in Table 3.19.[55] A cluster analysis was applied to the data in an effort to determine whether certain odors or tastes were commonly associated with one another. The association in cluster analysis is based on a similar rating of the intensity for individual tastes and odors. Odors reported when ClO_2 was in use formed seven clusters (Table 3.19a), and five clusters of tastes were formed (Table 3.19b). On the other hand, only one cluster of odors and two clusters of tastes were formed when ClO_2 was not in use (Table 3.19c). For the latter observation, the lack of clusters indicates that the intensities of tastes and odors were given similar rankings and no single taste or odor predominated. This interpretation of the cluster analysis "supports" previous reports that demonstrated taste and odor problems are associated primarily with the application of ClO_2.[57] Statistical analyses of the survey responses does, indeed, suggest that tastes and odors are intensified when ClO_2 is in use at water utilities. However, there was no indication of any mechanism for these observations.

INORGANIC COMPOUNDS

An unacceptable taste frequently may be imparted to drinking water from dissolved inorganic substances. These compounds may give the water a "mineral" taste or a "bitter metallic" taste. Some available research indicates that consumer acceptance of mineralized waters decreased as the total dissolved solids (TDS) increased.[58,59] Also, the corrosion products of iron and copper pipes impart a "bitter metallic" taste to drinking water. Again, the point may be made that the consumer judges the potability of drinking water by its taste characteristics.

Table 3.12a. Organic Compounds Probably Involved in Taste Impairment of Drinking Water in 20 Cities of the Netherlands.[a]

Compounds	Highest Concentration Detected (μg/L)	OTC in Water (μg/L)	C:OTC Ratio
Chlorination products			
Tribromomethane	10	300	0.03
Trichloromethane	60	100	0.06
Compounds of Biological Nature			
2-Ethyl-1-hexanol	3.0	300	0.01
Heptan-3-on	0.1	7.5	0.01
Heptanol	0.1	3.0	0.03
Octanol	0.03	0.7	0.04
Octene-1	0.03	0.5	0.06
Nanonal	0.1	1.0	0.1
Decanal	0.1	0.1	1.0
2-Methylisoborneol	0.03	0.002	1.5
Geosmin	0.03	0.02	1.5
Compounds of Industrial Nature			
bis-(2-Chloroisopropyl)ether	3.0	300	0.01
3,4-Dichloroaniline	0.03	3	0.01
o-Dichlorobenzene	0.1	10	0.01
Hexachlorobutadiene	0.1	6	0.02
Naphthalene	0.1	5	0.02
γ-Hexachlorocyclohexane	0.1	0.3	0.03
5-Chloro-*o*-toluidine	0.3	5	0.06
1,2,4-Trichlorobenzene	0.3	5	0.06
2-Chloroaniline	0.3	3	0.1
Biphenyl	0.1	0.5	0.2
1,3,5-Trimethylbenzene	1.0	3	0.3
p-Dichlorobenzene	0.3	0.3	1.0

[a] Reproduced from Zoeteman et al.,[47] courtesy of the American Water Works Association.

Table 3.12b. Organic Compounds Detected Most Frequently in 20 Types of Drinking Water in the Netherlands.[a]

Types of Compounds	Maximum Detection Frequency[b]	Concentration (mg/L)
Hydrocarbons		
Toluene	20	0.3
Xylenes	19	0.1
C-Benzenes	19	1.0
Decanes	18	0.3
Ethylbenzene	17	0.03
Fluoroanthene	16	0.05
Nonanes	15	0.3
Naphthalene	14	0.1
Oxygen Compounds		
Dibutyl Phthalate	17	0.1
1,1-Dimethoxyisobutane	13	0.3
Methyl Isobutyrate	13	1.0
Halogen Compounds		
Chloroform	16	60
Tetrachloromethane	15	0.7

[a] Reproduced from Zoeteman et al.,[47] courtesy of the American Water Works Association.

[b] Detection frequency is number of tap waters, among the 20 types, in which the compound was detected.

Table 3.12c. Correlation Between Average Water Table Rating and the Presence of Groups of Organic Micropollutants in Tapwater.[a]

Group of Organic Compounds	Correlation Coefficient (r)
Total Haloforms	0.45
Total Alkylbenzenes	0.47
Total Polycyclic Aromatics	0.17
Total Phthalates	0.27
Total Chlorobenzenes	0.56
Total Chlorinated Ethers	0.63
Total Anilines	0.55

[a] Reproduced from Zoeteman et al.,[47] courtesy of the American Water Works Association.

Table 3.13. Panel Test Thresholds of Free-Halogen Residuals in Aqueous Solution (mg/L).[a]

	Chlorine		Bromine		Iodine	
pH	Threshold Concentration	Threshold Range	Threshold Concentration	Threshold Range	Threshold Concentration	Threshold Range
5.0 ± 0.1	0.075	0.013–0.136	0.226	0.111–0.340	0.204	0.118–0.290
7.0 ± 0.1	0.156	0.020–0.290	0.212	0.078–0.346	0.190	0.001–0.394
9.0 + 0.1	0.450	0.144–0.760	0.215	0.118–0.313	0.147	0.001–0.420
Unadjusted						
5.3 ± 0.1	0050	0.001–0.220	0.168	0.043–0.291		
6.2 ± 0.1					0.155	0.056–0.252

[a] Reproduced from Bryan et al.,[50] courtesy of the American Water Works Association.

Table 3.14. Effects of Stepwise Chlorination of 1 ppm Phenol on Taste Intensity.[a]

Chlorine Added (ppm)	2-Hour Observations		24-Hour Observations			
	pH	Flash[b]	pH	Flash[b]	Residual (o-t.)	Dilutions to Threshold
0	7.8	—	8.0	—	0.00	0
0.5	7.9	—	8.2	—	0.00	100
1	8.1	—	8.2	—	0.00	200
1.5	8.2	—	8.3	—	0.00	200
2	8.3	—	8.3	—	0.00	400
3	8.2	—	8.2	—	0.00	100
4	8.1	—	8.2	—	0.00	0
5	7.9	—	7.9	—	0.00	0
6	7.8	+	7.9	—	trace	1
8	7.8	+	7.9	+	0.24	0
10	7.6	+	7.9	+	0.90	0

[a] Reproduced from Reference 53, courtesy of the American Water Works Association.

[b] Aminodimethylaniline flash test.

Table 3.15. Stepwise Free Residual Chlorination Studies of Some Phenolic Materials.[a,b]

Material	Dilution to Threshold, Unchlorinated	Chlorine at Maximum Taste (ppm)	Dilution to Threshold at Maximum Taste	Chlorine Added to Produce Free Residual (ppm)	Chlorine Required to Eliminate Taste (ppm)
Phenol	0[c]	2	400	7	4
o-Cresol	10	2	800	5	5
m-Cresol	4	1	1000	5	5
p-Cresol	50	2/3	2000	4	3
1-Naphthol	30	0	30	5	4
2-Chlorophenol	100	1/2	400	5	3
4-Chlorophenol	2	1	8	6	3
2,4-Dichlorophenol	4	0	4	6	2
2,4,6-Trichlorophenol	0[c]	—	0	3	—
2,4,5-Trichlorophenol	0[c]	—	0	2	—
2,3,4,6-Tetrachlorophenol	0[c]	—	0	1.5	—
Pentachlorophenol	0[c]	—	0	1.0	—

[a] Reproduced from Ettinger and Ruchhoft,[53] courtesy of the American Water Works Association.

[b] Contact time, 24 hr; 1 ppm solutions studied.

[c] Could not be tasted by observer.

"Mineralized" Water

Several laboratory studies and surveys have reported the consumer's assessment of the mineral taste in California public waters.[58–60] The consumer survey was composed of an interview schedule containing questions and attitude scales, and a taste scale rating procedure that was administered to respondents in their homes.[60] Scale values for the attitude taste scale and the taste scale rating procedure are given in Table 3.20. To complete the interview, the respondent tasted a sample of tap water under direction of the interviewer. The interviewee's response to this taste test was reported on the TSR scale. These surveys were performed for 29 water systems in California. Each system was selected carefully so that there were no tastes interfering with the TDS. Inverse statistical relationships were observed between TDS values and consumer acceptability of the water for the two attitude scales and the one taste scale (Table 3.20). For example, the linear regression equation for the TSR was: TSR = 9.09 − 0.00204 (TDS) where $r = -0.43$. Many variables affect consumer assessment of mineralized water. Nonetheless, there is qualitative value from this study of consumer acceptance of mineralized water. It is noted in Table 1.8 that there is an interim SMCL for TDS of 500 mg/L.

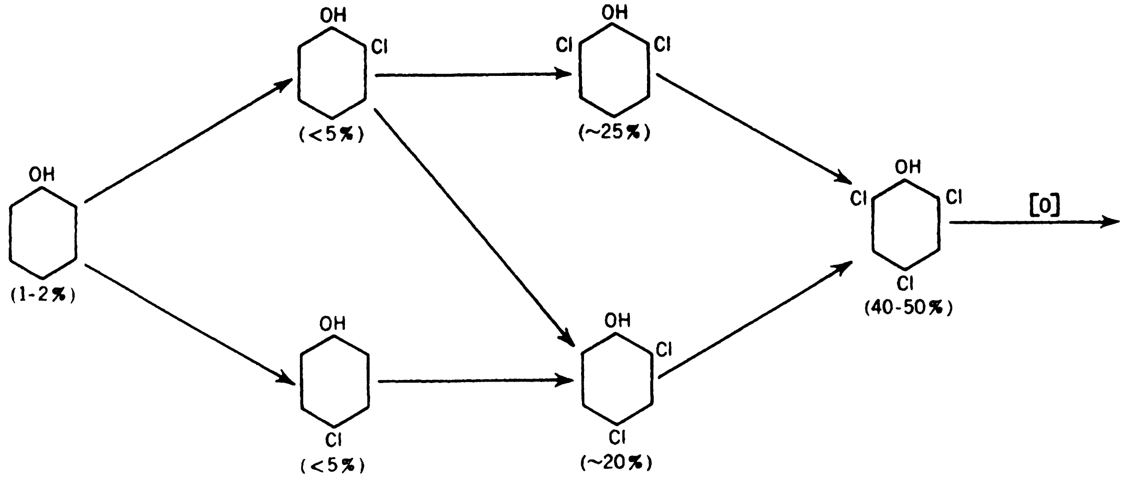


Figure 3.2. Course of chlorination of phenol. Reproduced from Burttschell et al.,[52] courtesy of the American Water Works Association.

Table 3.16. Products of Chlorination of Phenol to Maximum Taste.

Component	Percent of Product
Phenol	1–2
2-CP	2–5
4-CP	2-5
2,4-DCP	20
2,6-DCP	25
2,4,6-TCP	40–50
Carbonyl Compound (oxidation product)	Clearly present

Table 3.17. Taste and Odor Threshold Concentrations.[a,b]

	Geometric Mean Thresholds (ppb)	
Component	Taste	Odor
Phenol	>1,000	>1,000
2-CP	4	2
4-CP	>1,000	250
2,4-DCP	8	2
2,6-DCP	2	3
2,4,6-TCP	>1,000	>1,000

[a] All tests were made at room temperature, about 25°C.

[b] Reproduced from Burtschell et al.,[52] courtesy of the American Water Works Association.

Table 3.18. Effect of pH on Chlorophenolic Products.[a]

	Chlorine Residual (ppm)		
pH	2 hr	20 hr	Components Detected
6.0	<0.05	<0.05	Phenol; traces of 2-CP and 4-CP
8.0	<0.05	<0.05	2,4,6-TCP; much 2,4 and 2,6-DCP; traces of phenol, 2-CP, and 4-CP
9.0	0.15–0.20	<0.05	Same as for pH 8.0, except less 2,4,6-TCP
10.0	0.50	0.10–0.15	Same as for pH 9.0

[a] Reproduced from Burtschell et al.,[52] courtesy of the American Water Works Association.

The results of a laboratory study were reported in which a panel of 15 trained subjects rated the taste intensity of 125 to 2000 mg/L solutions of eight selected inorganic compounds: NaCl, $NaHCO_3$, Na_2SO_4, $CaSO_4$, $CaCl_2$, Na_2CO_3, $MgSO_4$, and $MgCl_2$.[61] For each compound, 3-mL coded samples of eight concentrations from 125 to 2000 mg/L were presented to the judge at room temperature (22 ± 1°C) in a random order. The judges were instructed to rate the total taste intensity on a 13-point scale, where 0 = none and 12 = extremely intense. A total of 45 replications (15 subjects × 3 test days) was obtained per sample. The average taste intensities of the eight mineralized solutions are shown in Figure 3.3. At concentrations between 750 and 2000 mg/L, the carbonates and chlorides were more intense than were the

Table 3.19a. Clusters of Odors Formed When Chlorine Dioxide Was Applied.[55]

Cluster Number	Odor Descriptors
1	Decayed vegetation, earthy, grassy, haylike, marshy, moldy, septic, sewage, swampy, woody
2	Organic solvent, phenolic, plastic, plastic pipe, rubber, varnish
3	Floral, fragrant, pigpen, wet paper
4	Antiseptic, cucumber, fishy, medicinal, potato, potato bin, sweet
5	Bleach, chlorinous, Clorox, Purex, swimming pool
6	Diesel fuel, gasoline, kerosene, natural gas
7	Cat urine, hydrocarbon, lighter fluid

Table 3.19b. Clusters of Tastes Formed When Chlorine Dioxide Was Applied.

Cluster Number	Taste Descriptors
1	Bleach, Clorox, diesel fuel, gasoline, kerosene, lighter fluid, natural gas, organic solvent, phenolic, plastic, plastic pipe, Purex, rubber, swimming pool, varnish
2	Cucumber, fishy, haylike, potato, potato bin, septic, sweet
3	Antiseptic, floral, fragrant, hydrocarbon, pigpen, wet paper
4	Decayed vegetation, earthy, marshy, moldy, sewage, swampy, woody
5	Cat urine, chlorinous, grassy, medicinal

Table 3.19c. Clusters of Tastes Formed When Chlorine Dioxide Was Not in Use.

Cluster Number	Taste Descriptors
1	Antiseptic, cat urine, cucumber, decayed vegetation, diesel fuel, fishy, floral, fragrant, gasoline, haylike, hydrocarbon, kerosene, lighter fluid, marshy, natural gas, organic solvent, phenolic, pig pen, plastic, plastic pipe, potato, potato bin, Purex, rubber, septic, sewage, swampy, sweet, swimming pool, varnish, wet paper, woody
2	Bleach, chlorinous, Clorox, earthy, grassy, medicinal, moldy

sulfates. The judges were required to report a descriptive term for each mineral: $CaCl_2$ is "bitter," $MgCl_2$ is slightly "bitter" and "sweet," and NaCl is unquestionably "salty." No distinguishing taste emerged for $CaSO_4$ and $MgSO_4$. These two salts had the lowest taste intensities of the eight minerals.

In communities where the drinking water contains a high percentage of unpalatable minerals, consumers remark that refrigeration of water greatly improves its taste. It is uncertain whether coolness of the water alone makes the water more acceptable, or whether perception of the undesirable tastes is diminished by the cold temperature. These considerations led to a study of the influence of temperature on taste intensity and the degree of consumer acceptance of the water.[62] Figure 3.4 shows some typical findings—namely, that taste intensities were lowest at 0°C and highest at 22°C. Also, intensity values were related to the TDS in the water. Consequently, the characteristic taste intensities of mineralized water were significantly reduced by lowering the solution temperature. The less the taste intensity, the greater the degree of consumer acceptance. Perhaps this can be explained by the preference of consumers in a warm climate for drinking cold rather than hot beverages.

An undesirable taste frequently occurs in waters that are chlorinated for disinfection purposes. The effect of 0.8 mg/L Cl_2 was reported for the taste intensities of several mineralized waters at 750 mg/L at 1 and 24°C.[61] As seen in Figure 3.5, chlorine was perceived with considerable difficulty in the Na_2CO_3 solutions, which averaged 63% correct, compared to 88% correct for $NaHCO_3$ and over 96% correct for the other compounds. The right half of Figure 3.5 gives the taste intensity of the chlorine solutions. $CaSO_4$ appears to enhance the taste, whereas $NaHCO_3$, $CaCl_2$ and Na_2CO_3 appear to suppress the taste.

Additional references exist on the taste intensity of mineralized water.[63–67]

Dissolved Oxygen

It is commonly believed that the flat, insipid taste of water is caused by a low content of dissolved oxygen (DO), or by mineral salts. Some laboratory data were obtained for the taste of water with various dissolved oxygen contents.[62,68]

Triangle tests[69] were employed to determine whether there was a significant difference between two extreme DO levels [3.25 and 18.8 mg/L (averages)]. The individual judge's ability to differentiate between the two contents of DO in distilled water and in 1000 mg/L NaCl at temperatures of 0 and 22°C is seen in Table 3.21. No significant differences were observed in any of the comparisons, as 18 correct separations in 36 trials are required for the chi-square to be significant at the $p = 0.05$ level. These data led to the conclusion that DO content had little, if any, effect on the taste of drinking water. This was confirmed later by Pangborn and Bertolero.[62]

Metals

Water occasionally acquires a "bitter," "metallic" taste due to such metals as copper, iron, manganese, and zinc. Three of these metals, Cu, Fe, and Zn, may arise from the corrosion of pipes through which water is conveyed. This is especially true of waters that are soft and acidic in nature. The threshold taste concentrations of these four metals were reported, as well as a review of the literature on this subject prior to 1960.[70]

A duo-trio test[71] with a panel of 18 or more judges was employed to provide threshold test values of the four metals in distilled water and spring water. A summary of these values is given in Table 3.22. Zinc was detected at the 5% frequency level (i.e., 5% of the panel) at 4.3 mg/L. The taste generally was characterized as bitter and, on occasion, it was detectable also by an astringent sensation which persisted for some time after tasting. Copper was detected at 2.6 mg/L at the 5% frequency level, and its taste persisted after the testing period. Of the four metals, iron was determined at the lowest concentration—0.04 mg/L—at the 5% level. Manganese was detected at 0.9 mg/L. Another indication of metallic taste sensitivity may be seen in the range of concentrations from the most acute level (5% of panel) to the level at which 95% of the panel tasted the metal. These ranges are seen also in Table 3.22. Copper appears to be the metal most universally tasted. Regulatory agencies take into consideration these threshold taste values of metals when they establish drinking water quality standards.

TREATMENTS FOR REMOVAL OF TASTES AND ODORS

Many treatments and/or combinations thereof are available to reduce, specifically, tastes and odors in raw water supplies. Historically, much of this originated from plant practice obtained by trial and error procedures. Plant operations adjusted feed rates, supplemental treatment with carbon and/or oxidants, or made other process changes in order to correct the problems and eliminate consumer complaints. However, the removal of tastes and odors from raw supplies has evolved into a highly sophisticated, technology-based science.[1] Advanced water utilities that have early warning systems in place are able to identify specific sources and/or compounds causing tastes and odors, and are able to implement specific treatments. In the majority of water utilities, however, taste and odor control still may be executed by trial and error. Several case histories and specific treatments are discussed below. Many other treatment processes cited in later chapters are capable of taste and odor control.

Table 3.20. Sample Items from the Attitude Taste Scale (ATS), Attitude Adjective Taste Scale (AATS), and the Taste Scale Rating (TSR) Procedure.[a]

Item	Scale Value
ATS	
Perfect	10.57
Good	7.67
Neither good nor bad	6.00
A little bad	4.33
Bad	2.16
AATS	
Delicious	10.57
Fine	8.04
Average	6.09
Inferior	3.54
Awful	1.94
TSR	
Excellent taste	10.67
Good taste	8.45
Neutral taste	6.00
Bad taste	2.95
Horrible taste	1.16

[a] Reproduced from Bruvold et al.,[60] courtesy of the American Water Works Association.

Early Warning Techniques

An obvious initial step before implementing treatment for taste and odor removal is to examine the source(s) that supply the water system. This is feasible if the utility has the capability and the resources to conduct a survey of the watershed and/or recharge area for potential sources of tastes and odors. This survey may include such items as land use practices, recreational activities, wastewater discharges, algal blooms, etc. Some utilities may have historical records that would indicate seasonal or other patterns influencing the occurrence of tastes and odors. Such a survey would lead to the establishment of an early warning system that, hopefully, would predict taste and odor episodes.

An example of an early warning system was developed by the Metropolitan Water District of Southern California for their extensive reservoir system.[70] The essence of this system is extensive sampling and shoreline inspection by "an alert microbiologist" for early detection of algal growth. In this case, earthy-musty odorants were usually detected

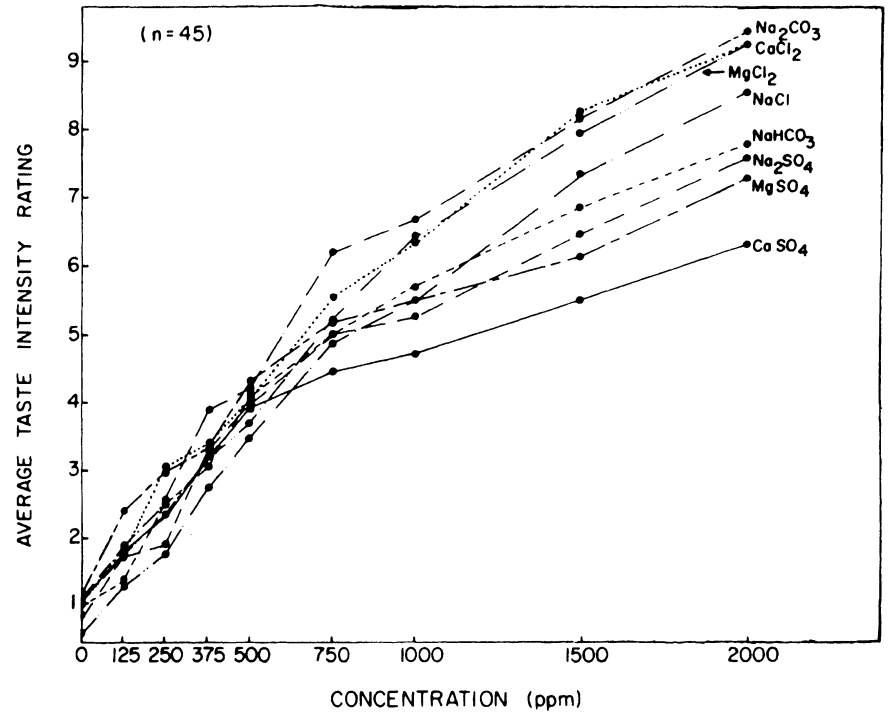


Figure 3.3. Rated taste intensity of distilled and mineralized waters at eight concentrations. Reproduced from Pangborn et al.,[61] courtesy of the American Water Works Association.

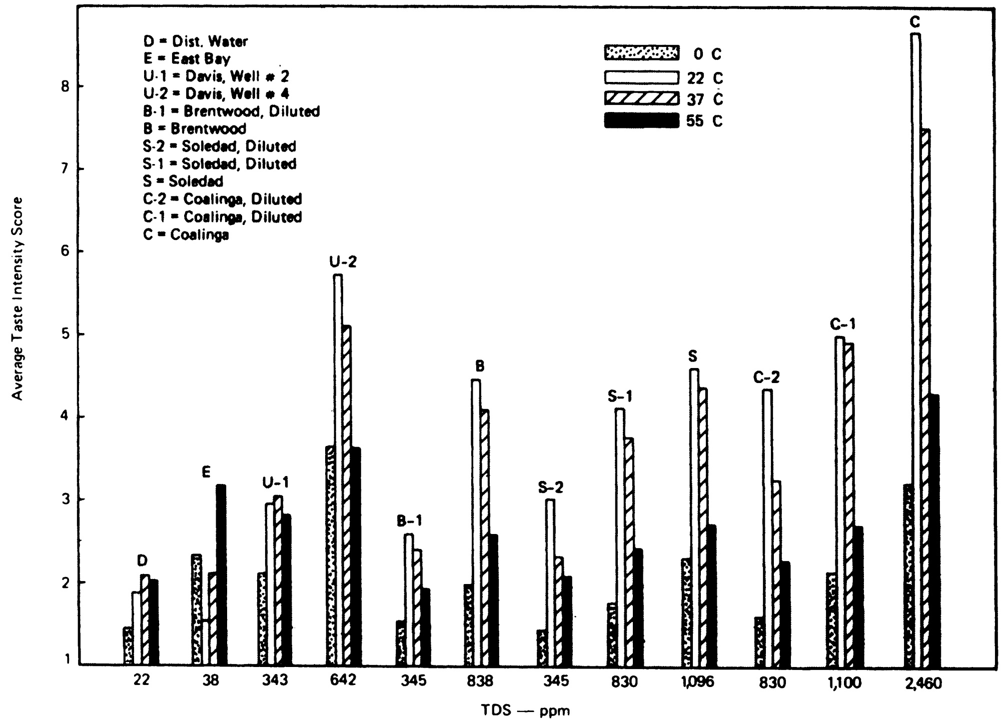


Figure 3.4. Taste intensity of distilled water, six natural waters and mixtures of the two at 0, 22, 37, and 55°C. Reproduced from Pangborn and Bertolero,[62] courtesy of the American Water Works Association.

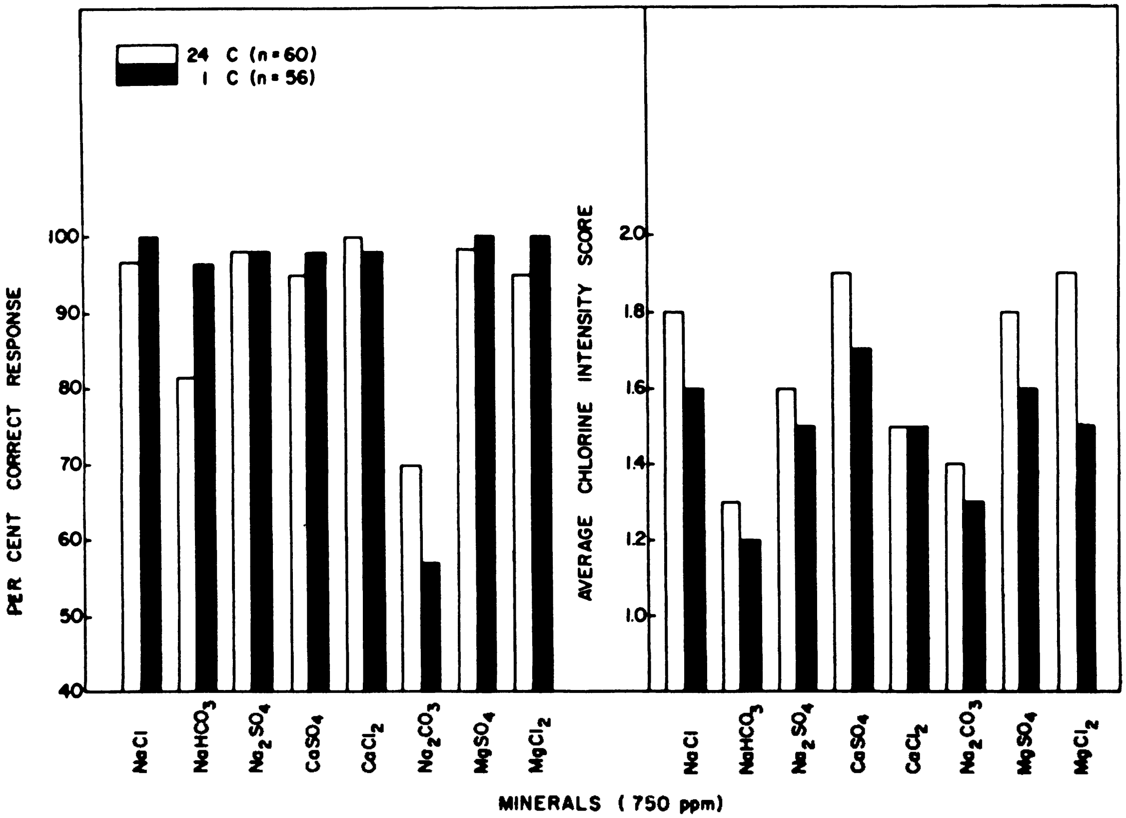


Figure 3.5. Sensory response to solutions of 0.8 ppm chlorine in mineralized waters at 24 and 1°C. Reproduced from Pangborn et al.,[61] courtesy of the American Water Works Association.

Table 3.21. Triangle Test Differentiation by Judges (A–F) Between Two Levels of DO in Distilled Water and in 1,000 mg/L Sodium Chloride Solutions.[a]

	A	B	C	D	E	F	Totals
Study I							
Dist. H_2O at 22°C	4	0	2	1	–1	3	11/36
Dist. H_2O at 0°C	4	2	3	4	3	0	16/36
NaCl at 22°C	1	4	0	2	2	1	10/36
NaCl at 0°C	3	2	1	2	2	3	13/36
	12	**8**	**6**	**9**	**8**	**7**	
Study II							
Dist. H_2O at 22°C	2	2	1	3	1	1	10/36
NaCL at 22°C	2	1	3	3	3	1	13/36
	4	**3**	**4**	**6**	**4**	**23**	Y

[a] Reproduced from Bruvold and Pangborn,[68a] courtesy of the American Water Works Association.

from which MIB and geosmin were identified by a closed-loop stripping analysis.[71] Once the taste and odor compounds were identified and the causative organisms isolated, it became necessary to learn more about their habitat and distribution throughout the reservoirs. The blue-green alga *Oscillatoria curviceps* was identified as the taste and odor producer. Control of this organism was difficult because of its growth pattern of attachment to various surfaces. A work barge was constructed for application of large quantities of chunk copper sulfate to the shorelines.[72] This treatment was effective but the organism grew rapidly. Regular treatment of the growth areas was necessary throughout the taste and odor season.

Specific Treatments

Should taste and odor problems occur in a treatment facility, specific treatments may be applied for their control. These treatments would supplement those in place and would be employed during the taste and odor season.

Sources

Perhaps the best treatment would be at its source, whether it be naturally occurring or anthropogenic. If the taste and odor is related to algal growth, then copper sulfate as described above may be the appropriate treatment.[73] Application methods include dissolving the copper sulfate crystals using porous bags pulled by a boat, using direct application by a hopper feeder, or spraying dissolved copper sulfate on the water surface. Timing of the application is extremely important, as cited above. Regular surveillance of the reservoir and/or lake is essential.

Another basic method of algal control involves reduction of the amount of nutrients available for algal growth and metabolism by controlling their inflow into the impounded water.[74] This approach involves a comprehensive monitoring program and close cooperation with pollution abatement authorities and officials.

Oxidation

Historically, such oxidants as Cl_2, ClO_2, O_3, and $KMnO_4$ have been employed for taste and odor control. Usually, these oxidants were applied in a pretreatment mode and on an intermittent basis during the taste and odor season. Trial and error techniques were employed with partial success. Recent technological advances in identification of actual compounds—namely, geosmin and MIB—have modified the uses of oxidants for taste and odor control. Frequently, oxidants enhance tastes and odors (see above). Consequently, oxidation may be effective only on a case-by-case basis for the removal, mainly, of organoleptic organic compounds.

Research within the past ten years or so has reported conflicting results from the oxidation of taste and odor organics. For example, it was concluded that Cl_2, chloramines, ClO_2, and $KMnO_4$ were not effective in reducing geosmin or MIB,[75] as previously reported.[76] On the other hand, there is some anecdotal evidence and experimental data[77] that when an odor or taste event occurs, oxidation may be effective on a case-by-case basis (see Case Histories below).

Oxidation studies were performed with Cl_2, ClO_2, O_3, and $KMnO_4$ on five earthy-musty smelling compounds in organic-free water.[76] These compounds were: geosmin, 2,3,6-trichloroanisole (TCA), 2-isopropyl-3-methoxy pyrazine (IPMP), 2-isobutyl-3-methoxy pyrazine (IBMP), and MIB. Figure 3.6 summarizes the results of this study. IPMP and IBMP, only, were completely removed by Cl_2, O_3, and MnO_2 (adsorption by the reduction product of $KMnO_4$). Generally, ClO_2 was the most effective oxidant for all five compounds. However, geosmin and MIB were oxidized to the extent of 50% or less. $KMnO_4$ was ineffective. Reaction times up to 16 hours were employed at a pH of 6.7. Oxidant dosages in the range of 10–20 mg/L are necessary for removal of the five odorous compounds.

Table 3.22. Range of Concentrations in Distilled Water Detectable by Panel Members[a]

Metal	Threshold Distribution 5%	95%
	Concentration (ppm)	
Zinc	4.3	62
Copper	2.6	15.8
Iron	0.04	256
Manganese	0.9	487

[a] Reproduced from Cohen et al.,[68b] courtesy of the American Water Works Association.

Some investigators feel that ozone is generally the most effective oxidant for use in taste and odor treatment; for example, an ozone dose of 2.5 to 2.7 mg/L with a contact time of several minutes results in an ozone residual of 0.2 mg/L and a "significant reduction in taste and odor."[78] Many odors are completely removed and others are significantly reduced when O_3 is used.[1] The use of ozone as a pretreatment to chemical coagulation and granular activated carbon wherein some taste and odor control is obtained is discussed in Chapter 4.

Various reports and case histories have indicated that $KMnO_4$ is useful in the elimination of taste and odors. Most investigators report that dosages from 0.3 to 1.5 mg/L are effective with sufficient contact time.[1] Higher dosages should be avoided due to the pink color that results from unreacted $KMnO_4$. Figure 3.6 shows the relative ineffectiveness (less than 20% removal) of $KMnO_4$ for the oxidation of finer odorous compounds. The relative effectiveness of MnO_2 suggests that adsorption on the reduction product rather than oxidation is the mechanism of removal.

Activated Carbon

Powdered activated carbon (PAC) and the granular form (GAC) have been employed successfully to treat tastes and odors. There is considerable historical and empirical data from treatment plant operation to support this statement. PAC is generally applied directly to the raw water, and is allowed to react prior to the addition of either oxidants or coagulants. This allows the carbon to react with the taste and odor compounds and not with the oxidant. GAC treatment occurs later in the treatment process, usually after coagulation and sedimentation (see Chapter 6).

Various researchers have determined the adsorptive efficiencies of PAC and GAC for specific taste and odor com-

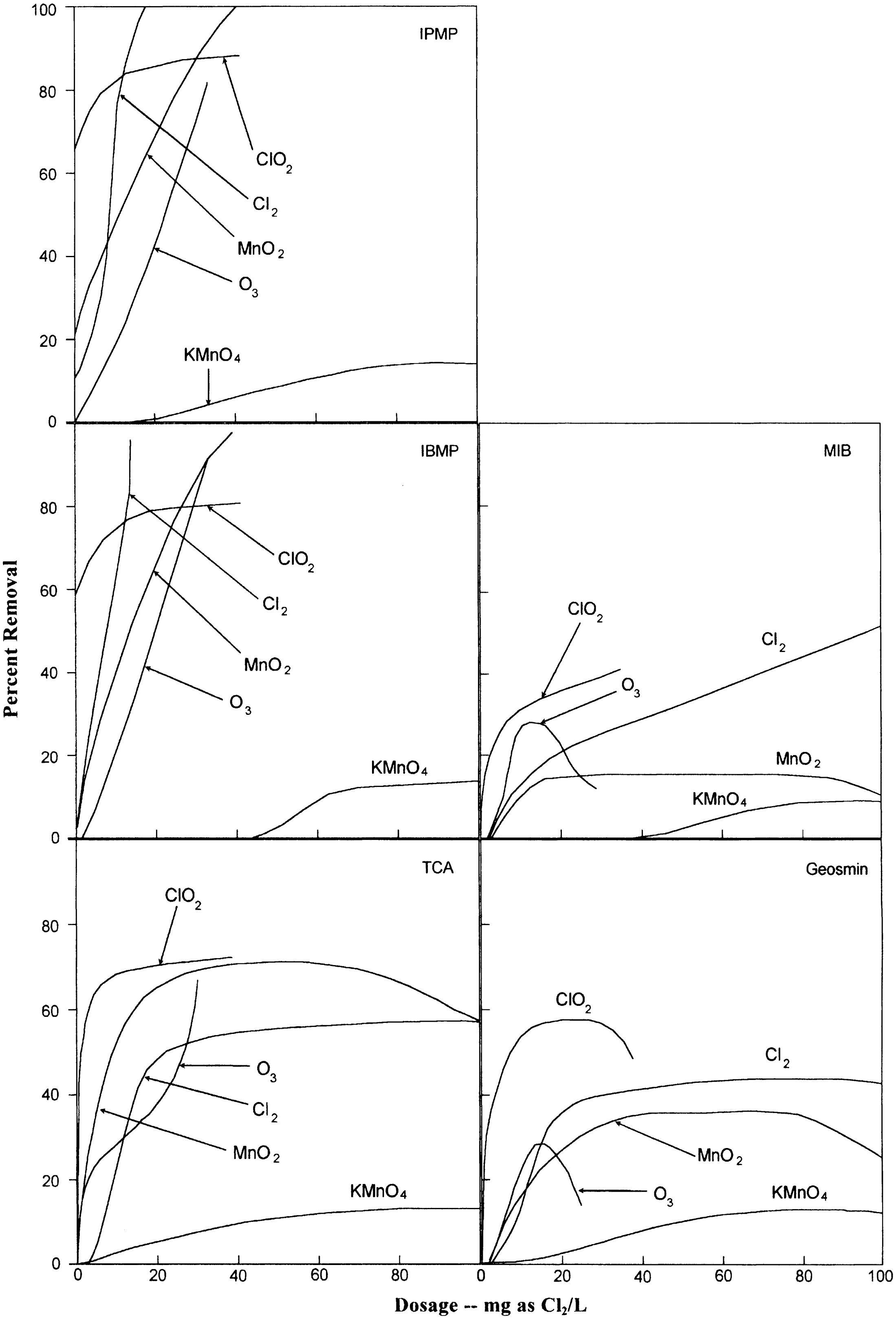


Figure 3.6. Comparison of removal efficiencies of different processes for taste and odor organics.[76]

pounds. For example, pilot plant work was conducted on the PAC removal of geosmin and MIB.[79] PAC doses ranged from 5 to 23 mg/L that effected reductions of MIB and geosmin concentrations of 66 ng/L to low levels (2 and 7 ng/L). PAC and GAC were evaluated for their removal of five taste and odor compounds (IPMP, IBMP, MIB, TCA, and geosmin).[80] Batch equilibrium studies were conducted in the laboratory for these evaluations. PAC dosages up to 20 mg/L were employed, with initial concentrations of the compounds in the 100 to 150 ng/L range for contact times of 3 hours. GAC dosages in the range of 0 to 100 mg/L were utilized with 10,000 ng/L of MIB and geosmin up to 7 days of equilibration time. For PAC, the order of increasing adsorbabilities was: TCA>IBMP>IPMP>geosmin>MIB. On the other hand, MIB and geosmin were removed with greater efficiency and capacity with GAC. Tables 3.23a and 3.23b give the Freundlich isotherm constants for PAC and GAC, respectively. That humic acid, a component of naturally occurring color, interferes with the GAC adsorption of geosmin and MIB is seen in Table 3.23b. Subsequent to these batch studies, a pilot plant operation was utilized to optimize the removal of geosmin and MIB by PAC.[81] Here, dosages of 10 mg/L PAC reduced concentrations of these two compounds up to 66 ng/L "down to acceptable levels" (2 and 7 ng/L, respectively). This study also indicated that chlorine, chloramine, and humic acid decreased the adsorptive capacities of geosmin and MIB on PAC.

Case Histories

Missouri River

The taste and odor qualities of Missouri River water historically have been extremely difficult treatment problems.[82] The causative agents are many and diverse: silt, decaying vegetation, algae, actinomycetes, and wastewaters from packing plants, stockyards and oil refineries. The taste and odor problem is especially apparent during heavy runoff in the early spring. In addition, there is usually a severe turbidity content due to silts and suspended sediments.

A schematic flow diagram of the Metropolitan Utilities Districts (Omaha, Nebraska) water treatment plant is seen in Figure 3.7.[82] There are long contact times for the carbon (presumed to be powdered) and alum treatments. Chlorine is added intermittently for taste and odor control. Applying it after the presedimentation basin was abandoned eventually, in favor of applying it after the upflow sludge contact. This move reduced the chlorine demand and also avoided a chlorinous or fishy odor in the finished water. Potassium permanganate had been applied unsuccessfully for taste and odor control. Table 3.24 shows operational data for odor control in the Missouri River water. That this is an extremely difficult treatment problem is seen in the odor values in the tap water. These data were obtained in March, when low water temperatures retarded the rate of chemical reactions for odor removal.

A flow diagram for the water treatment plant at Kansas City, Missouri, is seen in Figure 3.8.[83] Here the taste and odor were treated with potassium permanganate, chlorine, and powdered carbon. Turbidity was removed by the coagulants—ferric sulfate and alum—and hardness was reduced by lime and soda ash (see Chapter 7). Insofar as taste and odor control was concerned, "threshold odor values were reduced by the permanganate accompanied by a characteristic change. The chlorine did not reduce odor values and on two occasions increased them substantially."

Potassium permanganate and activated carbon were successfully applied for odor control to the waters of the Raccoon River at Des Moines, Iowa.[84] Carbon was fed during all periods of river intake, and when the OT exceeded 25, $KMnO_4$ was fed. An interesting comment was made: "The bland taste resulting from the activated carbon-potassium permanganate treatment has practically eliminated consumer complaints."

Kanawha River

Taste and odor problems with the drinking water from the Kanawha River (Nitro, West Virginia) may have ushered in the application of granular activated carbon (GAC) for their treatment.[85,86] The tastes and odors were due to a variety of organic compounds being discharged from a petrochemical complex upstream from Nitro (see Table 3.10). Figure 3.9 shows the flow diagram of the original system, an experimental system, and the eventual new system. In the latter system, the water is first double-aerated and then directed to a 24-hour sedimentation basin where alum is added to effect coagulation, and chlorine is used for disinfection. After sedimentation, the water passes through GAC beds, where filtration and adsorption occur. It is important to note the dual use of the GAC, where the adsorptive efficiency is decreased by filtered materials. Nonetheless, the treatment scheme was reasonably effective in reducing the OT value to below the PHS standard of 3.

Schuylkill River

Two episodes of unacceptable tastes and odors that corresponded to levels of geosmin in excess of 100 ng/L occurred in the Schuylkill River (Philadelphia, Pennsylvania) in 1985.[87] The source of one episode was a localized bed of blue-green algae in the river. Three control strategies were considered to maintain geosmin levels below 30 ng/L (a "threshold" concentration below which only one or two, if any, complaints were received). The treatment strategy employed PAC. Table 3.25 shows the combinations of PAC and Cl_2 and PAC alone that were tried to reduce the geosmin. A 73% removal with 42 mg/L PAC was achieved that was

Table 3.23a. Freundlich Isotherm Data[a] for PAC Adsorption of Taste- and Odor-Causing Organics Using Modified Jar-Test Technique.[80]

Carbon Type	Isotherm Parameter	Organic Compound				
		IPMP	IBMP	MIB	TCA	Geosmin
Carbon A	K_F	1.54	0.99	[b]	0.00	0.90
	1/n	0.21	0.52	[b]	5.5	0.59
	r^c	0.99	0.95	[b]	0.85	0.91
Carbon B	K_F	0.92	1.8	0.49	1.23	1.02
	1/n	0.83	0.69	0.91	0.96	0.92
	r^c	0.90	0.84	0.96	0.93	0.93

[a] Based on $q_r = K_F/C_r^{1/n}$, in which K_F and 1/n are isotherm constants, and equilibrium concentration C_r and amount adsorbed q_r are expressed in nanograms per liter and nanograms per milligram, respectively.

[b] The negative slope of this isotherm is probably due to analytical imprecision in obtaining the data point for the lowest amount of carbon, corresponding to the highest C_r value.

[c] r=correlation coefficient.

Table 3.23b. GAC Adsorption Equilibrium Parameters for Geosmin and MIB in the Presence and Absence of Humic Acids.[80]

Organic Compound	Background Solution	Concentration Range (ng/L)	Freundlich Isotherm Constant[a]		
			K_F	1/n	r^b
Geosmin	Organic-pure water	$300<C_r<10000$	346.7	0.35	0.99
		$20<C_r<200$	4.5	1.16	0.96
Geosmin	10 mg humic acid/L	$70<C_r<10000$	89.1	0.47	0.98
		$20<C_r<70$	5.3	1.10	0.97
MIB	Organic-pure water	$60<C_r<10000$	21.8	0.81	0.99
		$30<C_r<60$	0.19	2.0	0.98
MIB	10 mg humic acid/L	$400<C_r<10000$	260	0.38	0.98
		$30<C_r<400$	16.0	0.8	0.99

[a] Based on equilibrium concentration C_r and amount adsorbed q_r expressed in nanograms per liter and nanograms per milligram, respectively.

[b] r=correlation coefficient.

observed in plant operation. The second strategy, a hydraulic one, involved changes in intake pumping and dilution of water treated at the Belmont plant with other waters in the distribution system. Source control was the third strategy considered for the riverbed of blue-green algae. However, this became unnecessary when a hurricane raised the river flow 2500% in two days and scoured the algae from the river!

North Saskatchewan River

The city of Edmonton, Alberta, Canada obtains its water supply from the North Saskatchewan River, which flows eastward from the Canadian Rockies. Seasonal runoff, spring and summer, scours accumulated debris from city streets into storm sewers that discharge upstream of three of four water treatment plants. Prior to 1982, Edmonton water customers experienced and reported seasonal episodes of offensive drinking water. Table 3.26 summarizes all verified taste and odor complaints. The hydrocarbon (HC) taste and odor apparently resulted from runoff from streets, parking lots, etc. Such components as benzenes, naphthalenes, alkanes, and alkenes were recovered and identified in the storm sewer effluents. The chlorophenolic (CP) complaints came from in-plant chlorination of phenolic precursors naturally present in the runoff-season river water. Some musty, earthy, fishy, and chlorinous tastes and odors were also reported.

In early 1982, a full-scale implementation of ClO_2 was installed in three of Edmonton's treatment plants. Table 3.26 shows that high-yield ClO_2 treatment eliminated three of the five categories of taste and odor complaints. Only HC and Cl complaints were recorded in 1983. Subsequently, rectification of distribution and flow pattern problems eliminated recurring complaints based on slight elevation of chloramines, which were employed for disinfection. In 1984, HC tastes and odors remained in the finished water, for which PAC was applied. However, this treatment was not successful in eliminating the HC taste and odor complaints. Fixed-bed GAC adsorption was under consideration in late 1984.

Delaware River

Philadelphia, Pennsylvania draws its drinking water supply from two sources: the Delaware and Schuylkill Rivers (see

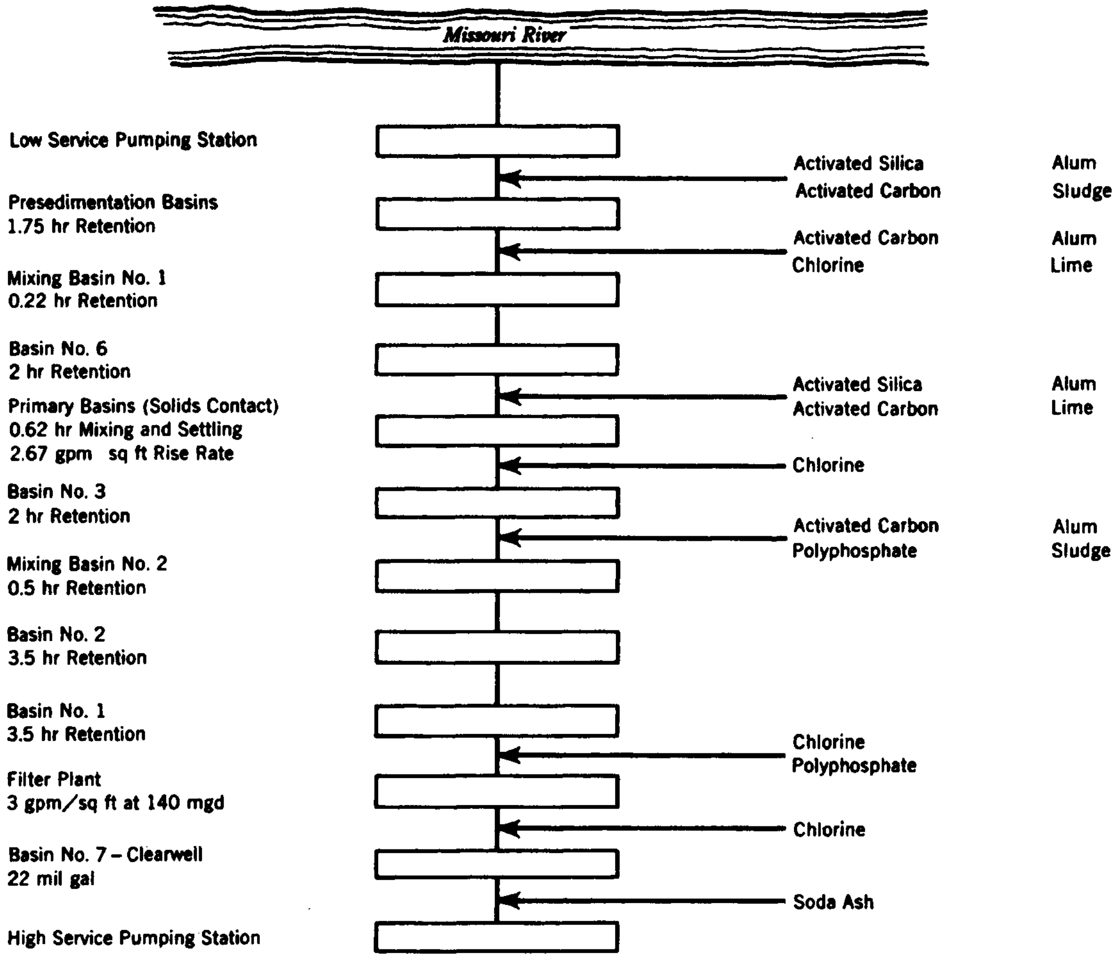


Figure 3.7. Schematic diagram of treatment at metropolitan utilities. All retention times are based on the maximum plant capacity of 140 mgd. Reproduced from Erdei,[82] courtesy of the American Water Works Association.

above). Since 1981, a seasonal cucumber flavor problem occurred at the Baxter Treatment Plant, which processes water from the Delaware River.[89] In 1990, the cucumber odor was traced more than 250 miles upriver to the Cannonsville Reservoir. Subsequently, the odor-causing compound was identified as *trans,* 2-*cis,* 6-nonadienal. This compound is an unsaturated, straight-chain aldehyde with two double bonds and the formula $C_2H_5CH{=}CHCH_2CH_2CH{=}CHCHO$. Algae growth beneath the winter ice produced the compound. The flagellate *Peridinium* showed the best relation to the cucumber odor and *trans,* 2-*cis,* 6-nonadienal. The remediation of this problem was simple and straightforward—chlorination. It had been observed that four other treatment plants on the Delaware River have never experienced a cucumber flavor problem, since they carried a free chlorine residual throughout their treatment processes and distribution system. Thereupon, the Baxter plant put on 2.4 mg/L of free chlorine at the intake, which provides 12 hours of contact in a raw-water basin. This treatment eliminated the cucumber flavor.

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Table 3.24. Operational Data for Odor Control of Missouri River Water.[a]

Day of Month	Odor[b]	Odor Numbers at Sampling Point				Tap Turbidity (ppm)	Carbon (ppm)[c]	$KMnO_4$ (ppm)[d]	Cl_2 (ppm)[e]
		Raw	Primary Influent	Primary Effluent	Lab. Tap				
8	M	5	5	2.5	2.5	0.10	6–4	1.5–1.0	
9	M	6		3.0	2.0	0.10	4		
10	E	8			2.0 M	0.10	4–8		
11	E&M	6 M	6	3.0	3.0 S&M	0.20	8–12	3–1–2	
12	B	22	6 B	5.0 M	4.0 M	0.30	12	2–3	
	O	24							
13	E	24	7 M	5.0	3.0	0.60	12	3–1–2	
14	E&M	13	6 E&M	12.0 OM	3.0	0.80	12	1–0	3
15	E&M	21	8 OM	6.0 OM	8.0 M	0.75	14	2–4	3–5
16	M	21	6	10.0 OM	6.0 M	0.45	14	3–2–3	5–3
17	M	17	8	10.0	5.0	0.25	14	3–2	3–4
18	M	18	12	7.0	4.0	0.25	14	2–0	4–5
19	M	17 M	10	8.0	4.0	0.25	14–10–8		5–3
		21 M							
20	M	10	7	8	5	0.25	10–8		3–2.5
	M	12							
21	M	7	8	14 G	5 M	0.20	8–10		2.5
	M	12							
22	M	17	8	7	4 S&M	0.20	10		2.5–2
23	E	12	8 M	6	4	0.15	10		2.0
24	E	8	6 M	6	4	0.15	10–8		2.0
25	M	18	8	5	3.5	0.15	8–10		2.0
	M	17							
26	M	9	6	6	3.5	0.10	10–4		2.0
	M	12							
27	M	15	8	5	3.0	0.10	4		2.0

[a] Reproduced from Erdei,[82] courtesy of the American Water Works Association.

[b] Odor description: B, barnyard; E, earthy; G, grassy; M, musty; O, offensive; S, sweet.

[c] Applied at presedimentation and Mixing Basin No. 2.

[d] Applied at clarification basin.

[e] Applied at primary effluent.

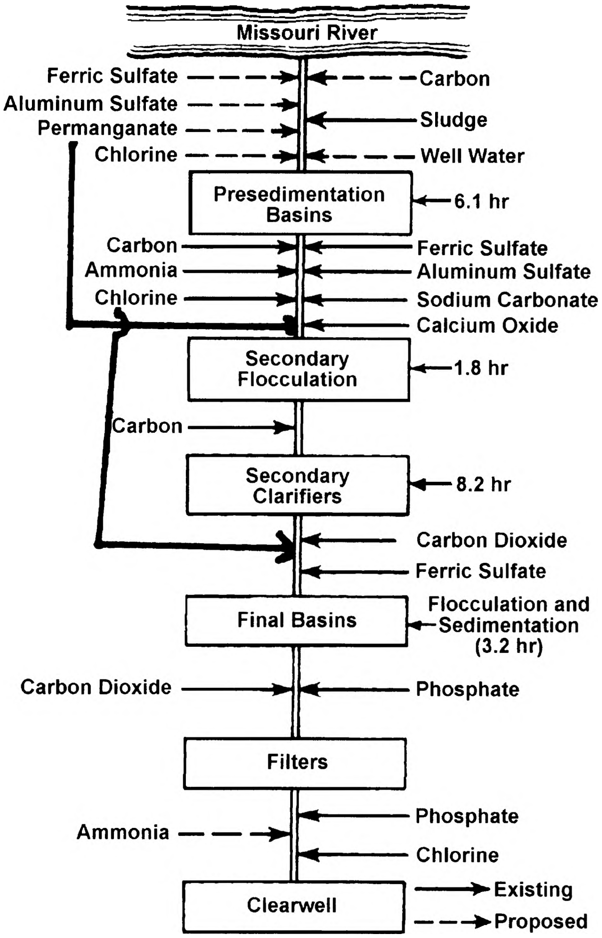

Figure 3.8. Flow diagram of the Kansas City, Missouri, water treatment plant. Reproduced from Popalisky and Pogge,[83] courtesy of the American Water Works Association.

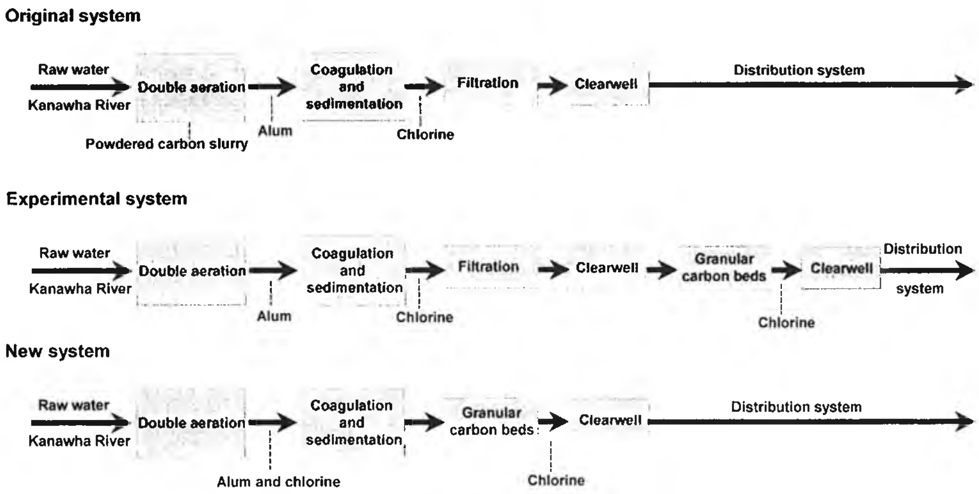

Figure 3.9. Flow diagram of Nitro, West Virginia, water purification plant. Reproduced from Hager,[85] courtesy of the American Water Works Association.

Table 3.25. Reduction in Geosmin Levels During Conventional Treatment and Powdered Activated Carbon Adsorption at the Belmont Treatment Plant.[87]

Treatment	Geosmin Levels Pretreatment (ng/L)	Posttreatment (ng/L)	Estimated Reduction (%)
Chlorination with primary sedimentation	57	62	
Chlorination with primary sedimentation	68	53	
Conventional treatment[a]	77	67	
Conventional treatment	57	52	
Conventional treatment	11	9	
12 mg PAC/L;[b] 1.8 mg Cl_2/L[c]	77	42	45
12 mg PAC/L; 6.6 mg Cl_2/L	38	28	26
12 mg PAC/L; 6.0 mg Cl_2/L	44	18	59
30 mg PAC/L; 3.6 mg Cl_2/L	68	24	65
30 mg PAC/L; 4.2 mg Cl_2/L	87	46	47
30 mg PAC/L	79	44	44
30 mg PAC/L	74	41	45
42 mg PAC/L	74	24	68
42 mg PAC/L	79	20	75
42 mg PAC/L	67	16	76

[a] Conventional treatment consisted of primary sedimentation followed by flocculation with alum, settling, and rapid sand filtration. Chlorination occurred at the primary sedimentation basins, rapid mix, and influent to the filters.

[b] PAC—WPH activated carbon, Calgon Corp., Pittsburgh, Pennsylvania.

[c] PAC and Cl_2 dosages together represent simultaneous addition at the rapid mix, where a negligible chlorine residual already existed.

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Table 3.26. Taste and Odor Complaints Received by the Edmonton Department of Water and Sanitation, Reflecting Changes in Treatment Applied.[88]

Month	Taste and Odor Complaints Received per Year							
	1981		1982		1983		1984	
	Number Received	Type[a]	Number Received	Type	Number Received	Type	Number Received	Type
January	7	HC, Cl	0		3	HC, Cl	11[b]	HC
February	27	HC	0		17[b]	HC	5[b]	HC
March	87	CP, HC	36[b]	HC	10[b]	HC, Cl	10[b]	HC
April	2	HC	1[b]	HC	21[b]	HC	4[b]	HC
May	7	HC, Cl	8[b]	HC	1[b]	HC	5[b]	HC
June	2	CP, HC	4	HC, M Act	5[b]	HC	37[b]	HC
July	2	M Act	4[b]	HC	1[b]	HC	8[b]	HC
August	3	CP, M Alg	3	PC, HC	2	CP, HC	5[b]	HC
September	1	HC	6	Cl, M Alg	3	HC, Cl	37[b]	HC
October	6	HC	32	HC, Cl	18	HC, Cl	0[b]	
November	6	HC, Cl	28	HC, Cl	14[b]	HC, Cl	0[b]	
December	14	CP, HC	21	CP, HC	3[b]	HC, Cl	1[b]	HC
Total	164		143		98		123	

[a] Abbreviations: CP—chlorophenols; HC—hydrocarbons; Cl—chloramines; M Act—metabolites, actinomycetes; M Alg—metabolites, algae.

[b] Water supply treated with ClO_2.

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Chapter 4

Removal of Organics and Inorganics by Activated Carbon

4

Removal of Organics and Inorganics by Activated Carbon

HISTORY OF ACTIVATED CARBON USE

Activated carbon has been long recognized as one of the most versatile adsorbents to be used for the effective removal of low concentrations of organic substances from solution. Charcoal, the forerunner of modern activated carbon whose ability to purify water dates back to 2000 BC, was used for medicinal purposes by ancient Egyptians. Its adsorptive properties for gases were first reported by Scheele in 1773 and later by Fontanna in 1777.[1] In 1785 Lowitz observed the ability of charcoal to decolorize many liquids. This led to the widespread application of wood and bone chars in the refinery of cane and beet sugars.[2] Several attempts were made during the nineteenth century to prepare activated carbons from other sources, such as blood, coconut, flour, and paper mill wastes. The development of modern commercial activated carbon is attributed to Ostrejka, who described a basic process for producing activated charcoal from vegetable materials.[2] This led to the manufacture of powdered activated carbon in Europe as a substitute for bone char in established operations. The real development of activated carbon began during World War I, when hard granular activated carbon (GAC) was developed for use in gas masks. These earlier carbons had relatively less adsorptive capacity than modern carbons. Further developments in the manufacture of activated carbon with sufficient hardness to resist abrasion and the ability to be regenerated for reuse paved the way for utilization of activated carbon in many industrial applications.[1,2] During the past two decades, increased awareness of the occurrence of many organic substances in natural waters and the need for their control led to the emergence of activated carbon adsorption as one of the most effective methods for removing these compounds from drinking waters.

PORE STRUCTURE AND SURFACE AREA

The properties of activated carbon are attributed mainly to its highly porous structure and relatively large surface area. A particle of activated carbon is composed of a complex network of pores that can be divided into two distinct classes with respect to size: macropores and micropores. The macropores are arbitrarily defined as pores greater than 500 Å in diameter. These pores are large capillaries that extend all through the interior of the particle. The micropores have diameters in the range of 10–500 Å and mostly branch off the macropores. Since the surface area of cylindrical or irregularly shaped pores increases considerably with decreasing diameter, the walls of the micropore system contribute to the major part of activated carbon's inner surface area, which may reach 500–1500 m^2/g of activated carbon.[3] This large surface area is one of the main reasons for the high adsorptive capacity of activated carbon. The pore size distribution depends on the type of starting material and the method of manufacturing the activated carbon. The macropores serve as conduits for transport of the adsorbate from the outer particle surface to the interior micropore surfaces where most of the adsorption occurs. A proper distribution of both types of pores is therefore required for the efficient utilization of activated carbon.

Determining Specific Surface Area

The most common method for determining the surface area of activated carbon and other porous adsorbents is the Brunauer, Emmett, and Teller (BET) method.[4–6] This method utilizes gas adsorption for the evaluation of monolayer capacity, Vm. This is defined as the volume of gas in cubic centimeters at standard temperature and pressure (STP) that would be required to cover the adsorbent with a monolayer. The specific surface area, $\Sigma(m^2/g)$, and Vm are related by:

$$\Sigma = \frac{V_m}{22{,}400} \times 6.03 \times 10^{23} \times 10^{-20} \times \sigma_m \qquad (1)$$

$$\Sigma = 0.269\, V_m \sigma_m \qquad (2)$$

where σ_m = area (Å^2) that one adsorbed molecule would occupy in a completed monolayer

Assuming an adsorbed molecule would have the same packing that a molecule of the condensed phase would have in their plane of closest packing, σ_m can be evaluated from:

$$\sigma_m = 3.646\left(\frac{M}{4 \cdot 2^{1/2} \cdot N \cdot \sigma}\right) \tag{3}$$

where M = molecular weight
N = Avogadro's number
σ = density of the condensed phase (solid or liquid at the temperature of the isotherm

The monolayer capacity V_m is determined by performing an adsorption isotherm of nitrogen gas on the activated carbon at liquid nitrogen temperature (–195.8°C). The adsorption isotherm is plotted according to the BET equation, which may be written in a linear form:

$$\frac{P}{V(P_o - P)} = \frac{1}{V_m C} = \left(\frac{C-1}{V_m C} \cdot \frac{P}{P_o}\right) \tag{4}$$

where P = equilibrium pressure
P_o = saturation pressure of nitrogen at the temperature of the experiment
V = volume of nitrogen adsorbed
C = constant characteristic of the gas-solid pair

A straight line is obtained by plotting $P/V(P_o–P)$ against P/P_o, and the value of V_m can be calculated from the slope $(C–1)/V_mC$.

Determining Pore Size Distribution

The pore size and pore size distribution of activated carbon are determined by an analysis of gas adsorption isotherms in the range where capillary condensation accompanies physical adsorption. The Kelvin equation[7] generally is applied to the desorption portion of the adsorption isotherm. The Kelvin equation relates the equilibrium vapor pressure of a curved surface, such as that of a liquid in a capillary or pore, to the equilibrium pressure of the same liquid on a plane surface. Equation 5 is a convenient form of the Kelvin equation:

$$\ln\frac{P}{P_o} = \frac{2\gamma\bar{V}}{rRT}\cos\theta \tag{5}$$

where P = equilibrium vapor pressure of the liquid contained in a narrow pore of radius r
P_o = saturation pressure of nitrogen at the temperature of the experiment
γ = surface tension
$\bar{V}$ = liquid molar volume
θ = contact angle at which the liquid meets the pore wall

The pore volume at each partial pressure (P/P_o) is given by:[8]

$$V_p = \frac{W}{\rho_L} \tag{6}$$

where V_p = the pore volume or the volume of adsorbate
W = the weight of adsorbate
ρ_L = the liquid density

A total pore volume can be obtained by determining the weight of the adsorbate at saturation pressure (i.e., $P/P_o \approx 1$). With each pore volume there is an associated surface area. If the pores are regarded as cylindrical segments, then for segments of radius r, the pore volume V and the surface area A are related by:

$$r = 2kV/A \tag{7}$$

where k = conversion factor for units of measurement

If the adsorbate is desorbed or adsorbed in small increments, and if the surface area is determined, a curve may be plotted showing the variation of surface area with the change in occupied pore space. The reciprocal of the slope of this curve at any pore volume is dV/dA and may be substituted into Equation 4 for V/A. With this information, pore size distribution curves (r vs. V or dV/dA vs. r) may be constructed.

Juhola and Wiig[9] applied the Kelvin equation to a water isotherm to determine the micropore size distribution in several activated carbons. This is the method most commonly used by carbon manufacturers. However, the adsorption isotherms of other adsorbates, such as benzene or nitrogen, can be used. The latter is used quite extensively for pore-size analysis of porous solids.

The useful range of the Kelvin equation is limited to the narrow micropore diameter range of 15–1000 Å. Above 1000 Å, the equation is not reliable, due to the rapid change of the pore diameter with relative pressure. At partial pressure P/P_o above 0.99, *ln* P/P_o approaches 1, and r rapidly approaches infinite size and the accuracy of the pore diameter measurement decreases.

Mercury porosimetry techniques are used to study macropore distribution above r=500 Å.[8] These techniques are based on capillary depression. Because of its high surface tension, mercury tends not to wet most solid surfaces and must be forced to enter a pore. When forced under pressure into a pore of radius r and length l, the amount of work

W required is proportional to the increased surface exposed by the mercury at the pore wall. Therefore, assuming cylindrical pores:

$$W = 2\pi r l \gamma \qquad (8)$$

where γ = surface tension of mercury

Since the wetting angle θ of mercury is greater than 90° and less than 180° on all surfaces with which it does amalgamate, the work required is reduced by $\cos\theta$, and Equation 8 becomes:

$$W_1 = 2\pi r l \gamma \cos\theta \qquad (9)$$

When a volume of mercury ΔV is forced into a pore under external pressure P the amount of work W_2 performed is:

$$W_2 = P\Delta V = P\pi r^2 l \qquad (10)$$

At equilibrium, Equations 9 and 10 are combined:

$$Pr = 2\gamma\cos\theta \qquad (11)$$

Because the product, Pr, is constant, and assuming constant γ and θ, Equation 11 indicates that, as the pressure increases, mercury will intrude into progressively narrower pores.[8] Consequently, pore size distribution can be measured by forcing mercury into a porous solid, e.g., activated carbon, and measuring the penetrating quantity V as a function of the pressure applied. From Equation 11, assuming the pores have a circular cross section, the pore radius r associated with P may be calculated. By plotting V as a function of r, the pore volume distribution curve, dV/dr as a function of r, can be obtained by graphical differentiation.[8]

The volume of mercury forced into the pores is usually monitored in a penetrometer, which is a calibrated stem of a glass cell containing the sample and filled with mercury. As intrusion occurs, the level in the capillary stem decreases. Modern porosimeters can achieve maximum pressures in the range of 50,000 to 60,000 psi, which corresponds to pore radii ranging from 10.7×10^3 Å at 1 psi to 18 Å at 60,000 psi. Figure 4.1 shows a pore size distribution curve for two carbons obtained by porosimetery.[10]

MANUFACTURING ACTIVATED CARBON

Activated carbons have been produced from every conceivable form of carbonaceous substance.[2] The most common materials are wood, coal, peat, lignin, nut shells, sawdust, bone, and petroleum coke. The nature of the starting materials does not have a significant effect on the properties of the resulting activated carbon, since different characteristics can be imparted by the selective introduction of additives, and by controlling the production processes.

The production of activated carbon involves two processes: carbonization followed by activation. Carbonization (pyrolysis) is sometimes called charring, which consists of slowly heating the starting material in the absence of air to temperatures usually below 600°C.[2] The carbonization of carbohydrate- or cellulose-containing materials (e.g., wood) can be controlled by use of dehydrating additives such as zinc chloride or phosphoric acid where a considerably greater pore system is obtained.[2] The dehydrating agents are usually recovered for reuse. During carbonization, volatile pyrolysis products are removed from the starting material, which leaves a residue called char or coke. Chars, frequently called amorphous carbon, have been shown by X-ray studies to be composed of crystals of submicroscopic dimensions termed microcrystallites.[11,12]

Activation consists of treating the chars with oxidizing agents such as steam, carbon dioxide, or oxygen at elevated temperatures, 800–900°C. The oxidizing agents selectively attack portions of the char, transforming it into gaseous products. The resulting hollow pores are systematically developed and enlarged. As a result of studies of the kinetics and mechanisms of activation,[3,13] the reaction now can be carefully controlled, enabling the production of a well-defined pore system in commercial activated carbons.

Before carbonization and activation, the starting materials must be brought to uniform size. Such physical properties of the final product as the granule size, shape, roughness, and hardness are influenced by production techniques.[3] Smooth uniform cylinders with particle sizes between 1 and 9 mm are prepared by extrusion—at high

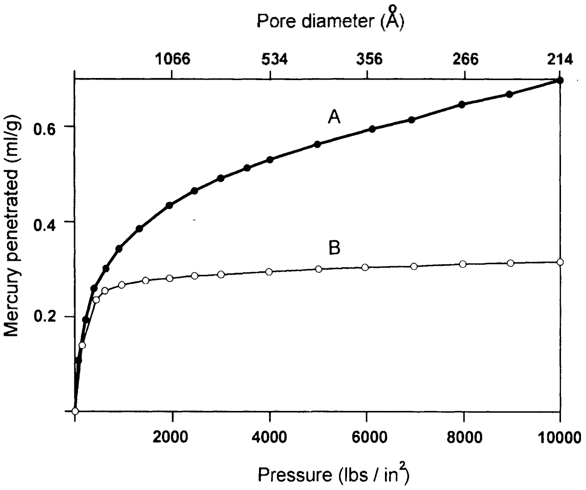


Figure 4.1. Mercury penetration into activated carbon. A = Darco carbon, B = Columbia carbon. Reproduced from Drake,[10] courtesy of the American Chemical Society.

pressures—of a blend of the pulverized material and a binder (sugar, tar, pitch, and lignin)[2] or a dehydrating agent such as zinc. Pelletization is used to produce relatively smooth spherical particles in the size range of 4–9 mm. Agglomeration with subsequent crushing and screening is used for shaping small particle base material. Starting materials with natural granularity can be shaped by crushing. The last two methods result in granules of irregular rough surface with a wide range of grain sizes, 1–10 mm. Pelletization and crushing result in final products with acceptable hardness, while extrusion or agglomeration result in products with very good hardness.[3]

Jüntgen[3] reported studies on changes in the properties of GAC during manufacturing. The shaping process of the granules seems to determine the macropore system. Most of the macropores are formed during the pyrolysis process in the void volume filled by the binder. The macropore volume depends on the forming pressure, particle size, and particle size distribution of the starting material in the granule. Large particles with a wide range of sizes result in a macropore system with a large volume and wide range of pore radii. On the other hand, smaller particle sizes and a narrow range of particle size distribution results in a low macropore volume and a very narrow range of pore radii.

The activation process has a decisive effect on the most important properties of activated carbon, as illustrated in Figure 4.2.[3] The degree of activation has a profound effect on the micropore system. The micropore volume increases almost linearly with the degree of activation. The sharp increase is due to the gasification reaction occurring predominantly on the inner surface of the coke; thus, the majority of pores formed are fine. The macropore volume undergoes a relatively moderate increase in the course of activation. In addition, pore size distribution of the macropore volume is not significantly influenced by the activation process. The average adsorption pore diameter increases sharply with activation, i.e., the carbon becomes increasingly wide-pored with activation. The inner surface area does not increase uniformly over the whole activation process. A sharp initial increase is followed by a slight decrease as activation is continued beyond a maximum value. The initial increase in the surface area is attributed to the formation of predominantly narrow pores which contribute largely to the inner surface area. Further activation causes a growth of smaller pores. Hence, the increase in the specific inner surfaces is slowed and eventually decreased. The bulk density decreases almost linearly with increasing degree of activation. The decrease of bulk density is due to the pore system becoming larger with increasing activation, due to a decrease in apparent density and the constant real density of the carbon. With increasing micropore and macropore volume, the carbon structure becomes more fragile and the impact hardness decreases, first fairly slightly, then at a more pronounced rate beyond medium values of degree of activation.

STRUCTURE OF ACTIVATED CARBON

The structure of activated carbon was shown, from X-ray diffraction studies,[11,12] to be composed of microcrystallites consisting of fused hexagonal rings of carbon atoms with a structure similar to graphite. The structure of graphite, as shown in Figure 4.3, is composed of infinite layers in which the carbon atoms are arranged in a hexagonal lattice.[14] Each graphitic layer is analogous to a very large polynuclear aromatic molecule (fused hexagons). Within each layer, three of each carbon atoms's four valence electrons form covalent bonds (σ bonds) with three neighboring carbon atoms, while the fourth electron resonates between several valence bond structures (π bond), giving each carbon-carbon bond a one-third double-bond character. The layers are stacked with a separation distance of 3.35 Å and are held together by weak van der Waals forces. The carbon layers form an ABAB stacking sequence in which one-half of the carbon atoms in any one plane lie above the center of the hexagons in the layers immediately below it.[14,15]

In microcrystalline carbon, the graphite-like layers are stacked parallel to each other in packets of 5–15 layers about 20–50 Å in height.[12] The diameter of each layer has been estimated to be 20–50 Å. The structure of microcrystallites, however, differs from that of graphite in many ways. Interior vacancies exist in the carbon microcrystallite, and their formation depends on the presence of impurities and the method of preparation. In addition, such foreign atoms as oxygen, sulfur, and hydrogen are always present in different amounts in microcrystallites, which may be bound at the edge of the planes to form heterocyclic ring systems or functional groups.[14] The functional groups terminating the planes interconnect the microcrystallites, and are at least partially responsible for the turbostratic character, in that they prevent orientation of the planes with respect to each other.

The size of microcrystallites is influenced by the temperature of carbonization and the structure of raw material.[2] Microcrystallites in chars prepared from carbohydrates (such as cellulose) increase in size with increasing temperature of carbonization. The macropore structure is developed by burnout of the reactive materials in the interstices between the microcrystallites and through the graphite regions. The micropores, on the other hand, are formed mainly by burnout of the microcrystallite basal planes during the process of activation.[16] As indicated above, the basal planes are composed mainly of fused hexagonal rings, and are thus expected to be fairly uniform. The involvement of carbon atoms in these planes in the formation of sigma bonds with the neighboring carbon atoms precludes the presence of any functional groups. Therefore, planar surfaces of the micropores, which contribute most of the surface area, are responsible for most of the adsorptive properties of activated carbon. Adsorption on these surfaces would be mostly physical due to weak van der Waals forces, although elec-

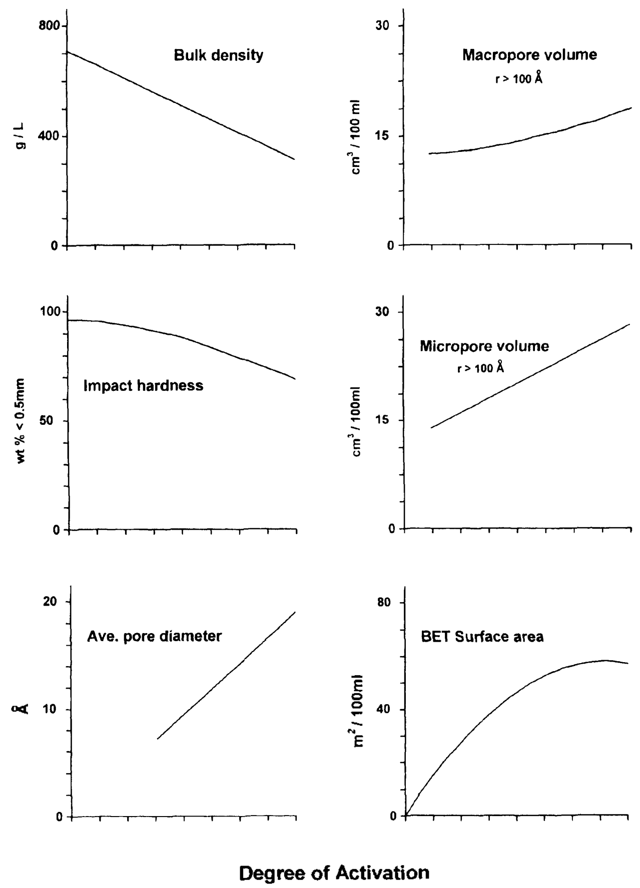


Figure 4.2. Manufacture of activated carbon, and influence of degree of activation.[3]

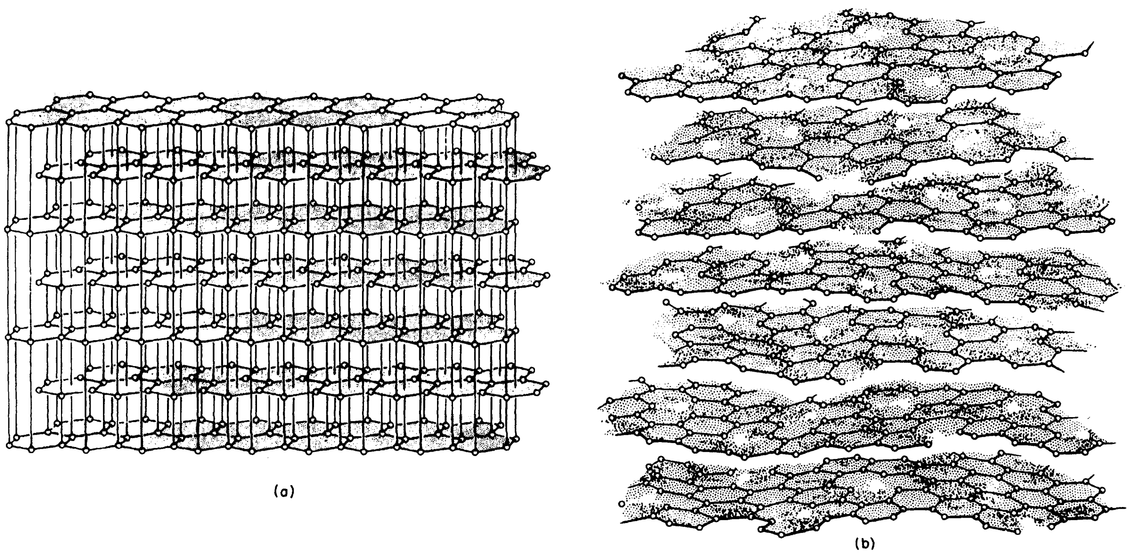


Figure 4.3. Schematic diagram comparing (a) a three-dimensional graphite lattice with (b) a turbostratic structure. Reproduced from Walker,[14] courtesy of *American Scientist*.

trons are available for bonding if the structure of the adsorbate molecule is conducive to such bonding.[17,18]

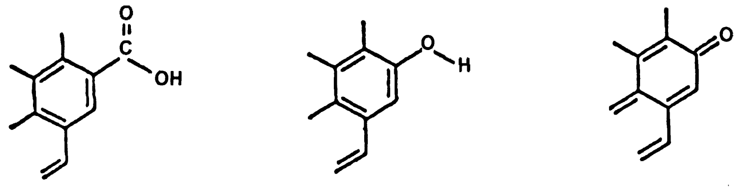
The edges of microcrystallites are more reactive and contain a wide variety of functional groups. During the process of carbonization, a large number of repaired electrons, which are resonance stabilized, are trapped in the microcrystallite due to bond breakage at the edge of the planar structures.[17,19] Foreign atoms such as oxygen and hydrogen interact with these electrons to form surface complexes or functional groups.[20] Surface sites associated with the functional groups constitute a small portion of the total surface area of activated carbon by participating in chemisorptive interactions or forming "specific adsorption" sites.[17,21] For example, presence of hydrogen on the surface of carbon imparts specific characteristics such that adsorption of iodine vapor on certain carbons is reported to be exclusively associated with that part of the surface associated with hydrogen sites.[22] Hydrogen exists at edges of the basal planes in the form of terminal groups or part of hydrocarbon functional groups.

The chemistry of carbon surfaces has been studied extensively by several investigators.[17,23-26] Several reviews have been presented by Weber and coworkers.[17,27] The relevant aspects of surface functional groups pertaining to activated carbons used in water purification are discussed below.

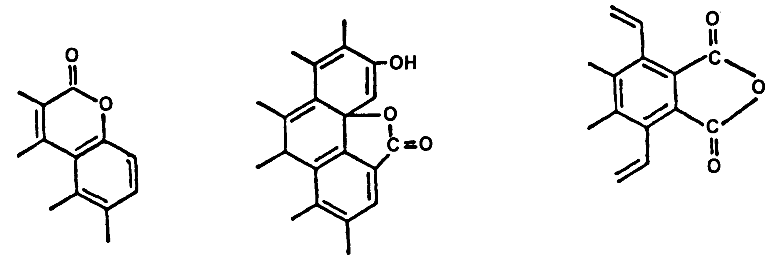
The type of starting material and the method of activation used in producing activated carbon determines, to a large extent, the nature of surface functional groups. The most important of these are the oxygen-containing surface groups, because of their probable effect on the adsorption process. The oxygen content of activated carbon ranges between 1 and 25%, and has been shown to vary considerably with the activation temperature.[28] The amount of oxygen decreases with an increase in the activation temperature, and a very low oxygen content is obtained at activation temperatures higher than 1000°C.[26] The major source of oxygen in activated carbon is the interaction of the oxidizing gases used in the process (oxygen, carbon dioxide, or steam). Here, the oxygen is chemisorbed and bound as surface oxides on the edges of the layer planes.[17,28]

Chemisorbed oxygen can be removed from activated carbon by heat, which evolves it as carbon dioxide, $CO_{2(g)}$, or carbon monoxide, $CO_{(g)}$, depending on the temperature. CO_2 is evolved at temperatures below 600°C, whereas CO is evolved between 500 to 800°C. The complete removal of all bound oxygen requires a temperature of about 1200°C. Under vacuum, the oxygen is completely removed as CO_2, CO, and H_2O.[30,31] The activation temperature has a significant effect on the type of surface oxide formed in activated carbon. Activation temperatures from about 200 to 500°C result in the formation of surface functional groups that are thermally removed as CO_2, while at the higher temperature range, functional groups form that are thermally removed as CO.[32,33] The nature of the surface oxides formed at different activation temperatures has been studied extensively by several investigators using acid-base titrations.[24,29,30,32,34] Carbons activated at low temperatures, 200–400°C, termed L-carbons, generally will develop acidic surface oxides and will lower the pH value of neutral or basic solutions. They sorb primarily bases from solutions, they are hydrophilic, and they exhibit a negative zeta potential. Those carbons activated at higher temperatures, 800–1000°C, termed H-carbons, will develop basic surface oxides and will raise the pH value of neutral or acidic solutions. They sorb acids and exhibit a positive zeta potential. However, cooling H-carbons in contact with air will change the zeta potential to negative, apparently due to formation of acidic surface oxides. Commercial activated carbons used in water treatment are activated at temperatures ranging between 500 and 900°C and exhibit amphoretic properties. Carbons activated by chemical treatment in aqueous solutions with such oxidizing agents as chlorine, permanganate, persulfate, H_2O_2, and nitric acid, develop the same characteristics as L-carbons. It has been suggested[30,34] that surface oxides thermally removed as CO_2 are responsible for the physicochemical properties of L-carbons, and that the oxides evolved as CO are responsible for H-carbons' characteristics.

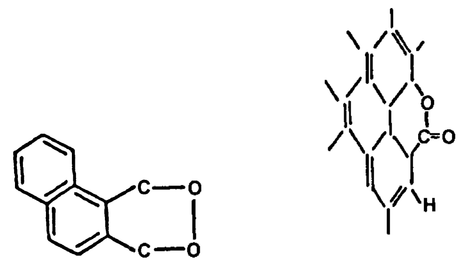
Many techniques have been used to identify the surface oxides of activated carbon. An acid-base titration is the method most extensively used.[24,25,30-34] For example, the acidic surface oxides can be identified by titration with a base of different strength. Other methods include the typical identification reactions of organic chemistry for such specific groups as carboxylic, phenolic, and ketones, etc.: polarography, infrared and internal reflectance infrared spectroscopy.[26] The groups most frequently suggested for the acidic surface oxides include carboxylic groups, phenolic hydroxyl groups, and quinone-type carbonyl groups. There are further suggestions of normal lactones, fluorescein type lactones, carboxylic acid anhydrides, cyclic peroxides, and the enol form of 1,3-diketone. Figure 4.4 shows schematic structural representations of these groups. The presence of acidic surface oxides on activated carbon has been shown to influence the extent of adsorption of aromatic compounds from aqueous solutions. Carboxylic surface oxides, resulting from wet chemical oxidation of carbon, have a negative effect on the adsorption of phenol from dilute solutions.[25] These groups impart a polar character to the surface of carbon which could result in preferential adsorption of water molecules on these sites. These water-oxygen functional group complexes could prevent the migration of organic molecules to a large portion of the surface area.[35] The presence of surface-carbonyl groups or quinonic structures, on the other hand, enhances adsorption of such aromatic compounds as phenol and *p*-nitrophenol due to the formation of a donor-acceptor complex involving the benzene ring's π electrons with the partial positive charge on the carbonyl groups.[26]



(a) Carboxylic group **(b) Phenolic hydroxyl group** **(c) Quinone-type carbonyl group**



(d) Normal lactone group **(e) Fluorescein-type lactone group** **(f) Carboxylic acid anhydride group**



(g) Cyclic peroxide group **(h) n-lactone**

Chromene - acid reaction:

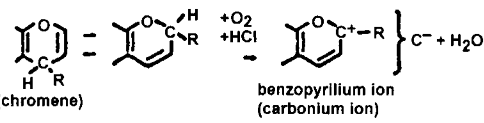


Figure 4.4. Oxygen surface functional groups.

The basic surface oxides on H-carbons that sorb acids from aqueous solutions were not as thoroughly investigated as acidic surface oxides. Garten and Weiss[36] proposed a chromene surface structure responsible for chemisorption of acids. Chromene groups contain active methylene groups, > CH_2 or > CHR, that can react with strong acids in the presence of oxygen to form carbonium ions and hydrogen peroxide (Figure 4.4). The evolution of hydrogen peroxide was observed earlier by Kolthoff[37] during the adsorption of acid by carbon. The carbonium ion tends to associate strongly with a negative anion, which accounts for the fact that sorbed acids are very difficult to wash from activated carbon.

ADSORPTION

Adsorption is defined as the increase in concentration of a particular component at the surface or interface between two phases. In any solid or liquid, atoms at a surface are subject to unbalanced forces of attraction normal to the surface plane. These forces are merely extensions of the forces acting within the body of the material. A molecule in the center of a liquid drop is attracted equally from all sides, while at the surface the attractive forces acting between adjacent molecules result in a net attraction into the bulk phase in a direction normal to the surface. Because of the unbalanced attraction at the surface, there is a tendency for these molecules to be pulled from the surface into the interior, and for the surface to shrink to the smallest area that can enclose the liquid. The work required to expand a surface by 1 cm^2 in opposition to these attractive forces is called the surface tension.

The above concept applies equally well to solids. Molecules in a solid surface are also in an unbalanced attractive field and possess a surface tension or a surface free energy. Whereas the surface tension of a liquid can be measured easily, that of a solid cannot, since, to increase the surface, extraneous work must be done to deform the solid.[38] Adsorption partially restores the balance of forces and is accompanied by a decrease in the system's free energy. Adsorption processes may be classified as physical or chemical, depending on the nature of the forces involved.

Physical adsorption on solids is attributed to forces of interactions between the solid surface and adsorbate molecules that are similar to the van der Waals forces between molecules. These forces, which involve the electrons and nuclei of the system, are electrostatic in origin, and are termed dispersion forces. The dispersion forces exist in all types of matter and always act as an attractive force between adjacent atoms and molecules, no matter how dissimilar. They are always present regardless of the nature of other interactions, and often account for the major part of the adsorbate-adsorbent potential.[38,39] The nature of the dispersion forces was first recognized in the 1930s by London.[40] Using quantum mechanical calculations, it was postulated that the electron motion in an atom or molecule would lead to a rapidly oscillating dipole moment. At any instant, the lack of symmetry of the electron distribution about the nuclei imparts a transient dipole moment to an atom or molecule that would average zero over a longer time interval. When in close proximity to a solid surface, each instantaneous dipole of an approaching molecule induces an appropriately oriented dipole moment in a surface molecule. These moments interact to produce an instantaneous attraction. These forces are known as dispersion forces because of their relationship, noted by London,[40] to optical dispersion. The dipole-dispersion interaction energy can be determined by:[40]

$$E = -C/r^6 \qquad (12)$$

where E = dispersion energy or potential
C = a constant
r = distance of separation between the interacting molecules

In addition to dipole-dipole interactions, other possible dispersion interactions contributing to physical adsorption include dipole-quadrapole and quadrapole-quadrapole interactions. If these two are included, the total dispersion energy becomes:[39,40]

$$E = C/r^6 - C'/r^8 - C''/r^{10} \qquad (13)$$

where C' = a constant for dipole-quadrapole interactions
C'' = a constant for quadrapole-quadrapole interactions

The contribution to E from the terms in Equation 13 clearly depends on the separation r between the molecules; therefore, the dipole-dipole interactions will be most significant. Quadrapole interactions involve symmetrical molecules with atoms of different electronegativities, such as CO_2. This molecule has no dipole moment, but does have a quadrapole ($^{-}O{-}^{+}C^{+}{-}O^{-}$) that can lead to interactions with polar surfaces.

When an adsorbate molecule comes very close to a solid surface molecule to allow interpenetration of the electron clouds, a repulsive interaction will arise. The overall interaction energy is expressed as:

$$E = C/r^6 + B/r^{12} \qquad (14)$$

where B = repulsive interaction constant

A more detailed discussion of interaction forces in physical adsorption can be found elsewhere.[39]

The second type of adsorptive interaction is chemisorption. This is characterized mainly by large interaction potentials that lead to high heats of adsorption approaching the value of chemical bonds. This fact, coupled with other spectroscopic, electron spin resonance, and magnetic susceptibility measurements, confirms that chemisorption involves the transfer of electrons and the formation of true chemical bonding between the adsorbate and the solid surface.[39] Because chemisorption involves chemical bonding, it often occurs at high temperatures and is usually associated with activation energy. Also, the adsorbed molecules are localized on specific sites and, therefore, are not free to migrate about the surface.

Physical adsorption can be distinguished from chemisorption according to one or more of the following criteria:

1. Physical adsorption does not involve the sharing or transfer of electrons, and thus always maintains the individuality of interacting species. The interactions are fully reversible, enabling desorption to occur at the same temperature, although the process may be slow because of diffusion effects. Chemisorption involves chemical bonding and is irreversible.
2. Physical adsorption is not site-specific; the adsorbed molecules are free to cover the entire surface. This enables surface area measurements of solid adsorbents. In contrast, chemisorption is site-specific; chemisorbed molecules are fixed at specific sites.

3. The heat of physical adsorption is generally low compared to chemisorption; however, heat adsorption is not usually a definite criterion. The upper limit for physical adsorption may be higher than 20 kcal/mol for adsorption on adsorbents with very narrow pores. The heat of chemisorption ranges from over 100 kcal/mol to less than 20 kcal/mol. Therefore, only very high or very low heats of adsorption can be used as a criterion for this type of adsorption process.[8]

FACTORS AFFECTING ADSORPTION

Nature of the Adsorbent

Surface Area and Pore Structure

Since the adsorption process results in a concentration of solutes at the surface, it is obvious that the surface area is one of the principal characteristics affecting the adsorptive capacity of an adsorbent. The adsorptive capacity of solid adsorbents generally is proportional to the specific surface area; that is, the adsorption of certain solutes increases with an increase of surface area. Table 4.1 shows the physical properties of 10 commercially available activated carbons that are employed in water treatment. Surface areas range from 750 to 1800 m^2/g. Sieve sizes, however, should be noted for comparison of each carbon's surface area. However, the specific surface area alone is frequently inadequate to explain the adsorptive capacity of porous solids, such as activated carbon, for different solutes. As discussed above, the pore size distribution in activated carbon indicates that micropores contribute a major portion of the specific surface area. Many of the micropores possess molecular dimensions. It is, therefore, reasonable to expect that a solute molecule will readily penetrate into a pore having a certain critical diameter and will be excluded from pores smaller than this size. In other words, the surface area accessible to the sorbate will be influenced by its molecular size, and only those pores that are accessible to the sorbate will contribute to the effective or measured surface area. Not only has such a molecular sieve effect been well established, but also a linear relationship between the specific surface area and sorbate molecular size has been demonstrated.[42]

Particle Size

The surface area of nonporous adsorbents increases considerably with a decrease in particle size. Consequently, the adsorptive capacity should increase with reduction in particle diameter. However, for such highly porous adsorbents as activated carbon, most of the surface area resides in the internal pore structure, and the adsorptive capacity is expected to be independent of the particle size. Zogorski[43] showed that crushing Columbia LCK carbon to particle sizes ranging between 0.66 and 1.4 mm had no effect on the N_2-BET surface area, and that the adsorptive capacity for 2,4-dichlorophenol and 2,4-dinitrophenol was independent of the particle size. This is in contrast to earlier findings by Weber and Morris[44] that a fourfold decrease in particle size of Columbia LCK activated carbon (0.502 to 0.126 mm) resulted in almost doubling the adsorptive capacity for 3-dodecylbenzenesulfonate. It was suggested by these authors that breaking up large particles served to open some tiny sealed channels in the carbon that might then become available for adsorption. This yielded the dependence of equilibrium capacity on particle size. The particle size of activated carbon has no apparent effect on the adsorptive capacity for such solutes of small molecular sizes as phenols (area per molecule is about 52 $Å^2$) that would have access to most of the small diameter micropores.[35] On the other hand, the capacity for solutes of larger molecular size such as the benzenesulfonates (area per molecule ranges between 100 and 280 $Å^2$)[45] may show dependence on particle size, probably due to the exposure of more accessible surface area by crushing of the larger particles.

Chemistry of the Surface

The presence of specific functional groups on the surface of the adsorbent imparts certain characteristics that affect the adsorption process. The formation of polar surface groups of chemisorbed oxygen during the activation process of activated carbon affects the adsorptive capacity for many solutes. Surface oxides consisting of acidic functional groups reduce the capacity of carbon for adsorption of many organic solutes, such as oxalic and succinic acids[35] and trihalomethanes from aqueous solutions.[46] This was attributed to the preferential adsorption of water, and hence blockage of a part of the surface.[35] On the other hand, the abundance of surface oxides consisting of carbonyl groups enhances the adsorption of such aromatic solutes as phenol, *p*-nitrophenol, and naphthalene. This enhanced adsorption was attributed to the interaction of aromatic ring π electrons with the carbonyl groups by a donor-acceptor mechanism involving the carbonyl oxygen as the electron donor and the aromatic ring as the acceptor.[26]

Nature of the Adsorbate

Adsorption by activated carbon in aqueous solutions is influenced by several physicochemical properties of the organic solutes. Solubility is, perhaps, the most significant property affecting the adsorptive capacity. In general, a higher solubility indicates a strong solute-solvent interaction or affinity, and the extent of adsorption is expected to be low because of the necessity of breaking the solute-solvent bond before adsorption can occur. A general rule for adsorption of organic solutes, known as Traube's rule,[47] states that the adsorption of organic substances from aque-

Table 4.1. Properties of 10 Commercially Available Activated Carbons.

Properties	Barney Cheney NL 1266	Barney Cheney SC 1548	Barney Cheney SK 1301	Calgon CAL	Calgon RB	ICI Darco S-51	Westvaco Nuchar WV-L	Westvaco Nuchar S-A	Westvaco WV-DC	Witco Witcarb 950
Surface area (m^2/g^1)	750–800	900	925	1100–1300	1100–1300	650	1000	1400–1800	1500–1700	1000–1100
Apparent density (g/cm^3)	0.18–0.25	0.48–0.53	0.48–0.53	0.44	0.41	0.24–0.29	0.43–0.47	0.38–0.41	0.24–0.29	0.46–0.53
Effective size (mm)	0.3–0.6	0.3–0.6	0.3–0.6	0.55–0.7			0.85–1.05	0.85–1.05	0.9–1.0	0.5–0.7
% passing No. 325					70	70				
Iodine	800	900	900	1000	1070	950	950	800	850	1050
Maximum moisture %	2	2	2	2	2	8	2	10	10	1
Source	Hardwood acid wash	Nutshell	Nutshell	Coal	Coal	Lignite	Bituminous coal	Bituminous coal	Wood	Petroleum
Size	30 × 50	30 × 50	30 × 50	12 × 40	Powder	Powder	8 × 30	8 × 30	10 × 25	18 × 40
Mean pore radius (Å)	100–150	20	20	50	18	30	19	23	23	20

Source: Reproduced from Netzer and Hughes,[41] courtesy of Pergamon Press.

ous solutions increases strongly and regularly as the homologous series is ascended. The adsorption of a series of aliphatic acids—formic through butyric—on activated carbon increases with an increase in the chain length. The increase in adsorption is due to the increase in hydrophobicity and the decrease in solubility with the increase in the chain length. The reverse order of adsorption of these species is observed for their adsorption from nonpolar solvents. Adsorption isotherms for the fatty acids—acetic, propionic, *n*-butyric, *n*-valeric, *n*-caproic and *n*-heptylic—on carbon were shown by Hansen and Craig[48] to be superimposable when plotted as the amount adsorbed vs. the reduced concentration. The latter is the equilibrium concentration divided by the solubility at the temperature of measurement, and is equivalent to the partial pressure P/P_0 in gas adsorption. Dividing the solute concentration by its solubility normalizes the solute-solvent interactions, which are considered to be the same for each member of the homologous series.

The molecular weight and size of the adsorbate molecule also affects the adsorptive capacity. Weber[27] and Weber and Morris[44] showed that the adsorptive capacity of activated carbon increases with an increase in molecular weight of a series of sulfonated alkylbenzenes ranging from the unsubstituted and up to the sulfonated tetradecylbenzene. The increase in the side chain length increases the hydrophobicity of the molecule, which results in greater adsorption.

The properties of solute molecules are discussed better in terms of polarity, which has a profound effect on adsorbabilty from water. As indicated above, a major portion of the carbon surface is nonpolar or hydrophobic; therefore, hydrophobic interactions become important. These interactions originate from a net repulsion between the water and nonpolar regions of the carbon surface as well as the nonpolar moieties of the solute or adsorbate. As a consequence of these repulsive interactions and the high cohesive energy of water, the nonpolar molecules and nonpolar regions of the surface can associate when they are in close proximity to each other.[49,50] In other words, in aqueous systems, nonpolar solutes are more strongly adsorbed on activated carbon than polar solutes. Polarity of organic compounds results when the centers of opposite charges in a molecule do not coincide. These charges (positive and negative) in a molecule originate from unequal distribution of electron density between two atoms of different electronegativities (electron-attracting ability). The introduction of functional groups imparts polar characteristics to the molecule. Polarity of the functional groups is thought to follow the order:[51,52] $-COOH > -OH > -C{=}O > -C-O-C$. Since solubility of organic solutes in water involves formation of hydrogen bonding between the partially positive hydrogen atoms of water and the partially negative atoms of the organic molecule, increasing the polarity is expected to increase solubility and, in turn, decrease adsorbability.

Several investigators evaluated the effects of functionality, molecular weight, branching, solubility, and polarity of solutes on carbon adsorption.[53,55] Giusti et al.[53] reported that functionality has a substantial effect on adsorption, which is interrelated with solubility and polarity. For straight-chain aliphatic compounds, the relative adsorbability on carbon for compounds of less than four carbon atoms are: undissociated organic acids > aldehydes > esters > ketones > alcohols > glycols. An increase in molecular weight due to an increase in chain length in any series results in a decrease in solubility; therefore, there is an increase in adsorptive capacity.[27,44,53] Branching in the chain generally results in reduction in adsorbability. For example, adsorption decreases in the alcohol series in the following order: normal > iso > tertiary.[49] Branching presumably results in changes in the geometry of molecules, which become more spherical, and, hence, have less surface area for interaction with the carbon surface.

The adsorptive capacity of carbon for aromatic compounds is influenced by substitution in the ring structure. Introduction of substituent groups to phenols results in increased adsorbability in the following order:[49,54] $-OCH_3 > -CH_3 > -Cl > -NO_2$. The position of the substituents seems to have no effect on adsorbability.[27,54,56,57] Thus, the adsorptive capacity for ortho-, meta-, or para-cresol, or ortho- or para-chlorophenol, is the same for each series. Adsorption is enhanced when the number of substituents on the phenol molecule is increased. The disubstituted phenols: 2,3-, 3,4- and 2,6-dimethylphenol, are more strongly adsorbed than *o*-, *m*-, or *p*-cresol.[56] For chlorinated phenols, adsorbability increases in the following order: 2,4,6-trichlorophenol > 2,4- or 2,6-dichlorophenol > 2- or 4-chlorophenol > phenol.[57] Length of the side chain also increases adsorption according to the following order: 2-isopropylphenol > dimethylphenol > ethylphenol > methylphenol > phenol.[56]

Effect of $[H_3^+O]$

The adsorption of nonelectrolytes by activated carbon from aqueous systems is generally not affected by the solution pH, although some exceptions can occur. However, the effect of $[H_3^+O]$ on the adsorption of weak electrolytes, both acids and bases, is quite pronounced. Extensive studies have been reported for the adsorption, at different pH values, of phenolic compounds[26,57,61] and organic acids[26,44,62-64] that may occur as contaminants in natural waters. The adsorption characteristics of these compounds follow more or less a general pattern. Both the undissociated and ionized forms of a species can be adsorbed on activated carbon, with undissociated forms being more strongly adsorbed than ionized forms. The adsorption behavior of a weakly acidic compound is illustrated in Figure 4.5. This shows the adsorption versus pH curve for 2,4-dinitrophenol (pK_a=4.09) developed from the adsorption data reported by Zogorski.[43] This adsorption curve follows the dissociation curve of 2,4-dinitrophenol in a general way, although it is shifted by a few pH units. This behavior is observed for adsorption of most organic acids on activated carbon. At alkaline pH values greater than the pK_a of a weak organic acid, the adsorptive capacity is greatly reduced, and the anions are adsorbed when no undissociated molecules are present in bulk solution. The adsorptive capacity increases with a decrease in pH, and a maximum occurs in the range where pH is numerically equal to pK_a, i.e., where both anions and undissociated molecules exist in equal concentrations. At pH values more acidic than the pK_a value, the adsorptive capacity usually decreases.

The dependence of activated carbon's adsorptive capacity for weakly acidic compounds on the solution pH has been attributed to changes in the characteristics of the adsorbent and the solute molecules. Activated carbon can adsorb both acids (H_3^+O) or bases (OH^-)[23,24,26,27] from aqueous solution, which could result in changes of the surface characteristics. The decrease in capacity at pH values higher than pK_a values has been attributed to the development of repulsive forces between the anions and the carbon surface or between the anions themselves.[58] The negative surface charge of the carbon may be increased by adsorption of hydroxyl ions on the surface, or by ionization of the very weak acidic functional groups on the surface, or both.[58] The increased adsorptive capacity for carboxylic acids as the pH value is decreased to the range of pK_a was attributed by Getzen and Ward[63] to the adsorption of hydronium ions as well as anions. Since the concentration of H_3^+O ions rapidly exceeds that of the weak electrolyte anions, the former adsorb on the carbon far in excess of the anions, and subsequently enhance anion adsorption, i.e., a synergistic effect occurs. The decrease in adsorptive capacity at pH values much more acidic than pK_a was suggested to be due to the competitive interaction of the hydronium ions with the carbonyl oxygen groups on the carbon surface.[64]

Manes[65] considered the effect of pH on adsorption of weak acids to be due to competitive adsorption between the acid and its anion where the ratio of both is controlled by the pH. An anion is much more weakly adsorbed than its conjugate acid at the same concentration, because of the greater solubility of the anion over the acid and the increased negative entropy of concentration of the anion. The latter arises from the necessity to concentrate two particles (the ions) rather than one (the neutral molecule) in the course of adsorption. As a result, the net free energy driving force for the anion will be much smaller, and, therefore, can be readily displaced by the strongly adsorbed neutral species.

Hydronium ion concentration, i.e., pH, is, of course, an important operational variable at drinking water treatment plants. This is especially true for chemical coagulation (see Chapter 5) and also for activated carbon removal of ionizable contaminants. The influence of [H_3^+O] on the GAC removal of organic contaminants expressed as total organic carbon (TOC) and TTHM formation potential has been demonstrated in the laboratory.[66] Water samples from the Mississippi River at Minneapolis were pretreated with chemical coagulation (alum) and then passed through miniature columns of GAC at pH values of 5.0, 6.1, 7.0, and 8.7. The breakthrough curves in Figure 4.6 clearly show that, as the pH values increase, the extent of adsorption decreases. An adjustment of pH value in treatment plant operation is not recommended to optimize removal of TOX and TTHM formation potential organics. Acidic conditions would lead to unnecessary corrosion of plant equipment. Rather, operational personnel should be aware that efficiency of adsorption of organics is affected by pH (i.e., [H_3^+O]).

Effect of Foreign Ions

The inorganic composition (Ca^{2+}, Mg^{2+}, etc.) of water can also have an important effect on adsorption of selected organics from water by activated carbon. For example, the effect of calcium chloride ($CaCl_2$) addition on the extent of fulvic acid adsorption is seen in Figure 4.7.[67] After 70 days of continuous operation, a small GAC column was nearly saturated with fulvic acid. Addition of $CaCl_2$ at this point resulted in a large increase in adsorbability of fulvic acid that is seen in the reduced column effluent. After 140 days, elimination of the $CaCl_2$ resulted in desorption of much of the fulvic acid. The calcium ion apparently complexes with the fulvic acid and the carbon's surface to make it more adsorbable.[67,68] Many other divalent ions can act in a similar manner, but Ca^{2+} has special interest because of its ubiquitous distribution in natural waters. Similar effects are expected for other anionic adsorbates. However, foreign ions are not expected to have an appreciable effect on adsorption of neutral adsorbates.

Effects of Temperature

Since the process of adsorption is spontaneous, it is accompanied by a decrease in the system's free energy. There is always a decrease in entropy due to loss of degrees of freedom of the solute in passing from the dissolved state to the adsorbed state.[39] It follows from the relationship

$$\Delta G = \Delta H - T\Delta S \qquad (15)$$

that the adsorption process must always be exothermic, i.e., ΔH must have a negative value regardless of the nature of the interaction forces. The enthalpy change, ΔH, for physical adsorption is in the range of 2–15 kcal/mol.[8] An increase in temperature, therefore, will result in a reduction of the equilibrium adsorptive capacity, whereas lower temperatures will favor an increased capacity. Morris and Weber[45] reported a reduction in the capacity of activated carbon for

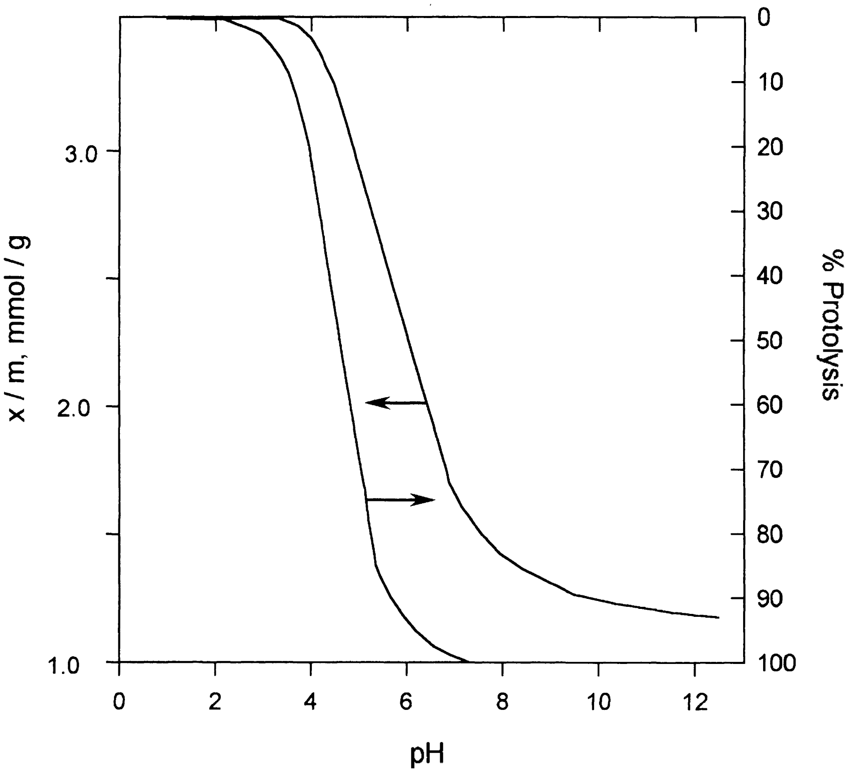


Figure 4.5. Effect of pH on adsorption of 2,4-dinitrophenol.[43]

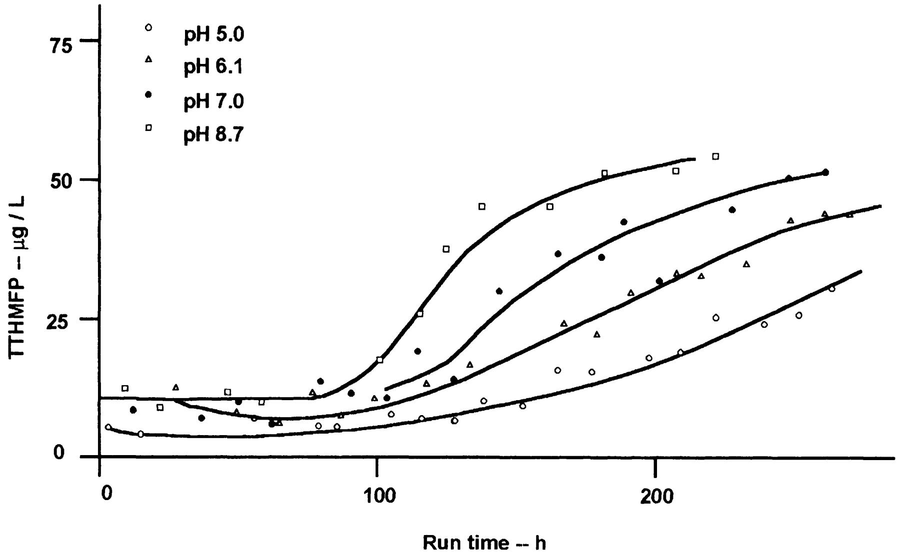


Figure 4.6. The effect of pH on the removal of THM precursors by GAC (influent TTHM formation potential = 101 μg/L; alum dose = 50 mg/L; pH of coagulation = 5; EBCT = 1.15 min).[66]

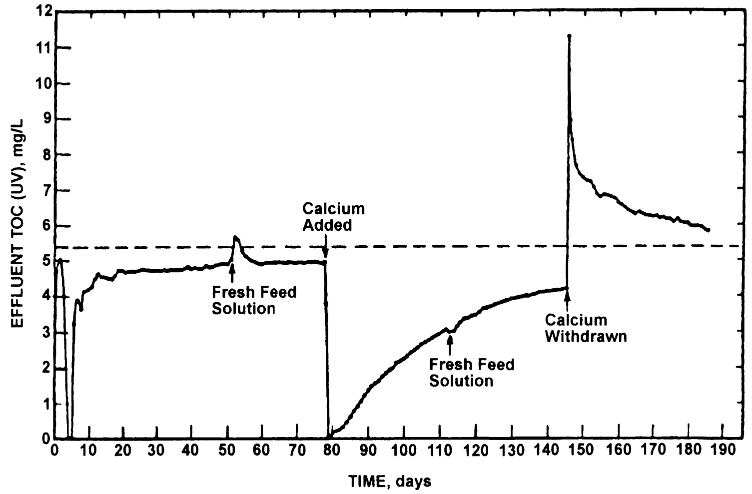


Figure 4.7. The effect of calcium chloride addition and withdrawal on column performance (pH = 8.3; TOC = 5.37 mg/L), peat fulvic acid; buffer = 1.0 m*M* $NaHCO_3$).[67]

adsorption of benzenesulfonate by increasing the temperature from 9.5 to 48.5°C. Similar results were obtained by Snoeyink et al.[58] for the adsorption of *p*-nitrophenol.

Zogorski[43] showed that the effect of temperature on adsorption of phenol is more pronounced at low surface coverage or at low initial concentrations, as shown in Table 4.2. Thus, at a phenol concentration of 30 μmol/L, an increase in temperature from 8 to 29°C results in a 42% decrease in the adsorptive capacity of activated carbon. At initial concentrations higher than 200 μmol/L, the temperature effect is relatively small.

The temperature of natural surface waters in northern states fluctuates widely during the year, ranging from 34°F (≈ 0.5°C) during the winter months to 95°F (≈ 32°C) during the summer months. Such a wide range of temperature has a significant effect on the adsorptive capacity of activated carbon used to remove the relatively low concentrations of organic contaminants encountered in surface waters used for drinking water.

The heat of adsorption ΔH in gas-solid adsorption is measured by introduction of a definite quantity of gas to the adsorbent sample in a thermally insulated calorimeter. The adsorption process produces a temperature rise in the entire system, and the heat of adsorption is obtained by multiplying the temperature rise by the heat capacity of the system. Direct measurement of the heat of adsorption from solutions, however, is not possible by this method because of the interaction of the solvent with the solid surface. Morris and Weber[45] measured the differential heat of adsorption by computing the monolayer capacity X_m at two different temperatures from the Langmuir equation and by using the van't Hoff equation in the form:

$$\Delta H = 2.303R\frac{(T_1T_2)}{(T_2 - T_1)}(\log X_{m,2} - \log X_{m,1}) \qquad (16)$$

The differential heat of adsorption for benzenesulfonate was reported to be ΔH=1.4 kcal/mol.[45] The negative sign of ΔH confirms that the adsorption is an exothermic process, and the value 1.4 kcal/mol is within the expected range for physical adsorption.

Temperature dependence of adsorption on AC has been evaluated for chloroform ($CHCl_3$), bromodichloromethane ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$), and bromoform ($CHBr_3$) at 4, 15, 30, and 45°C.[69] Coefficients of Langmuir and Freundlich isotherms (see below) were determined from which isoteric heats of adsorption (ΔH) were calculated by statistical methods. These ΔH values are: –7.9 ± 2.4, –5.9 ± 1.3, –5.2 ± 2.2, and –4.1 ± 2.2 kcal for the aforementioned THMs, respectively, with an average of –5.8 ± 2.0 kcal/mol. These values are well within the range of physical adsorption cited above. It was concluded "that the characteristic decrease in GAC capacities with increasing temperature is significant, even for THMs, which are weakly adsorbed, and have a relatively small heat of adsorption...."[69]

ADSORPTION EQUILIBRIA

Adsorption from aqueous solutions involves concentration of the solute on the solid surface. As the adsorption

Table 4.2 Adsorptive Capacity of Columbia LCK Carbon for Phenol as a Function of Temperature and Initial Adsorbate Concentration.[43]

Concentration of Phenol (µmol/L)	$X_{8^{\circ}C}$[a] (µM/g)	$X_{29^{\circ}C}$ (µM/g)	Decrease in Adsorptive Capacity of Adsorbent (%)
30	895	520	42
50	1040	780	25
100	1250	1050	16
200	1480	1320	11
300	1620	1500	7
400	1710	1625	5
500	1800	1725	4

[a] Amount of phenol adsorbed per unit weight of carbon at the temperature indicated.

process proceeds, the sorbed solute tends to desorb into the solution. Equal amounts of solute eventually are being adsorbed and desorbed simultaneously. Consequently, the rates of adsorption and desorption will attain an equilibrium state, called adsorption equilibrium. At equilibrium, no change can be observed in the concentration of the solute on the solid surface or in the bulk solution. The position of equilibrium is characteristic of the entire system—the solute, adsorbent, solvent, temperature, pH, and so on. Adsorbed quantities at equilibrium usually increase with an increase in the solute concentration. The presentation of the amount of solute adsorbed per unit of adsorbent as a function of the equilibrium concentration in bulk solution, at constant temperature, is termed the adsorption isotherm. Typical adsorption isotherms for adsorption from water systems are shown in Figure 4.8.[57] Isotherms of this type are typical for adsorption by activated carbon from aqueous solutions when adsorption does not proceed beyond a monomolecular layer,[6] whereas multilayer adsorption in these systems is not usually encountered.

The surface of activated carbon is heterogenous, not only in surface structure but also in the distribution of surface energy. During the course of adsorption, the heat of adsorption is not constant for each incremental increase in adsorption. Usually the initial portions of adsorbed solute have greater differential heats of adsorption than subsequent ones. Thus, a steep initial drop of the heat of adsorption, with an increase of the amount adsorbed, indicates that the first molecules to arrive at the bare surface are preferentially adsorbed on the most attractive sites, or on positions on the surface where their potential energy will be a minimum.[39,42] As adsorption proceeds, the less active sites become occupied. Therefore, adsorption occurs on sites of progressively decreasing activity. Smooth adsorption isotherms are usually obtained because of the presence of sufficiently large number of sites which may occur in patches of equal energy or randomly distributed sites of unequal energy.[39] Several models can be used for the description of the adsorption data with Langmuir[70] and Freundlich[71] isotherms as the ones most commonly used.

Langmuir Adsorption Isotherm

The basic assumptions underlying Langmuir's model, which is also called the ideal localized monolayer model, are: (1) the molecules are adsorbed on definite sites on the surface of the adsorbent; (2) each site can accommodate only one molecule (monolayer); (3) the area of each site is a fixed quantity determined solely by the geometry of the surface; and (4) the adsorption energy is the same at all sites. In addition, the adsorbed molecules cannot migrate across the surface or interact with neighboring molecules. The Langmuir equation was originally derived from kinetic considerations.[65] Later, it was derived on the basis of statistical mechanics, thermodynamics, the law of mass action, theory of absolute reaction rates, and the Maxwell-Boltzmann distribution law.[39] The Langmuir adsorption isotherm is expressed as:

$$X = \frac{X_m b C_e}{1 + b C_e} \qquad (17)$$

where X = x/m, the amount of solute adsorbed x per unit weight of adsorbent m
C_e = equilibrium concentration of the solute
X_m = amount of solute adsorbed per unit weight of adsorbent required for monolayer capacity
b = a constant related to the heat of adsorption Q [$b \ \alpha \ \exp(-\Delta H/RT)$][39]

Equation 17 indicates that X approaches X_m asymptotically as C_e approaches infinity. For linearization of the data, Equation 17 can be written in the form:

$$\frac{C_e}{X} = \frac{1}{bX_m} + \frac{C_e}{X_m} \qquad (18)$$

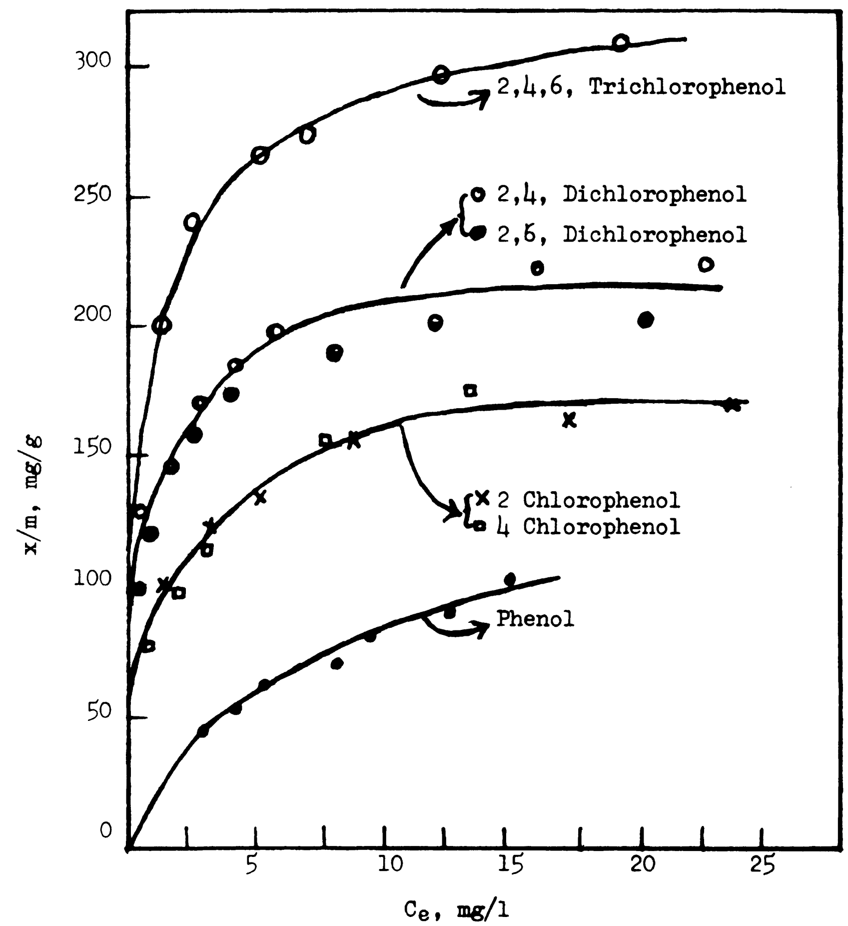


Figure 4.8. Adsorption isotherms of phenolic compounds on activated carbon.[57]

When C_e/X is plotted vs. C_e, a straight line, should result, having a slope $1/X_m$ and an intercept $1/bX_m$. Another linear form can be obtained by dividing Equation 18 by C_e:

$$\frac{1}{X} = \frac{1}{X_m} + \left(\frac{1}{C_e}\right)\left(\frac{1}{BX_m}\right) \tag{19}$$

Plotting $1/X$ against $1/C_e$, a straight line is obtained having a slope $1/bX_m$ and an intercept $1/X_m$. Figure 4.9 shows a typical Langmuirian plot using Equation 19 for adsorption of COD (surrogate parameter for organic contaminants in water) on activated carbon.[72] These reciprocal plots are used to evaluate the band X_m constants in the Langmuir equation. An example calculation is (modified from Reference 72):

Example Calculation 4.1: An adsorption study is set up in the laboratory by adding a known amount of activated carbon to six flasks which contain 200 m of an industrial waste. An additional flask containing 200 m of waste but no carbon is run as a blank. Plot the data according to the Langmuir equation, and determine the values of the constants b and X_m.

Flask No.	Wt. of Carbon, m (mg)	Volume in Flask (mL)	Final COD, C (mg/L)	Wt. of Adsorbate Adsorbed (mg)	x/m (mg/mg)
1	804	200	4.70	49.06	0.061
2	668	200	7.0	48.6	0.073
3	512	200	9.31	48.1	0.094
4	393	200	16.6	46.7	0.118
5	313	200	32.5	43.5	0.139
6	238	200	62.8	37.4	0.157
7	0	200	250	0	0

Solution:

1. Calculate the values of x and x/m from the data:
   For Flask #1:

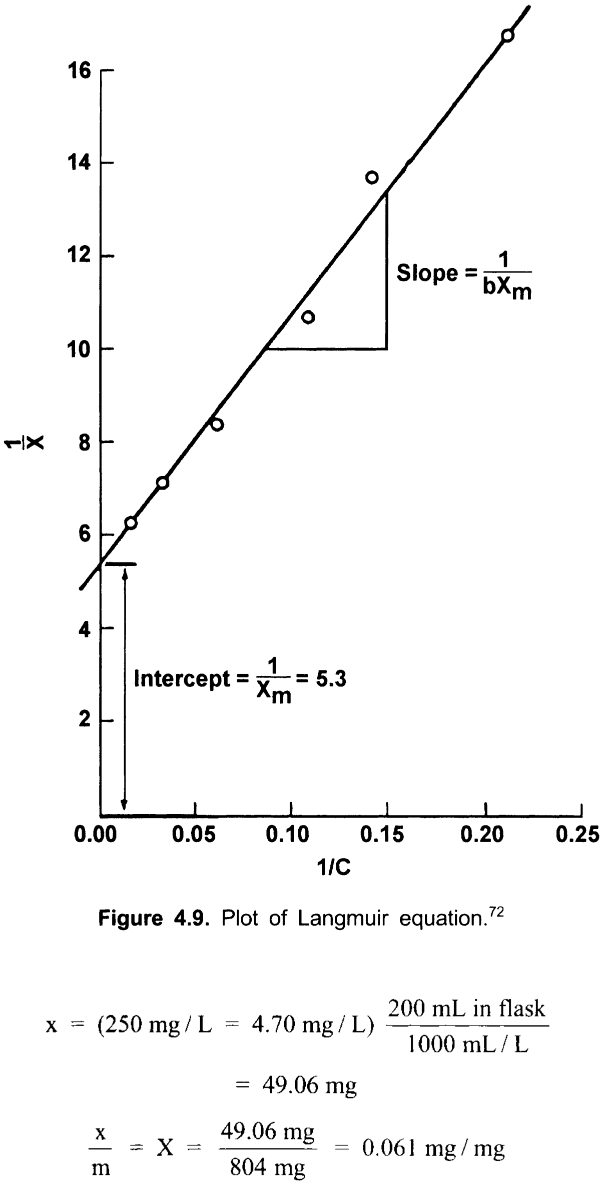


Figure 4.9. Plot of Langmuir equation.[72]

$$x = (250\ \text{mg}/\text{L} = 4.70\ \text{mg}/\text{L})\ \frac{200\ \text{mL in flask}}{1000\ \text{mL}/\text{L}}$$

$$= 49.06\ \text{mg}$$

$$\frac{x}{m} = X = \frac{49.06\ \text{mg}}{804\ \text{mg}} = 0.061\ \text{mg}/\text{mg}$$

2. Plot values of $1/C_e$ vs. $1/X$ as shown in Figure 4.9.
3. Determine the values of the constants b and X_m
   (a) Read value of intercept = $1/X_m$ = 5.3:

$$X_m = \frac{1}{5.3} = 0.189\ \text{mg}/\text{mg}$$

   (b) Calculate slope:

$$\frac{13.42 - 10.0}{0.15 - 0.085} = \frac{3.42}{0.065} = 52.615$$

   (c) Since slope = $1/bX_m$ and X_m = 0.189,

$$b = \frac{1}{52.615\ (0.189)} = 0.101\ \text{L}/\text{mg}$$

4. The Langmuir equation is

$$\frac{1}{X} = \frac{1}{0.189} - \frac{1}{(0.101)\ (0.189)\ C_o}$$

$$= 5.3 - \frac{52.615}{C_o}$$

The monolayer capacity X_m determined from the Langmuir isotherm defines the total capacity of the adsorbent for a specific adsorbate. Also, it may be used to determine the specific surface area of the adsorbent by utilizing a solute of known molecular area. Reliable X_m values can be obtained only for systems exhibiting type I isotherms of Brunauer's classification shown in Figure 4.10.[6,39]

It must be indicated that conformity to the algebraic form of Langmuir's equation does not constitute conformity to the ideal localized monolayer model, even if reasonable values of b and X_m are obtained. Therefore, a constant value of b [b α exp($-\Delta H/RT$)] may be due to cancellation of variations in ΔH. In turn, constancy of ΔH may be due to internal compensation of opposing effects, such as attractive lateral interactions and surface nonuniformity.[39] In addition, the assumption that the area of the sites and, in turn X_m, is determined solely by the nature of the solid and is independent of the nature of the solute is contrary to what is encountered in adsorption systems. However, orientation of solute molecules on the surface of activated carbon has been shown to affect the monolayer capacity X_m as determined from the area occupied by the molecules.[6,35,45] Therefore, nonconformity with the physical model should not detract from the usefulness of the Langmuir isotherm for analytical description of adsorption systems that do not proceed beyond monomolecular layers and conform to type I isotherms.[6]

Freundlich Adsorption Isotherm

The Freundlich adsorption equation is perhaps the most widely used mathematical description of adsorption in aqueous systems. The Freundlich equation is expressed as:[71]

$$\frac{x}{m} = KC_e^{1/n} \qquad (20)$$

where x = the amount of solute adsorbed
m = the weight of adsorbent
C_e = the solute equlibrium concentration
K,1/n = constants characteristic of the system

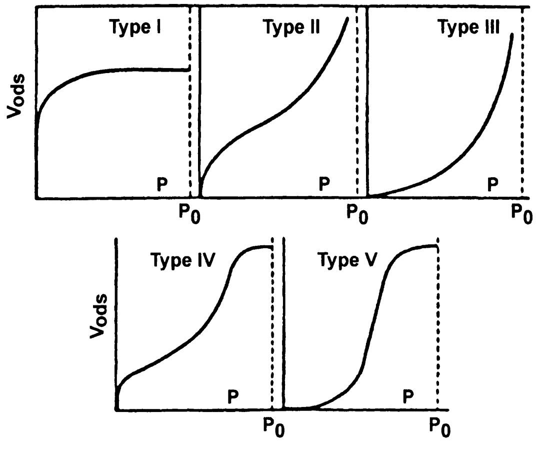


Figure 4.10. The five typical shapes of isotherms for physical adsorption. Reproduced from Young and Crowell,[39] courtesy of Butterworths, Ltd.

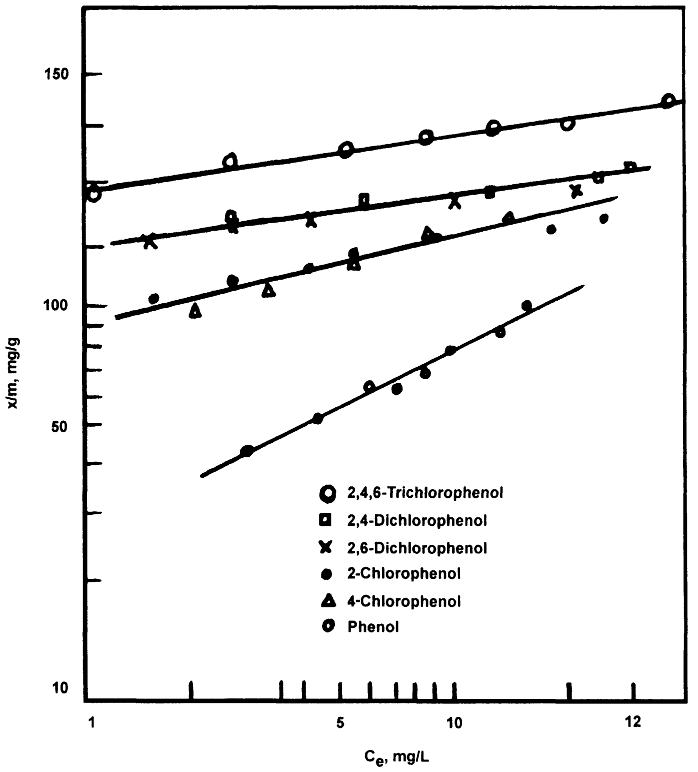


Figure 4.11. Logarithmic form of Freundlich adsorption isotherms for phenolic compounds on activated carbon.[57]

The Freundlich equation is an empirical expression that encompasses the heterogeneity of the surface and the exponential distribution of sites and their energies.[39,73] For linearization of the data, the Freundlich equation is written in logarithmic form:

$$\log\frac{x}{m} = \log K + \frac{1}{n}\log C_e \qquad (21)$$

Plotting log x/m vs. log C_e, a straight line is obtained with a slope of l/n, and log K is the intercept of log x/m at

$\log C_e=0(C_e=1)$. The linear form of the isotherm can be obtained conveniently by plotting the data on log-log paper (Figure 4.11). The value of l/n obtained for adsorption of most organic compounds by activated carbon is <1. Steep slopes, i.e., l/n close to l, indicate high adsorptive capacity at high equilibrium concentrations, which rapidly diminishes at lower equilibrium concentrations covered by the isotherm. Relatively flat slopes, i.e., l/n << 1, indicate that adsorptive capacity is only slightly reduced at the lower equilibrium concentrations. As the Freundlich equation indicates, the adsorptive capacity or loading factor on the carbon, x/m, is a function of the equilibrium concentration of the solute. Therefore, higher capacities are obtained at higher equilibrium concentrations.

Example Calculation 4.2: The following laboratory data were collected in a batch adsorption study of Sevin on PAC. Plot the data according to the Freundlich Equation 21 and determine the values of l/n and K.

Carbon added, m (mg/L)	Initial Conc., C_o (mg/L)	Equilibrium Conc., C_e (mg/L)	Amount Adsorbed, x (mg)	x/m (mg/mg)
2	3.2	2.8	0.4	0.200
5	3.2	2.3	0.9	0.180
10	3.2	1.7	1.5	0.150
15	3.2	1.2	2.0	0.133
20	3.2	0.8	2.4	0.120
30	3.2	0.4	2.8	0.093
40	3.2	0.2	3.0	0.075

1. Plot the values of x/m vs. C_e on log-log graph paper (Figure 4.12).
2. Determine the value of K from the interception of the line on the log-log plot where the abscissa (C_e) is equal to 1.0 (mg/L). In this example:

$$K = 0.130\ (\mathrm{mg/mg})/(\mathrm{mg/L})^{1/n}$$

3. Determine the value of l/n from the slope of line on the log-log plot.

$$\text{Slope} = \frac{1}{n} = \frac{Y_2 - Y_1}{X_2 - X_a}$$

$$= \frac{\log 0.20 - \log 0.75}{\log 2.8 - \log 0.2} = \frac{-0.698-(1.125)}{0.447-(-0.698)}$$

$$\frac{1}{n} = 0.373\ ,\ n = 2.68$$

4. The Freundlich equation becomes:

$$\frac{x}{m} = 0.130\, C_e^{\ 0.373}$$

The Freundlich equation can be used for calculating the amount of activated carbon required to reduce any initial concentration to a predetermined final concentration. By substituting x in Equation 21 for C_o–C_e, where C_o is the initial concentration:

$$\log\left(\frac{C_o - C_e}{m}\right) = \log K + \frac{1}{n}\log C_e \qquad (22)$$

Equation 22 is useful for comparing different activated carbons in removal of different compounds or removal by the same carbon.

Example Calculation 4.3: Determine the carbon dosage, mg/L to a residual concentration of 0.1 mg/L from Equation 22:

$$\log\left(\frac{1.0 - 0.1}{m}\right) = \log 0.130 + 0.373 \log 0.1$$

$$\log m = \log 0.9 - \log 0.130 - 0.373 \log 0.1$$

$$m = 20\ \mathrm{mg/L}$$

Therefore, 20 mg/L PAC would be required to remove 0.9 mg/L of Sevin from this water supply.

Most of the adsorption studies reported in the literature have been conducted in distilled water systems. However, inorganic salts have been shown to affect the adsorptive capacity of activated carbon for certain solutes. Snoeyink at al.[58] and Zogorski[43] reported on the enhancement of adsorptive capacity of activated carbon for some phenolic compounds at high pH values (anionic species) in the presence of inorganic salts. This effect was suggested to be due possibly to a reduction of the repulsive forces between adsorbed molecules and the carbon surface or between anions adsorbed on the surface. Although the concentrations of the inorganic salts used in these studies were too high to be encountered in drinking water supplies, the implication of the potential effects of inorganic ions on the carbon's adsorptive capacity should not be overlooked. Indeed, Weber et al.[74] showed that the presence of low concentrations of calcium and magnesium salts enhances the adsorption of humic acids on activated carbon, possibly due to the formation of an ion-humate-carbon complex. Adsorption isotherms of humic acid in tap water systems showed higher carbon adsorptive capacities than those in distilled water systems. Therefore, adsorption studies for application of

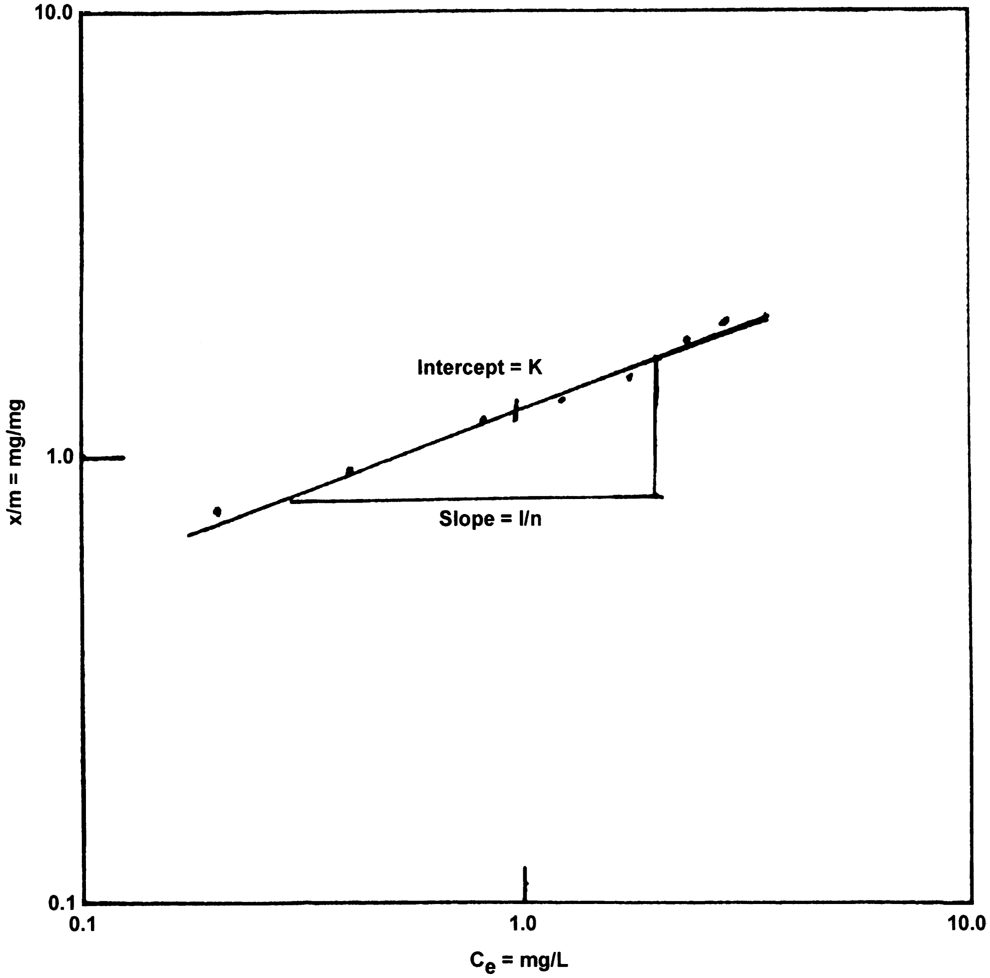


Figure 4.12. Evaluation of Freundlich constants.

activated carbon in water treatment plants should be conducted using the natural water or a synthetic medium of equivalent composition. In addition, the isotherms should be conducted within the concentration range corresponding to the levels likely to be encountered for the compound of interest, since extrapolation of the isothermal data can lead to erroneous results.

ADSORPTION KINETICS

Evaluating the performance of unit processes utilizing adsorption requires an understanding of the kinetics of uptake or the time dependence of the concentration distribution of the organic solute in both bulk solution and solid adsorbent and identification of the rate-determining step. Adsorption of organics from aqueous solution by a porous adsorbent such as activated carbon can be described by three consecutive steps.[27,75,76]

The first step is the transport of the adsorbate from bulk solution to the outer surface of the adsorbent granules by molecular diffusion. This is called external or film diffusion. There is no actual film surrounding the granule, but the term is used generally to describe the resistance to mass transfer at the surface of the particle. The mass transfer coefficient K_f in film theory is related to the free liquid diffusivity of the solute, D_e, and the thickness of the diffusional sublayer δ as follows:

$$K_f = D_e / \delta \tag{23}$$

The concentration gradient in the liquid film around the granule is the driving force in film diffusion.

The second step, termed internal diffusion, involves the transport of the adsorbate from the particle surface into interior sites by diffusion within the pore-filled liquid and migration along the solid surface of the pore (surface diffusion).[27,76–79] Because these two transport processes act in parallel, the more rapid one will control the overall rate of transport. Keinath and Weber[78] found that, for a typical water or wastewater sorption system, the rate parameter for surface diffusion was two to four orders of magnitude greater than the liquid-phase pore diffusion.

The third step is adsorption of the solute on the active sites on the interior surfaces of the pores. Since the adsorption step is very rapid, it does not influence the overall kinetics.[27,74] The overall rate of the adsorption process, therefore, will be controlled by the slowest step, which would be either film diffusion or internal diffusion. However, control might also be distributed between intraparticle and external mechanisms in some systems.[27,76,79,80]

The nature of the rate-limiting step in batch systems can be determined, in a general way, from the properties of the solute and the adsorbent. Rates of adsorption are usually measured by determining the change in concentration of the solute in contact with the carbon as a function of time. Linearization of the data is obtained by plotting the amount adsorbed per unit weight of adsorbent, x/m, vs. $t^{0.5}$ for the initial fraction of the reaction.[43,45]

The adsorption rates, determined from the slope of the line with units of $mg/g/hr^{0.5}$ or $mmol/g/hr^{0.5}$ or equivalent, are not true reaction rates, but relative rates useful for comparative purposes. For processes controlled by film diffusion, the adsorption rate is expected to be proportional to the first power of concentration. Zogorski[43,60] showed that the adsorption of 2,4-dichlorophenol by activated carbon is film diffusion–controlled at concentrations less than 400 µmol/L, and that a direct linear relationship existed between the initial concentration and the adsorption rate. At concentrations of 2,4-dichlorophenol greater than 500 µmol/L, the reaction rate was shown to be intraparticle diffusion–controlled.

Variation of the rate with concentration was not linear, which is expected from the diffusion theory.[27] Therefore, the concentration dependence of the adsorption rate can be used to identify the rate-limiting step. It is also recognized that the adsorption rate is film diffusion–controlled during initial stages of the adsorption process in batch reactors and initial breakthrough in fixed-bed reactors. As the carbon becomes loaded with the adsorbate, the reaction rate becomes controlled by intraparticle diffusion.[79,81]

For processes controlled by intraparticle diffusion, the size and configuration of the adsorbate molecule should affect the overall rate of adsorption. The larger the molecule or the more branched, the lower should be the rate at which it diffuses. Hence, the adsorption rate should be lower. Morris and Weber[45] reported that a linear relationship existed between observed adsorption rates and molecular weight for a series of alkylbenzenesulfonates ranging from 2-hexylbenzenesulfonate to 2-tetradecylbenzenesulfonate. An increase in the chain length by a $-CH_2-$ group resulted in reduction of the adsorption rate. An increase in the chain length apparently reduces mobility of the molecule and also increases its affinity to the carbon surfaces in accord with Traube's rule. Both effects result in a decrease of the surface diffusion inside the pores and, hence, an overall decrease in the observed adsorption rate. Adsorbates that exhibit high affinity to activated carbon usually result in intraparticle diffusion control of the adsorptive process.[79] This is attributed to a decrease of surface diffusion of adsorbates that is tightly held, and thus, is less flexible to migrate on the internal surfaces of the carbon. Branching of the adsorbate molecule also results in a decrease of the observed adsorption rate due to a decrease in surface diffusion rate. Morris and Weber[45] showed that 6-dodecylbenzenesulfonate, which contains a bifurcated chain, and the extensively branched technical benzenesulfonate exhibited lower adsorption rates than the less branched 2-dodecylbenzenesulfonate.

Characterization of the rate-limiting step in adsorption by activated carbon can be obtained by determining variation of the rate with particle size of the adsorbent. For a film diffusion–controlled process, the rate of adsorption is expected to vary as the reciprocal of the diameter of the particles for a given total weight of adsorbent. This is because the rate, in this case, is a first-order function of exterior surface area which, in turn, is inversely proportional to particle diameter. Zogorski[43,60] showed that the adsorption rate of 2,4-dichlorophenol, at concentrations less than 400 µmol/L, exhibited a linear relationship with the reciprocal of the activated carbon particle's diameter in the range of 0.16 to 1.41 mm. This supports the conclusion that the adsorption rate was film diffusion–controlled. On the other hand, for internal diffusion–controlled processes, the rate of adsorption is expected to vary as the reciprocal of some higher power of the particle's diameter. This relationship was demonstrated for the adsorption rates of benzenesulfonates on activated carbon, which were internal diffusion–controlled. The adsorption rates were shown to vary as a function of the inverse of the diameter squared.[43,45]

The nature of the rate-controlling step can also be obtained by determining the activation energy of the process. This can be achieved by studying the effect of temperature on the rates of adsorption, which are expected to increase with an increase in temperature. This relationship was shown for adsorption of 2,4-dichlorophenol[43] and alkylbenzenesulfonates.[45] The activation energy can be computed from:

$$\ln\frac{k_1}{k_2} = \frac{E_a(T_1 - T_2)}{RT_1T_2} \qquad (24)$$

where k_1, k_2 = observed adsorption rates at temperatures T_1 and T_2 in °K

R = ideal gas law constant (1.987 cal/mol/°C)

The activation energy for internal diffusion-controlled processes is expected to be in the range of 3-5 kcal/mol. The activation energy for adsorption of 3-dodecylbenzenesulfonate was reported to be 4.3 kcal/mol, which indicates a diffusion-controlled process.[45]

Application of adsorption kinetics has been in the predictive modeling and design of fixed-bed GAC absorbers. Several mathematical models have been developed that deal with the relative contribution of film diffusion and intraparticle diffusion and methods for calculating the film diffusion coefficient and the intraparticle diffusion coefficient.[27,76,79,81] The reader is directed to Reference 82 for a comprehensive discussion of the various kinetic and mass transfer models that have been developed for adsorption on GAC.

MULTISOLUTE ADSORPTION

The occurrence of a wide variety of organic substances in natural waters results in simultaneous adsorption of different species by activated carbon used for treatment. Since adsorption from solution is usually restricted to a monolayer, multisolute adsorption involves competition between different compounds for the available sites on the carbon surface. Mutual reduction in the adsorptive capacity of each of the competing species is usually encountered in aqueous systems. The extent of such reduction depends on the affinity of each solute for the carbon surface, relative concentrations, molecular sizes, and possible mutual interactions during adsorption. Competitive adsorption is illustrated in Figure 4.13, which shows carbon adsorption equilibria of the bisolute system phenol/*p*-nitrophenol.[80] The upper family of curves shows adsorption isotherms for *p*-nitrophenol in the presence of different initial concentrations of phenol, whereas the lower graph shows the adsorption of phenol in the presence of *p*-nitrophenol.

Mutual inhibition of the adsorptive capacity of the two solutes is apparent, but the extent of the interference is different. There is only a slight reduction in the adsorptive capacity of *p*-nitrophenol in the presence of phenol, whereas the uptake of phenol is very much reduced by the strongly adsorbed *p*-nitrophenol. Several similar studies have been reported on the kinetics and equilibria of adsorption of simple bisolute mixtures on activated carbon in batch systems that indicate that competitive adsorption generally results in mutual inhibition of the adsorptive capacity of each solute.[27,43,56,61,83]

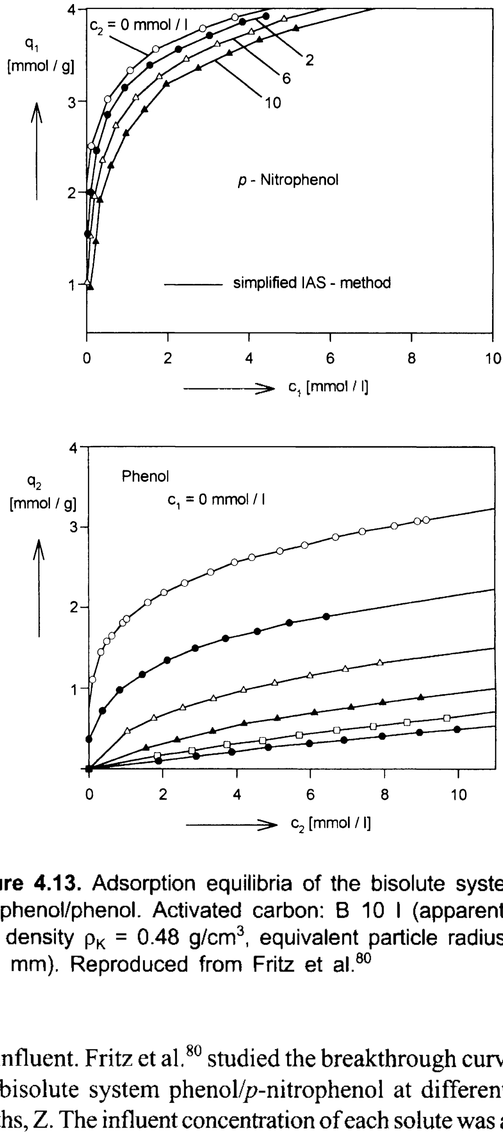


Figure 4.13. Adsorption equilibria of the bisolute system *p*-nitrophenol/phenol. Activated carbon: B 10 I (apparent particle density ρ_K = 0.48 g/cm^3, equivalent particle radius R = 0.62 mm). Reproduced from Fritz et al.[80]

In fixed-bed adsorbers, which are used in water treatment, competitive adsorption results in displacement of weakly adsorbed species by more strongly adsorbed ones, resulting in the "chromatographic effect." This means that under certain conditions, the effluent of the carbon bed contains concentrations of certain compounds higher than in the influent. Fritz et al.[80] studied the breakthrough curves of the bisolute system phenol/*p*-nitrophenol at different bed depths, Z. The influent concentration of each solute was about 5.0 μM/L. An early breakthrough of phenol always occured at any bed depth, and its concentration in the effluent increased sharply up to 70%, at a bed depth of 20 cm, above the influent concentration. After the initial phenol breakthrough, the effluent did not contain any *p*-nitrophenol for some time, until it started to appear in the effluent. The increase of *p*-nitrophenol concentration in the effluent was generally gradual, i.e., the breakthrough curve was not as steep as the one for phenol. The increase of phenol concentration in the effluent can be explained by the fact that as the influent is introduced into the column, the more strongly adsorbed *p*-nitrophenol is adsorbed on the top carbon layers. The weakly adsorbed phenol is subsequently adsorbed at lower bed depths, essentially as a single solute without competition. As the influent continues to flow into the column, additional *p*-nitrophenol is introduced, which displaces the previously adsorbed phenol into lower bed depths and eventually into the effluent at a higher concentration. This behavior is well recognized in chemical separations by chromatographic techniques. The relative concentrations of each solute in the binary mixture determine the positions of the breakthrough curves.[79,80] A higher relative concentration of the strongly adsorbed species results in earlier breakthrough of the weakly adsorbed one.

Several mathematical models have been developed for predicting the adsorptive behavior of mixed solutes from knowledge of the adsorptive properties of the individual components. The Langmuir competitive model developed by Butler and Ockrent[84] has been used by several investigators for predicting equilibrium concentrations of a mixture in batch systems. This model allows calculation of X_i, which is the amount of species i adsorbed per unit weight of adsorbent at an equilibrium concentration C_e in the presence of a j-solute mixture.

$$X_i = \frac{X_{m,i} b_i C_i}{1 + \sum_{j=1}^{n} (b_j C_j)} \tag{25}$$

The constants X_m and b are obtained from single-solute systems. Equation 25 or modifications of it have been applied by several investigators[27,56,61,83] for predicting equilibrium concentrations in bisolute systems where the Langmuir isotherm is obtained for pure components.[39,56] This model, however, has not been tested for a mixture of several solutes.

A Freundlich-type multicomponent isotherm equation has been developed to describe adsorption data of various bicomponent systems.[85,86] The isothermal equation for component i in a k-component system is:

$$\left(\frac{x}{m}\right)_i = K_i C_i \left(\sum_{j=1}^{k} a_{ij} C_j\right)^{(n_i - 1)} \tag{26}$$

This equation applies to systems in which each component obeys the Freundlich isotherm:

$$\left(\frac{x}{m}\right)_i = K_i C_i^{n_i} \tag{27}$$

K_i and n_i are determined from the monocomponent systems.

The competitive coefficient, a_{ij}, describes inhibition to adsorption of component i by component j. It can be determined from thermodynamic data or experimentally from bicomponent systems. "The proposed isotherm is clearly superior to the commonly employed competitive Langmuir isotherm when the components follow the Freundlich isotherm since fewer parameters are required for the Freundlich isotherm than for the multisection Langmuir isotherm."[85] This statement is interpreted to mean the Freundlich equation was fitted to their adsorption data better than the Langmuir equation. So it is with carbon adsorption.

The proposed isotherm was employed to describe the adsorption data of phenol, PBP, and BS on GAC (F-400, mesh unknown) from the respective bicomponent and tricomponent aqueous solutions (1 week for equilibrium).[85] The bicomponent equation can be written:

$$\frac{C_1}{C_2} = \frac{1}{C_2}\beta_1 - a_{12}\,;\quad \frac{C_2}{C_1} = \frac{1}{C_1}\beta_2 - a_{21} \tag{28}$$

with

$$\beta_i = \left(\frac{K_i C_i}{(x/m)_i}\right)^{1/(1-n_i)} \tag{29}$$

where the C terms are equilibrium concentrations and ß and a are competition coefficients that are determined experimentally.

Isotherm constants for these three compounds (mg/L contents) are:

i	**Solute**	K_i	n_i	e_{i1}	a_{i2}	a_{i3}
1	Phenol	0.037	0.371	1.0	9.7	0.26
2	PBP	0.130	0.225	0.1	1.0	0.025
3	BS	0.013	0.352	3.85	42	1.0

The extent of reduction due to adsorptive competition for each component in a multicomponent system is exhibited by a plot of curves of C_{eq} values versus carbon load, m, for respective monocomponent systems, along with the multicomponent systems.[88] Figure 4.14 shows such plots. For this situation, BS and phenol were inhibited in the multicomponent system, whereas the strongly adsorbed PBP was almost unaffected by the presence of the other two constituents.

Another important operational aspect of carbon adsorption is the influence of natural organic matter (NOM) on the removal of specific compounds. Especially significant is the presence of humic and fulvic acids (see Chapter 2), which provide competition for adsorption sites on PAC and GAC for smaller sized and lower-molecular-weight compounds. Several model studies have been conducted to demonstrate this competitive effect. For example, two naturally occurring odorous compounds, MIB and geosmin, were investigated for their adsorption on GAC (F-200 and F-400, 40 × 50 mesh) in equilibrium studies (4 to 5 days) with and without humic acid.[87] Figure 4.15a is a log-log plot of the data for MIB in the absence and presence of humic acid. The latter was included to interfere with adsorption of MIB and

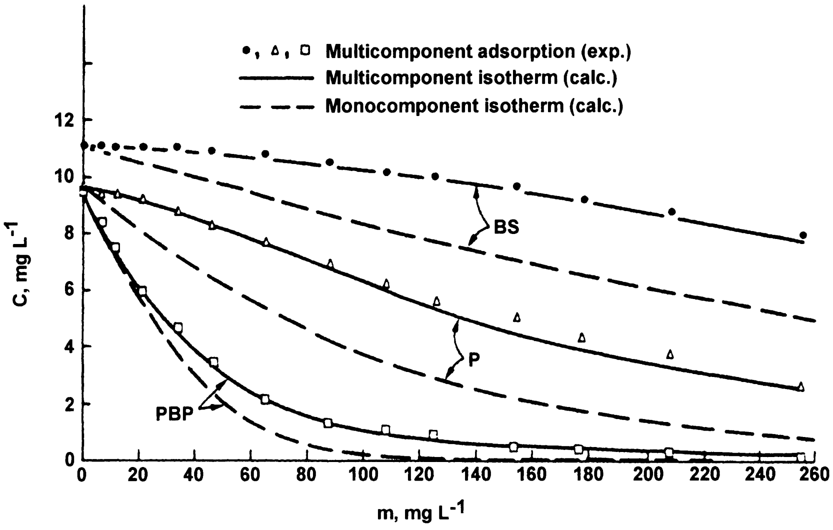


Figure 4.14. Description of adsorption in a three-component system by the proposed isotherm employing the bicomponent competition coefficients: correlation between experimental (exp.) and calculated values (calc.). Reproduced from Sheindorf et al.,[85] courtesy of Pergamon Press.

geosmin. At 1 μg/L MIB, 0.9 mg/g was adsorbed on the GAC from distilled water solutions. The presence of humic acid did inhibit adsorption of MIB. That geosmin was adsorbed to a greater extent is seen in Figure 4.15b, where 4 mg/g was the surface coverage when $C_e = 1$ μg/L. Again, humic acid interfered with adsorption of geosmin.

Column breakthrough curves were constructed for MIB and geosmin in the presence and absence of humic acid.[87] These are seen in Figure 4.15c, about which the authors state: "An obvious characteristic of these curves is the manner in which they level off rather than converge to $C_e/C_i = 1$. This suggests that a portion of the capacity is being utilized very slowly and that a long operational time would be required for complete saturation." This may be true, but it does not guarantee that the earthy, musty odor would be eliminated from the water within the same time frame. Other examples of the interference of NOM on the carbon adsorption of several organic contaminants are given in Reference 82.

POWDERED ACTIVATED CARBON

The use of powdered activated carbon in most modern water treatment plants processing surface water is a routine practice. The first application in American waterworks dates back to 1929 for taste and odor control;[88] its use in water treatment subsequently became widespread. Almost 90% of water treatment plants worldwide that use activated carbon use it in the powdered form.[89] The particle size distribution is such that at least 80% of the carbon should pass No. 325 mesh, or measure less than 44 μm. Manufacturers' specifications of some commercially available PACs are given in Table 4.3.[90]

Several design and operational parameters affect the performance of PAC for potable water treatment. Important criteria for selecting the point with addition of PAC include: (a) the provision of good mixing or good contact between the PAC and all the water under treatment, (b) sufficient contact time for adsorption of the contaminant(s), (c) a minimum of interference by other treatment chemicals with the adsorption process, and (d) no degradation of the finished water quality.

Powdered carbon is usually applied to raw water in the form of a slurry at any treatment stage before filtration (in a batch-type system). The optimum point of application should allow adequate dispersion of the carbon and sufficient contact time to ensure maximum adsorption. The carbon slurry may be added to the mixing tank or a flocculation tank ahead of the settling tanks. This application point allows adequate contact time and the carbon can be removed easily with the settled sludge. However, the carbon particles may become embedded in the coagulant flocs, leading to a reduction of adsorption efficiency. In addition, many organic compounds are adsorbed that would be removed by coagulation alone, therefore requiring more activated carbon. The cost of increased carbon use is offset in many instances by savings in the coagulant dose due to improvement in the flocculation process as a result of a seeding effect of the carbon particles. Another point of application of powdered activated carbon would be to the filter's influent. A small dose of a polymer usually is added as well, to improve the filter's ability to retain carbon particles. Addition of carbon to the sand filter's influent should not normally exceed 4 mg/L; however, multimedia beds possess a high capacity for stor-

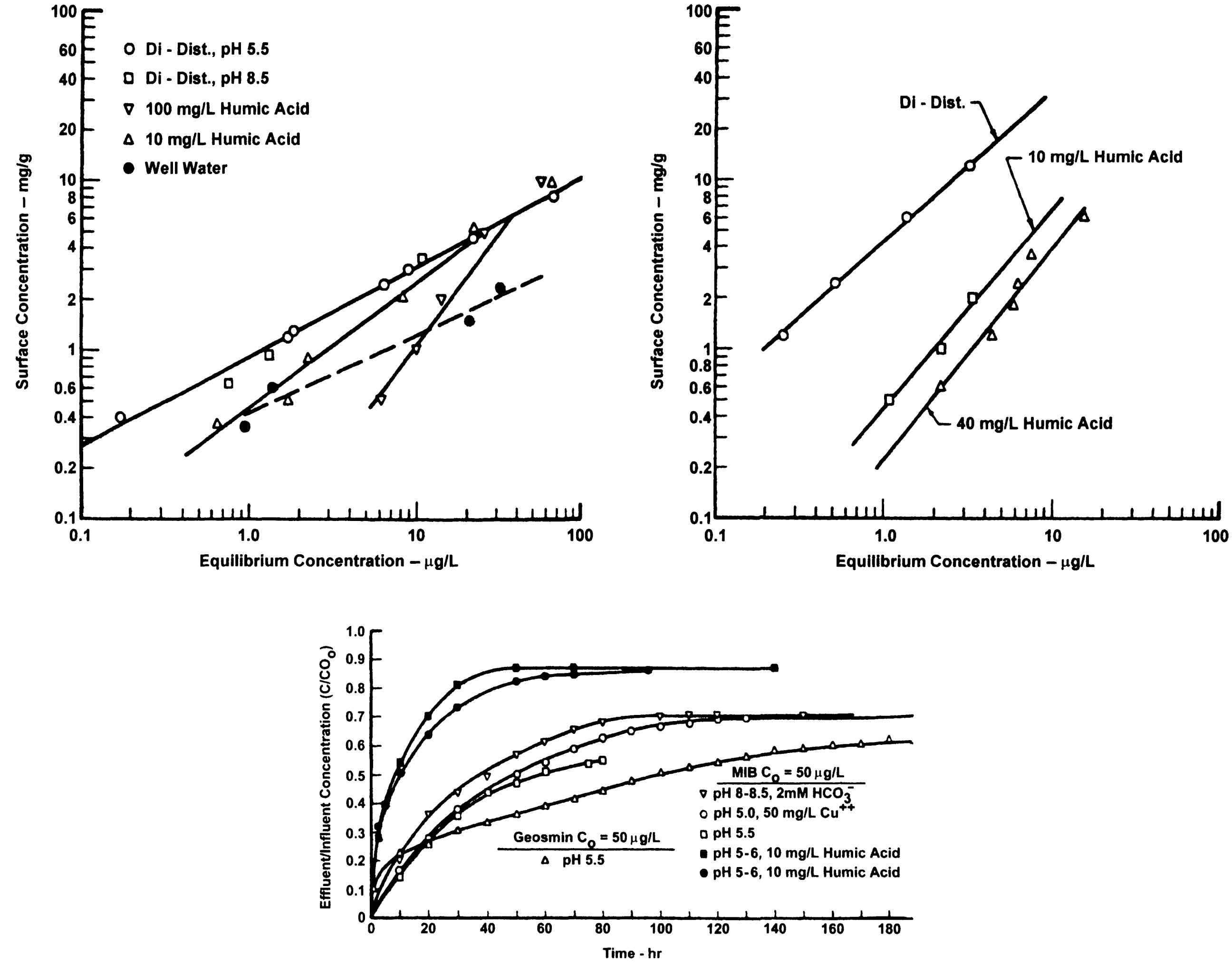


Figure 4.15. (a) Adsorption of MIB. (b) Adsorption of geosmin. (c) Column breakthrough curves for MIB and geosmin. Reproduced from Herzing et al.,[87] courtesy of the American Water Works Association.

Table 4.3. Manufacturers' Specifications of Some Commercially Available PACs.[90]

Parameter	PAC 1[a]	PAC 2[b]	PAC 3[c]	PAC 4[d]	PAC 5[e]	PAC 6[f]
Iodine number (mg/g)	800	1,199	600	900	1,000	550
Molasses decolorizing index	9			14	18	
Moisture as packed (%)	5	3	5	10	10	4
Apparent density (g/cm^3)	0.64	0.54	0.74	0.38	0.38	0.50
Ash content (%)		6		3–	3-5	
Passing 100 mesh (%)	99		99	95–100	95–100	99
Passing 200 mesh (%)	97		97	85–95	85–95	95
Passing 325 mesh (%)	90	98	90	65–85	65–85	90

[a] Aqua-Nuchar, Westvaco, Covington, West Virginia.
[b] WPH, Calgon Corp., Pittsburgh, Pennsylvania.
[c] Aqua, Westvaco, Covington, West Virginia.
[d] Nuchar S-A, Westvaco, Covington, West Virginia.
[e] Nuchar SA-20, Westvaco, Covington, West Virginia.
[f] Hydrodarco B, American Norit, Jacksonville, Florida.

age of solids. Therefore, carbon doses up to 10 mg/L can be tolerated for short durations.

Simultaneous addition of chlorine and activated carbon should be avoided because of carbon's dechlorination capability. In such cases where chlorine addition is required, the activated carbon should be applied at a point upstream or ahead of the chlorine. This allows the use of lower carbon doses, reduces the potential of formation of trihalomethanes and other chlorination products, and avoids the potential loss of the carbon's adsorptive capacity due to formation of oxidized surface groups. The effect of other treatment processes should be considered also in the application of powdered activated carbon. For example, the addition of softening chemicals produces high pH values that are not favorable for adsorption of most organic compounds, whereupon high carbon doses would be required. Advantages and disadvantages of different points of addition of PAC are summarized in Table 4.4.[90]

In situations where large quantities of activated carbon are required to reduce the concentration of organic compounds, adding the carbon in two steps (split dose) usually results in reducing the total amount of carbon. This can be readily determined from the Freundlich adsorption isotherm parameters and computation of the amount of carbon needed to reduce organic compounds to a desired level for a single dose and a split dose using Equation 22. The first dose can be applied ahead of the settling tank, and the second dose ahead of the filter.

The use of powdered activated carbon in water treatment is more adaptable to applications where relatively low contaminant levels require less carbon. Also, when applications are periodical or seasonal in nature, such as taste and odor problems in some surface water supplies, the capital investment in equipment is relatively small, and the carbon addition can be adjusted to changes in water quality. However, if continuous application of activated carbon is required, or if the contaminants have low adsorbability, the powdered form may be more costly and may generate sludge disposal problems. In addition, batch systems do not allow efficient utilization of the adsorptive capacity, since the carbon will be in contact with a continuously decreasing solute concentration.

Various alternative techniques are available for applying PAC to improve its adsorption of large, slowly diffusing compounds. Adding PAC to a solids contact clarifier has potential for improved adsorption efficiency because the carbon can be kept in contact with the water for a longer time than when it is added to the rapid mix of a conventional plant. For example, mean carbon residence times ranging from 9 hours to 8.5 days were reported when PAC was added to a solids contact slurry recirculating clarifier (SCSRC).[91] Also, it was found that very high concentrations of PAC (>4000 mg/L) would be accumulated in an SCSRC. However, isotherm tests showed that the adsorptive capacity of PAC-containing slurry for $CHCl_3$ appeared to decrease somewhat when the residence time of the PAC in the clarifier was longer than 100 hours.[92] Other investigators have had similar experiences with SCSRCs, PAC, and adsorption of various organics.[93,94]

Another innovation in the PAC treatment of water is the hollow-fiber ultrafiltration (UF) system. The UF is a low-pressure membrane process that is available in four basic configurations: tubular, hollow-fiber (HF), plate-type, and spiral-wound modules.[95] HF modules have the highest surface-area-to-volume ratio and are easy to backflush because of the self-supporting nature of the fibers. A pilot system was evaluated for the PAC-UF removal of 2,4,6-trichlorophenol and TOC from groundwater.[96] The PAC-UF system has promise for full-scale drinking water treatment. Considerably more research, however, must be conducted in laboratory and pilot-plant systems before full-scale application.

The reader is directed to References 90 and 97 for a critical review of the application of PAC in potable water treatment in the 1980s and 1990s.

GRANULAR ACTIVATED CARBON

GAC is used in water treatment in the form of fixed beds where the water is contacted with the carbon by gravity flow downward through the bed. The carbon beds may be placed in structures similar to conventional filters in a water treatment plant, or in the sand filters after replacing the medium with the carbon. In the latter case, carbon will function both as a filtering medium and adsorber. Pressure-type cylindrical filters are also widely used in the food processing and bottling industries. After the carbon is exhausted, it is either replaced with fresh carbon or removed and reactivated for further reuse. A considerable amount of research has been conducted in recent years on the use of GAC in water treatment in response to the Safe Drinking Water Act Amendments of 1986 (see Chapter 1). The use of GAC adsorption and filtration is recommended as the best available technology (BAT) for removing a broad spectrum of organic contaminants from drinking water supplies (see Table 1.7, Chapter 1). Commercially available particle sizes of GAC expressed in limiting U.S. Standard Sieve sizes include 8×16, 8×30, 10×30, 12×40, 14×40, and 20×40, with effective sizes ranging from 0.55 mm to 1.35 mm.[98]

The fixed-bed continuous flow operation results in maximum utilization of the carbon's adsorptive capacity. The carbon in the column acts like a series of layers, with each layer in contact with fresh solution of constant solute concentration. This results in maximum loading of the carbon (x/m) (from the solute's adsorption isotherm) at constant solute concentration in batch processes.

Table 4.4. Advantages and Disadvantages of Different Points of Addition of PAC.[90]

Point of Addition	Advantages	Disadvantages
Intake	Long contact time, good mixing	Some substances may be adsorbed that would otherwise probably be removed by coagulation, thus increasing carbon usage rate (this still needs to be demonstrated).
Rapid mix	Good mixing during rapid mix and flocculation, reasonable contact time	Possible reduction in rate of adsorption because of interference by coagulants; contact time may be too short for equilibrium to be reached for some contaminants; some competition may occur from molecules that would otherwise be removed by coagulation.
Filter inlet	Efficient use of PAC	Possible loss of PAC to the clearwell and distribution system.
Slurry contactor preceding the rapid mix	Excellent mixing for the design contact time, no interference by coagulants, additional contact time possible during flocculation and sedimentation.	A new basin and mixer may have to be installed; some competition may occur from molecules that may otherwise be removed by coagulation.

Figure 4.16 illustrates the concentration of adsorbed species on the surface of the adsorbent (x/m) with bed depth.[99] Under operational conditions, adsorbed material accumulates at the top of the bed until the amount adsorbed is in equilibrium with the influent contaminant concentration. At this time, the adsorbent is loaded to capacity and that portion of the bed is exhausted. Below this zone is a second zone where dynamic adsorption is occurring, i.e., the contaminant is being transferred from the liquid solute to the adsorbed phase. This zone is called the "mass transfer zone," and its depth is controlled by many factors, depending on the contaminant being adsorbed, characteristics of the adsorbent, hydraulic factors, and others. The depth of the mass transfer zone is a measure of physical/chemical resistance to mass transfer. Once formed, the mass transfer zone moves down through the adsorbent bed until it reaches the bottom, whereupon the effluent concentration of the contaminant in the aqueous phase begins to rise (Figure 4.17). Figure 4.17a shows the concentration gradient of adsorbed material (x/m) in an adsorber as the mass transfer zone moves down the column with time. As the mass transfer zone reaches the bottom of the column, "breakthrough" of the contaminant occurs, as shown by a detectable increase in effluent concentration (Figure 4.17b). When the adsorber is operated to exhaustion (at equilibrium, $C_{in} = C_{out}$), the breakthrough profile (plot of effluent concentration with time) takes on the classical "S" shape—a shape controlled by the shape and length of the mass transfer zone. Steeper slopes for the breakthrough curves generally are obtained for systems that exhibit high film transfer coefficients, high internal diffusion coefficients, or flat Freundlich adsorption isotherms, i.e., smaller 1/n values.[77] The areas A and B in Figure 4.17b show deviation of the behavior of the adsorbers from ideal plug flow projection, i.e., leakage of the solute appears long before exhaustion of the carbon bed. When an adsorber is removing all of a contaminant, the mass transfer zone in Figure 4.16 may also be called the "critical depth" because this is the minimum design depth for an adsorber that will allow it to remove all of a contaminant.

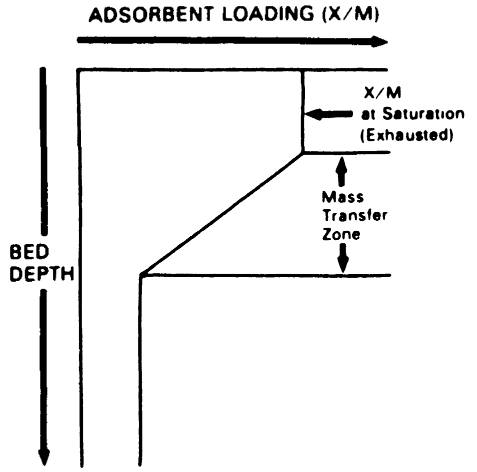


Figure 4.16. Mass transfer zone in a GAC adsorber.[99]

The time or volume of water treated to the breakthrough point generally is decreased by: (1) increased particle size, (2) increased solute concentration in the influent, (3) increased pH value of the water in the case of adsorption of weak electrolytes, (4) increased flow rate—usually expressed as gal/min/ft^2, and (5) decreased bed depth.[27,43,45,59] The typical smooth S-shaped breakthrough curve described above is obtained for single-solute systems where the influ-

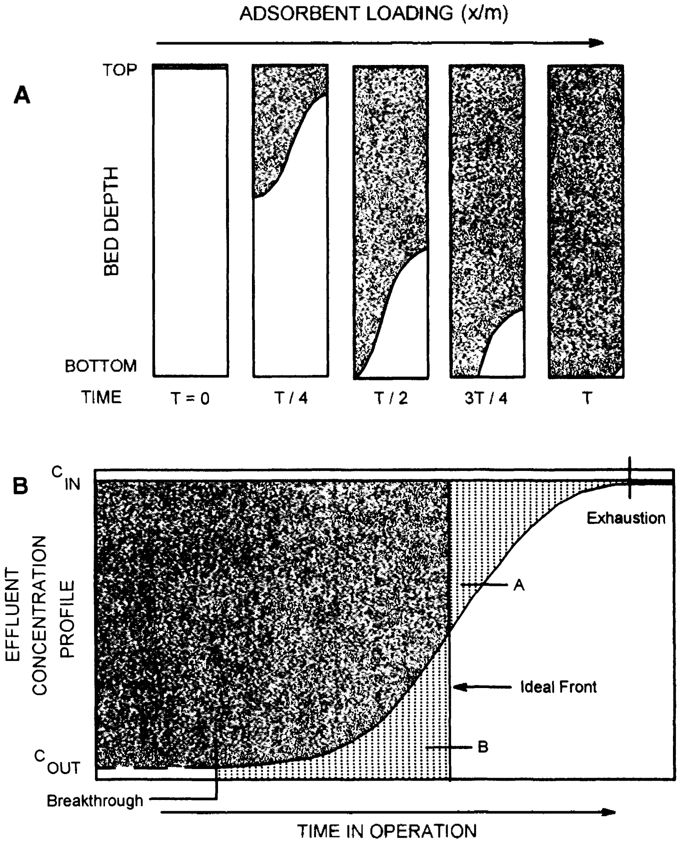


Figure 4.17. Typical adsorption column performance.[99]

ent concentration to the carbon column is assumed to be constant. However, in natural water systems, there is a broad spectrum of organic contaminants, and a wide variation in the concentration of any single compound is not unusual. Competitive adsorption, displacement of weakly adsorbed compounds by strongly adsorbed ones (chromatographic effect), and concentration variations complicate the prediction of the shape and position of the breakthrough curves. Therefore, pilot-plant tests must be conducted at the treatment plant site employing the carbon to be used and the water to be treated in order to select the appropriate design parameters for the carbon beds.

Several factors are involved in the design of GAC adsorption columns: type of GAC, surface loading rate (gal/min/ft^2), empty bed contact time (EBCT in min), contaminant type and concentration, contaminant competition, and carbon depth and usage.[100] The reader is directed to Reference 82 concerning details for each of these factors. However, contact between the influent and GAC is the primary factor in determining the size and capital cost of a GAC treatment system. The EBCT is the time required for water to pass through the empty column (absent of GAC). Typical effective EBCTs are approximately 10–15 minutes for removal of most organic compounds. This is, of course, an oversimplification of the GAC column operation. Kinetics of adsorption of individual compounds may or may not be appropriate for these EBCTs. Molecular size of the adsorbate is a key factor, with many compounds too large to diffuse into the pore structure; e.g., humic and fulvic acids. In any event, GAC is a recommended BAT for many of the organic priority pollutants. Designers and operators should be aware of the limitations of GAC operation.

A proposal by the U.S. Environmental Protection Agency (EPA) for use of GAC for control of organics in drinking water describes two adsorption schemes.[101] The first is to retrofit an existing water treatment plant by replacing the filtration media with GAC, and the second, called postfilter adsorption, requires separate contactors following the filtration step. The major design parameters to be evaluated for the GAC adsorbers are the contact time, or the EBCT, and the carbon usage rate. Pilot studies should be conducted at the site to optimize the design, which should incorporate several "empty bed contact times" (EBCT). The choice of this criterion is based on the assumption that adsorption is dependent on contact time; i.e., true equilibrium is not achieved in column operation. EBCT is not a true measure of the contact time between the water and the carbon, but an "apparent contact time" can be obtained by multiplying EBCT by the porosity of the carbon. EBCT is related to the different operating parameters as follows:

$$\text{EBCT} = \frac{\text{bed volume (ft}^3) \times 7.48}{\text{hydraulic surface loading (gal / min / ft}^3) \times \text{bed surface area (ft}^2)} \tag{30}$$

where

$$\text{bed volume} = \frac{\text{weight of carbon (lb)}}{\text{carbon bulk density (lb / ft}^3)}$$

$$\text{EBCT} = \frac{\text{bed volume (ft}^3) \times 7.48}{\text{flow rate (gal / min)}} \tag{31}$$

$$\text{EBCT} = \frac{\text{bed depth (ft)}}{\text{linear velocity (ft / min)}} \tag{32}$$

$$\text{EBCT} = \frac{\text{bed depth (ft)} \times 7.48}{\text{hydraulic surface loading (gal / min / ft}^2)} \tag{33}$$

The carbon dosage is calculated from:

$$\begin{array}{c}\text{usage rate} \\ \text{(lb / 1000 gal)}\end{array} = \frac{\text{weight of carbon in column (lb)}}{\text{volume at breakthrough (gal)}} \times 1000 \tag{34}$$

The EBCT has a significant impact on the performance of the GAC column. Given a critical depth of GAC and a corresponding minimum EBCT for a given situation, these conditions must be exceeded if the adsorber is to produce water of acceptable quality. As EBCT increases, the bed life (expressed in bed volumes of product water to breakthrough) will increase until a maximum value is reached. Correspondingly, the activated carbon usage rate will decrease to a minimum value. Figure 4.18 shows the relationship of length of carbon service to bed depths or contact times used in a pilot study at a water treatment plant in Miami, Florida.[99] This shows that the operating time or service time of a column will increase with increasing depth, although this increase may not always be linear with depth. Also, the mass of organic matter adsorbed per unit mass of activated carbon increases as percent exhaustion increases. Correspondingly, the number of bed volumes of water that can be processed before breakthrough will also increase to a maximum value. EBCTs for current use of GAC units range from a few minutes for some filter adsorbers[102] to more than 4 hours for removal of high concentrations of some specific contaminants.[103] Hydraulic application rates vary from 0.4 to 12 gpm/ft^2 (1–30 m/h), with a typical value being 3 to 4 gpm/ft^2 (7–10 m/h).

Example Calculation 4.4: Design a GAC system to treat water containing 10 mg/L alkylbenzenesulfonates to a residual concentration of 0.5 mg/L at a flow of 20,000 gal/day.

Given:

1. The Freundlich adsorption isotherm developed from a batch equilibrium study was favorable.
2. A pilot-scale study using three columns having an inside diameter of 1 inch in series gave the results that follow.[103]

Solution Using EBCT Method:

1. A plot of carbon usage rate (lb/1,000 gal) vs. EBCT is constructed as shown in Figure 4.19. Note that the carbon usage rate decreases rapidly with the increase in EBCT, and that the curves for the through-flow rates converge at high contact time.
2. Low carbon usage rate is obtained at a 15 minute contact time. Increasing the EBCT beyond this value results in a minor reduction in usage rate. Therefore, design EBCT = 15 minutes.
3. Volume of carbon (ft^3)=EBCT (min) × flow (ft^3/min).

$$\text{Flow (ft}^3\text{ / min)} = \frac{\text{Daily flow (gal / day)}}{\text{min / day} \times 7.48 \text{ gal / ft}^3}$$

$$= \frac{20{,}000}{1{,}440 \times 7.48}$$

$$= 1.86 \text{ ft}^3 \text{ / min}$$

$$\text{Volume of carbon (ft}^3) = 15 \times 1.86 = 27.9 \text{ ft}^3$$

4. Weight of carbon (assume the bulk density of the carbon = 25 lb/ft^3):

$$\text{Weight of carbon} = 27.9 \times 25 = 697.5 \text{ lb}$$

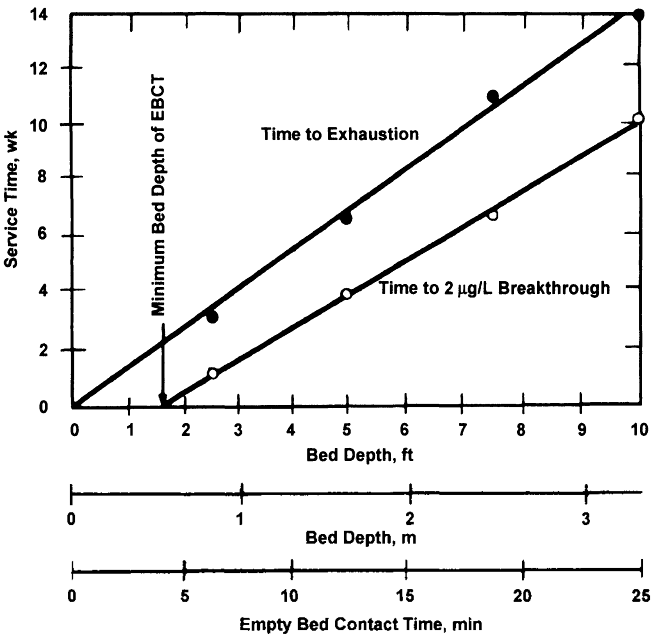


Figure 4.18. Bed depth vs. service times for the removal of chloroform in Miami, Florida water by GAC.[99]

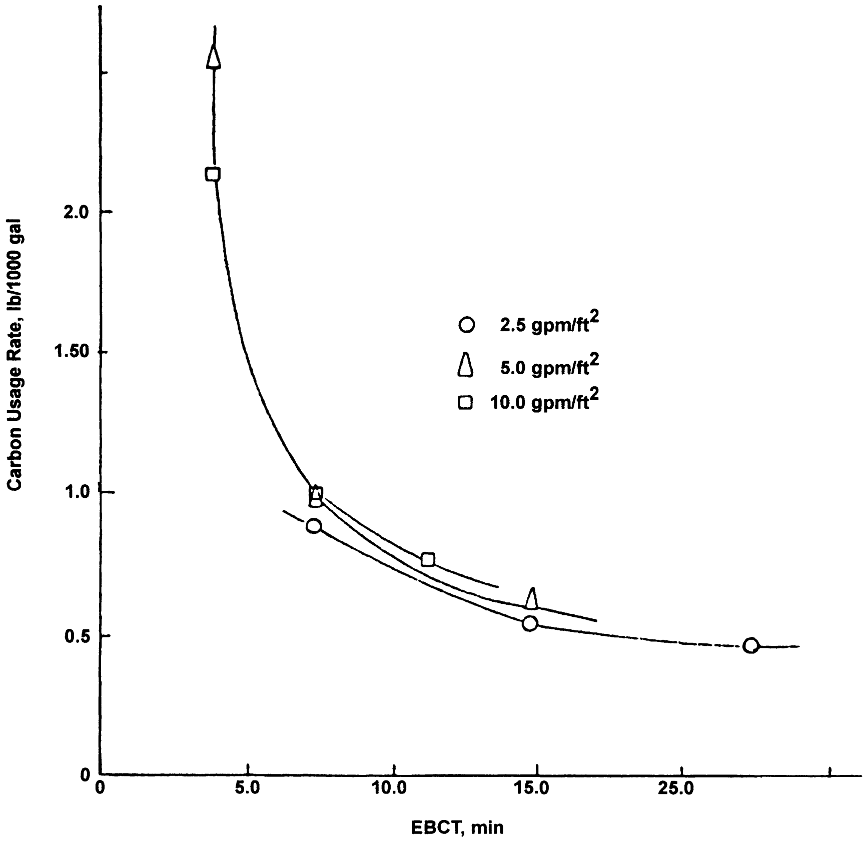


Figure 4.19. EBCT plot.

5. Adsorber sizing (assume linear flow rate = 2.5 gal/min/ft^2):

$$\text{Adsorber area (ft}^2\text{)} = \frac{\text{flow (gal / min)}}{\text{linear flow rate (gal / min / ft}^2\text{)}}$$

$$= \frac{20{,}000}{1{,}440 \times 2.5}$$

$$= 5.6\ \text{ft}^2$$

Assume a circular adsorber is used.

$$\text{Diameter of adsorber} = \sqrt{\frac{4 \times 5.6}{\pi}}$$

$$= 2.7\ \text{ft}$$

$$\text{Carbon bed depth} = \frac{\text{volume of carbon (ft}^3\text{)}}{\text{area of adsorber (ft}^2\text{)}}$$

$$= \frac{27.9}{5.6}$$

$$= 5\ \text{ft}$$

Sidewall height (ft) (allow 50% freeboard for bed expansion):

$$\text{Sidewall height} = 1.5 \times 5$$

$$= 7.5\ \text{ft}$$

Select the nearest commercially available sizes, and adjust the linear flow rate accordingly.

6. Carbon bed cycle time:

$$\text{Cycle time of bed (days)} = \frac{\text{lb carbon in adsorber}}{\text{lb carbon usage / day}}$$

Carbon usage rate determined from Figure 4.19 = 0.55 lb/1,000 gal

$$\text{Cycle time of bed} = \frac{697.5\ \text{lb}}{0.55\ \text{lb / 1000 gal} \cdot 20{,}000\ \text{gal / day}}$$

$$= 63.4\ \text{days}$$

$$= 1{,}522\ \text{hours}$$

To optimize the design, a higher EBCT can be used for sizing the adsorber, and an economic analysis is conducted. The EBCT that gives the lowest total annual cost should be selected.

The normal course of events in the design of a full-scale and operational GAC column is: (a) laboratory tests for the determination of adsorption kinetics, isotherm constants, and adsorption capacity, (b) laboratory-scale studies of column operation for breakthrough curves, and (c) pilot-plant scale operation of carbon columns. This is a time-consuming and expensive protocol for the ultimate design, construction, and operation of a full-scale GAC treatment plant. To circumvent and/or to shorten the time line, rapid methods for the design of large-scale fixed-bed adsorbers from small columns have been developed (see Reference 105 for several citations). Rapid small-scale column tests (RSSCTs) have been developed which do not require the use of complicated models, but are based on fixed-bed mass transfer models. Similarity of operation of the RSSCTs is assured by properly selecting the particle size, hydraulic loading, and EBCT of the small adsorber.

The essence of the RSSCT is a comparison of its performance to that of a larger column.[105] The EBCT of the RSSCT—EBCT$_{SC}$—is determined from intraparticle mass transfer resistances. If the dependence of the pore and surface diffusion coefficient on particle size is known, similarity may be achieved by equating the dimensionless groups that consider the intraparticle diffusion resistances in the small and large columns. If the void fractions, bulk densities, and capacities are identical for the carbons that are used in the RSSCT and full-scale process, the proper scaling between the small- and large-column EBCTs can be determined from this equation:

$$\frac{\text{EBCT}_{SC}}{\text{EBCT}_{LC}} = \left(\frac{d_p,\ SC}{d_p,\ LC}\right)^{2-x} = \frac{t_{SC}}{t_{LC}} \tag{35}$$

in which EBCT$_{SC}$ and EBCT$_{LC}$ are the EBCTs of the small and large column; $d_{p,SC}$ and $d_{p,LC}$ are the adsorbent particle sizes for the small and the large GAC; and t_{SC} and t_{LC} are the corresponding elapsed times in the small- and large-column tests, respectively; x defines the dependence of the intraparticle diffusion coefficient on particle size. Furthermore, the bed life, bed volumes fed, carbon usage rate, and volume of water that may be treated per mass of carbon (the specific volume) for the full-scale adsorber can be determined from the RSSCT bed life (Equation 35).

Several studies have been conducted to evaluate the reliability of the RSSCT to predict GAC performance of pilot- and/or full-scale columns (see Reference 105). In one of these studies,[105] dissolved organic carbon (DOC) removal from five surface waters and one groundwater by RSSCT and pilot performances were compared. Table 4.5 summarizes the results of 11 comparisons of RSSCT and pilot columns that involved the adsorption of background organic matter as measured by total or DOC or UV absorbance. In all of the studies given in Table 4.5, good comparisons between RSSCT and pilot columns were obtained using a pore diffusion (PD) design. It appears, therefore, that RSSCTs may be useful in the ultimate design and operation of full-scale GAC columns. However, the reader is directed to References 105 and 108 for limitations of the RSSCT.

Estimates of GAC loading and bed life can be obtained from adsorption isotherms (see above). In order to perform these estimates, it is necessary to assume that: (a) all of the GAC in the bed will reach equilibrium with the influent concentration, and (b) the adsorptive capacity, obtained by extrapolating the isotherm data to the initial concentration, is a reasonably good value. Whereupon the bed life, in volumes of water, can be calculated. If $(x/m)_0$ is the mass of a contaminant adsorbed (mg/g) when $C_e = C_0$, the bed life Y (volume of water treated per unit volume of carbon, can be calculated from:

$$Y = \frac{(x/m)_0}{(C_0 - C_1)} \times \rho_{GAC} \tag{36}$$

where C_0 = influent concentration, mg/L
C_1 = average effluent concentration for entire column run, mg/L
ρ_{GAC} = apparent density of GAC

C_1 is zero for strongly adsorbed compounds that have sharp breakthrough curves. It also represents the concentration of nonadsorbable compounds whenever they are present. Consequently, the carbon usage rate (CUR) can be estimated from:

$$CUR = \frac{(C_0 - C_1)}{(x/m)_0} \tag{37}$$

where CUR is expressed as g/L.

Example Calculation 4.5: Estimate the bed life and carbon usage rate for a GAC adsorber that is to remove 10 mg/L of bromoform from solution, given r_{GAC} = 500 g/L.

Solution.

1. K = 20 (mg/g) $(L/mg)^{1/n}$ and 1/n = 0.52 for bromoform (Table 4.8).
2. Applying the Freundlich equation (Equation 20), we have

$$(x/m)_0 = KC^{1/n}$$

$$= 20\,(mg/g)\,(L/mg)\,(0.01\ mg/L)^{0.52}$$

$$= 1.82\ mg/g$$

3. Applying Equation 36, assuming that $C_1 = 0$, gives

$$Y = \frac{(x/m)_0\ (mg/g)}{(C_0 - C_1) mg/L} \times \rho_{GAC}(g/L)$$

$$= \left(\frac{1.82\ mg/g}{0.01\ mg/L}\right) 500\ g/L$$

$$= 91{,}000\ L\ H_2O/L\ GAC = \text{bed life}$$

4. Applying Equation 37 to obtain CUR gives

$$CUR = \frac{(C_0 - C_1) mg/L}{(x/m)_0 mg/g}$$

$$= \frac{0.01\ mg/L}{1.82\ mg/g}$$

$$= 0.0055\ g\ GAC/L\ H_2O$$

Note: The bed life will be reduced and the CUR will be increased if other organics that compete for adsorption sites are in the water.

(This example calculation was graciously supplied by V.L. Snoeyink, Chapter 13 in *Water Quality and Treatment,* 4th Edition, American Water Works Association, 1990).

The use of isotherm data to estimate GAC usage rate has several limitations. It is valid only for columns in series or for very long columns where the carbon is in equilibrium with the influent concentration. Any biological activity is not considered. Finally, competitive effects observed in batch tests are not the same as those in a column where the molecules will separate according to strength of adsorption. In a column operation, the GAC may be exposed to a greater variety of organics through the bed life than GAC in a batch test. This may be true for the competitive effects of NOM on trace quantities of organics.

APPLICATIONS OF ACTIVATED CARBON

Taste and Odor Removal

The use of activated carbon for taste and odor control represents the earliest successful application of carbon adsorption in water treatment. Most modern water treatment

Table 4.5. Results of RSSCT and Pilot Studies Using DOC to Measure Adsorption of Background Organic Matter.[105]

Water Source	Target Compound	Influent Concentration, C_0 (mg/L) Pilot	Influent Concentration, C_0 (mg/L) RSSCT	RSSCT Design	EBCT Pilot (min)	EBCT RSSCT (s)	Loading Rate (V) m/h Pilot	Loading Rate (V) m/h RSSCT	Comments
Fuhrberg humic substances in tap water preadsorbed by GAC	Humic substances	8.72	8.93	CD	4.5	30.0	9.3	30.3	The CD RSSCT effluent profiles appeared before the pilot-plant effluent profiles. Diameter of GAC particles: pilot = 0.085 cm, RSSCT = 0.026 cm.
	Humic substances	8.72	8.93	CD	8.4	50.0	9.3	30.3	
Fuhrberg humic substance in tap water preadsorbed by GAC	Humic substances	8.03	8.72	CD	15.6	272.1	5.0	9.3	The CD RSSCT effluent profiles appeared before the pilot-plant effluent profiles. Diameter of GAC particles: pilot = 0.158 cm, RSSCT = 0.085 cm.
	Humic substances	8.03	8.72	CD	28.2	505.4	5.0	9.3	
Fuhrberg humic substances in tap water preadsorbed by GAC	Humic substances	8.03	8.93	CD	15.6	30.0	5.0	30.3	The CD RSSCT effluent profiles appeared before the pilot-plant effluent profiles. Diameter of GAC particles: pilot = 0.158 cm, RSSCT = 0.026 cm.
	Humic substances	8.03	8.93	CD	28.2	50.0	5.0	30.3	
Fuhrberg humic substances in tap water preadsorbed by GAC	Humic substances	8.72	8.93	PD	1.6	30.9	9.3	30.3	The PD RSSCT effluent profiles adequately predicted the large-column effluent profiles. Diameter of GAC particles: pilot = 0.085 cm, RSSCT = 0.026 cm.
	Humic substances	8.72	8.93	PD	2.7	50.0	9.3	30.3	
Fuhrberg humic substances in tap water preadsorbed by GAC	Humic substances	8.03	8.93	PD	3.0	30.9	5.0	30.3	The PD RSSCT effluent profiles adequately predicted the large-column effluent profiles. Diameter of GAC particles: pilot = 0.158 cm, RSSCT = 0.026 cm.
	Humic substances								
Fuhrberg humic substances in tap water preadsorbed by GAC	Humic substances	8.03	8.72	PD	3.0	97.3	5.0	9.3	The PD RSSCT effluent profiles adequately predicted the large-column effluent profiles. Diameter of GAC particles: pilot = 0.158 cm, RSSCT = 0.026 cm.
	Humic substances	8.03	8.72	PD	15.6	505.4	5.0	9.3	
Colorado River water, LaVerne, CA. coagulated and filtered, pretreated with ClO_2	DOC	2.64	2.33	CD	15.0	30.0	1.2	6.6	The CD RSSCT effluent profile appeared before that of the pilot column. The PD RSSCT effluent profiles adequately predicted the pilot-column profiles. As EBCT increased, the RSSCT effluent profiles appeared after the pilot-plant profiles. Diameter of GAC particles: pilot = 0.103 cm, RSSCT = 0.021 cm.
	DOC	2.64	2.22	PD	15.0	165.9	1.2	2.9	
	DOC	2.64	2.11	PD	30.0	331.8	1.2	2.3	
	DOC	2.64	2.09	PD	60.0	662.4	1.2	1.7	

Table 4.5. Results of RSSCT and Pilot Studies Using DOC to Measure Adsorption of Background Organic Matter.[105] (Continued)

Water Source	Target Compound	Influent Concentration, C_0 (mg/L)		RSSCT Design	EBCT		Loading Rate (V) m/h		Comments
		Pilot	RSSCT		Pilot (min)	RSSCT (s)	Pilot	RSSCT	
State project water, LaVerne, CA, coagulated and filtered, pretreated with ClO_2	DOC	2.64	2.24	PD	15.0	165.9	1.2	1.7	The PD RSSCT effluent profiles predicted the pilot-column effluent profiles. Diameter of GAC particles: pilot = 0.103 cm, RSSCT = 0.021 cm.
Ohio River water, Cincinnati, OH, coagulated and filtered prior to disinfection with chlorine	DOC	2.00	2.17	PD	15.0	165.9		2.9	A good comparison was obtained between the PD RSSCT and the pilot-column effluent profiles. Diameter of GAC particles: pilot = 0.103 cm, RSSCT = 0.021 cm.
Mississippi River water, Jefferson Parish Water District, LA, coagulated and filtered prior to disinfection with chlorine	DOC	2.69	2.69	PD	20.0	165.9		1.7	A good comparison was obtained between the PD RSSCT and the pilot-column effluent profiles. Diameter of GAC particles: pilot = 0.103 cm, RSSCT = 0.021 cm.
Delaware River water, Philadelphia Water Department, coagulated and filtered prior to disinfection with chlorine dioxide	DOC	2.72	2.72	PD	15.0	165.9		1.7	A good comparison was obtained between the PD RSSCT and the pilot-column effluent profiles. Diameter of GAC particles: pilot = 0.103 cm, RSSCT = 0.021 cm.

plants use powdered activated carbon for control of tastes and odors of biological or industrial origin in batch processes, as discussed earlier in this chapter. The use of GAC was revived in the early 1960s, first at Hopewell, Virginia, in 1962, and next at the Nitro, West Virginia, water treatment plants in 1966 for taste and odor control.[109,110] Replacement of the sand with carbon allowed the filters to serve a dual adsorption and filtration function. The success of GAC beds for controlling taste and odor at these plants led to the acceptance of the practice in other water utilities. A 1977 survey indicated that about 35 plants are using GAC, either alone or on top of some sand medium as both a filter medium for particulate removal and as an adsorptive medium for taste and odor control.[10] The effective service life of these filters ranged between 2 and 4 years, and the odor breakthrough occurred much later than the breakthrough of other organics.[10] The exhausted carbon is usually replaced by virgin carbon, and reactivation is not practiced.

Geosmin and 2-methylisoborneol (MIB), the causative agents of the earthy-musty odor in water supplies, were shown to adsorb strongly to activated carbon.[61,111,112] Tables 3.22a and 3.22b give the Freundlich isotherm parameters for removal of geosmin, MIB, IPMP, IBMP, and TCA and geosmin and MIB by PAC, respectively.[113,114] That NOM (i.e., humic substances) significantly reduces the adsorptive capacity of PAC and GAC for these compounds was discussed above for batch equilibrium systems. Similar results were obtained for column studies.[61,87] Additional studies were conducted for PAC (100 × 200 mesh) adsorption of MIB.[115] In this case, four bituminous coal-based carbons and one lignite-based carbon were employed in equilibrium systems (7 days) for MIB alone and in the presence of 10 mg/L humic acid.

Phenolic compounds, especially the chlorinated species, impart medicinal iodine-like tastes to drinking water (see Chapter 3). Most of these tastes arise from the chlorination treatment for disinfection and taste and odor control. PAC and GAC have been used in the water treatment industry for many years in a rather empirical manner for taste and odor removal. Only since the late 1950s and early 1960s have PAC and GAC treatment found quantitative application in laboratory and pilot plant operation.

Table 4.7 contains Freundlich and Langmuir adsorption constants for phenol and several chlorinated phenols on GAC under a wide range of experimental conditions (see Reference 82 for original references). Adsorption capacities (k values) ranged from 25 to 138 mg/g (when $C_e = 1.0$ mg/L). These capacities are modest for carbon adsorption of organic compounds. However, it is feasible to use carbon for removal of these phenolic compounds where batch contact times (15–60 minutes) are somewhat less than those reported in Table 4.6. Langmuir monolayer coverage—X_m values—ranged from 85 to 380 mg/g when $C_e = 1$ µmol/L. All of these studies were conducted on GAC, whose capacities are less than for PAC.

Trichlorophenol was employed as a model compound in a study of the effect of particle size and background NOM on the adsorption efficiency of PAC.[116] Freundlich constants for various mesh-sized PAC particles (100–400) were: K = 19.6 (mg/g)/(µg/L)$^{1/n}$ and l/n = 0.3144 (7-day batch systems). Apparently carbon particle size did not affect the isotherm and its constants, but there was the expected effect on the kinetics of adsorption. Similar results were obtained for TCP on various particle sizes of PAC in concert with a hollow-fiber ultrafiltration system.[96]

Hydronium ion concentration (pH) affects the associated-dissociated state of the adsorbate, and this in turn affects the extent of adsorption. Table 4.8 gives some Freundlich isotherm constants for 2,4-DCP and 2,4-DNP at pH values ranging from 2 to 10.9.[43] Comparison of the K values [(mg/g)(mg/L)^{ln} when $C_e = 1.0$ mg/L] shows the obvious effects of [H_3^+O]. Lesser quantities of 2,4-DCP were adsorbed at pH values of 2, 8.3, and 10.9 than at 6.3. As indicated, there is a competitive effect of HO on 2,4-DCP adsorption under acid conditions. Maximum adsorption of 2,4-DCP occurred at pH values just below its pK_a value of 7.8. In contrast, 2,4-DNP showed its maximum adsorption at a pH value of 2.0, whereupon it decreased as the [H_3^+O] was decreased. Apparently, 2,4-DNP competes better with H_3^+O than 2,4-DCP because it is a stronger acid ($pK_a = 4.0$). It is doubtful, however, that the [H_3^+O] would be a major factor under treatment plant conditions because most phenols are weak acids in water and would be dissociated to a small extent.

Removal of Organics

General Considerations

The ability of granular activated carbon to remove a broad spectrum of organic compounds from water is well documented. Table 4.6 shows adsorption isotherm data developed by Dobbs and Cohen[117] for some of the compounds studied as single solutes in aqueous systems. These data illustrate clearly the wide range of organic compounds of different structures, sizes, functionality, etc., that can be adsorbed by GAC (ground to a powdered form). It can also be seen that these compounds exhibit different adsorption characteristics, i.e., some are strongly adsorbed, whereas others are weakly adsorbed. Their adsorption behavior is expected to be affected by the different factors discussed so far in this chapter, either in batch processes or continuous-flow systems.

In natural surface waters, however, contaminants do not exist as single solutes but rather as mixtures comprising, perhaps, hundreds of compounds. In removing these compounds by GAC beds, competitive effects of the different species for the available sites and displace-

Table 4.6. Freundlich Adsorption Isotherm Constants for Toxic Organic Compounds.[117]

Compound	K (mg/g)/(mg/L)$^{l/n}$	l/n
bis(2-Ethylhexyl) phthalate	11,300.0	1.5
Butylbenzyl phthalate	1,520.0	1.26
Heptachlor	1,220.0	0.95
Heptachlor epoxide	1,038.0	0.70
Endosulfan sulfate	686.0	0.81
Endrin	666.0	0.80
Fluoranthene	664.0	0.61
Aldrin	651.0	0.92
PCB-1232	630.0	0.73
beta-Endosulfan	615.0	0.83
Dieldrin	606.0	0.51
Hexachlorobenzene	450.0	0.60
Anthracene	376.0	0.70
4-Nitrobiphenyl	370.0	0.27
Fluorene	330.0	0.28
DDT	322.0	0.50
2-Acetylaminofluorene	318.0	0.12
alpha-BHC	303.0	0.43
Anethole	300.0	0.42
3,3-Dichlorobenzidine	300.0	0.20
2-Chloronaphthalene	280.0	0.46
Phenylmercuric acetate	270.0	0.44
Hexachlorobutadiene	258.0	0.45
gamma-BHC (Lindane)	256.0	0.49
p-Nonylphenol	250.0	0.37
4-Dimethylaminoazobenzene	249.0	0.24
Chlordane	245.0	0.38
PCB-1221	242.0	0.70
DDE	232.0	0.37
Acridine yellow	230.0	0.12
Benzidine dihydrochloride	220.0	0.37
beta-BHC	220.0	0.49
n-Butylphthalate	220.0	0.45
n-Nitrosodiphenylamine	220.0	0.37
Phenanthrene	215.0	0.44
Dimethylphenylcarbinol	210.0	0.34
4-Aminobiphenyl	200.0	0.26
beta-Naphthol	200.0	0.26
alpha-Endosulfan	194.0	0.50
Acenaphthene	190.0	0.36
4,4'-Methylene-*bis*-(2-choloroaniline)	190.0	0.64
Benzo [k] fluoranthene	181.0	0.57
Acridine orange	180.0	0.29
alpha-Naphthol	180.0	0.32
4,6-Dinitro-*o*-cresol	169.0	0.27
alpha-Naphthylamine	160.0	0.34
2,4-Dichlorophenol	157.0	0.15
1,2,4-Trichlorobenzene	157.0	0.31
2,4,6-Trichlorophenol	155.0	0.40
beta-Naphthylamine	150.0	0.30
Pentahlorophenol	150.0	0.42
2,4-Dinitrotoluene	146.0	0.31
2,6-Dinitrotoluene	145.0	0.32
4-Bromophenyl phenyl ether	144.0	0.68

Table 4.6. Freundlich Adsorption Isotherm Constants for Toxic Organic Compounds[117] (Continued).

p-Nitroaniline	140.0	0.27
1,1-Diphenylhydrazine	135.0	0.16
Naphthalene	132.0	0.42
1-Chloro-2-nitrobenzene	130.0	0.46
1,2-Dichlorobenzene	129.0	0.43
p-Chlorometacresol	124.0	0.16
1,4-Dichlorobenzene	121.0	0.47
Benzothiazole	120.0	0.27
Diphenylamine	120.0	0.31
Guanine	120.0	0.40
Styrene	120.0	0.56
1,3-Dichlorobenzene	118.0	0.45
Acenaphthylene	115.0	0.37
4-Chlorophenyl phenyl ether	111.0	0.26
Diethyl phthalate	110.0	0.27
2-Nitrophenol	99.0	0.34
Dimethyl phthalate	97.0	0.41
Hexachloroethane	97.0	0.38
Chlorobenzene	91.0	0.99
p-Xylene	85.0	0.19
2,4-Dimethylphenol	78.0	0.44
4-Nitrophenol	76.0	0.25
Acetophenone	74.0	0.44
1,2,3,4-Tetrahydronaphthalene	74.0	0.81
Adenine	71.0	0.38
Dibenzo[a,h]anthracene	69.0	0.75
Nitrobenzene	68.0	0.43
3,4-Benzofluoranthene	57.0	0.37
1,2-Dibromo-3-chloropropane	53.0	0.47
Ethylbenzene	53.0	0.79
2-Chlorophenol	51.0	0.41
Tetrachloroethene	51.0	0.56
o-Anisidine	50.0	0.34
5-Bromouracil	44.0	0.47
Benzo[a]pyrene	34.0	0.44
2,4-Dinitrophenol	33.0	0.61
Isophorone	32.0	0.39
Trichloroethene	28.0	0.62
Thymine	27.0	0.51
Toluene	26.0	0.44
5-Chlorouracil	25.0	0.58
N-Nitrosodi-n-propylamine	24.0	0.26
bis(2-Chloroisopropyl) ether	24.0	0.57
Phenol	21.0	0.54
Bromoform	20.0	0.52
Carbon tetrachloride	11.0	0.83
bis(2-Chloroethoxy) methane	11.0	0.65
Uracil	11.0	0.63
Benzo[g,h,i]perylene	11.0	0.37
1,1,2,2-Tetrachloroethane	11.0	0.37
1,2-Dichloropropene	8.2	0.46
Dichlorobromomethane	7.9	0.61
Cyclohexanone	6.2	0.75
1,2-Dichloropropane	5.9	0.60
1,1,2-Trichloroethane	5.8	0.60

Table 4.6. Freundlich Adsorption Isotherm Constants for Toxic Organic Compounds[117] (Continued).

Trichlorofluoromethane	5.6	0.24
5-Fluorouracil	5.5	1.0
1,1-Dichloroethylene	4.9	0.54
Dibromochloromethane	4.8	0.34
2-Chloroethyl vinyl ether	3.9	0.80
1,2-Dichloroethane	3.6	0.83
1,2-*trans*-Dichloroethene	3.1	0.51
Chloroform	2.6	0.73
1,1,1-Trichloroethane	2.5	0.34
1,1-Dichloroethane	1.8	0.53
Acrylonitrile	1.4	0.51
Methylene chloride	1.3	1.16
Acrolein	1.2	0.65
Cytosine	1.1	1.6
Benzene	1.0	1.6
Ethylenediaminetetraacetic acid	0.86	1.5
Benzoic acid	0.76	1.8
Chloroethane	0.59	0.95
N-Dimethylnitrosamine	6.8×10^{-5}	6.6

Table 4.7. Adsorption of Phenolic Compounds by Carbon in Batch Systems.[82]

	Type of Carbon	Contact Time		Freundlich Constants		Langmuir Constants	
Phenol			pH	K $(mg/g)/(mg/L)^{1/n}$	1/n	X_m (mg/g)	b^{-1}
Phenol	GAC	24 hr	9.0	25.0	0.37	—	—
4-chloro-	GAC	24 hr	7.0	82.0	0.29	—	—
4-chloro-	GAC	24 hr	9.0	78.0	0.20	—	—
2,4-dichloro-	GAC	24 hr	9.0	70.0	0.27	—	—
2,6-dichloro-	GAC	24 hr	7.0	138.0	0.13	—	—
2,6-dichloro-	GAC	24 hr	9.0	25.0	0.57	—	—
Phenol	GAC	1-2 wk	?	—	—	103.0	9.26[a]
Phenol	GAC	4 wk	4.0	—	—	123.0	13.0[a]
Phenol	GAC	4 wk	12.0	—	—	34.45	45.0[a]
Phenol	GAC	10 days	7.0	—	—	99.0	7.7[a]
Phenol	GAC	10 days	9.5	—	—	85.0	12.5[a]
2,4-dichloro-	GAC	10 days	7.0	—	—	380.0	0.93[a]
2,4-dichloro-	GAC	10 days	9.5	—	—	233.0	33.3
4-Cl-	GAC	100 hr	6.5	—	—	272.0	19.0[a]
Phenol	GAC	2 days	?	50.0	0.26	213.0	—
p-Cl-	GAC	4 wk	?	126.0	0.25	434.0	—

[a] μmol/L.

ment effects where the more strongly adsorbed compounds displace the weakly adsorbed ones will affect the shape and position of the breakthrough curves. In addition, the concentration of many contaminants in surface water is quite variable and may result in the establishment of different equilibrium conditions in the carbon beds. These effects may result, for certain compounds, in early breakthrough or effluent concentrations exceeding those in the influent to carbon beds. Computer-reconstructed gas chromatographic profiles have demonstrated the displacement effects (chromatographic effects) in GAC beds treating surface waters.[46,118]

Phase I Organics

GAC is the recommended BAT for removal of seven of the eight Phase I organic contaminants (see Table 1.7). Packed tower aeration (PTA) is recommended for vinyl chloride. Numerous laboratory and pilot plant studies have been conducted for the PAC and GAC removal of these com-

Table 4.8. Freundlich Constants for 2,4-DCP and 2,4-DCP at Several pH Values.[a,b]

		Freundlich Constants	
Compound	**pH**	**K (mg/g)/(mg/L)$^{1/n}$**	**l/n**
2,4-DCP[c]	2.0	275.0	0.114
	6.3	322.0	0.100
	8.3	306.0	0.117
	10.9	109.0	0.207
2,4-DNP[d]	2.1	321.0	0.145
	6.0	166.0	0.156
	8.0	129.0	0.128
	10.4	116.0	0.147

[a] Adapted from Zogorski.[43]
[b] GAC, 2 weeks contact time.
[c] pK_a = 7.8; 25°C.
[d] pK_a = 4.0; 25°C.

pounds. Table 4.9 summarizes the Freundlich constants for seven of the Phase I organics on PAC and GAC under a wide range of contact times and equilibrium concentration ranges. There is a wide range of adsorption capacities for these compounds. Some are poorly adsorbed (e.g., benzene and CCl_4), whereas some are strongly adsorbed (1,2-dichloroethane). Some Phase I compounds also have PTA as an alternative or a supplemental treatment (see Table 1.7).

Phase II Organics

There are 30 organic compounds regulated under Phase II of the Safe Drinking Water Act Amendments of 1986 (see Table 1.7). Removal of 29 of these Phase II organics (acrylamide controlled by treatment techniques) by GAC and PTA is recommended. Table 4.10 shows the Freundlich adsorption constants and the concentration ranges for these organics. Here again, a wide range of adsorption capacities is noted. These adsorption characteristics should indicate their behavior on carbon columns in a treatment situation. Also, it may be necessary to utilize PTA in conjunction with GAC for some of the poorly adsorbed compounds. Ethylenedibromide (EDB) is a candidate for this dual treatment process, for example.

GAC point-of-entry filters are efficiently removing EDB from contaminated groundwater throughout Florida.[121a] An extensive study was conducted on the design, performance, and operational problems of these filters that assessed the possibility of extending the interval between the GAC replacement from the current six months. Florida's EDB-fumigant filter program consists of nearly 1,000 POE GAC filter systems that were installed to treat the polluted groundwater. The major concern was the consistency of EDB loadings on these filters that include mass transfer resistances and competitive adsorption effects. An equilibrium column model was developed from the Freundlich equation:

$$q_{column} = 12 * Co^{0.85}$$

where q_{column} = loading in µg EDB/g GAC
Co = column feed concentration in µg/L EDB

This model was employed to predict breakthrough of the EDB from the column, hence the time for carbon replacement.

Phase V Organics

Eighteen organic compounds and/or groups are regulated under Phase V of the SDWAA. All are to be removed by GAC and/or PTA except dichloromethane (methylene chloride), which requires PTA. Table 4.11 contains the available GAC adsorption data as of 1995. Phase V regulates some of the most hazardous and carcinogenic compounds, e.g., polynuclear aromatic hydrocarbons (PAH) and dioxin. Additional adsorption data are given below for the PAHs.

Parenthetical note to Tables 4.9, 4.10, and 4.11: Freundlich adsorption constants should be interpreted with caution. The values of K and l/n are approximate estimates of the values that will be obtained in waters other than distilled-deionized water (DDW) systems and with other activated carbons. In Reference 90, there are several K and l/n values for surface and groundwaters that are significantly different than those from DDW systems.

The removal efficiency of intermittently applied pesticides (Simazine, Napropamid, Bentazon, Asulum, and Hymexazol) by a GAC bed preloaded with background organic matter (BOM) was examined using the RSSCT.[129c] As expected, preloading with BOM decreased the removal efficiency of these pesticides, which was a function of the amount of BOM adsorbed. It was unrelated to the influent concentration of the pesticides. The ideal adsorbed solution theory and a linear driving force expression for intraparticle surface diffusion adequately modeled these phenomena (see Reference 82 for explanation of these models). For example, the removal efficiency of intermittently applied pesticides was well described with first-order kinetics vs. bed depth, and the rate coefficient was a function of the amount of BOM preloaded onto the GAC.

Polynuclear Aromatic Hydrocarbons (PAH)

Polynuclear aromatic hydrocarbons (PAH), some of which are known carcinogens, have been detected in many surface and groundwaters at low concentrations.[123,125] Effective removal of these compounds in natural waters can be achieved by activated carbon treatment.[124,125] Borneff[124] showed that several types of activated carbon removed 99 to 99.9% of solubilized PAH under laboratory conditions. Use of activated carbon for removal of PAH from natural waters is shown in Table 4.12, where a two-stage treatment consisting of powdered activated carbon followed by GAC

Table 4.9. Freundlich Adsorption Constants and Concentration Ranges for Phase I Organics.

Compound	Type of Carbon	Contact Time (min)	Equilibrium Range (mg/L)	Maximum Adsorbed (mg/g)	Freundlich Constants K (mg/g)/(mg/L)$^{l/n}$	Freundlich Constants l/n	Carbon Dosage to Reduce 1 mg/L to 0.1 mg/L	Reference
Benzene	PAC	120.0	4.0–19.8	58.3	1.0	1.6	35,000.0	82^{a}
Benzene	PAC	120.0	21.0	95.0	—	—	—	82^{a}
Benzene	PAC–A	120.0	1.4–10.0	—	26.8	1.3	678.0	82
Benzene	PAC-B	120.0	2.0–10.0	—	18.5	1.2	705.0	82
Benzene	PAC	15.0	0.0–25.0	—	65.0	0.42	—	82
Benzene	GAC	2 d	0.0–20.0	—	36.0	0.48	—	82
Benzene	GAC-A	550.0	0.005–0.5	—	0.73^{c}	0.61	—	82
Benzene	GAC-B	550.0	0.005–0.5	—	1.07^{c}	0.48	—	82
Benzene	GAC-C	550.0	0.005–0.5	—	1.12^{c}	0.39	—	82
Benzene	GAC-D	550.0	0.005–0.5	—	1.18^{c}	0.36	—	82
Benzene	PAC	120.0	5.5–76.6	—	207.0	0.61	—	82
Benzene	GAC	5 d	0.01–0.2	—	1.14^{d}	0.398	—	82
Benzene	PAC	15 m	3.0–50.0	—	3.57^{c}	0.42	—	90
Benzene	PGAC^{b}	7 d	5.76x10^{-6}M	—	1140.0^{d}	0.398	—	119
Carbon tetrachloride	PAC	120.0	0.02x1.0	2.85	11.1	0.83	550.0	82
Carbon tetrachloride	GAC-A	550.0	0.0005–0.1	—	0.16^{c}	0.75	—	82
Carbon tetrachloride	GAC-B	550.0	0.0005–0.1	—	0.22^{c}	0.69	—	82
Carbon tetrachloride	GAC-C	550.0	0.0005–0.1	—	0.23^{c}	0.74	—	82
Carbon tetrachloride	GAC-D	550.0	0.0005–0.1	—	0.13^{c}	0.68	—	82
Carbon tetrachloride	GAC	2 d	0.0025–0.063	—	11.6	0.73	—	82
Carbon tetrachloride	GAC	?	?	—	38.1	0.7	—	82
Carbon tetrachloride	PGAC	7 d	1.21x10^{-6}M	—	224.0^{d}	0.63	—	119
Carbon tetrachloride	PAC	60.0	0.0025–0.12	—	0.12^{d}	0.84	—	90
1,4-dichlorobenzene	PAC	?	0.33–16.7	265.0	121.0	0.47	22.0	82
1,4-dichlorobenzene	GAC	?	4.0–10.1	206.0	—	—	—	82
1,4-dichlorobenzene	GAC	550.0	0.005–5.0	—	17.1^{c}	0.37	—	82
1,2-dichloroethane	PAC	120.0	0.012–1.0	2.46	3.57	0.83	1700.0	82
1,2-dichloroethane	PAC	120.0	15.8–84.0	—	140.5	0.75	—	82
1,2-dichloroethane	PGAC	7 d	1.25x10^{-6}M	—	37.9^{d}	0.83	—	119
1,2-dichloroethene	PAC	120.0	0.007–1.0	2.83	4.91	0.54	640.0	82
1,1,1-trichloroethane	PAC	120.0	0.0035–1.0	2.4	2.48	0.34	800.0	82
1,1,1-trichloroethane	GAC	2 d	0.09–0.8	—	42.7	0.57	—	82
Trichloroethylene	PAC	120.0	0.005–1.0	8.7	28.0	0.62	130.0	82
Trichloroethylene	GAC-C	?	?	—	32.0	0.45	—	82
Trichloroethylene	PAC-A	?	?	—	16.5	0.54	—	82
Trichloroethylene	PAC-B	?	?	—	28.0	0.52	—	82
Trichloroethylene	PAC-C	?	?	—	11.0	0.67	—	82
Trichloroethylene	GAC	?	?	—	26.2	0.5	—	82
Trichloroethylene	PGAC	7 d	10.0x10^{-6}M	—	3261.9^{d}	0.41	—	119

Trichloroethylene	ACF[e]	120.0	—	—	52.0–150.0	0.75	—	120
Trichloroethylene	PAC	60.0	0.00015–0.063	—	0.66[c]	0.5	—	90
Trichloroethylene	PAC	7 d	0.003–0.031	—	1.35[c]	0.51	—	90
Trichloroethylene	PAC	7 d	0.004–0.032	—	0.9[c]	0.51	—	90

[a] See Reference 82 for original citation.

[b] PGAC = pulverized granular activated carbon.

[c] When Ce = 1.0 µg/L.

[d] K in units of $(\mu g/g)/(\mu g/L)^{1/n}$.

[e] ACF = activated carbon fibers.

Table 4.10. Freundlich Adsorption Constants and Concentration Ranges for Phase II Organics.

Compound	Type of Carbon	Contact Time (min)	Equilibrium Range (mg/L)	Maximum Adsorbed (mg/g)	Freundlich Constants		Carbon Dosage to Reduce 1 mg/L to 0.1 mg/L	Reference
					$K\ (mg/g)/(mg/L)^{1/n}$	1/n		
Alachlor	PAC	14 d	0.0006–0.512	—	80.2^c	0.26	—	90
Alachlor	PAC	18 d	0.0002–0.477	—	62.0^c	0.33	—	90
Alachlor	PAC	11 d	0.0026–0.046	—	10.5^c	0.38	—	90
Alachlor	?	?	?	—	679.0	0.26	—	121
Aldicarb	?	?	?	—	132.0	0.40	—	121
Aldicarb	PAC	13 d	0.0013–0.274	—	8.4^c	0.40	—	90
Aldicarb	PAC	12 d	0.019–0.171	—	4.52^c	0.41	—	90
Atrazine	PAC	?	0.042–0.785	—	283.0	0.29	—	90
Atrazine	PAC	?	0.0006–0.317	—	294.0	0.36	—	90
Carbofuran	PAC	7 d	0.003–0.111	—	16.2^c	0.41	—	90
Carbofuran	PAC	7 d	0.0022–0.365	—	11.9^c	0.36	—	90
Carbofuran	?	?	?	—	266.0	0.41	—	121
Chlorobenzene	?	?	?	—	100.0	0.35	—	121
Chlorobenzene	PAC	120.0	1.4–25.9	1700.0	91.0	0.99	—	82^a
Chlorobenzene	PAC	60.0	1.4–17.5	—	0.11^c	0.98	—	90
Chlorobenzene	PAC	11 d	0.015–0.73	—	9.0^c	0.35	—	90
Chlorobenzene	PAC	10 d	0.014–0.401	—	9.9^c	0.31	—	90
Chlordane	?	?	?	—	190.0	0.33	—	121
Chlordane	PAC	120.0	0.0005–0.22	87.0	245.0	0.38	8.8	82
1,2-Dibromochloropropane	PAC	120.0	0.008–0.996	34.7	53.0	0.47	50.0	82
1,2-Dibromochloropropane	?	?	?	—	224.0	0.51	—	121
1,2-Dibromochloropropane	PAC	8 d	0.0002–0.069	—	6.61^c	0.51	—	90
1,2-Dibromochloropropane	PAC	8 d	0.0002–0.086	—	3.84^c	0.46	—	90
1,2-Dichlorobenzene	PAC	11 d	0.0144–1.06	—	19.1^c	0.38	—	90
1,2-Dichlorobenzene	PAC	10 d	0.059–0.293	—	8.4^c	0.58	—	90
1,2-Dichlorobenzene	?	?	?	—	263.0	0.38	—	121
1,2-Dichlorobenzene	PAC	120.0	0.33–27.5	952.0	129.0	0.43	19.0	82
1,2-Dichlorobenzene	GAC-C	?	?	—	300.0	0.43	—	82
1,2-Dichlorobenzene	PAC-A	?	?	—	360.0	0.56	—	82
1,2-Dichlorobenzene	PAC-B	?	?	—	140.0	0.31	—	82
1,2-Dichlorobenzene	PAC-C	?	?	—	89.0	0.50	—	82
cis-1,2-Dichloroethene	PAC	3 d	0.005–0.615	—	0.2^c	0.59	—	90
cis-1,2-Dichloroethene	PAC	31 d	0.019–0.23	—	0.15^c	0.64	—	90
cis-1,2-Dichloroethene	PAC	15 d	0.010–0.214	—	0.12^c	0.63	—	90
cis-1,2-Dichloroethene	?	?	?	—	12.0	0.59	—	121
cis-1,2-Dichloroethene	$PGAC^g$	7 d	$5.23 \times 10^{-6} M$	—	357.0^h	0.556	—	119
trans-1,2-Dichloroethene	PAC	10 d	0.0135–0.415	—	0.62^c	0.45	—	90
trans-1,2-Dichloroethene	PAC	10 d	0.059–0.406	—	0.63^c	0.39	—	90

trans-1,2-Dichloroethene	?	?	?	—	14.0	0.45	—	121
trans-1,2-Dichloroethene	PAC	120.0	0.005–1.0	2.10	3.05	0.51	950.0	82
2,4-Dichloroethene	PAC	30.0	?	—	18.0	0.56	31.0	82
2,4-Dichloroethene	?	?	?	—	67.0	0.27	—	121
2,4-D Isopropylester	PAC	30.0	?	—	283.0	0.63	14.0	82
2,4-D Butylester	PAC	30.0	?	—	200.0	0.52	15.0	82
2,4-D Isooctylester	PAC	30.0	?	—	117.0	0.33	16.0	82
1,2-Dichloropropane	PAC	120.0	0.015–1.0	3.6	5.86	0.6	600.0	82
1,2-Dichloropropane	PAC	3 d	0.0041–0.196	—	0.3[c]	0.59	—	90
1,2-Dichloropropane	PAC	10 d	0.0046–0.126	—	0.4[c]	0.48	—	90
Ethylbenzene	PAC	120.0	2.1–24.3	720.0	53.0	0.79	110.0	90
Ethylbenzene	PAC	120.0	18.0[b]	19.0	—	—	—	82
Ethylbenzene	PAC	15.0	6.0–15.0	—	120.0	0.29	—	82
Ethylbenzene	GAC	2 d	2.0–21.0	—	100.0	0.40	—	82
Ethylbenzene	?	?	?	—	175.0	0.53	—	121
Ethylbenzene	PAC	60.0	2.1–22.5	—	0.23[c]	0.79	—	90
Ethylbenzene	PAC	15.0	3.0–50.0	—	16.2[c]	0.29	—	90
Ethylenedibromide	PAC	4 d	0.0002–0.123	—	0.9[c]	0.46	—	90
Ethylenedibromide	PAC	10 d	0.0011–0.139	—	0.77[c]	0.54	—	90
Ethylenedibromide	?	?	?	—	22.0	0.46	—	121
Heptachlor	?	?	?	—	9320.0	92.0	—	121
Heptachlor	PAC	120.0	0.0058–0.17	132.0	1220.0[i]	0.95	6.6	82
Heptachlor	GAC	?	0.006–0.056	12.3	—	—	—	82
Heptachlor epoxide	PAC	120.0	0.0004–0.1	70.6	1038.0	0.70	—	82
Heptachlor epoxide	?	?	?	—	2120.0	0.75	—	121
Lindane	?	?	?	—	285.0	0.43	—	121
Lindane	PAC	120.0	0.006–1.02	230.0	256.0	0.49	11.0	82
Lindane	PAC	?	?	—	4.5[c]	0.74	—	90
Lindane	PAC	6 d	0.002–0.170	—	15.4[c]	0.43	—	90
Lindane	PAC	?	?	—	0.31[c]	0.34	—	90
Lindane	PAC	7 d	0.0006–0.149	—	14.5[c]	0.39	—	90
Methoxychlor	PAC	?	0.00002–0.46	—	10.0[c]	0.36	—	90
Methoxychlor	PAC	?	0.1–1.0	—	28.0[c]	0.17	—	90
Methoxychlor	PAC	?	0.04–0.5	—	5.83[c]	0.46	—	90
Methoxychlor	?	?	?	—	115.0	0.36	—	121
Pentachlorophenol	?	?	?	—	436.0	0.34	—	121
Pentachlorophenol	PAC	120.0	0.22–9.23	350.0	150.0	0.42	16.0	82
Pentachlorophenol	PAC	60.0	0.22–8.18	—	8.24[c]	0.42	—	90
Pentachlorophenol	PAC	7 d	0.0004–0.041	—	42.4[c]	0.34	—	90
Pentachlorophenol	PAC	7 d	0.0053–0.322	—	14.4[c]	0.36	—	90
PCB-1221	PAC	120.0	0.001–0.611	108.0	242.0	0.7	19.0	82
PCB-1232	PAC	120.0	0.0001–0.353	147.0	630.0	0.73	7.7	82
PCB-1016	GAC	550.0	0.0005–0.1	—	3.44[c]	0.66	—	82
PCB-1016	GAC-A	550.0	0.0005–0.1	—	13.7[c]	0.27	—	82
PCB-1016	GAC-B	550.0	0.0005–0.1	—	15.4[c]	0.25	—	82
PCB-1016	GAC-C	550.0	0.0005–0.1	—	6.7[c]	0.36	—	82
PCB-1016	GAC-D	550.0	0.0005–0.1	—	4.1[c]	0.46	—	82

Table 4.10. Freundlich Adsorption Constants and Concentration Ranges for Phase II Organics (Continued).

Compound	Type of Carbon	Contact Time (min)	Equilibrium Range (mg/L)	Maximum Adsorbed (mg/g)	Freundlich Constants		Carbon Dosage to Reduce 1 mg/L to 0.1 mg/L	Reference
					K (mg/g)/(mg/L)$^{1/n}$	1/n		
PCB-1016	PAC	48 hr	0.0007–0.02	—	3.44^c	0.644	—	82
PCB-1016 + 5 mg/L humic acid	PAC	48 hr	0.001–0.02	—	3.16^c	0.56	—	82
PCB-1254	PAC	48 hr	0.001–0.007	—	0.73^c	1.14	—	82
PCB-1254	GAC	550.0	0.0005–0.05	—	0.73^c	1.14	—	82
PCB-1254	PAC	28 d	0.000011–0.00017	—	11.46^c	1.03	—	90
Styrene	PAC	12 d	0.012–0.148	—	12.1^c	0.48	—	90
Styrene	?	?	?	—	327.0	0.48	—	121
Styrene	PAC	120.0	0.07–6.45	316.0	120.0	0.56	—	82
Styrene	PAC	120.0	18.0^d	28.0	—	—	—	82
Tetrachloroethylene	PAC	120.0	0.007–1.0	35.8	50.8	0.56	64.0	82
Tetrachloroethylene	GAC	2 d	0.06–0.5	—	57.7	0.48	—	82
Tetrachloroethylene	GAC	5 d	?	—	274.0^c	0.56	—	82
Tetrachloroethylene	GAC	?	?	—	84.1	0.41	—	82
Tetrachloroethylene	ACF	120.0	—	—	130.0–390.0	0.77	—	120
Tetrachloroethylene	PGAC	7 d	$9\times10^{-6}M$	—	10388.0^h	0.46	—	119
Toluene	PGAC	7 d	$4.04\times10^{-6}M$	—	991.7^h	0.33	—	119
Toluene	PAC	120.0	1.71–18.5	160.0	26.1^h	0.44	96.0	82
Toluene	GAC	?	1.6–4.4	8.75	—	—	—	82
Toluene	PAC	120.0	66.0^f	50.0	—	—	—	82
Toluene	PAC	15.0	6.0–15.0	—	110.0	0.28	—	82
Toluene	GAC	2 d	2.0–20.0	—	90.0	0.30	—	82
Toluene	PAC	120.0	2.8–49.0	—	348.0	0.48	—	82
Toluene	PAC	?	?	—	40.0	0.35	—	82
Toluene	?	?	?	—	100.0	0.45	—	121
Toluene	PAC	15.0	3.0–50.0	—	15.9^c	0.28	—	90
Toluene	PAC	4 d	0.0023–0.104	—	4.5^c	0.45	—	90
Toluene	PAC	15 d	0.0025–0.672	—	6.3^c	0.37	—	90
Toluene	PAC	30.0	0.014–0.180	—	8.72^c	0.45	—	90
Toxaphene	PAC	28 d	0.000064–0.0005	—	5.73^c	0.74	—	90
Toxaphene	PAC	28 d	0.00032–0.0022	—	2.97^c	0.81	—	90
Toxaphene	?	?	?	—	950.0	0.74	—	121
2,4,5-TP(Silvex)	?	?	?	—	215.0	0.38	—	121
m-Xylene	?	?	?	—	230.0	0.75	—	121
p-Xylene	?	?	?	—	200.0	0.42	—	121
o-Xylene	?	?	?	—	175.0	0.53	—	121
p-Xylene	PAC	120.0	1.5–18.0	130.0	85.0	0.19	15.0	82
o-Xylene	PAC	15.0	5.0–15.0	—	130.0	0.27	—	82
o-Xylene	GAC	2 d	1.5–20.0	—	120.0	0.22	—	82
m-Xylene	PAC	3 d	0.0056–0.166	—	1.3^c	0.75	—	90

o-Xylene	PAC	15.0	3.0–50.0	—	20.13[c]	0.27	—	90
o-Xylene	PAC	8 d	0.0069–1.8	—	7.1[c]	0.47	—	90
o-Xylene	PAC	10 d	0.0105–0.522	—	9.9[c]	0.47	—	90
p-Xylene	PAC	60.0	1.5–12.0	—	28.15[c]	0.16	—	90
p-Xylene	PAC	9 d	0.0016–0.0327	—	11.1[c]	0.42	—	90
p-Xylene	PAC	15 d	0.0029–0.232	—	7.6[c]	0.46	—	90

[a] See Reference 82 for original citation.

[b] From an initial concentration of 115.0 mg/L.

[c] When Ce = 1.0 μg/L.

[d] From an initial concentration of 3.7 mg/L.

[e] When Ce = 1.0 *M*.

[f] From an initial concentration of 3.7 mg/L.

[g] Powdered granular activated carbon.

[h] Units of $(\mu g/g)/(\mu g/L)^{l/n}$.

[i] Believed to be in error. Correct value should be 100.

Table 4.11. Freundlich Constants and Concentration Ranges for Phase V Organics.

Compound	Type of Carbon	Contact Time (min)	Equilibrium Range (mg/L)	Maximum Adsorbed (mg/g)	Freundlich Constants K (mg/g)/(mg/L)$^{1/n}$	Freundlich Constants l/n	Carbon Dosage to Reduce 1 mg/L to 0.1 mg/L	Reference
Adipates								
Dalapon								
Dinoseb								
Diquat	PAC	30.0	0.44–0.86	—	17.4	0.20	82.0	122
Diquat	PAC	60.0	—	—	19.4	0.09	57.0	122
Endothall								
Endrin	PAC	120.0	0.0006–0.11	51.0	666.0	0.8	8.5	82[a]
Endrin	GAC	?	0.00007–0.015	23.6	—	—	—	82[a]
Endrin	PAC	?	?	—	5.0	0.85	—	90
Glyphosate								
Hexachlorobenzene	PAC	120.0	0.079–0.753x10^{-3}	6.2	450.0	0.6	8.0	82
Hexachlorocyclopentadiene	PAC	120.0	0.004–0.8	307.0	370.0	0.17	3.6	82
Oxamyl (vydate) PAHS:								
3,4-Benzofluoranthene	PAC	120.0	0.04–0.583x10^{-3}	4.4	57.0	0.37	37.0	82
3,4-Benzofluoranthene	PAC	120.0	0.172–0.583x10^{-3}	4.3	55.5	0.37	—	82
Benzo(k)fluoranthene	PAC	120.0	0.013–0.194x10^{-3}	1.4	181.0	0.57	18.0	82
Benzo(k)fluoranthene	PAC	120.0	0.065–0.164x10^{-3}	683.0	183.0	0.57	18.4	82
Benzo(ghi)perylene	PAC	120.0	0.015–0.267x10^{-3}	0.61	10.7	0.37	200.0	82
Benzo(ghi)perylene	PAC	120.0	0.071–0.27x10^{-3}	24.6	10.6	0.36	197.0	82
Benz(a)pyrene	PAC	120.0	0.03–0.32x10^{-3}	1.1	33.6	0.44	74.0	82
Benz(a)pyrene	PAC	120.0	1.35–1.6x10^{-3}	1.64	33.6	0.44	—	82
Phthalates[b]	PAC	120.0	—	—	—	—	—	82
Picloram simazine	PAC	?	0.00002–0.0165	—	151.0	0.23	—	90
Picloram simazine	PAC	?	0.002–0.77	—	190.0	0.31	—	90
2,3,7,8-TCDD (Dioxin)								
1,2,4-Trichlorobenzene	PAC	120.0	0.38–15.0	500.0	157.0	0.31	—	82
1,2,4-Trichloroethane	PAC	120.0	0.006–1.0	3.8	5.81	0.6	620.0	82

[a] See Reference 82 for original citation.

[b] See Table 4.6 for several phthalates.

Table 4.12. Removal of PAH by Activated Carbon Treatment (Pittsburgh, Pennsylvania).[125]

Compound	Concentration (ng/L)[a] Raw	Concentration (ng/L)[a] Finished
Fluoranthene	408.3	ND[b]
Benzo[j]fluoranthene	35.7	0.3
Benzo[k]fluoranthene	19.1	0.2
Benzo[a]pyrene	42.1	0.4
Indeno[1,2,3-c,d]pyrene	60.4	1.2
Benzo[g,h,i]perylene	34.4	0.7

[a] Two-stage activated carbon treatment; powdered activated carbon, then GAC filtration (≈30–40 min of EBCT).

[b] ND—Not detected; limits ranging from 0.1 to 4.6 ng/L.

Table 4.13. Freundlich Adsorption Parameters for Several Polynuclear Aromatic Hydrocarbons on Powdered Activated Carbon[a].[126]

Compound	K (mg/g)/(mg/L)$^{1/n}$	l/n	r^2
Naphthalene	277	0.430	0.87
Acenaphthylene	266	0.302	0.88
Acenaphthene	624	0.457	0.87
Fluorene	674	0.604	0.90
Phenanthrene	273	0.406	0.84
Anthracene	330	0.620	0.81
Fluoranthene	242	0.314	0.81
Pyrene	389	0.386	0.78
Triphenylene	532	0.685	0.55
Benz(a)anthracene	216	0.500	0.67
Chrysene	716	0.458	0.62

[a] F–400, 200 mesh, contact time = 1–2.5 days.

filtration reduced the concentration to extremely low levels.[125] The presence of naturally occurring humic acids was shown not to interfere with the rate of adsorption of a model PAH, anthracene.[63]

Polycyclic aromatic hydrocarbons are considered to be naturally occurring because their origin is usually in petroleum. They are released into the environment through a pyrolytic industrial operation of some sort. Examples are preparation of acetylene from natural gas; hydrolysis of kerosene to benzene, toluene, and other organic solvents; and pyrolysis of wood. There is a legitimate concern about the occurrence of these compounds in the human environment because of the carcinogenic properties exhibited in laboratory animals exposed to some PAHs. For example, 3,4-benzpyrene (BP) is, perhaps, the most carcinogenic of all PAHs.

Freundlich isothermal data for 11 PAHs from water into F-400 GAC (200 mesh) at 25°C were generated by batch shake testing for 1 to 2.5 days.[126] Table 4.13 is a summary of the K [(mg/g)/(mg/L)$^{1/n}$] and l/n values for these PAHs, which are adsorbed readily due to their hydrophobic nature and low solubility in nature.

Total Trihalomethanes

The discovery that disinfection of drinking waters containing low concentrations of naturally occurring organic matter with chlorine results in formation of trihalomethanes led the EPA to amend the National Interim Primary Drinking Water Standard to include a maximum contaminant level of 0.10 mg/L for total trihalomethanes (see Chapter 1 for amendments). Compounds covered by the regulation are: chloroform, bromodichloromethane, dibromochloromethane, and bromoform. Consequently, removal of these compounds by activated carbon adsorption has been studied extensively in both pure systems and pilot and full-scale studies.[82] For example, these THMs were examined for their adsorption on Nuchar WV-6 GAC also in equilibrium and column modes.[82] Table 4.14 shows Freundlich constants for their adsorption on GAC, whereas their removal in a column operation is seen in Table 4.15. The order of appearance of the four compounds coming off the column is predicted quite well from isothermal data. $CHClBr_2$ and $CHCl_2Br$ are transposed in the column study, perhaps because of similar adsorptive characteristics. However, quantities of the four

Table 4.14. Freundlich Constants and Concentration Ranges for Total Trihalomethanes.

Compound	Type of Carbon	Contact Time (min)	Equilibrium Range (mg/L)	Maximum Adsorbed (mg/g)	Freundlich Constants		Carbon Dosage to Reduce 1 mg/L to 0.1 mg/L	Reference
					K (mg/g)/(mg/L)$^{1/n}$	1/n		
Chloroform	PAC-A	7 d	1.67x10^{-6}*M*	—	42.2^{a}	0.75	—	119
Chloroform	PAC-C	7 d	3.1x10^{-6}*M*	—	106.0^{a}	0.65	—	119
Chloroform	PAC-D	7 d	3.74x10^{-6}*M*	—	159.0^{a}	0.63	—	119
Chloroform 4°C	PAC	7 d	0.02–0.256	—	0.24^{b}	0.61	—	69
Chloroform 15°C	PAC	7 d	0.024–0.184	—	0.081^{b}	0.855	—	69
Chloroform 30°C	PAC	7 d	0.047–0.376	—	0.119^{b}	0.64	—	69
Chloroform 45°C	PAC	7 d	0.062–0.359	—	0.053^{b}	0.79	—	69
Chloroform	ACF^{c}	120	—	—	0.084^{b}	0.73	—	69
Chloroform	ACF	120	—	—	0.110	0.73	—	127
Chloroform	PGAC^{d}	300	—	—	0.0323	0.73	—	127
Chloroform	GAC	360	—	—	0.0165^{e}	0.60	1900.0	127
Bromodichloromethane	ACF	120	—	—	0.378^{b}	0.71	—	82
Bromodichloromethane	PGAC	300	—	—	0.119^{b}	0.71	—	127
Bromodichloromethane	ACF	120	—	—	0.267^{b}	0.71	—	127
Bromodichloromethane	PAC	120	0.011–1.0	6.2	7.9	0.61	—	127
Bromodichloromethane	GAC	5 d	?	—	24.6	0.75	—	82
Bromodichloromethane	GAC	360	?	—	0.15^{e}	0.51	500.0	82
Bromodichloromethane	PAC-A	7 d	?	—	143.0^{a}	0.745	—	82
Bromodichloromethane 4°C	PAC	7 d	0.01–0.265	—	0.525^{b}	0.58	—	119
Bromodichloromethane 15°C	PAC	7 d	0.017–0.085	—	0.303^{b}	0.71	—	69
Bromodichloromethane 30°C	PAC	7 d	0.012–0.13	—	0.164^{b}	0.75	—	69
Bromodichloromethane 45°C	PAC	7 d	0.015–0.13	—	0.152^{b}	0.73	—	69
Dibromochloromethane 4°C	PAC	7 d	0.01–0.17	—	0.79^{b}	0.605	—	69
Dibromochloromethane 15°C	PAC	7 d	0.01–0.09	—	0.641^{b}	0.592	—	69
Dibromochloromethane 30°C	PAC	7 d	0.01–0.107	—	0.344^{b}	0.733	—	69
Dibromochloromethane 45°C	PAC	7 d	0.01–0.13	—	0.231^{b}	0.775	—	69
Dibromochloromethane	GAC	360	?	—	0.13^{e}	0.62	410.0	82
Dibromochloromethane	PAC	120	0.0009–1.0	5.6	4.8	0.34	410.0	82
Dibromochloromethane	PAC	60	?	—	0.1^{e}	0.93	—	90
Dibromochloromethane	ACF	120	—	—	0.393^{b}	0.71	—	127
Dibromochloromethane	ACF	120	—	—	0.578^{b}	0.71	—	127
Dibromochloromethane	PGAC	300	—	—	0.119^{b}	0.71	—	127
Bromoform	PAC	120	0.013–1.0	12.6	19.6	0.52	150.0	82
Bromoform	GAC	5 d	0.005–0.33	25.3	73.1	0.63	—	82
Bromoform	GAC	360	—	—	0.185^{e}	0.32	—	82
Bromoform	PAC	60	—	—	0.62^{e}	0.83	—	90

Bromoform 4°C	PAC	7 d	0.01–0.122	—	3.35[b]	0.36	—	69
Bromoform 15°C	PAC	7 d	0.01–0.178	—	1.34[b]	0.49	—	69
Bromoform 30°C	PAC	7 d	0.011–0.097	—	0.89[b]	0.56	—	69
Bromoform 45°C	PAC	7 d	0.011–0.184	—	0.503[b]	0.654	—	69

[a] $(\mu g/g)(\mu g/L)^{1/n}$.

[b] $(mg/g)/(\mu g/L)^{1/n}$.

[c] Activated carbon fibers.

[d] Powdered granular activated carbon.

[e] When Ce = 1.0 μg/L.

Table 4.15. GAC Performance for Removal of Light Halogenated Hydrocarbons on Columns[a].[82]

Compound	C_0 (mg/L)	Breakthrough Point	Amount Adsorbed from a Mixture	Amount Adsorbed as Single Compounds
$CHCl_3$	1.20	0.10	0.593	0.829
CCl_4	1.89	0.094	1.88	—
$CHCl_2Br$	3.69	0.10	3.14	3.22
$CHClBr_2$	2.99	0.10	3.64	—
$CHBr_3$	11.14	0.05	11.12	20.45

[a] Phosphate buffer, pH 7. Temperature = 24°C.

Table 4.16. THM Concentrations in PAC Experiments, Louisville, Kentucky Tap Water[a].[128]

PAC Dose (mg/L)	Exposure Time (min)	$CHCl_3$ (μg/L)	Percent Removal	THMs[b]		$CHBr_2Cl$ (μg/L)	Percent Removal	TTHM (μg/L)	Percent TTHM Removal
				$CHBrCl_2$ (μg/L)	Percent Removal				
0	0	35.2	—	12.3	—	0.7	—	48.2	—
(Control)	5	30.3	—	10.3	—	1.1	—	41.7	—
	15	31.8	—	10.2	—	0.7	—	42.7	—
	30	30.2	—	10.5	—	0.7	—	41.4	—
	60	29.4	—	8.7	—	0.5	—	38.6	—
25	0	35.2	0	12.3	0	0.7	0	48.2	0
	5	26.3	13	7.2	30	0.3	73	33.8	19
	15	24.1	24	5.9	42	0.3	57	30.3	29
	30	23.2	23	5.3	50	0.2	71	28.7	31
	60	19.2	35	3.9	55	0.1	80	23.2	40
50	0	35.2	0	12.3	0	0.7	0	48.2	0
	5	25.0	17	4.9	52	0.2	82	30.1	28
	15	18.1	43	3.1	70	0.1	86	21.3	50
	30	17.7	41	2.7	74	0.1	86	20.5	50
	60	15.5	47	2.1	76	0.1	80	17.7	54
100	0	35.2	0	12.3	0	0.7	0	48.2	0
	5	17.4	43	2.8	73	0.1	91	20.3	51
	15	13.2	58	1.4	86	0.0	100	14.6	66
	30	10.1	67	1.0	90	0.0	100	11.1	73
	60	9.7	67	0.8	91	0.0	100	10.5	73

[a] Free chlorine residual = 0.12 mg/L.
[b] No bromoform found.

compounds adsorbed in the carbon column suggest this mode of treatment is somewhat inefficient. This inefficiency is seen (Table 4.14) also in the quantities of PAC needed to reduce an initial 1.0 mg/L to 0.1 mg/L. All those PAC dosages in Table 4.14 are much too high for normal water treatment plant operation.[82]

A laboratory study confirmed the inefficiency of PAC to remove total trihalomethanes (TTHM) from drinking water.[128] Various quantities of PAC were added to tap water that contained some free chlorine residual, 0.12 mg/L (Table 4.16). Among other things, at least 50 mg/L PAC are needed to effect a 50% removal of TTHM within a treatment time of 60 minutes. This study was also consistent with others where the bromine-containing compounds were removed more efficiently than chloroform.

Pilot-plant and full-scale plant studies have confirmed many of the conclusions of the above laboratory experiments.[129] Apparently, the inefficiency of PAC and GAC in adsorbing the THMs prompted the USEPA to recommend alternative disinfectants, precursor removal, and the discontinuance of pre-Cl_2 as the BAT for removal of these DBPs (Table 1.7).

The proposed Information Collection Rule (see Chapter 1) provides for the use of the rapid small-scale column test (RSSCT) to assess the effectiveness of GAC for control of DBP under a simulated distribution system (SDS). This test was developed several years ago to evaluate the GAC adsorption of various organics in a small-column configuration under laboratory conditions.[82] Consequently, this technique has been adapted for the prediction of control of DBP formation by GAC where TTHMs and total organic halide (TOX) were measured in the influents and effluents of the laboratory- and field-scale columns.[129a] In this study, one set of laboratory RSSCTs (Cincinnati, Ohio) and one set of field- or pilot-scale absorber runs (Palm Beach County, Florida) were conducted. The latter was a groundwater with a high TOC. Two bituminous-based and one lignite-based GAC were employed in both the laboratory- and field-scale situations. Throughout the operation of these columns, the removals of NOM [as measured by TOC and UV absorbance of 254 nM(SAC)] and DBP precursors (as measured by TOX and TTHMs) were evaluated under SDS conditions.

The laboratory-based RSSCTs were effective in prediction of the field-scale breakthrough behavior of NOM and subsequent DBP formation with the three GACs.[129a] For each parameter evaluated, except TOC, the nonabsorbable fractions measured in the field-scale fractions break through "immediately" and presumably serve as precursors for DBPs. Other parameters that were predicted well by the RSSCT-laboratory scale were the initial rise in the effluent concentration and time to 50% breakthrough. These predictions compared well with the field/pilot-scale observations of the performance of the three carbons with respect to TOC, SAC, TOXSDS, and TTHMSDC. After the initial breakthrough, the shapes of the breakthrough curves for the individual TTHMs were well predicted by the RSSCTs in 9 of 12 runs. For this water, the breakthrough behavior of TOC seems to predict that of TTHMSDC. UV-absorbing substances were removed better by the GACs compared to TOC. SAC "seemed" to predict the breakthrough behavior of TOXSDS. For the individual TTHM species, GAC adsorption worked best in controlling the formation of $CHCl_3$ and worst for $CHBr_3$.

The use of RSSCT in the laboratory as a predictor for field/pilot-scale behavior seems to work well in the OH/FL study.[129a] However, the removal of NOM and DBP precursors by the three GACs was not particularly effective. This is not surprising in view of the adsorption isothermal data cited earlier in this chapter. Nonetheless, the authors conclude: "this study shows that the RSSCT can reasonably predict the field-scale behavior of GAC for controlling DBP formation."[129a]

The RSSCT study described above was extended to an examination of several raw water sources and four GACs for the removal of DBP precursors as measured by TOC.[129b] Here again, the authors conclude that the RSSCT was successful in predicting the NOM breakthrough in pilot- or full-scale GAC columns. Several parameters were examined: control of DBPs, TOC, and UV_{254}, seasonal influent water quality, operation of the columns to breakthrough for stage 1 and 2 target MCLs for TTHMs and HAA5 (TTHM levels control reactivation frequency), carbon usage rate as affected by the empty bed contact time, and capital costs associated with GAC contactors. There is a considerable amount of pragmatic operational data in this RCCST study.

A laboratory study evaluated the effect of the presence of molecular oxygen on the adsorptive behavior of chloroform, chlorobenzene, and dibromochloropropane on PAC.[129d] Experiments were conducted for the VOC solutions in deionized water and in water supplemented with BOM. Apparently molecular oxygen did not exert any influence on the adsorptive capacities (via Freundlich isotherms) of the PAC (Filtrasorb 400) for these three VOCs when the isotherms were conducted in deionized water. On the other hand, molecular oxygen significantly increased the adsorption of BOM that was attributed to its "conglomeration" of BOM on the carbon's surface. Again, the presence of BOM reduced the adsorptive capacities of PAC for the VOCs. Subsequently, the presence of molecular oxygen further reduced the adsorptive capacities of the PAC for the VOCs in the presence of BOM. This, of course, is attributed to a reduction in the available surface area of the carbon for the VOCs. No satisfactory explanation was given for the mechanistic role of molecular oxygen for increasing the adsorption of BOM on the PAC.

Disinfectants/Disinfection By-Products (Phase VIa)

The 1991 Drinking Water Priority List (Table 1.5) lists several inorganic disinfectants and their reaction by-products that may be regulated in the late 1990s. These include: chloramines, chlorate, chlorite, chlorine dioxide, cyanogen chloride, hypochlorite ion, and several halogenated organic compounds (see Chapter 2). Historically, the principal use of chlorination in water treatment is disinfection (see Chapter 11). However, chlorination is also practiced for taste and odor control (superchlorination), control of odor-causing algae and microorganisms, and control of ammonia by breakpoint chlorination. The chlorine doses required to achieve any of the above goals, whether using free residual chlorination or combined residual chlorination, can be sufficiently high that dechlorination may be required. GAC adsorption has proved to be an effective dechlorination process. However, recent concern about the possible human health effects of chlorine and its by-products (see Chapter 1) has led to the discontinuation of such treatments as prechlorination and superchlorination. In the 1990s, PAC and GAC are being evaluated for by-product removal.

Surface Reactions with Activated Carbon

Free Chlorine

The reaction between free chlorine and activated carbon has been reported to proceed as:[130–132]

$$C^* + HOCl = CO^* + H^+ + Cl^- \qquad (38)$$

where C = an activated carbon site
CO* = a surface oxide on the carbon.

If OCl^- is the free chlorine species, then no H^+ would be expected as an end product unless the oxide is acidic and liberates a proton.[133] At pH values below 6.6, HOCl predominates, while at pH values higher than 8.6, the hypochlorite ion (OCl^-) is the predominant species. Both forms of free chlorine are converted to the chloride ion.

Combined Chlorine

The reaction of chloramines with activated carbon has been studied by Bauer and Snoeyink,[34] who proposed the following stoichiometric relationship for the interaction of dichloramine with carbon:

$$\begin{aligned} &C^* + 2NHCl_2 + H_2O = \\ &CO^* + 4H^+ + 4Cl^- + N_2 \end{aligned} \qquad (39)$$

The nitrogen in the dichloramine is converted to nitrogen gas. Also, two dichloramine molecules react with carbon to produce one surface oxide, while each molecule of free chlorine is capable of forming such an oxide. Therefore, four times as much dichloramine (expressed as Cl_2) is needed to react with active carbon to produce an equivalent amount of surface oxides, compared to free chlorine.[132] The capacity of activated carbon for dechlorination of dichloramine is, therefore, much higher than for free chlorine.

The reaction between monochloramine and activated carbon is proposed[134] to proceed according to:

$$\begin{aligned} &C^* = NH_2Cl + H_2O = \\ &CO^* + H^+ + Cl^- + NH_3 \end{aligned} \qquad (40)$$

The monochloramine is reduced to ammonia and a surface oxide group is formed. However, in the presence of an already existing surface oxide group on the carbon, the following reaction occurs:[134]

$$\begin{aligned} &CO^* + 2NH_2Cl = \\ &C^* + 2H^+ + 2Cl^- + H_2O + N_2 \end{aligned} \qquad (41)$$

In this case, the monochloramine is oxidized to nitrogen and the carbon is regenerated by removing the surface oxide. Therefore, in a continuous-flow operation, surface oxides formed according to Reaction 37 are regenerated according to Reaction 38, and a steady state is reached whereby the amount of ammonia produced would be equal to the net reduction in chloramine-N (NH_3-N plus NH_2Cl-N).[132,134]

Chlorine Dioxide, Chlorite, and Chlorate

ClO_2 reacts rapidly with activated carbon, but the nature of the reaction changes as pH changes. At pH 3.5, Cl^-, ClO_2^-, and ClO_3^- are products found in the effluent of a column receiving only ClO_2, but Cl^- is the predominant product. At pH 7.9, the same end products are formed, but ClO_2^- is now the predominant species. The ClO_2^- concentration in the column effluent is initially low, but then rapidly increases, as would be expected if the carbon initially reacted with the ClO_2^- and then its capacity to react with it was used up.[135]

Separate experiments consisting of ClO_2^- solutions at pH 7 applied to GAC columns showed that fresh carbon readily destroyed ClO_2^-, presumably by the reaction:[136]

$$ClO_2^- + C^* \rightarrow C^*O_2 + Cl^- \qquad (42)$$

The reaction capacity of the fresh carbon was saturated after 80 to 90 mg ClO_2^- reacted per gram of GAC.

Solutions of ClO_2^- were contacted with several concentrations of PAC for 15 and 30 minutes, and for 7 days in a laboratory study with organic-free water.[137] PAC dosages ranged from 0 to 100 mg/L and the pH value was not controlled. When the contact time was 15 minutes, ClO_2^- was reduced to Cl^-, and ClO_3^- was not formed. However, when the contact time was extended to 30 minutes and 7 days, ClO_2^- was reduced to Cl^- and oxidized to ClO_3^-, a disproportionation reaction (Figure 4.20). This is an undesirable reaction, inasmuch as ClO_3^- may have adverse health effects on humans. However, when PAC was enmeshed in alum floc, ClO_2^- removals were improved significantly, with no mention of ClO_3^- formation.

Pilot- and full-scale plant GAC columns for removal of ClO_2^- were evaluated at three surface water treatment plants.[138] Virgin and preloaded GAC with EBCT ranging from 1.65 to 6.2 minutes were operated for 21–49 days in the pilot-plant. Influent ClO_2^- concentrations ranged from 1.01 to 2.31 mg/L and ClO_3^- contents ranged from 113 to 0.52 mg/L. Similar conditions existed for the full-scale plant experiments. In summary, it was concluded that GAC filtration was not a feasible means of removing ClO_2 by-products. Removal efficiencies for ClO_2^- and ClO_3 declined rapidly from the onset of the filter runs. Sulfur-based reduction of the by-products was unsuccessful also.

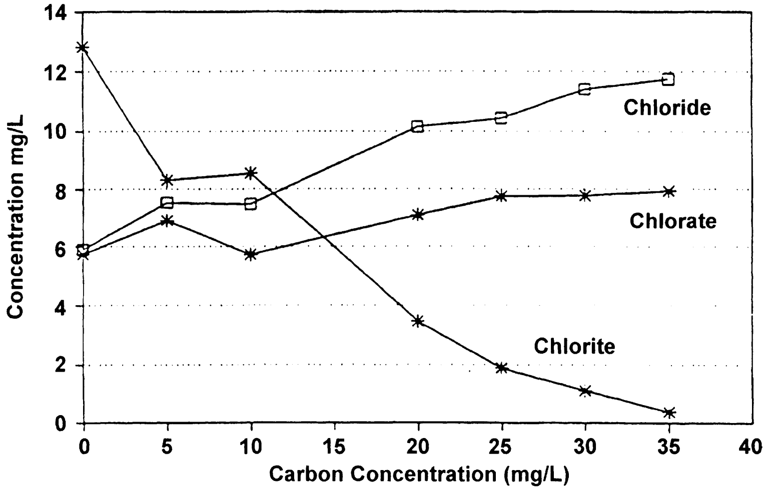


Figure 4.20. Chlorite, chloride, and chlorate remaining in distilled water after one week of contact with varying concentrations of powdered activated carbon.[137]

Removal of Inorganic and Organic Mercury

Considerable research has been conducted on the activated carbon removal of various inorganic species from water.[82] Several ions, notably the "heavy" metals, can be removed by PAC and GAC, but the capacity for many substances is quite "low." Of those inorganics regulated in potable water, the BAT of GAC is recommended for mercury only (Table 1.7). Consequently, the efficacy of PAC and GAC for mercury removal is evaluated here.

The MCL for mercury in drinking water is 0.002 mg/L (Table 1.7). There are few historical data on the occurrence of Hg in ground, surface, and finished waters in the United States. Mercury contents of < 0.5 to 6.8 μg/L have been reported for several surface waters in the United States. Only a few Hg-bearing minerals occur in nature. The most common are sulfides [cinnabar and metacinnabar (HgS)] and native mercury. In aqueous systems, mercury can exist in one of these oxidation states: the free metal, Hg^0, the mercurous ion, Hg_2^+, or the mercuric ion, Hg_2^{2+}. Mercury readily forms complexes with many inorganic anions and organic constituents, for which methylation reactions have been documented. An important characteristic of Hg is its tendency to adsorb and adhere to various types of surfaces, which has immediate application to potable water treatment.

Several investigations have been conducted on the utilization of PAC and GAC for Hg removal. Figure 4.21a shows the log-log plot of the adsorption data for inorganic Hg and CH_3Hg^+.[139] These data indicate that each milligram per liter of PAC (Nuchar Aqua A) removes 0.0001 mg of inorganic Hg and CH_3Hg^+. Pilot plant studies with PACs (Dacro-B and Dacro-M) and GACs (Hydrodarco 1030 and Filtrasorb 100) were conducted.[140] When PAC was used in conjunction with ferric sulfate, Hg removals were greater than by either treatment alone. Cumulative removals for inorganic mercury by GAC filtration ranged from 49 to 97%, whereas organic Hg removals ranged from 80 to nearly 100%.[140] Exhausted GAC was as effective as fresh GAC. Figure 4.21b shows the effect of pH on removal of inorganic mercury by PAC (Dacro HDB).[140] Figure 4.21c shows the adsorption of CH_3Hg^+ by three different types of PACs: PAC-1, lignite base (Dacro HDB); PAC-2, petroleum base (Amoco PX-21); and PAC-3, bituminous base (Nuchar Aqua).[141] With the exception of PAC-3, methyl mercury removals were decreased as the pH value was increased from 7 to 9. PAC-1 apparently was the most effective of the three powdered carbons. At pH 7, the MCL for Hg was reached by 80 to 100 mg/L PAC-1.[141] Batch and column tests were conducted for Hg removal by PAC (Filtrasorb 300, 270 mesh) and GAC (Filtrasorb 300, 8 x 30 mesh).[142] Typical log-log plots of the adsorption data from batch tests for pH values of 4 and 10 are seen in Figure 4.22. Experimental conditions were 2.0 g carbon, 200 mL of 10.0 mg/L Hg (II), and 6 hours of agitation at 20°C. Greater adsorption occurred at the lower pH value of 4. For example, at 1 mg/L Hg, the quantity adsorbed was 0.14 mg Hg/g carbon at pH 10, whereas the quantity at pH 4 was 1 mg Hg/g. Breakthrough curves for the carbon columns are seen in Figure 4.23 for pH values 4 and 10. For the latter system, Hg broke through within the first day, whereas no breakthrough occurred within 5 days at pH 4. PAC has been employed with conventional coagulation treatment to enhance the removal of mercury. For example, a PAC dosage of 65 mg/L and an alum dosage of 30 mg/L effected a reduction in excess of 70% in the inorganic mercury content. This was greater than the 40% removal with only alum in Ohio River water.[139] Similar results were obtained with another PAC (Nuchar

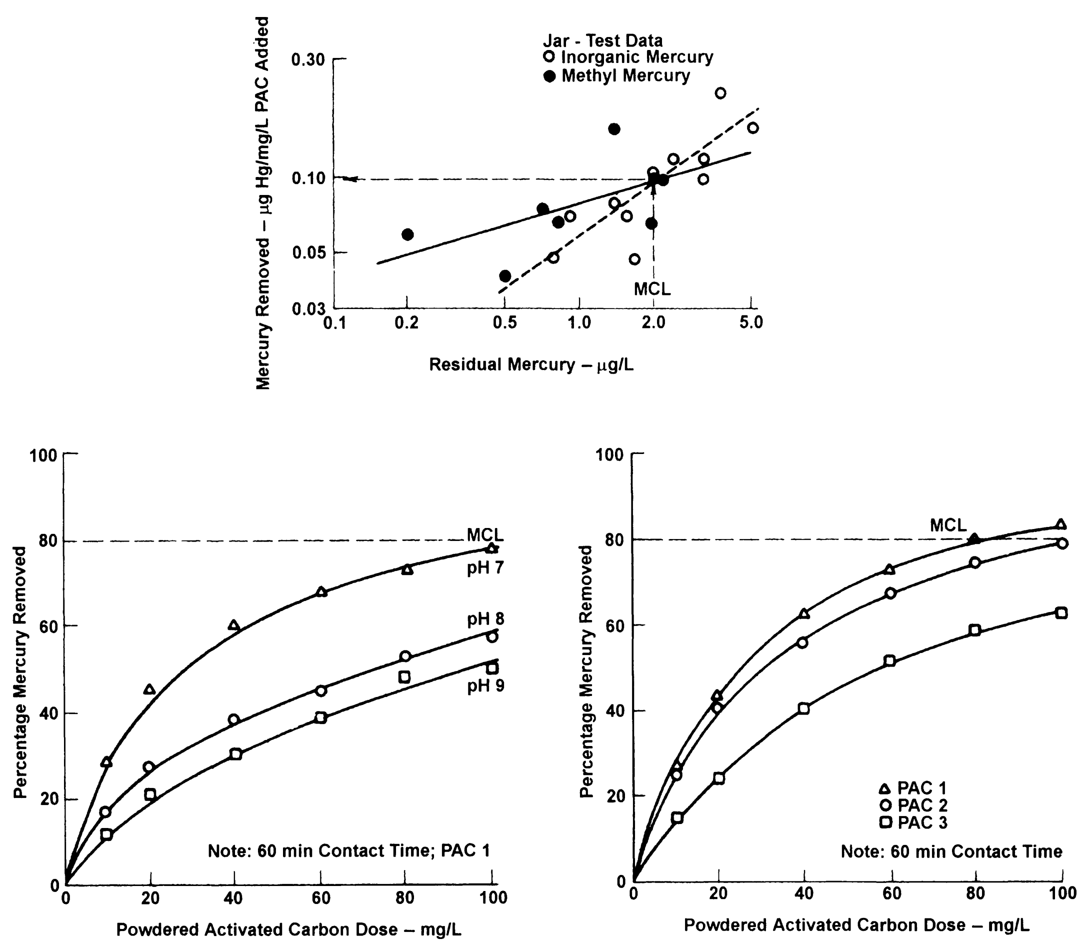


Figure 4.21. (a) Freundlich isotherms for mercury adsorption with PAC. Reproduced from Logsdon and Symond,[139] courtesy of the American Water Works Association. (b) Effect of pH on removal of inorganic mercury (0.010 mg/L) with PAC treatment. Reproduced from Thiem,[141] courtesy of the American Water Works Association. (c) Removal of methyl mercury (0.010 mg/L as Hg) by PAC at pH 7. Reproduced from Sorg,[140] courtesy of the American Water Works Association.

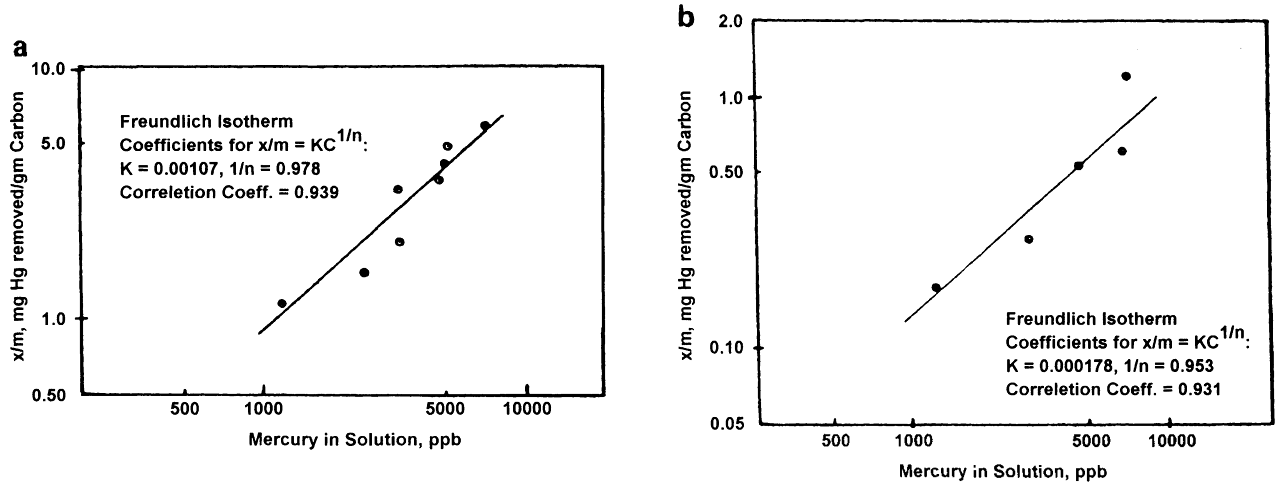


Figure 4.22. Adsorption isotherm for Hg(II) and PAC at 20°C and (a) pH 4 and (b) pH 10. Reproduced from Humenick and Schnoor,[142] courtesy of the American Society of Civil Engineers.

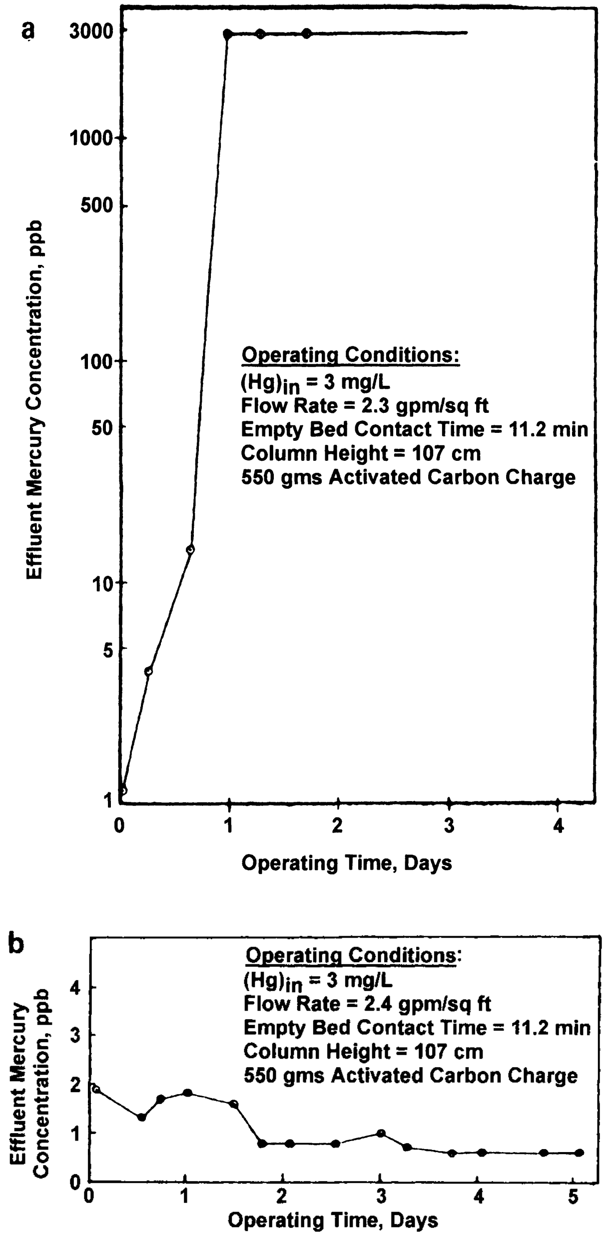


Figure 4.23. Carbon-only system: column run at 25°C and (a) pH 10 and (b) pH 4. Reproduced from Humenick and Schnoor,[142] courtesy of the American Society of Civil Engineers.

W-C1000N) used in conjunction with either alum or iron coagulants.[143] A 30 mg/L quantity of this PAC increased mercury (0.5 mg/L) removals from 35 to 73% for alum systems and from 67 to 85% for iron systems.

Several pilot-plant experiments have evaluated the additional benefits of PAC with conventional water treatment for organic (methyl) mercury removal.[140] Table 4.17a shows results of these experiments, and Table 4.17b shows results from studies on the removal of inorganic mercury. The presence of PAC apparently increases mercury removal when used in conjunction with conventional treatments.[140] (Some researchers do not consider ferric sulfate to be a conventional coagulant.) The increase in mercury removal is attributed to PAC and GAC adsorption. Also, the reduction data for virgin and exhausted activated carbon columns suggest continued mercury removal after the carbon has been exhausted for organics removal. This may or may not be due to mercury adsorption. Chelation of mercury may be significant here. Some experimental evidence exists to support this.[141]

Eleven different brands of commercial activated carbon were evaluated for their removal of Hg (II) in a laboratory study.[144] A very high percentage (99 to 100%) of total Hg removal was obtained by all types of activated carbons, especially at pH values of 4 to 5 with dosages of 1,000 mg/L. Above and below these pH values, removal of Hg decreased considerably. Freundlich isotherms were used to describe the adsorption, with K values ranging from 6.3 (pH 11) to 62.9 (pH 4) μmol/g. Adsorption and reduction were thought to be the mechanisms of removal. In another PAC study, Freundlich constants of K = 20 mg/g, and $1/n = 0.46$ were obtained on F-400.[145] A GAC dosage of 100 mg/L, a pH value of 7.0, and a contact time of 60 min produced a Freundlich isotherm with a K value of 0.5 $(\mu g/mg)/(\mu g/L)^{1/n}$ and $1/n = 0.25$.[146] The GAC in this study was sized in the 12 × 32 mesh range.

PRETREATMENT FOR REMOVAL OF ORGANIC COMPOUNDS

Treatment prior to adsorption is especially appropriate because the quantity of organic matter presented to the carbon is reduced considerably. Also, characteristics of the organic compounds may be rearranged whereby their adsorptive properties and their biological degradability are altered.[147] Several techniques are available: chemical coagulation, aeration for volatilization, and oxidation by O_3, ClO_2, and Cl_2. Most of the research on pretreatment has been on a full-scale water treatment plant. Consequently, the results are applicable immediately. An example is seen in Figure 4.24, where four adsorption isotherms are given for different pretreatments.[148] Ozonated Rhine River bank filtrate was coagulated with $FeCl_3$ and $Al_2(SO_4)_3$ prior to adsorption. The isotherm from the $FeCl_3$ coagulated water shows very little effect, whereas the $Al_2(SO_4)_3$ system gave a higher isotherm. This suggests a better adsorption of the remaining organic compounds after coagulation. Another example is seen in Figure 4.25, where five adsorption isotherms are given for Rhine bank filtrate.[149] The combination of ozonation and clarification resulted in better

Table 4.17a. Results of Conventional Coagulation and PAC Pilot Plant Tests for Organic Mercury Removal.

PAC (mg/L)	Length of Test (hr)	Test Water	Coagulant		pH of Treated Water	Turbidity of Raw Water (ntu)	Average Raw Water Mercury Concentration (mg/L)	Percentage Mercury Removed				
									Filtered Water			
									Dual-Media Filter	GAC Filters		
			Type	Dose (mg/L)				Settled Water		Virgin GAC	Exhausted GAC	Virgin GAC
9[a]	54	Cincinnati tap[c]	Ferric sulfate	31	7.0	<1.0	0.0054[d]	24	31	100[e]	100[f]	86[g]
17[a]	54	Cincinnati tap	Ferric sulfate	31	7.0	<1.0	0.0045	32	38	99	100	99
7[b]	57	Cincinnati tap	Ferric sulfate	35	7.0	<1.0	0.0056	27	40	100	100	98
7[b]	40	Cincinnati tap	Ferric sulfate	28	7.0	<1.0	0.0055	5	8	100	100	99
0	61	Cincinnati tap	Ferric sulfate	28	6.8	<1.0	0.0037	0	19	100	97	84

[a] Darco-B, ICI Americas, Inc., Wilmington, Delaware.
[b] Darco-M, ICI Americas, Inc., Wilmington, Delaware.
[c] Water spiked with CH_3 HgCl.
[d] Detectable limit of 0.0005 mg/L was used to compute percentage where effluent was at or below detectable limit; value reported with > symbol.
[e] Hydrodarco 1030, ICI Americas, Inc., Wilmington, Delaware.
[f] Filtrasorb 100, Calgon Corp., Pittsburgh, Pennsylvania.
[g] Filtrasorb 200, Calgon Corp., Pittsburgh, Pennsylvania.

Source: Reproduced from Sorg,[140] courtesy of the American Water Works Association.

Table 4.17b. Results of Conventional Coagulation Pilot Tests for Inorganic Mercury Removal.

Length of Test (hr)	Test Water	Coagulant		pH of Treated Water	Turbidity of Raw Water (ntu)	Average Raw Water Mercury Concentration (mg/L)	Percentage Mercury Removed				
								Filtered Water			
								Dual-Media Filter	GAC Filters		
		Type	Dose (mg/L)				Settled Water		Virgin GAC	Exhausted GAC	Virgin GA
93	Ohio River	Ferric sulfate	28	8.0	5	0.0055	13	20	55	49	—
99	Ohio River	Alum	30	8.0	31–76	0.007	63	74	—	87	>93
91	Ohio River	Ferric sulfate	29	8.1	10–20	0.008	73	73	—	80	88

[a] Turbidity of tap water adjusted with bentonite clay.
[b] Raw water spiked with $HgCl_2$.
[c] Filtrasorb 200, Calgon Corp., Pittsburgh, Pennsylvania.
[d] Hydrodarco 1030, ICI Americas, Inc., Wilmington, Delaware.

Source: Reproduced from Sorg,[140] courtesy of the American Water Works Association.

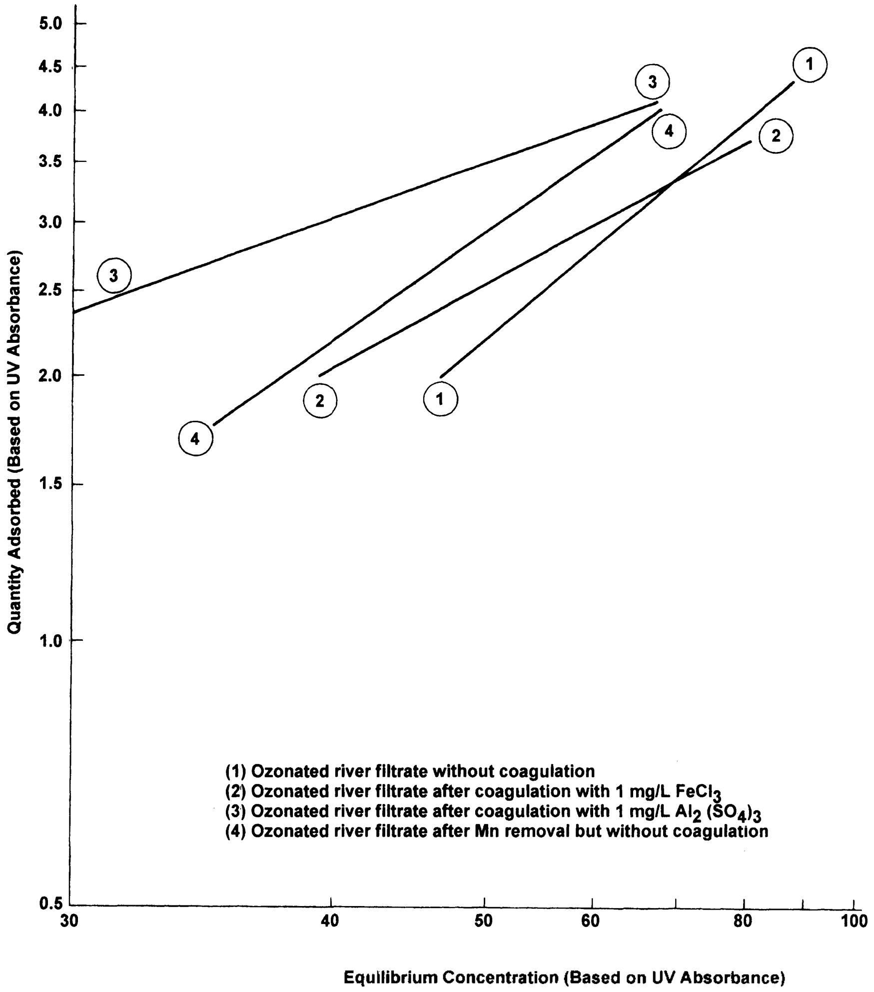


Figure 4.24. Adsorption isotherms after coagulation under various conditions. Reproduced from McCreary and Snoeyink,[147] courtesy of the American Water Works Association.

adsorption of organics than either process alone. Details of the efficiencies of the various pretreatments are documented well in Reference 82.

BIOLOGICAL GROWTH IN CARBON BEDS

GAC beds used in water treatment develop substantial microbial growth after a short period of operation, both in the carbon granules and the effluent water.[46,99,101,150–155] This increase in bacterial population is encountered irrespective of the pretreatment method, including prechlorination. Residual chlorine in the influent is adsorbed in the top carbon layers and is rendered ineffective in controlling the bacterial population. The main source of the microorganisms is the influent water population, which is readily adsorbed by the carbon. Also, virgin carbon may contain a significant number of bacteria. Several batches of GAC were analyzed in the author's laboratory and were found to contain an average of 2000 cells/g of carbon (standard plate count at 35°C). Establishment of the bacterial population is attributed to an increased concentration of adsorbed organics on the carbon surfaces that serve as nutrients, and the large surface area of the carbon granules that serve as an attachment medium. Attachment of the microorganisms to the carbon surface has been shown by scanning electron microscopy to be in sparsely scattered single bacterial clumps.[152,153,156] A small fraction of the surface appears to be occupied by the bacteria, and no uniform biofilm around the carbon granules was observed. The highest bacterial density is reported to be in the macropores. Individual bacterial cells are small enough to fit into the macropores (50–100 μm in size) of the GAC, where they are protected from shear forces. On the other hand, bacteria are too large (1–16 μm) to fit into the micropores, some of which are less than 0.5 μm in di-

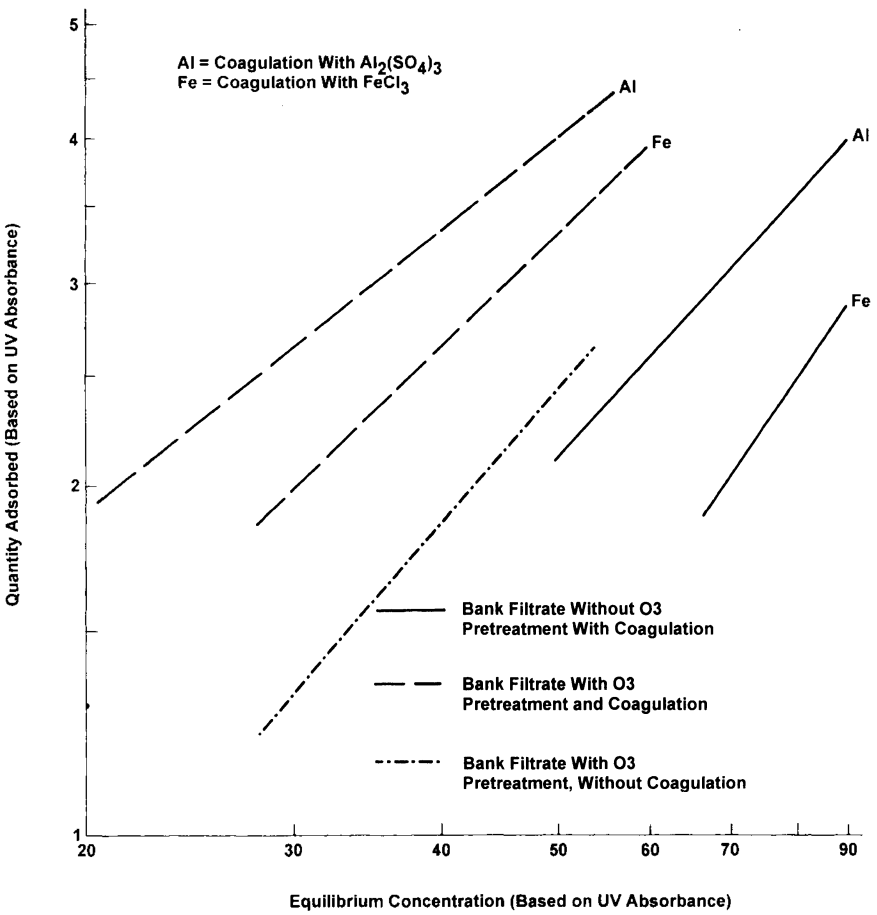


Figure 4.25. Adsorption isotherms after various pretreatments (Düisberg-Wittlaer). Reproduced from McCreary and Snoeyink,[147] courtesy of the American Water Works Association.

ameter. Since the micropores are about 99% of the available carbon surface area, bacteria would occupy only 1% of the total GAC surface area and, therefore, would not interfere with the adsorption process.[154,156] Bacterial growth is attributed to the utilization of adsorbed organics by one of two mechanisms: the dissolved organics adsorbed on the external surface and the macropores are utilized rapidly, or the organics adsorbed in the micropores are dissolved and are utilized slowly. Desorption can occur by displacement of the loosely adsorbed, biodegradable compounds by more strongly adsorbed organics or by enzymes secreted by bacteria present in the outer macropores. Neither of these proposed mechanisms has been demonstrated conclusively to date.[157] The mechanism of surface attachment of the bacteria has been discussed recently by Marshall.[158] Attachment apparently can be either reversible, with detachment produced by shearing action of fluid mixing and by mobility of the sorbed bacteria, or it can be irreversible, mediated by extracellular enzymes.

The bacterial density in carbon beds and effluent waters has been discussed by several investigators. Conflicting results have been reported due to variation in operating conditions, sample locations, and nonuniformity in the bacterial measurement techniques (type of medium, incubation temperature, and incubator period). However, the general trend is that the bacterial population increases rapidly in the carbon granules almost immediately after startup. It may reach values in the range of 10^3–10^5 cells/g of wet carbon and continues to rise until a pseudo-state cell level in the range of 10^5–10^8 of wet carbon is reached. The bacteria level in the filter effluent also rises sharply after startup from 10^1 to 10^5 cells/mL of water.[99,150,153] Size of the population within the filter and in the effluent varies with changes in the organic content of the water and with seasonal changes in tem-

Table 4.18. Bacterial Counts[a] From Top, Mid-Point, and Bottom of an Activated Carbon Bed and from its Effluent.[99]

Column Age[b] (days)	Organisms/0.5 g dry wt[c]			Effluent (counts/mL)
	Top	Mid-Point	Bottom	
6	[d]	58,000	55,000	250,000
11	550,000	45,000	28,000	135,000
17	130,000	4,400,000	2,700,000	30,000
20	2,790,000	460,000	320,000	44,000
25	7,700	90,000,000	50,000,000	520,000

[a] R2-A pour plates (35°C); incubation for 6 days.
[b] Ambient room temperature.
[c] Activated carbon particles sonicated for 4 min.
[d] Not run.

perature, usually increasing during warmer weather.[99] Distribution of the bacteria in the carbon filter varies with the adsorber bed age and perhaps the hydraulic flow rate or approach velocity. Flow rate is probably critical because it affects nutrient transport to the microorganism on the carbon granules.[99] Table 4.18 shows the bacterial distribution in a GAC bed and the filter's effluent.[99] These data indicate that the bacterial density near the bottom does not correlate with the bacterial density of the effluent. Also, the bacteria appear to become established in the lower part of an adsorber bed. Furthermore, these populations may pulse widely in densities because they reflect numerous variables in the adsorber column ecosystem.[99]

The microbial population in GAC beds and in the effluent has been identified by several investigators[99,153,157,159] and a list of the species identified is shown in Table 4.19. It is noted that all the identified species are nonpathogenic in nature and are found in naturally occurring soils and waters. Concern has been expressed regarding the possible formation of endotoxins in GAC adsorbers because of bacteriological activity.[101] Endotoxins are pyrogenic lipopolysaccharide-protein complexes produced in the cell walls of gram-negative bacteria. The EPA Health Effects Research Laboratory has monitored bacterial endotoxin concentration in untreated water and effluent from GAC units. There was no increase in pyrogenic activity in the effluent from the GAC beds.[101]

Attempts to reduce the bacterial population in the carbon beds by frequent backwashing with finished water or highly chlorinated water results only in an initial reduction in the population density, followed by a gradual buildup to the higher levels in a few days.[150] Therefore, it is expected that carbon-filtered waters will contain high total plate counts, with the levels depending on the quality of the influent water to the carbon beds. In addition, some cases have been reported where coliform bacteria penetrated the carbon bed and appeared in the filter effluent.[99,160] Both the potential penetration of coliforms in the carbon beds, which may not be a common occurrence, and the high standard plate counts make it essential to disinfect the carbon-filtered water before final distribution. It is fortunately the common practice of water treatment plants in the United States to maintain a high disinfectant residual in the distribution system, thus assuring the safety of the delivered water.

BIOLOGICAL ACTIVATED CARBON

Biological activated carbon (BAC) is a process being used increasingly in European water treatment works where biological activity is deliberately enhanced in the GAC beds. The process, therefore, allows removal of soluble organic matter by utilization of the adsorptive capacity of the carbon and the biological oxidation provided by the microorganisms. The benefits claimed for the BAC process include: biological oxidation of organic compounds, biological nitrification of ammonia, and partial biological regeneration of the GAC.[157]

Aerobic biological growth in the activated carbon filters is promoted by introduction of sufficient dissolved oxygen into the water ahead of the contactor. If the water to be treated contains easily biodegradable organics, then simple aeration—or perhaps oxygenation—would provide adequate dissolved oxygen. Drinking water treatment plants along the upper Rhine River in Germany are utilizing this approach where pollution is mostly from municipal sewage.[157]

However, the presence of organics that are not readily biodegradable in water requires the addition of an oxidant ahead of the carbon filters. To date, this has involved the use of ozone. Preozonation converts larger, less biodegradable organic compounds into smaller, more biodegradable molecules.[99,151,157] The extent of such conversion depends on the ease of oxidation of the specific organics present, and on the amount of ozone employed. At the same time, ozonation introduces a large quantity of oxygen into the water, which promotes aerobic bacterial growth. Slowly, biodegradable organic molecules can be sorbed onto the activated carbon, where the microorganisms can metabolize

Table 4.19. Microbial Species Found in Effluents of GAC.[99,153,159]

Pseudomonas alcaligenes
Pseudomonas cepacia
Pseudomonas facilis
Pseudomonas fluorescens
Pseudomonas lemoignei
Pseudomonas mendocina
Pseudomonas ruhlandii
Pseudomonas stutzeri
Pseudomonas sp.
Gluconobacter oxidans
Azomonas agilis
Azomonas insignis
Azomonas macrocytogenes
Chromobacterium violaceum
Neisseria sicca
Acinetobacter calcoaceticum
Micrococcus luteus
Staphylococcus saprophyticus
Bacillus cereus
Bacillus circulans
Bacillus licheniformis
Bacillus megaterium
Bacillus pumulis
Bacillus thuringensis
Corynebacterium sp.
Micromonospora sp.
Pseudomonas putida
Pseudomonas maltophilia
Pseudomonas pseudoalcaligenes
Achromobacter sp.
Alcaligenes odorans
Flavobacterium odoratum
Citrobacter freundii
Enterobacter cloacae
Klebsiella pneumonia
Klebsiella oxytoca
Moraxella sp.
Filamentous Fungi
Phialophora hoffmannii
Phialophora mutabilis
Taphrina sp.
Yeasts
Rhodotorula minuta var. *texensis*
Cryptococcus uniguttulatus
Candida guillermondii var. *guillermondii*
Hansenula anomala var. *anomala*

them. This reactivates the formerly occupied carbon sites,[154,157] which leads to an extended life of the activated carbon before it is replaced. High-molecular-weight, naturally occurring humic acids are not readily adsorbed by activated carbon. Preozonation of water containing these compounds results in their conversion into lower-molecular-weight and more readily biodegradable organic compounds[157,161,162] that can be easily removed in biologically activated carbon beds. The activated carbon, therefore, will not become saturated rapidly with biorefractory materials, and the bed service life will be extended. Additional information on the role of microbial activity in BAC and carbon beds can be obtained in a publication by the AWWA Research and Technical Practice Committee.[154]

Miller et al.[157] have reviewed in detail the development and current practices and operation of BAC systems where an estimated 46 full-scale drinking water treatment plants are presently in operation in Europe. The BAC process currently being utilized in the water treatment plant in Mulheim, Germany[150,157,163] is discussed here briefly for illustrative purposes. The raw water for this plant is the River Ruhr, which until mid-April 1977 was treated by breakpoint chlorination for ammonia removal, flocculation, and sedimentation, and by GAC for dechlorination, and finally by ground and/or sand filtration and disinfection. The chlorine dose required for ammonia removal was as high as 10–50 mg/L. This resulted in the formation of chlorinated organics that were not completely removed by the activated carbon beds. Regeneration of the activated carbon columns was required every 4–8 weeks. A two-year pilot-plant study was conducted on the use of preozonation followed by activated carbon adsorption for removing ammonia and organics. The results indicated that breakpoint chlorination could be eliminated completely, and at the BAC was reliable for removing ammonia. At the same time, the dissolved organic carbon (DOC) was reduced to the desired levels. This process subsequently involves ozonation ahead of sand filtration and GAC adsorption. It was installed in the plant and began operating in mid-April 1977. The newly installed process involves preoxidation with about 1 mg/L ozone for manganese oxidation. After flocculation and sedimentation, 2 mg/L of ozone is added to oxidize dissolved organics where a retention time of 15–30 min is provided. The water is then filtered through sand filters and finally through BAC, where the bulk of DOC and ammonia is removed. The treated water is subsequently chlorinated before discharge into the distribution system. Table 4.20 lists the old process and the new process and compares their performance. The life of the full-scale carbon columns is estimated to be 2 years, and the filters are backwashed every 10 days.

Additional information about the biological activated carbon treatment of potable water is found in Chapter 9 of Reference 82.

REACTIVATION OF GRANULAR ACTIVATED CARBON

Exhaustion of the adsorptive capacity of GAC requires its removal from the adsorber so that it can be regenerated. Regeneration involves removing the adsorbate and simulta-

Table 4.20. Process Parameters and DOC Data at the Dohne Waterworks (Mulheim, Germany) Before and After Treatment Changes.[a]

Treatment Step	Old Treatment (Before 1977)		New Treatment[b] (April–July 1977)	New Treatment (November 1977–June 1978)
Preoxidation	10–50 mg/L Cl_2		1 mg/L O_3	1 mg/L O_3
Dosing	4–6 mg/L Al^{3+}		4–6 mg/L Al^{3+}	4–6 mg/L Al^{3+}
Power Input	0.1 kW/m^3		2.5kW/m^3	2.5 kW/m^3
	Ret. time—1.5 hr		Ret. time—0.5 min	Ret. time—0.5 min
Flocculation	5–15 mg/L $Ca(OH)_2$		5–15 mg/L $Ca(OH)_2$	5–15 mg/L $Ca(OH)_2$
Sedimentation	Ret. time—1.5 hr		Ret. time—1.5 hr	Ret. time—1.5 hr
Ozonation			2 mg/L O_3	2 mg/L O_3
			Ret. time—5 min	Ret. time—5 min
Filtration with Preflocculation	v^c = 10.7 m/hr		v = 9 m/hr	10 mg/L pure oxygen
			0.2 mg/L Al^{3+}	
			0.1 mg/L polyelectrolyte	
Activated Carbon Filter	v = 22 m/hr		v = 18 m/hr	v = 18 m/hr
	h^d = 2 m		v = 2 m	h = 4 m
Ground Passage	Ret. time—12–50 hr		Ret. time—12–50 hr	Ret. time—12–50 hr
Safety Chlorination	0.4–0.8 mg/L Cl_2		0.2–0.3 mg/L Cl_2	0.2–0.3 mg/L Cl_2
DOC Data (mg/L)	1975	1976		
Raw Water (Ruhr)	3.9	5.0	3.6	2.4-3.7
After Flocculation and Sedimentation	3.2	4.0	2.9	1.8–3.0
After Filtration	3.2	3.8	2.6[b]	1.7–3.1
After Activated Carbon	3.0	3.7	2.3	1.0–2.6
After Ground Passage	1.8	2.1	0.9	—

[a] Reproduced from Miller et al.[157]

[b] Filters filled with fully exhausted GAC, used during pre-1977 treatment.

[c] Velocity.

[d] Bed height.

neously reestablishing the original adsorptive capacity of the virgin carbon. The most commonly used method is thermal regeneration, where the spent carbon is heated in an inert atmosphere at high temperatures (800°C) in the presence of oxidizing gases such as steam, carbon dioxide, and oxygen.[99,164,165] The regeneration process proceeds in three steps:[164,165] (1) a drying step where the water in the wet carbon is driven off at temperatures above 100°C; (2) a pyrolysis step where the adsorbed materials are volatilized at high temperatures (during this step a fraction of the organic matter undergoes polymerization or condensation and carbonization); and (3) an activation step where residues in the micropores are oxidized by activation gases. Some loss of the activated carbon generally occurs during the regeneration due to burnoff and mechanical attrition. Figure 4.26 shows a typical flow diagram of a carbon reactivation system.

The carbon slurry must be received and dewatered before it is fed into the furnace. There are several ways to accomplish this. Usually, a carbon slurry is withdrawn from a column and conveyed to a storage tank, and then to a dewatering tank prior to heating. The dewatering and storage are frequently combined into one tank. A surge tank is placed below the dewatering tank and prior to the furnace. Feeding equipment is usually one of these types: belt, screw feeder, or rotary valve type.

A typical multiple-hearth furnace is seen in Figure 4.27 that consists of a steel sheet-lined refractory inside the unit. This refractory can be castable for small 30-inch units, or it can be brick, as used for large units. Other types of furnaces are: rotary kiln, fluidized bed furnace, and infrared tunnel.[99] The total regeneration time ranges from 20 to 30 minutes.

Loss of carbon mass during regeneration is extremely important because of its impact on the cost of using activated carbon. Total losses (transport plus loss in the furnace) have been reported to be 16 to 19% in an experimental system at Cincinnati.[166] Others have reported a 9% loss at Jefferson Parish, Louisiana.[167] Proper design of the transport system is very important because of the high losses that occur in a poorly designed system.[121] Overall, carbon losses are a function of the transport system design, the type of adsorbate, the loading of adsorbate on the carbon, and the type of furnace.[168]

The properties of the regenerated carbon depend on the proper control of reactivation conditions. Several investiga-

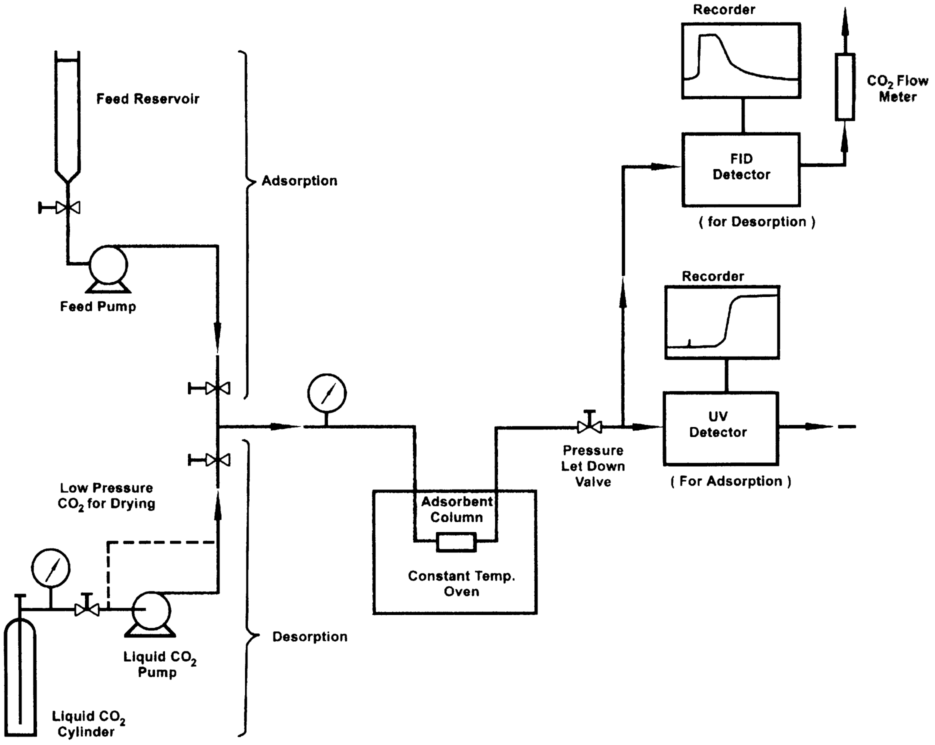


Figure 4.26. Carbon reactivation system. Reproduced from DeMarco et al.,[166] courtesy of the American Chemical Society.

tors reported changes in the pore size distribution[99] and specific surface area[169] of the regenerated carbon. However, Jüntgen[164] showed that it is possible to determine the conditions of desorption and activation enabling the best possible restoration of the original surface area and pore size distribution with minimum loss of the activated carbon during regeneration. Figure 4.28 shows the effect of activation residence time on the changes in activity and weight of activated carbon during regeneration.[164] It indicates, in this case, that an activation temperature at 800°C for 20 min does not significantly change the properties of activated carbon. Studies by Weber and Van Vliet[76] illustrate that the regeneration process may not result in significant changes in the pore-size distribution of the activated carbon.

Onsite regeneration at potable water treatment plants is not practiced extensively in the United States.[168] The general practice is to replace the spent carbon (which is usually returned to the manufacturer) with virgin carbon. Most of these plants in the United States use GAC for taste and odor control, where the service life of the carbon ranges from two to five years. When the MCLs (Table 1.7) for VOCs, SOCs, pesticides, and DBPs are implemented, the onstream life of carbon beds will be reduced significantly. Consequently, the economics may be more favorable for onsite reactivation or offsite custom reactivation. Additional information on carbon regeneration may be found in Chapter 8 of Reference 82.

SYNTHETIC ADSORBENTS FOR REMOVAL OF ORGANICS

The potential use of a wide range of synthetic adsorbents as alternatives to GAC for removing organics from drinking water has received considerable attention in recent years. The types that have been considered for potential use in water treatment are: polymeric adsorbents, carbonaceous adsorbents, and ion-exchange resins. All of these adsorbents are based on cross-linked polymers having polystyrene, phenol-formaldehyde, or acrylate structures (matrices), as shown in Figure 4.29.[170] A major advantage of using these adsorbents is claimed to be the ease of regeneration in place with suitable regenerants.[170,171] Synthetic adsorbents may be a BAT in the future for organics. Currently, they are recommended (Table 1.7) for use in removal of inorganics by ion exchange processes. However, additional information is found in Chapter 10 of Reference 82 for their use as adsorbents.

An example of the application of a synthetic adsorbent (Ambersorb 563) in removing TCE from a groundwater containing NOM was compared with that of GAC (Filtrasorb F-400).[172] Adsorption equilibrium, kinetic, and pilot plant

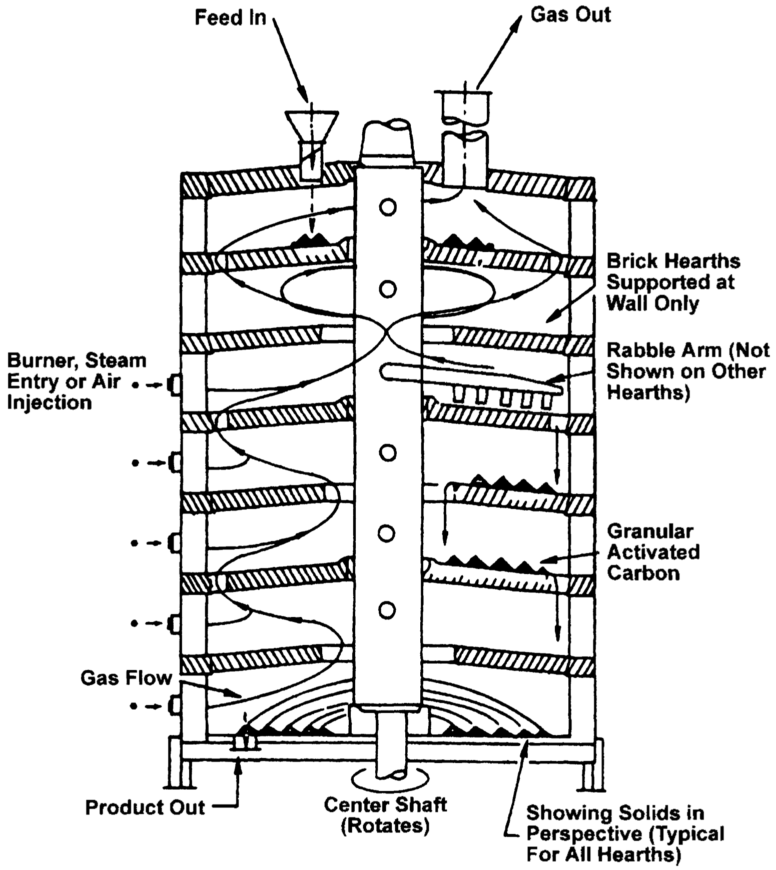


Figure 4.27. Cross section of multi-hearth furnace.[99]

experiments were used to compare the adsorbents. Adsorption isotherm (Myers equation from a log-log plot[173]) studies showed that the synthetic adsorbent had 3 to 4 times the TCE capacity than GAC over the TCE concentration range of 10–2000 μg/L. When this synthetic adsorbent was preexposed for 24 weeks to a groundwater containing NOM, it showed an average 12% loss in capacity compared with the single-solute isotherm performed on the virgin adsorbent. On the other hand, GAC showed an average 35% loss in its virgin capacity for a preexposed time of only 10 weeks. RSSCTs and pilot plant data confirmed that the synthetic adsorbent is more efficient than GAC in removing TCE.

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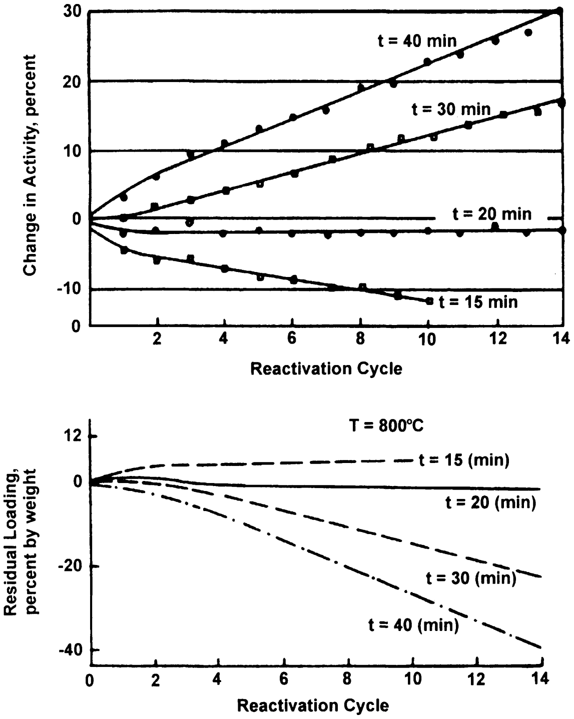

Figure 4.28. Effect of residence time on activity and change of weight of activated carbon.[164]

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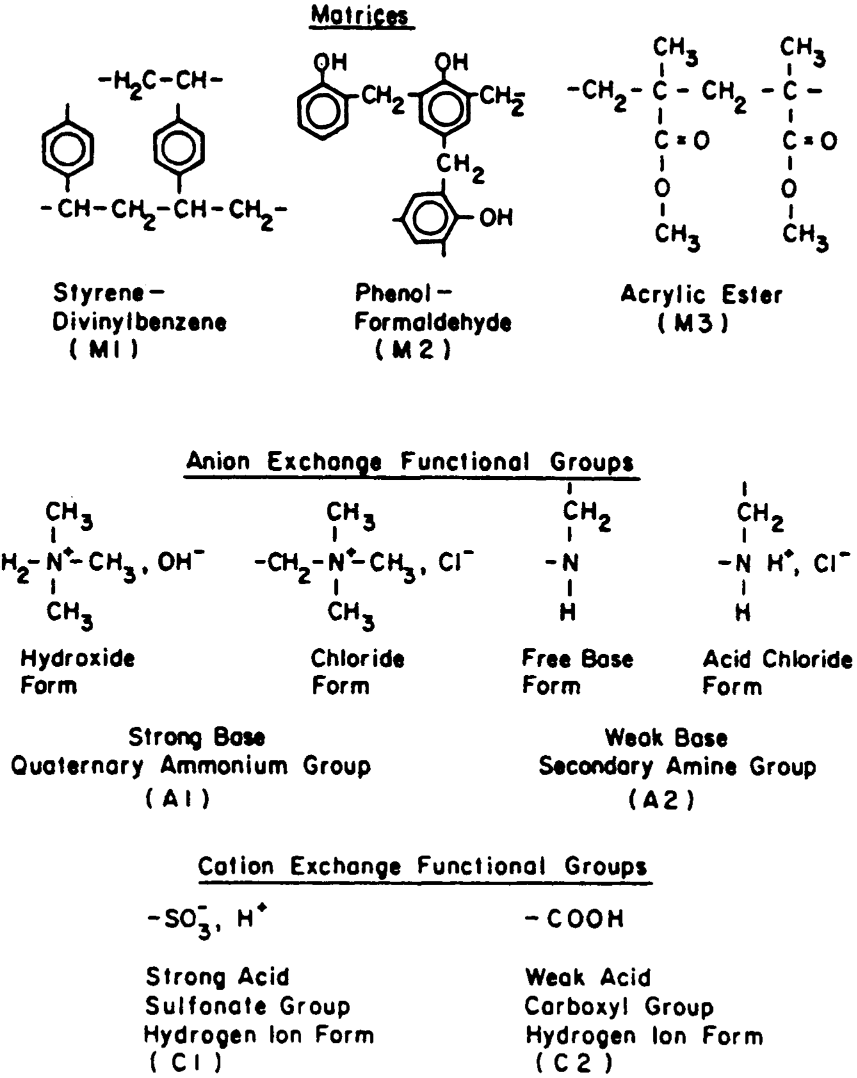

Figure 4.29. Matrices and functional groups of resins commonly used for water purification. Reproduced from Kim et al.,[170] courtesy of the Water Pollution Control Federation.

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Chapter 5

Aeration

5

Aeration

Aeration in water treatment is the process of bringing air into intimate contact with the water for the purpose of exchanging gases between the two phases. The applications include:

1. Exchange of gases from the air to the water. This process is used mainly for introducing oxygen into the water (oxygenation) for oxidation of reduced species such as sulfides or iron and manganese. The latter is the most widely used application. The addition of carbon dioxide for the recarbonation of excess lime softened water is often conducted by the same methods used in aeration.
2. Exchange of gases from the water into the air. This process is commonly referred to as stripping, and includes:
   a. Removal of hydrogen sulfide from certain groundwaters for taste and odor control.
   b. Removal of carbon dioxide from waters to reduce the demand for lime in the lime softening treatment and for raising the pH of waters in iron and manganese removal.
   c. Removal of volatile organic chemicals (VOCs) from waters. This process gained rapid acceptance during the past decade as a result of the discovery of the presence of many of these compounds in natural waters, specifically groundwaters. Maximum Contaminant Levels (MCLs) have been established for many of the VOCs, and aeration—packed-tower aeration (PTA)—was determined to be one of the Best Available Technologies (BAT) for achieving these MCLs under the Safe Drinking Water Act.

THEORETICAL OVERVIEW OF GAS TRANSFER

Solubility of Gases

The solubility of gases in water is an important consideration in determining the rate and amount of gas transfer in and out of the water. The solubility is affected by two basic mechanisms. Either the gas reacts with water, as in the case of hydrogen sulfide, carbon dioxide, ammonia, and chlorine, or the gas does not chemically react with water, as in the case of oxygen, methane, chloroform, and most of the volatile organic compounds.

When a gas reacts with water, the chemical reaction is known as hydrolysis, soluble ionic species are formed, and the gas solubility is completely dependent upon the degree to which the reaction takes place. The significance of these reactions in aeration is that they are reversible; that is, the ionic species can reassociate to form the gas. This is illustrated by the reaction of hydrogen sulfide with water:

$$H_2S + H_2O \rightleftharpoons H_3O^{\dagger} + HS^{-} \tag{1}$$

$$H^{2}5 + H_2O \rightleftharpoons H_3O^{\dagger} + S^{2-} \tag{2}$$

The pH of the solution determines the total sulfide species as well as the free hydrogen sulfide gas. As acid is added, the hydrogen ion concentration is increased, the reaction is shifted to the left, and the amount of free gas is increased. In removal of hydrogen sulfide (H_2S) from water by air stripping, only that portion of the total sulfide that is hydrogen sulfide can be stripped.[1]

When a gas does not react with water, its solubility or diffusion through the water is opposed by the attraction of water molecules to themselves. Therefore, for a gas to increase its solubility it must overcome the forces that attract the water molecules together. Water molecules are held together by the forces of hydrogen bonding, forming a tetrahedral structure. A constant interaction of bond formation and bond breaking occurs, producing short-lived clusters of water molecules. For a gas to solubilize, it must be more attracted to water than the water to itself. For example, the solubility of the unsaturated compound ethylene (C_2H_4) is twice as much as that of the saturated compound ethane (C_2H_4) because of the difference in the ability to break the hydrogen bonding between the water molecules. Ethane molecule has all the valence electrons utilized in localized single bonds. The ethylene molecules, on the other hand, include a delocalized double bond. The excess electrons at the double bond attract the positive end of the water dipole. This produces a dipole-induced attraction between water and ethylene, resulting in greater solubility in water. A similar comparison can be made between oxygen and nitrogen. The molecules of both gases are slightly polarized in water because each has delocalized electrons. Oxygen, however, contains two unpaired electrons that are more susceptible to attraction by water molecules and therefore it is more soluble in water than nitrogen.[1]

Gas-Liquid Equilibrium

When oxygen-deficient water is exposed to air, oxygen will dissolve or transfer into the water. A portion of the oxygen molecules in the water will transfer back to the air phase. When the number of molecules leaving the air phase and entering the water equals the number of molecules leaving the water and entering the air, a state of equilibrium is reached where the concentration in the water is constant. The equilibrium concentration or saturation value of a dissolved gas depends mainly upon the temperature of the water and partial pressure of the gas in the atmosphere in contact with the water. According to Henry's law, the higher the partial pressure, the greater the solubility of the gas in water. At a constant partial pressure, the solubility decreases with increase in temperature. Also, gas solubility is reduced by an increase in dissolved solids.

In the aeration process, the equilibrium concentration or saturation value has a considerable practical significance because the driving force for interchange of gas between air and water is the difference between the saturation value of a gas and its actual concentration in the water. The rate of approach to equilibrium is also important in aeration, since under similar conditions, the farther the air-water system from equilibrium, the more rapid will be the interchange of gas in the direction of attainment of equilibrium.

Henry's Law

In dilute aqueous solutions, the tendency of a compound to escape to the gas phase is described by Henry's law. Henry's law states that at equilibrium, the concentration or partial pressure of a substance in the gas phase is proportional to its concentration in the liquid phase.

$$p = \frac{HC}{P_T} \tag{3}$$

where p = mole fraction of gas in air = mol gas/mol air
C = mole fraction of gas in water = mol gas/mol water
H = Henry's constant = atm, = $\dfrac{\text{atm(mol/gas/mol air)}}{\text{mol gas/mol water}}$
P_T = total pressure = atm, usually = 1

A useful conversation factor when calculating C is that 1 L of water contains 55.6 mol of water. Henry's law can also be reported by utilizing concentration units, which is very useful in water treatment. The total pressure P_T is usually defined as 1, and therefore is dropped off the equation, and atm is dropped from the units of H.

$$p = H_uC \tag{4}$$

where p = concentration units; e.g., kg/m^3, mol/L, mg/L
H_u = unitless
C = same units used for p

The concentration of a contaminant in the gas phase, therefore, is proportionate to its concentration in the liquid phase. The larger the Henry's constant, the greater will be the equilibrium concentration of the contaminant in the air. Henry's law constant, sometimes called the partition coefficient, can be calculated from experimental data by dividing the concentration of the contaminant in the air by its concentration in water at equilibrium. This constant can be estimated from the special case conditions where the concentration of the contaminant is at saturation in both the liquid and vapor phase, causing the partial pressure of the contaminant to be equal to the vapor pressure of the pure material.[2,3] Thus, Henry's law constant, H, becomes:

$$H \propto \frac{P_v}{S} \tag{5}$$

where P_v = vapor pressure of the pure liquid
S = solubility of the contaminant in water

Thus, lower compound solubility and higher vapor pressure (volatility) result in a higher Henry's law constant. By conversion of partial pressure units to concentration in the gas phase, a dimensionless Henry's constant is obtained:

$$H = \frac{C_a}{C_w} \tag{6}$$

where C_a = concentration of the contaminant in air, µg/L
C_w = concentration of the contaminant in water, µg/L

There have been conflicting reports in the literature concerning the effect of the contaminant's concentration on its Henry's constant.[4] Recent studies, however, showed good agreement between experimental Henry's constants and those predicted from vapor pressure and solubility data.[5] Therefore, if reliable vapor pressure and solubility data are available, this method of prediction should yield equally reliable estimates of Henry's constants. However, because the range of solubility values (20°C) reported in the literature could be substantial, careful selection is extremely important.

Henry's law constants determined in waters containing a mixture of several volatile organic compounds showed that the values obtained with distilled water were in excellent agreement with those obtained for each compound individually in distilled water, indicating that the constants obtained were independent of the presence of other compounds.[5] Similarly, no effect of solute concentration on the solute's Henry's constant was observed up to solute mole fractions of $\sim 10^{-3}$.[5]

Therefore, most volatile organic compounds of interest in water treatment follow Henry's law quite satisfactorily in the range of concentrations experienced in domestic water supplies. Table 5.1 shows Henry's constants for several compounds at 20°C. For those compounds that are liquids at 20°C, the Henry's constant was computed from solubility data and the partial pressure of the pure liquid at the system temperature and atmosphere total pressure.[6]

It must be pointed out that although Henry's constant values determined experimentally or derived thermodynamically for many volatile organic compounds are published in the literature, it is not uncommon to find many different measured values for the same VOC. Therefore, the applicability of the published values must also be considered carefully for conditions other than pure water. For example, the composition of natural waters, i.e., dissolved solids (370–700 mg/L) and humic material (20 mg/L) was reported to have little, if any, effect on the values of Henry's constants for the trihalomethanes[7] ($CHCl_3$, $CHCl_2Br$, $CHClBr_2$, and $CHBr_3$). On the other hand, the presence of salts, surfactants, and humic materials had a profound effect on the measured value of Henry's constants of trichloroethylene (TCE) and toluene.[8] This indicates that Henry's constant for organics in contaminated and natural waters can deviate unpredictably from pure water value because of poorly understood and complex molecular interactions. Therefore, it is prudent to obtain experimentally determined Henry's constant values for the VOCs of interest in the same natural water for which an aeration removal system is to be designed.

Henry's Constant Temperature Dependence

Temperature has a strong influence on Henry's constants, like any other equilibrium constant. In general, increasing temperature will decrease the solubility of volatile compounds in water. The strong temperature dependence of Henry's constant can be described by the following van't Hoff-type relationship:

$$\log Hc = \frac{-H^\circ}{2.3RT} + K \tag{7}$$

where Hc = Henry's constant, atm
H° = heat absorbed in the evaporation of 1 mol of gas from solution, kcal/kmol
R = universal gas constant, 1.987 kcal/kmol
T = absolute temperature, °K
K = constant

Table 5.2 shows values of H° and K for some VOCs and other compounds of interest in water treatment.[6] These data indicate that a temperature difference of 10°C can affect Henry's constant by a factor of two or three.[6] Therefore, temperature is considered one of the most important operating parameters that will affect the extent of removal of volatile compounds in water treatment aeration systems.

Mass Transfer

The rate of transfer of a volatile solute (gas, VOC) from the aqueous phase into the gaseous phase is commonly described by the two-resistance theory. The theory is based on a model in which two films exist at the gas-liquid interface: one liquid and one gas, as shown in Figure 5.1. For transfer of gas molecules from the gas phase to the liquid phase, a concentration gradient in the direction of transfer in each phase must exist. The concentration of the gas in the bulk of the air phase, p_G, falls to a lower value at the interface, p_I, hence a concentration gradient is set up from the bulk to the interface. A similar concentration gradient is set up in the liquid phase, where the concentration decreases from the interface c_I to the bulk liquid c_L. Lewis and Whitman[9] assumed that the only resistances to the transfer of the solute are those in the two phases, and no resistance exists at the interface itself. The concentration gradients provide the driving force necessary for mass transfer through the aqueous and gas phases. The interfacial concentrations are at equilibrium and can be described in dilute solutions by Henry's law:

$$p_I = Hc_I \tag{8}$$

Basing overall mass transfer on liquid phase concentration and using Henry's law to describe the equilibrium partitioning at the film interface, the overall mass transfer rate constant, K_L, can be expressed in terms of separate gas and liquid phase coefficients by the following relationship:

Table 5.1. Henry's Constants for Selected Compounds.[a]

Compound	Henry's Constant (atm)
Vinyl chloride[b]	3.55×10^5
Oxygen	4.3×10^4
Nitrogen	8.6×10^4
Methane	3.8×10^4
Ozone	3.9×10^3
Toxaphene[b]	3.5×10^3
Carbon dioxide	1.51×10^3
Radon	2.26×10^3
Carbon tetrachloride[b]	1.29×10^3
Tetrachloroethylene[b]	1.1×10^3
Trichloroethylene[b]	5.5×10^2
Hydrogen sulfide	5.15×10^2
Chloromethane[b]	4.8×10^2
1,1,1-Trichloroethane[b]	4.0×10^2
Toluene	3.4×10^2 (25°C)
1,2,4-Trimethylbenzene[b]	3.53×10^2 (25°C)
Benzene	2.4×10^2
1,4-Dichlorobenzene[b]	1.9×10^2
Chloroform[b]	1.7×10^2
1,2-Dichloroethane[b]	61
1,1,2-Trichloroethane[b]	43
Sulfide dioxide	38
Bromoform[b]	35
Ammonia	0.76
Pentachlorophenol[b]	0.12
Dieldrin	0.0094

[a] Temperature 20°C except where noted otherwise.

[b] Computed from water solubility data and partial pressure of pure liquid at specified temperature.

Source: Reproduced from Kavanaugh,[6] courtesy of the American Water Works Association.

Table 5.2. Henry's Constant Temperature Dependence.

Compound	ΔH° (kcal/kmol) $\times 10^{-3}$	K
Benzene	3.68	8.68
Chloroform	4.00	9.10
Carbon tetrachloride	4.05	10.06
Methane	1.54	7.22
Ammonia	3.754	6.31
Chloromethane	2.48	6.93
1,2-Dichloromethane	3.62	7.92
1,1,1-Trichloroethane	3.96	9.39
1,1-Dichloroethane	3.78	8.87
Trichloroethylene	3.41	8.59
Tetrachloroethylene	4.29	10.38
Carbon dioxide	2.07	6.73
Hydrogen sulfide	1.90	5.96
Chlorine	1.74	5.75
Chlorine dioxide	2.93	6.76
Sulfur dioxide	2.40	5.68
Difluorochloromethane	2.92	8.18
Oxygen	1.45	7.11
Nitrogen	1.12	6.85
Ozone	2.52	8.05

Source: Reproduced from Kavanaugh,[6] courtesy of the American Water Works Association.

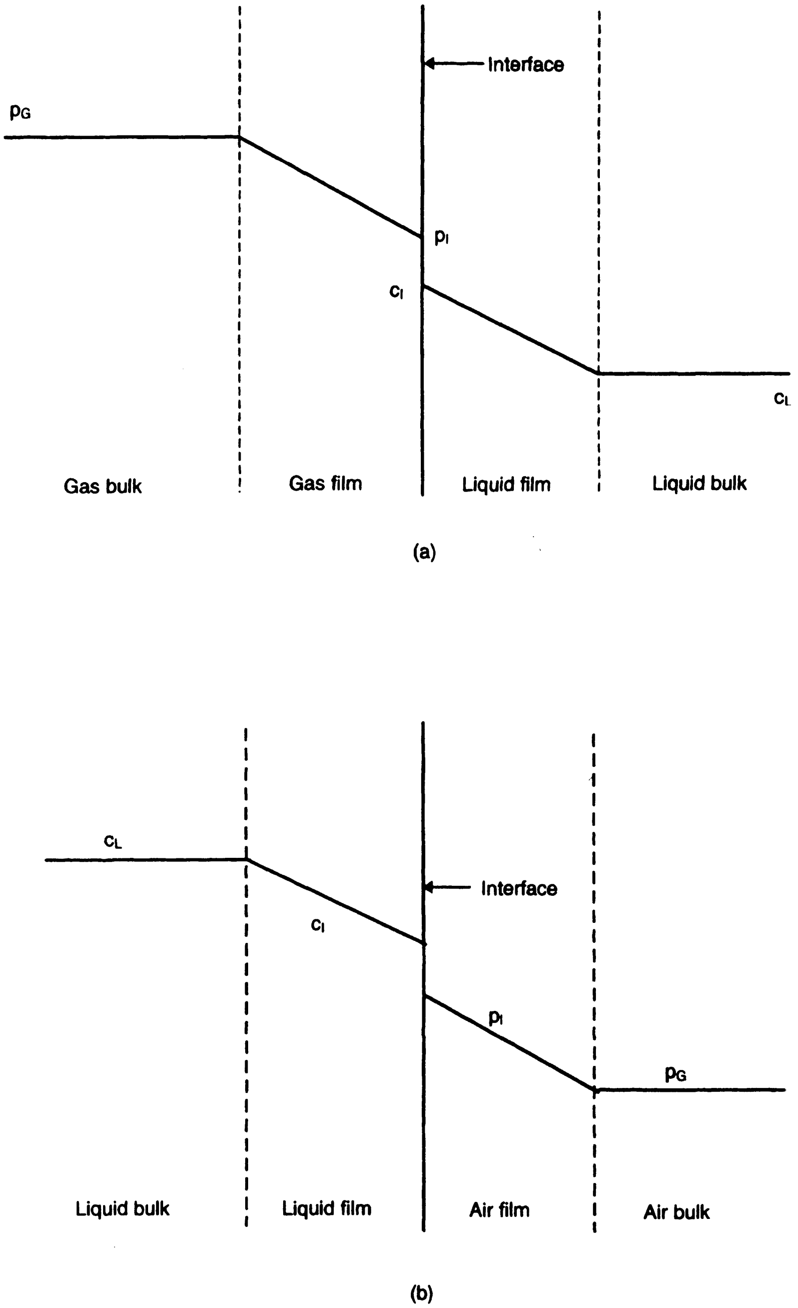

Figure 5.1. (a) Two-resistance concept, gas adsorption; (b) Two-resistance concept, stripping. Reproduced from Cornwell,[1] courtesy of the American Water Works Association.

$$\frac{1}{K_L} = \frac{1}{Hk_G} + \frac{1}{k_L} \tag{9}$$

where K_L = overall mass transfer coefficient
H = Henry's constant
k_G = gas phase transfer coefficient (length/time)
k_L = liquid phase transfer coefficient (length/time)

If Henry's constant is large, such as for highly volatile compounds, then Equation 9 shows that the liquid phase resistance controls the transfer rate. Compounds of interest in water treatment tend to be liquid phase controlled or a combination of liquid and gas phase controlled.[1] The steady state rate of mass transfer from the liquid (water) to the gas (air) phase (air stripping) can be expressed as:

$$J = \frac{dc}{dt} = K_L \frac{A}{V} (C - C^*) \qquad (10)$$

The term A/V may be replaced by "a"

where J = rate of mass transfer of the solute, kmol/s
K_L = overall mass transfer coefficient, based on the liquid phase driving force, m/s
A = interfacial area through which mass transfer occurs, m^2
V = volume containing interfacial area, m^3
a = specific interfacial area = interfacial area per volume across which mass transfer occurs, m^2/m^3
C = average molar concentration of solute in the liquid phase, $kmol/m^3$
C^* = concentration of the solute in aqueous phase in equilibrium with the gas phase concentration, $kmol/m^3$, and is given by:

$$p^* = HC^* \qquad (11)$$

where p^* = concentration of solute in gas phase in equilibrium with the liquid phase concentration, $kmol/m^3$
H = Henry's constant, mass concentration/mass concentration

The product K_La is called the overall mass transfer rate constant and is dependent on the type of mass transfer equipment and water quality factors. The K_La values may be determined from pilot studies[1] or by using empirical correlations to extrapolate mass transfer data provided in the literature.[10–14]

AERATION METHODS

There are several types of aeration processes used in the drinking water treatment field. The key consideration in the selection of an aeration method is the feasibility of the process to achieve high mass transfer efficiency at the lowest cost.

Diffused Aeration

In diffused aeration, air bubbles are brought in contact with the water in a mixing or contact chamber. Compressed air is released at the bottom of the tank through perforated pipes, porous diffuser tubes, or various sparger devices that allow uniform distribution through the water cross section. The bubbles rising through the water create turbulence and provide opportunity for exchange of the volatile materials between the bubbles and the water, and between the water and the air at the turbulent interface. In typical applications, the untreated water is allowed to enter the tank from the top and exit from the bottom in a counterflow pattern to the air, which is introduced at the bottom. The efficiency of diffused aeration is improved by using fine bubbles (0.2 cm diameter) as compared to coarse bubbles (2.5 cm diameter), by increasing the water depth (9–15 ft), by improving the basin geometry (width-to-depth ratio not to exceed 2), or by increasing the retention time (10–30 minutes).[1,15]

Diffused aeration has not been widely used in the drinking water treatment field because large air-to-water ratios are needed to achieve high removal efficiencies. Therefore, it did not prove to be a cost-effective method compared to other aeration processes for removal of volatile compounds. It has been used for aeration of water supply reservoirs, and found limited application for VOC removal. Generally, diffused aeration is considered when the process can take place in the existing clearwells, such as seasonal or summer removal of trihalomethanes where such application eliminates the capital costs associated with the construction of other aeration systems. The most common use of diffused aeration in water treatment is for addition of gases, such as oxygenation or ozonation systems.

Spray Aeration

In this aeration process, the water is sprayed through fixed nozzles installed on a pipe grid. The sprayed water is broken into small drops, thus providing high area-to-volume ratio for efficient gas transfer. The spray nozzles direct the water upward, vertically or at an inclined angle, and are generally designed as fountain type, spraying into the open atmosphere.

Several nozzle designs are used to obtain optimum dispersion of the water. These include full cone nozzles, hollow cone nozzles, rifled nozzles, centrifugal nozzles, and impinging, rotating, and reaction nozzles. The dispersion action of the nozzle determines the drop size and hence its air volume ratio. The smaller the drop diameter, the larger the interfacial area. Generally, nozzles that produce drops with diameters of 2–10,000 μm are selected. The nozzles are mostly 1.0 to 1.5 inch in diameter, and have discharge ratings of about 75–150 gpm at approximately 10 psi, with spacing varying from 2–12 ft.

The removal efficiency of these aerators—and in turn the mass transfer—increases with the decrease in the drop diameter and the increase in contact time between the water drops and the atmosphere. The contact time, on the other hand, can be increased by increasing the spray angle, or increasing the operating water pressure, which in turn increases the exit velocity of the drops from the nozzles. The above concepts are described by the following relationships:[1,15]

$$a = \frac{6}{d} \qquad (12)$$

$$t = \frac{2\upsilon_d \sin\alpha}{g} \tag{13}$$

$$\upsilon_d = C_v(2gh)^{1/2} \tag{14}$$

$$C_e - C_i = (C_s - C_i)\,[1 - \exp(-K_L\, at)] \tag{15}$$

where a = specific interfacial area
d = mean diameter of the drop, obtained from manufacturer
t = time of contact of the water drop with the atmosphere
υ_d = exit velocity of the drop from the nozzle
α = angle of the spray from the horizontal
g = acceleration of gravity
C_v = velocity coefficient of nozzle, from manufacturer, 0.4 to 0.95
C_e = effluent concentration
C_i = influent concentration
C_s = equilibrium concentration, in open atmosphere is constant = 0

The limitations or the use of spray aeration in water treatment include the large area requirement of about 50–150 ft^2/day/million gallons, freezing weather conditions, short contact time, and the relatively high head requirements. These aerators are not cost-effective for the removal of dissolved volatile organic compounds because of the relatively low K_L and the unrealistic requirement of high operating pressure for obtaining moderate removal efficiencies. The major uses, however, are for applications of gas transfers where high efficiencies (50–80% removal) are obtained because of the rapid transfer between the water drops and the air. These applications include the removal of carbon dioxide from water, the removal of hydrogen sulfide from water, and the addition of oxygen to the water for iron and manganese removal.

Multiple-Tray Aerators

In multiple-tray aerators, the water to be treated is distributed and allowed to trickle through a series of trays equipped with slats, perforated or wire mesh bottom. The treated water is collected in a basin at the bottom of the trays. Coarse media such as coke, ceramic balls, or stone are placed in the trays to increase the surface area and allow better distribution of the water. Mass transfer takes place during surface aeration within the tray and in falling laminar sheets.

Mass transfer data for these aerators are not available in the literature because the air-to-water ratio is not controlled. However, this design is mostly based on experience and manufacturer's recommendations. The area required for these aerators is approximately 50 ft^2/day/million gallons. Generally, 3 to 9 trays are used with spacing of 12–30 inches between trays. The water application rates range from 20 to 30 gpm per square foot.[15]

The tray aerators are usually housed, and adequate ventilation is provided for efficient operation. In certain types, forced aeration is provided by blowers in an enclosed structure. Such aerators are operated in a counterflow mode, where the air is supplied at the bottom of the enclosure and travels upward counter to the downward flow of the water.

These aerators are used mainly for mass transfer of gases. The principal applications in water treatment include removal of carbon dioxide, removal of hydrogen sulfide, and addition of oxygen for iron and manganese removal. Some systems, however, are operated for the removal of VOCs. Efficiencies for transfer of gases range between 50 to 80%. The efficiency of tray aerators with coarse media such as coke seems to be enhanced by the catalytic effects of deposited manganese oxides for iron and manganese removal, and by growth of biological slimes over the large surface area which mediate the oxidation of sulfides.

Cascade Aerators

In cascade aerators, the water is allowed to flow downward over a series of steps which causes the water to fall in thin layers from one level to the other. This results in increasing the area-volume ratio and the exposure time for mass transfer. Increasing the number of steps increases the exposure time, and the addition of baffles to produce turbulence will increase the area-volume ratio.

These aerators are used mainly for gas transfer, such as removal of carbon dioxide, where sufficient space and drop are available at the plant. The space requirements are on the order of 40–50 ft^2/day/million gallons and head requirement varies from 3 to 10 ft.[15] The efficiency of these aerators for removal of carbon dioxide ranges from 25–45%.

Packed Tower Aeration

In packed tower aeration, commonly called air stripping, a cylindrical-shaped tower is filled with randomly dumped packing material that provides larger surface area of contact between the water and the air. The packing material usually consists of commercially available small-diameter individual pieces of different shapes made of ceramic, stainless steel, or various plastic materials. Self-supporting or fixed packing material consisting of prefabricated sheets can also be used.[16] In water treatment, lightweight plastic random packing material is commonly used.[1,4,14,16–18]

The tower is commonly operated in a countercurrent flow pattern. The untreated water is distributed on the top of packing material, where it falls downward by gravity. The air is blown at the bottom and forced upward through the tower. This flow pattern allows continuous contact between the water and the air and minimizes the thickness of the water layer to allow efficient mass transfer. As clean air moves upward, the volatile compounds transfer from the water phase into the air phase. The treated water with low concentration of the contaminants exits from the bottom, and the air containing the volatile compounds is discharged from the top of the tower. A typical configuration of a packed tower[18] is shown in Figure 5.2. The other components of a packed tower stripper include the water pump and air blower, the liquid distribution and redistribution trays, the mist eliminator, the piping, and the control instrumentation.

Countercurrent packed tower aeration (PTA) is used for the removal or stripping of gases such as carbon dioxide and hydrogen sulfide. During the past decade, it gained wide application as a cost-effective process for the removal of volatile organic compounds (VOCs) from contaminated waters.

Theory of Operation

The performance of a packed tower is affected by two key parameters: Henry's constant of the contaminant and the overall mass transfer coefficient for the water-to-air contaminant transfer.

The importance of Henry's constant can be understood by considering the performance of an "ideal" tower.[3] In an ideally operated countercurrent packed tower, the concentration of the contaminant to be removed from the water is in equilibrium with the concentration of the contaminant in the air at any point in the system. In addition, according to Equation 6, the concentration in the water is equal to the concentration in the air divided by Henry's law constant, at any point in the aerator. Because the concentration of the contaminant in the air coming into the bottom of the system is zero, in a "perfect" tower the concentration of the contaminant in the water must also be zero, to satisfy the definition of an ideal tower being at equilibrium at every point. Thus, the perfect system would remove all of the contaminant in question. The loss of contaminant from the water would be equal to the gain of the contaminant in the air, and the mass balance relationship would be:

$$(C_i - C_e)\,L = (p_e - p_i)\,G \tag{16}$$

where C_i = influent concentration of the contaminant in the water
C_e = effluent concentration of the contaminant in the water
p_i = influent concentration of the contaminant in the air
p_e = effluent concentration of the contaminant in the air
L = volume of water
G = volume of air

In the perfect column, which is at equilibrium throughout, from Equation 11, at any point:

$$\frac{p^*}{C^*} = \frac{P_e}{C_i} = H \tag{17}$$

Therefore, at the top of the tower

$$P_e = H\,C_i \tag{18}$$

Substituting in Equation 16 yields

$$(C_i - C_e)\,L = (H\,C_i - P_i)\,G \tag{19}$$

Because both C_e and P_i are zero in the ideal system, Equation 19 becomes:

$$C_i\,L = H\,C_i\,G \tag{20}$$

Canceling yields

$$\frac{L}{G} = H \tag{21}$$

or

$$\frac{G}{L} = \frac{1}{H} \tag{22}$$

This means that in the "perfect" system, the minimum air-to-water ratio—which will achieve complete removal of the contaminant in—question is the reciprocal of its Henry's law constant.[3]

The above relationship can be illustrated for the removal of trihalomethanes in an ideal counterflow tower. Henry's law constants were reported to be 0.152 for chloroform, 0.095 for bromodichloromethane, 0.035 for dibromochloromethane, and 0.024 for bromoform.[3] Experience has shown that compounds with Henry's law constants greater than 0.05 could be removed relatively easily by aeration.[20] The theoretical minimum air-to-water ratios required to achieve complete removal in a perfect tower are calculated from Equation 22 to be 6.7:1, 10.2:1, 28:1, and 41:1 for chloroform, bromodichloromethane, dibromochloromethane, and bromoform, respectively. The relative difficulties of removing each of the trihalomethanes can be seen by comparing the above minimum air-to-water ratio required for removal of each compound. It is clear that chloroform would be the easiest to remove and that bromoform would be the most difficult of the four compounds to remove by aeration.

In actual water treatment practice, no aeration system is perfect, so less than 100% removal always occurs, even with air-to-water ratios much higher than the theoretical minimum. This occurs because several design factors in-

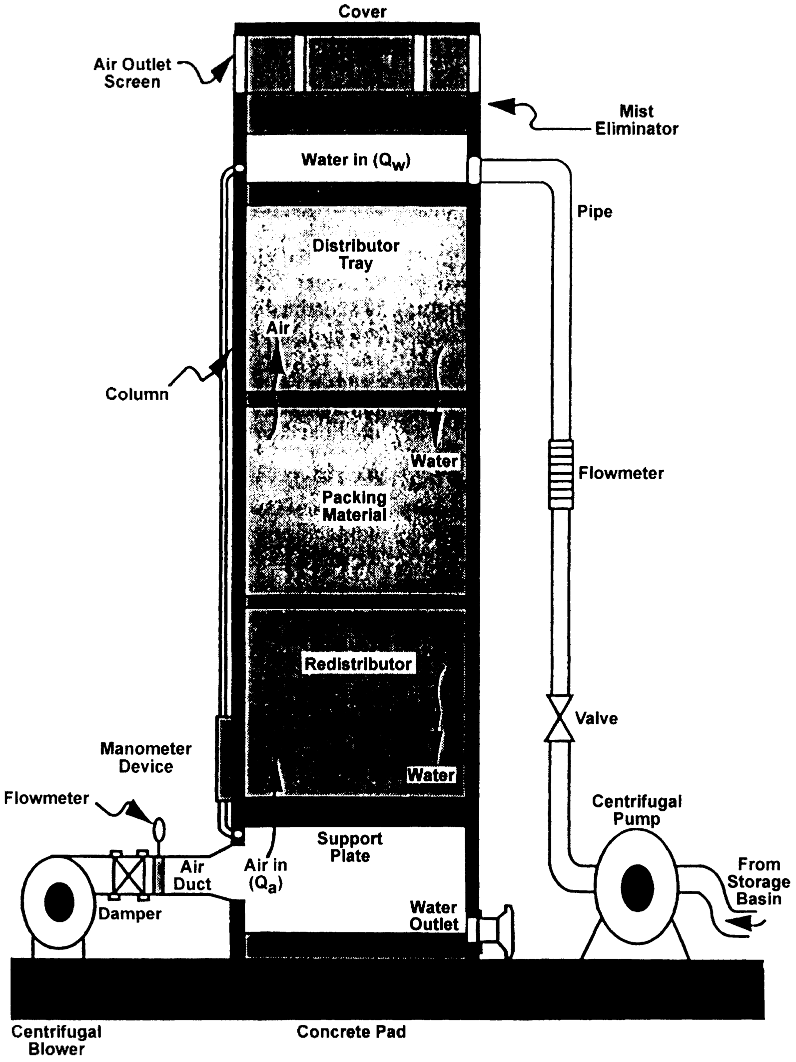

Figure 5.2. Air-stripping tower configuration. Reproduced from D.A. Dzombak,[18] courtesy of the American Water Works Association.

fluence the rate of mass transfer from the liquid phase (water) to the gas phase (air). The rate of transfer in any point within a packed tower is stated in Equation 10 and can be expressed as:

$$J = K_La\ (C - C^*) \tag{23}$$

From Equation 23, the rate of stripping of a volatile contaminant from water depends on the driving force for mass transfer $(C - C^*)$, the overall mass transfer coefficient K_L and the interfacial area, a. The driving force is proportional to the degree of deviation from the equilibrium conditions. Therefore, departure from the equilibrium condition provides the driving force that causes the contaminant to move across the air-water interface. This driving force is greater when conditions are not near equilibrium and becomes small as equilibrium is approached. Thus, aeration system design becomes exceedingly important in facilitating mass transfer if the low, theoretical minimum air-to-water ratios to achieve good removal are to be approached in actual practice.[3] Some important factors considered in improving the performance of the tower include optimizing the air and water flow rate to increase the driving force, selection of packing material to optimize the surface area and increase the overall mass transfer rate, K_La, and to optimize the transfer unit height (contact time).

The design of packed towers (air strippers)—including the development of model equations and process design procedures—is well established in the chemical engineering literature[1,6,14,17–19] and is beyond the scope of this book.

However, in order to gain insight into the practical factors affecting the performance of the tower as it relates to the mass transfer theory, the four basic relationships used for the design—to determine the tower configuration (diameter and height of packing material) and the air and water loading rates—are briefly discussed here:

$$Z = \text{packing height} = \text{HTU} \times \text{NTU} \tag{24}$$

$$\text{HTU} = \text{height of transfer unit} = \frac{L}{K_L a C_o} \tag{25}$$

$$\text{NTU} = \text{number of transfer units}$$

$$= \frac{R}{R-1} \ln \frac{\left[\left(\frac{C_i}{C_e}\right)(R-1)+1\right]}{R} \tag{26}$$

$$R = \text{stripping factor} = \frac{G}{L} \times \frac{H}{P_T} \tag{27}$$

where L = liquid loading rate, mass/area × time
G = gas loading rate, mass/area × time
C_o = density of liquid, mass/volume
C_i = influent concentration of the contaminant, mass/volume
C_e = effluent concentration of the contaminant, mass/volume
H = Henry's constant of the contaminant, dimensionless
P_T = ambient pressure, atm = 1

The HTU term in Equations 24 and 25 is inversely proportional to the product of the overall liquid phase mass transfer coefficient and interfacial area $K_L a$, and characterizes the efficiency of mass transfer from water to air. In general, the HTU value will decrease as the hydraulic loading decreases, the air flow rate increases, or the packing height increases.

The term NTU represents the equilibrium side of the aeration process, and characterizes the difficulty of removing the contaminant from the liquid phase. The stripping factor R in the NTU term represents a basic equilibrium parameter. If $R > 1$, enough capacity in the gas exists to convey all of the compound from the liquid into the gas, given a tall enough tower. In water treatment applications, a stripping factor (R) of 1.2 to 5 is typically used. Increasing R beyond 5 is uneconomical and does not yield significant improvement in removal efficiency. When $R < 1$, the packed tower aeration is potentially limited by equilibrium as well as mass transfer. In this case, removal is asymptotic to the value of R, and complete removal of the compound is impossible.[6,14]

APPLICATIONS OF AERATION

Removal of Volatile Organic Compounds

Packed Tower Aeration

Applications

Packed tower aeration (PTA) is considered the most common water treatment technology for the removal of volatile organic compounds (VOCs) from surface and groundwaters. The technology proved to be cost-effective in achieving 95–99% removal of most VOCs, and is considered one of the Best Available Technologies (BAT) to meet the current Maximum Contaminant Levels (MCLs) for the VOCs regulated by the Safe Drinking Water Act.

The theory of countercurrent packed tower aeration has been previously discussed in this chapter. Application in water treatment includes removal of trihalomethanes, volatile halogenated solvents, and other volatile hydrocarbons. Table 5.3 shows the parameters for some actual water treatment applications.

Exhaust Gas Treatment

1. Granular Activated Carbon Adsorption. As indicated earlier, during the air stripping process, the volatile organic compounds are transferred from the water to the gas (air) phase. These VOC emissions may have to be controlled in certain air quality regions. Removal of the VOCs from the exhaust or offgas by adsorption on fixed-bed granular activated carbon (GAC) was shown to be cost-effective.[21]

During this process, air from the top of the air stripper is heated to reduce the relative humidity (RH) and then the VOCs are removed by GAC. Reducing the relative humidity is important, since at high RH values a majority of the GAC pores are filled with water and the carbon capacity is substantially reduced. As the temperature increases, the RH is reduced, drying more of the pores and increasing the capacity. As soon as the pores are mostly dry, however, further heating reduces the capacity. At RHs between 40 and 50% the effects of RH and temperature balance out and a maximum loading is obtained.

Steam regeneration of the exhaust carbon bed onsite proved to be ineffective for the gas phase GAC at low concentrations because of the loss in capacity of the carbon with successive adsorption regeneration cycles. In addition, high steam-to-carbon ratio was required for good VOC removal from the GAC adsorption system. Approximately 15–20 kg steam (212°F, 1 atm) was needed to desorb some of the VOCs and effective regeneration required the use of saturated steam at a temperature as high as 338°F at a rate of 50 kg steam/kg carbon for total removal of one of the common VOCs, PCE. These steam requirements make the onsite steam regeneration neither feasible nor cost-effective. The alternative is the use of offsite regeneration at a dedicated facility or the use of virgin carbon for replacement of the

Table 5.3. Air Stripping Tower Parameters for Some Water Treatment Applications.

		Air Stripper Design	
Site (Reference)	**Treatment Goal**	**Design Item**	**Actual Value**
Tacoma Well 12A, Washington	89% removal of 1,1,2,2-tetrachloroethane at 300 ppb, flow rate 700 gpm each in five towers	Tower height	9.75 m
		Tower diameter	3.66 m
		Packing height	7.01 m
		Air-flow rate	29,000 cfm
		Air-to-water ratio	310
Brewster Well Field, New York	Removal of tetrachloroethylene from 215 to 5 ppb, flow rate 300 gpm	Tower height	8.22 m
		Tower diameter	1.45 m
		Packing height	5.41 m
		Air flow rate	2,000 cfm
		Air-to-water ratio	50
Brewster Well Field, New York	Removal of 99% tetrachloroethylene, flow rate 600 gpm at 9°C	Packing height	5.41 m
		Tower diameter	1.45 m
		Air-to-water ratio	33
Wurtsmith Air Force Base, Michigan	90% removal of trichloroethylene, flow rate 1,200 gpm each through two columns, temperature 10°C	Tower height	9 m
		Tower diameter	1.5 m
		Packing height	5.5 m
Wright-Patterson Air Force Base, Ohio, Site A	96% removal of trichloroethylene, present at 15 ppb, flow rate 950 gpm	Tower height	8.4 m
		Tower diameter	1.8 m
		Packing height	4.5 m
		Air-to-water ratio	60
Wright-Patterson Air Force Base, Ohio, Site B	95% removal of trichloroethylene, present at 16 ppb, flow rate 1,750 gpm	Tower height	15.5 m
		Tower diameter	2.6 m
		Packing height	5.33 m
Wausau, Wisconsin	95% removal of trichloroethylene, present at 72 ppb, flow rate 1,500 gpm and temperature 10°C	Packing height	7.47 m
		Tower diameter	2.44 m
		Air-to-water ratio	30
		Air flow rate	6,000 cfm

Source: Reproduced from D.A. Zombak,[18] courtesy of the American Water Works Association.

exhausted carbon. Bench-scale experiments demonstrated that liquid carbon dioxide extraction appeared to be technically feasible, but the economic viability of this approach had not been determined.

The removal of VOCs by air stripping followed by offgas GAC treatment was shown to be cost-effective compared to the treatment of the contaminated water with GAC.[21] The GAC usage rates for gas phase adsorption were less than half those for aqueous phase adsorption. Because gas phase adsorption kinetics are much faster than aqueous phase adsorption kinetics, the required bed depth and diameter are much smaller for gas phase beds than for aqueous phase beds.

2. Closed-Loop Air Stripping Process. The closed-loop air stripping process was recently evaluated[22] as an alternative to granular activated carbon treatment for the control of VOCs in the offgas from air strippers. This process couples air stripping with an ultraviolet (UV) photooxidation process that destroys the VOCs. In this process, the exhaust from PTA is irradiated with UV light in a photooxidation chamber, and the VOCs are destroyed by photolysis and oxidation processes that occur in the gas phase. Phosgene, $COCl_2$, and other hydrolyzable intermediates are formed; the end products of irradiation are carbon dioxide, hydrochloric acid, and ozone.[22] The treated air is recycled to the PTA, where additional VOCs are stripped from the water and the gaseous products of the photooxidation process are reabsorbed into the water stream. Therefore, no gases are released to the atmosphere. The process, therefore, is a dynamic system where the VOCs are transferring back and forth between the phases in the stripper.

The process has been tried in a bench-scale study and proved to be technically feasible for the removal of the compounds studied; namely, 1,1,2-trichloroethane (TCA), chloroform, trichloroethylene (TCE), tetrachloroethylene (PCE), and carbon tetrachloride (CTC). The universal application of the process needs to be evaluated since it would be feasible only for the control of those compounds that are amenable to photooxidation where the oxidation kinetics—i.e., the rate of photooxidation—is favorable for the process to be cost-effective. In addition, the quality of the treated water needs to be evaluated with respect to the levels and significance of the photooxidation intermediates and by-products.

Fouling of Packing Media

1. Causes of Fouling. Fouling of the packing media is one of the major operational problems affecting the performance of the PTA process. The quality of the water to be treated influences the degree and severity of fouling of the media. Fouling is caused mainly by:

- scale formation on the surfaces of the media due to the precipitation of calcium and magnesium salts in hard waters
- oxidation and precipitation of iron salts in the incoming water
- microbial growth and slime formation on the media

The buildup of fouling agents results in a pressure drop in the tower and the loss of efficiency. In extreme cases the buildup can be so severe as to fill the voids in the media and result in unacceptable total pressure drop through the tower, therefore reducing the performance of high-efficiency packing media. The following is a brief overview of the causes of fouling.[17,23]

(a) Carbonate Scaling. Waters having high carbonate hardness (calcium and magnesium bicarbonate) content will have high scale-forming tendency during packed tower aeration. As the water moves from the pressurized inlet port of the tower to the atmospheric pressure of the packed section of the tower, a substantial pressure drop causes the liberation of CO_2 gas. This results in shifting the carbonate equilibrium system toward the precipitation of calcium carbonate:

$$Ca(HCO_3)_2 = CaCO_3\downarrow + CO_{2(g)}\uparrow + H_2O \quad (28)$$

The removal or stripping of the $CO_{2(g)}$ results in an increase in the pH value of the water, which causes further precipitation of the calcium carbonate.

The calcium deposits precipitated on the surface of the packing media usually take the form of a brittle cement-like scale that dissolves readily by the addition of acid solutions.

(b) Iron Oxide Scaling. The aeration of waters containing naturally occurring iron salts—such as some groundwaters—results in the rapid oxidation of the ferrous into the ferric forms. The latter are precipitated on the packing media as hydrated ferric oxides ($Fe_2O_3 \bullet XH_2O$). The removal of CO_2 during aeration increases the pH of the water and subsequently increases the rate of the oxidation and precipitation of the oxidized iron salts. The ferric oxides take the form of rust-colored amorphous mass or rust to black colored gel.

(c) Microbial Growth. The high surface area of the packing media creates an excellent medium for microbial growth in the form of slimes that attach to the media. The presence of iron in the incoming water promotes the growth of iron bacteria which are capable of forming dense slimes at a rapid rate. These bacteria derive their energy from the catalytic oxidation of the ferrous to the ferric forms. The slimes collect the oxidized iron and form a rusty colored, densely packed stringy and/or slimy material which can completely fill all the void spaces in the packing.[23]

2. Control of Fouling. (a) Water Pretreatment. Pretreatment of the water for removal of the fouling-causing agents, such as hardness and/or iron and manganese, before the PTA process is one of the options to be considered. However, this option is feasible only if the pretreatment (softening or iron removal) is a part of the overall treatment strategy of producing drinking water, otherwise the aeration process would not be cost-effective.

Waters containing low levels of hardness or iron salts may be pretreated by acid addition for pH adjustment to mitigate the rapid buildup of scales on the media.[17] This approach is useful for prolonging the use of the tower before serious buildup of the scales takes place. Obviously, it is not advisable to lower the pH below 7.0, otherwise the water will become corrosive to the equipment and the distribution system without subsequent adjustment.

Attempts to control iron scale formation by the addition of chelating agents such as hexametaphosphate at levels as high as 2 mg/L were unsuccessful in the reduction or elimination of iron oxidation in the tower.[23]

(b) Packing Media Cleaning. The buildup of scales and microbial growth can be effectively controlled by cleanup of the media on a regular basis. Successful cleanup was achieved by recirculation in the tower of a solution containing 500 ppm citric acid (pH<3.0), followed by another 2 hour acid wash with 10% muriatic acid solution.[23] A recirculation line must be installed in the tower for this purpose. The use of acids will result in severe foaming problems. However, this can be controlled by the addition of a defoaming compound in both acid solutions.

The media cleanup process has to be repeated on a regular basis as a part of the routine maintenance program for the tower that includes visual inspection of the media. The frequency of the acid cleanup can be determined accordingly. In severe cases, a cleaning frequency every two weeks was found to be necessary.[23]

The selection of the packing media for the treatment of waters that have scaling and biofouling tendencies is a very important consideration for the operation of the PTA process. The randomly packed (dumped) media that are usually used have relatively small void spaces which can be rapidly plugged up by fouling agents, resulting in a large pressure drop and ultimately loss of performance of the tower. Also, these media cannot be effectively cleaned. Therefore, serious consideration should be given to self-supporting structured media. These bundle-type packing media have more open area for less restricted air and water flow, and no horizontal surfaces on which stagnant water may support the colonization of iron bacteria. These media have lower mass transfer coefficients than the randomly packed media and therefore a higher air-water ratio will be required in order to achieve the same performance efficiency. However, the ease of cleanup of the media and the fact that no serious pressure drop across the tower would occur allows the continued operation of the PTA system when the routine maintenance program described above is implemented.

Shallow-Tray Aeration

During the past decade, low profile compact air stripping systems have been developed for the treatment of VOC-contaminated groundwaters mostly at remediation sites. The most common style is the tray-type unit, in which a shallow layer of water is allowed to flow along one or more shallow baffled trays where forced-draft, countercurrent air stripping takes place.[24]

The contaminated water is sprayed into the inlet chamber of the unit through a coarse-mist spray nozzle. The water flows over a flow distributor weir and along the baffled aeration tray. The air is blown up through 3/16 inch diameter holes in the aeration tray. The air forms a froth of bubbles generating a large mass transfer surface area for stripping of the VOC compounds. In these systems, high air-water ratio is used because large volumes of air are required to transform water in the tray into a froth.

Performance of these systems can be improved by the use of more trays for increasing the residence time. In a multi-tray system, when the water reaches the end of one tray, it falls onto the next for additional treatment.

The fouling problems encountered in packed tower units are easily managed in the low profile units. Each tray can be removed for maintenance, and scraping clean the calcium, iron, and boiling fouling residues in relatively short time. The compactness of these systems also allows their use in cold climate regions since they can be easily housed in a heated building.

The shallow-tray systems are capable of achieving removal efficiencies as high as 99.99% for volatile organic compounds such as benzene, toluene, ethylbenzene, and xylenes (BTEX) and many chlorinated VOCs from groundwaters.

Technological Developments

a. Inclined Cascade Aeration

The removal of VOCs from waters using an inclined cascade process has been evaluated recently in an experimental system.[25] In this system, the water to be treated is pumped to the top of an inclined plane, where it cascades by gravity down a transversely corrugated surface. Because most of the resistance to mass transfer of low-solubility solutes is generally liquid phase–controlled, induced liquid turbulence greatly enhances the mass exchange of dissolved VOC from the liquid to the gas phase. In addition, the gas phase is never saturated with VOCs because it is continually replenished with fresh air in the open atmosphere.

The experimental system consisted of a cascade surface or board that was 16 ft long and 2 ft wide and was located in the open air. The transversely corrugated surface was standard fiberglass corrugated, semicircular, 1 inch in diameter, and sinusoidal (alternate ridge-trough). The inclination angle of the board was adjustable from 30° to 70° in 5° increments. City water spiked with chlorinated hydrocarbons and trihalomethane compound was applied at flow rates ranging from 10 gpm to 30 gpm.

Inclined cascade aeration proved to be effective for stripping VOCs from drinking water. The overall mass transfer rate constants (K_La) for the compounds studied were higher than those reported for PTA due to higher degree of liquid turbulence. Removal rates greater than 99% were reported to be possible with reasonable treatment surface lengths and angles of inclination. A cascade angle of 60° was found to be effective for compounds having Henry's constants greater than 300 atm. Compounds with Henry's constant values less than 300 atm (less volatile) were more effectively stripped at steeper angles and reached the maximum at 90° or freefall.

As with the conventional cascade aeration, which is used mostly for the removal of gases, the inclined cascade aeration process will be limited by space availability, freezing weather conditions, and possibly cost-effectiveness.

b. Membrane Air Stripping

Air stripping of VOCs with microporous polypropylene hollow-fiber membranes has been introduced as an alternative method to PTA, with advantages over PTA in both size and operation.[26,27]

Membrane air-stripping involves pumping water contaminated with VOCs through the interior bundle of microporous hollow-fiber membranes while stripping air is passed countercurrently on the exterior of the fibers. The membranes used in this process are hydrophobic; therefore, the water does not pass through the pores of the membrane. The VOCs respond to a concentration gradient that exists between the water in the fibers and the air flow outside the fibers and diffuses through the water to the surface of the membrane, into the air-filled membrane pores, and then into the flowing air. Because of the high specific surface area provided by the membranes, membrane air-stripping is very effective in removing VOCs from water, reaching VOC mass transfer rates an order of magnitude greater than those achievable by PTA under similar operating conditions. Stated another way, the large area for contact between the water and air phases in the membrane system allows equivalent removal efficiencies at stripping factors that are much lower than in PTA.[27] Here the stripping factor R is defined as the product of the dimensionless Henry's law constant of the compound of interest and the volumetric air flow rate, divided by the water flow rate ($R = Q_gH/Q_w$). Therefore, it is possible to utilize smaller treatment systems for membrane air stripping, and space reduction may be realized. However, the performance of membrane air stripping when in continuous operation has not been established.

Membrane air stripping can be used at various locations within a treatment train. It can be used alone for nondisinfected waters to remove VOC contamination. It can also be used to remove VOC contamination or volatile disinfection by-products (DBPs) or both from disinfected waters. In addition, it can be used before or after conventional treatment to remove VOC contamination or volatile DBPs. Regardless of where the process is located within a treatment train, however, there are certain characteristics of treated and untreated waters that may affect the performance and durability of the membranes when in continuous operation.

The majority of drinking water sources are disinfected with chlorine; ozone is the next most popular disinfectant of choice. If the proposed Ground Water Disinfection Rule is promulgated, all groundwater sources will require some form of disinfection. Membrane air stripping would most likely be employed after disinfection to prevent biological fouling of membranes and to remove any volatile DBPs, such as trihalomethanes.

A recent study assessed the performance of polypropylene membrane air stripping in continuous operation, while exposed to different pH levels, oxidants (ozone and free chlorine), and oxidant concentration.[27] The results of this study indicated that microporous polypropylene hollow-fiber membranes are generally unaffected by continuous exposure to low-pH waters (pH 5 to 7), exhibiting no damage and consistent performance. However, on exposure to pH 9 solutions, membrane air stripping with polypropylene membranes exhibited significant performance reduction and pore area reduction. Consistent performance and durability at lower pH is promising for the use of these membranes as a treatment technology for control of VOCs in groundwaters. With pH adjustment, higher-pH surface waters could also be treated with this process.

All membranes tested in that study were relatively resistant to chlorine at low concentrations, exhibiting consistent performance and durability throughout exposure periods. However, a higher chlorine concentration caused a marked pore area reduction in polypropylene type membranes and damage to the epoxy potting material. It is anticipated that long-term exposure to high chlorine concentrations will adversely affect membrane performance, and use of this process in highly chlorinated waters is not recommended. This result also points out that the useful life of membranes exposed to low chlorine concentrations may be shorter than for nonchlorinated waters.

All membranes exposed to ozonated waters were damaged. Use of membrane air stripping with ozonated waters is not recommended, unless the process is located far enough downstream of ozone introduction that concentrations degrade to acceptable levels. Biological fouling of membranes would need to be addressed if the process is located in this manner.

Although the membrane air stripping process shows considerable promise for the removal of VOCs from drinking waters, further research work is needed for design optimization and performance evaluations under natural water conditions before its full-scale application in water treatment.

Removal of Volatile Odorous Substances

Removal of Hydrogen Sulfide

Most of the odors caused by organic substances in drinking waters are not volatile enough to be removed effectively by aeration. The principal volatile odorous compound in many groundwaters is hydrogen sulfide gas, which imparts a characteristic rotten egg smell. Since hydrogen sulfide is a reactive gas, the aeration process will only remove that portion of the gas that is in the gaseous state.[1] The reaction of hydrogen sulfide with water results in the formation of HS^- and S^{2-} species according to the following equations:

$$H_2S + H_2O = H_3O^+ + HS^- \quad K_1 = 1 \times 10^{-7} \qquad (29)$$

$$HS^- \; H_2O = H_3O^+ + S^{2-} \quad K_2 = 1 \times 10^{-15} \qquad (30)$$

From Equation 29, the amount of total sulfides as H_2S is calculated to be 50% at pH 7.0. At other pH values, the amount of H_2O is calculated by:

$$\%H_2S = 100 \frac{[H^+]^2}{[H^+]^2 + K_1[H^+] + K_1K_2} \qquad (31)$$

The amount of H_2S gas at pH 8, for example, is calculated from Equation 31 to be about 10% of the total sulfur species. Therefore, if the aeration process is 100% efficient, only 10% of the gas will be removed. Most natural waters containing hydrogen sulfide also contain carbon dioxide. During the air stripping process, the carbon dioxide is also removed. This will result in increasing the pH and therefore cause disocciation of H_2S to HS^-, thus reducing the removal efficiency.

The aeration process also results in increasing the dissolved oxygen concentration in the water, which may oxidize some of the remaining HS^- species. The chemistry of oxidation of reduced sulfur species has been discussed in detail in Chapter 9. However, it is important to repeat that the oxidation of HS^- is pH-dependent. At pH values less than 6.0, the oxidation reaction is very slow where H_2S is the predominant species. As the pH value is increased above 6.0, the oxidation rate increases rapidly, reaching a maximum between pH 8 and 8.5.

The net result of the removal of hydrogen sulfide by aeration is that a portion will be stripped off and a fraction will be oxidized, depending on the pH conditions of the water. Any of the aeration methods discussed previously can be used for hydrogen sulfide removal.

Removal of Iron and Manganese

Aeration is used for the transfer of oxygen from the air into the water for the oxidation of iron and manganese as the initial step for their removal from natural waters. The chemistry of oxidation and removal of iron and manganese is discussed in detail in Chapter 9. However, it is important to mention that the rate of oxidation of Fe(II) with oxygen is strongly pH-dependent. Above pH 6, an increase in pH value of one unit results in a 100-fold increase in the oxidation rate. For the oxidation of iron, 1 mg of oxygen is required for the oxidation of 7 mg of iron, according to the following equation:

$$4Fe^{2+} + O_{2(g)} + 10H_2O = 4Fe(OH)_3(s) + 8H^+ \quad (32)$$

Therefore, the oxygen demands—and, correspondingly, the oxygen gas transfer requirements—are very small. The equipment need not be sophisticated to accomplish the necessary oxygen transfer.[1] Any of the aeration methods—such as spray nozzle, cascade, coke tray, and coarse bubble aeration—can be used to accomplish this step.

The oxidation of manganese by oxygen is very slow, and the aeration process is not practical at the normal pH conditions in natural waters. Therefore, strong oxidants are needed for manganese removal.

Removal of Radon

Radon is a water-soluble radioactive gas that is naturally occurring in many groundwaters. The removal of radon from waters, like many other soluble gases, can be readily achieved by aeration. For this reason, EPA proposed aeration to be the Best Available Technology (BAT).

All the aeration methods presented in this chapter can be applied for the removal of radon. However, the selection of an appropriate method must be determined based on the specific local conditions where the treatment is needed and an evaluation of the cost-effectiveness of the selected option. There are not many treatment systems already installed for radon removal; however, the following is a brief discussion of some types of aeration technology that have been evaluated.[28]

Spray Jet Aeration System

The spray jet aeration system is a high-intensity end-of-line aerator. Water enters the nozzle-shaped unit at right angles to the body of the spray jet unit through precisely engineered orifices. This creates a vacuum that draws air in through the rear of the unit. The pressured water stream (20 psi) causes a violent mixing of the water and air within the interior of the spray jet unit, resulting in the stripping of volatile gases. The air-to-water ratio can be varied by inserting a replaceable orifice ring in the unit.

The results of evaluation of the spray jet aeration system using groundwater having radon levels of 1,700 to 1,900 pCi/L indicated that this system was marginally capable of reducing the radon level to 300 pCi/L.[28] The air-to-water ratio was 6:1 and the contact time was 20 minutes. Variations in the air-to-water ratio had negligible effect in improving the 75% removal efficiency. In addition, the orifices of the spray jet unit were susceptible to clogging and a resultant decline in removal efficiency. It was concluded that the spray jet aeration system is not suitable for radon removal applications.

Multi-Stage Bubble Aerator System

This is a diffused aeration system in which the water flows through a series of compartments (staged flow regime) in a single basin. Each compartment is equipped with aerator assembly for producing fine air bubbles in the water. An outside air compressor is used to supply the air to the different assemblies. The compartments are usually about 3 ft in depth, which allows efficient mixing of the water and the air bubbles.

This system was shown to be capable of radon removals of 97–99%.[28] Because of their compact size, the units can be housed entirely within a wellhouse building and appear to be particularly suited to sites where aesthetics are of primary concern.

Packed Tower Aeration System

This system was shown to be extremely effective, with radon removal efficiency ranging from 93 to 98%. For 10 ft tower height, 98% radon removal was achieved at an air-to-water ratio of 8:1 and a loading rate of 25.5 gpm/ft^2.[28]

A packed tower aeration system was installed recently to treat a small community water system in a small town in Colorado.[29] The system was designed for a flow of 30 gpm and was constructed after an iron removal system. Removal efficiencies of 96 to 98% were consistently achieved for a 9 ft high PTA at 20 gpm/ft^2 with a counterflow of 100 cfm/ft^2 of air using polypropylene spheres as the packing media.

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Chapter 6

Removal of Particulate Matter by Coagulation

6

Removal of Particulate Matter by Coagulation

Almost all natural surface waters contain particulate matter and/or colloidal substances that are not removed rapidly by sedimentation. Consequently, it is necessary to catalyze this sedimentation by physical and/or chemical coagulation. The term flocculation is occasionally used interchangeably with coagulation. LaMer and Healey[1] have defined these two terms in a mechanistic fashion:

> We propose that coagulation be used for the general kinetic process obeying the simple Smoluchowski equation independent of θ, whereby colloidal particles are united (L. *coagulare*—to be driven together) as typified by the effects of electrolytes upon gold sols. Coagulation is brought about primarily by a reduction of the repulsive potential of the electrical double layer in accordance with the ideas advanced by Derjaguin, Landau, Verwey, and Overbeek.
>
> We propose that the term flocculation should be restricted more in accordance with original usage corresponding to the Latin meaning of "floc" (L. *flocculus*—a small tuft of wool or a loosely fibrous structure).
>
> Flocculation is usually brought about by the action of high-molecular-weight materials (potato starch and polyelectrolytes, in general) acting as linear polymers of the dispersion into a random structure which is three-dimensional, loose, and porous.

Defined operationally, coagulation includes the addition of the chemicals, floc formation, coagulation, and sedimentation prior to sand filtration. This chapter will use both the mechanistic and operational definitions of the term coagulation.

HISTORICAL ASPECTS

Clarification of water as an aid to sedimentation of particulate matter has been practiced from ancient times. The predominant chemical agent has been, since those times, aluminum sulfate [$Al_2(SO_4)_3$], whose common name is alum. Lime [$Ca(OH)_2$] has been employed also, either alone or with alum, and with such iron salts as ferric sulfate [$Fe_2(SO_4)_3$] or ferric chloride ($FeCl_3$). Some other interesting substances have been improvised for use as coagulants: almonds, beans, nuts, toasted biscuits, and Indian meal.[2]

The Egyptians practiced a form of coagulation as early as 2000 BC. After they collected water from streams and transported it in camel-skin bags, they placed it in wide, round-belly and oblong vessels. Then they smeared the mouth of the vessel with five sweet almonds, after which a person would plunge his arm into the water up to the elbow and twist it with a vigorous motion for an appropriate period of time. The arm was withdrawn and the crushed almonds were left in the jar. After about three hours of sedimentation the water would be clear enough to store in little earthen jars, where it would become clearer and cooler.[3] Reports claim that this technique was also applied to the waters from the Nile River.

Alum was also known to the early Romans of 2000 BC.[4] Pliny (ca. 77 AD) was, perhaps, the first to mention use of alum as a coagulant when he described the use of both lime (chalk of Rhodes) and alum (argilla of Italy) in making bitter water potable. The Egyptians apparently used alum as an important item of trade long before its usefulness for water treatment was known. The purification of alum eventually reached proportions large enough for its manufacture. An attempt in 1461 by Pope Pius II to develop a monopoly on the production of alum led, eventually, to a manufacturing force of approximately 8000 workmen. By 1757, muddy water in England was treated with 2–3 grains of alum per quart, followed by flocculation and filtration of the supernatant.[2] This eventually led to the coagulation of municipal water supplies at Balton, England, in 1881. Alum was added by a dosage of 1.5 grains per imperial gallon at the intake of the water treatment plant. From about 1885, coagulation was employed ahead of sand filtration.

In 1884 the first patent was granted to Isaiah Smith Hyatt for the perchloride of iron coagulation of the New Orleans Water Company's supply. A year later, the Somerville and Raritan Water Company of New Jersey installed Hyatt's coagulation-filtration system, which, in turn, established these processes as full-scale treatments.

The first scientific investigation into the use of alum for coagulation was conducted and reported by Austen and Wilbur of Rutgers University in 1885.[5] They concluded that, "by the addition of two grains of alum to the gallon (~34 ppm), or half an ounce to 100 gallons, water can be clarified by standing, and that neither taste nor physiological properties will be impaired to it by this treatment." Later, a series of experiments was conducted on turbid Ohio River water at Louisville, Kentucky, in the years 1895–1897.[6] Of the several compounds tried—alum, potash alum, and lime—alum was found to be the most suitable. These experiments led to widespread use of alum coagulation as an adjunct to rapid sand filtration in the United States. There was concurrent research on the use of such iron compounds as ferrous sulfate, ferric chloride, chlorinated copperas (Cl_2 added to ferrous sulfate), and ferric sulfate as coagulants. These compounds are reasonably effective in certain situations (see below), but alum remains the most widely used coagulant today.

NECESSITY

It is inferred from the above passages that chemical coagulation is required to clarify turbid waters. In turn, turbidity is composed of various kinds of biotic species, i.e., bacteria, plankton, etc., and of abiotic substances such as inorganic and organic colloids. Table 6.1[7] gives the kinds of particle sizes of particulate matters found in water. Plain sedimentation removes gravel, coarse and fine sands, and, perhaps, some of the silt fraction. The finer particles—bacteria, plankton, and colloids—require coagulation to larger particle sizes that can settle within two hours. The large surface areas of colloids play an important role in their coagulation by a variety of coagulants. The primary drinking water standard is 0.5 to 1.0 ntu, based on a monthly average (see Chapter 1). Even high-quality treated water meeting this standard will contain a number of particles.[9] Assuming a suspended solids content of 0.1 mg/L and spheres with a 1 μm diameter and a specific gravity of 1.01, a liter of treated water will contain about 2×10^8 particles.

Several inorganic salts of iron and aluminum are available commercially for coagulation. These are seen in Table 6.2,[9] with their availability in dry or liquid forms (frequently alum appears with $18H_2O$). As stated above, alum finds almost exclusive application in drinking water treatment, whereas the iron compounds are used predominantly in treating domestic and industrial wastewaters. When these coagulants are added to water, their hydrous oxides are precipitated. For alum, the stoichiometric coagulation reaction is:

$$Al_2(SO_4)_3 \bullet 18H_2O + 3Ca(HCO_3)_2 = 2Al(OH)_{3(s)} + 3CaSO_4 + 6CO_{2(g)} + 18H_2O \quad (1)$$

In this reaction, calcium bicarbonate represents the natural or added alkalinity needed to form $Al(OH)_{3(s)}$. It is important to note that 1 mg/L of alum with 18 H_2O requires 0.45 mg/L of alkalinity as $CaCO_3$ and releases 0.9 mg/L of $CO_{2(g)}$ as $CaCO_3$ if all of the alkalinity is bicarbonate. A representative iron coagulation reaction is:

$$Fe_2(SO_4)_3 + 3Ca(HCO_3)_2 = 2Fe(OH)_{3(s)} + 3CaSO_4 + 6CO_{2(g)} \quad (2)$$

CHEMISTRY OF COAGULATION

The chemical coagulation of turbid and or naturally colored surface waters involves the interaction of particulates and/or colloids with a destabilizing agent. The essential purpose of coagulation is to aggregate these particles into larger sizes that will settle quickly within an hour or two and/or will be filtered by sand or other media. This aggregation process is also called destabilization of colloidal systems.

Colloids are characterized by their size and by the mechanism by which they are stabilized in water. Figure 6.1 shows a size spectrum of waterborne particles and of filter pores.[10] Colloids have diameters usually less than 10 μm and remain suspended in water because their sedimentation by gravity is less than 10^{-2} cm/sec. It should also be noted from Figure 6.1 that bacteria and algae are sized in the upper colloid range, whereas viruses are at the lower range. These microorganisms should be removed, in part, by coagulation.

The time periods over which colloidal systems are stable can range from a few seconds to several years. This is noted in Table 6.1, as is the increase in total surface area as the particle size decreases. The latter is also an important factor in the stability of colloidal systems. The interface of large surface areas represents a substantial free energy that, by agglomeration, tends to lower values. Thus, the coagulation of many small particles into fewer large particles is favored in a thermodynamic sense.

Another characteristic of colloids is their affinity for the solvent in which stabilization occurs. This is the process of "solvation." "Lyophilic" is the general term given to colloids "loving" the solvent. In water, this becomes hydrophilic, and such colloids are stabilized by the formation of adherent thick layers of oriented water molecules around the particle. "Lyophobic" is the general

Table 6.1. Effect of Decreasing Size of Spheres.[a]

Diameter of Particle (mm)	Order of Size	Total Surface Area[b]	Time Required to Settle[c]
10	Gravel	0.487 in.^{2}	0.3 sec
1	Coarse sand	4.87 in.^{2}	3 sec
0.1	Fine sand	48.7 in.^{2}	38 sec
0.01	Silt	3.38 ft^2	33 min
0.001	Bacteria	33.8 ft^2	55 hr
0.0001	Colloidal particles	3.8 yd^2	230 days
0.00001	Colloidal particles	0.7 ac	6.3 yr
0.000001	Colloidal particles	7.0 ac	63 yr (minimum)

[a] Reproduced from Powell,[7] courtesy of the McGraw-Hill Book Company.

[b] Area for particles of indicated size produced from a particle 10 mm in diameter with a specific gravity of 2.65.

[c] Calculations based on a sphere with a specific gravity of 2.65 to settle 1 ft.

Table 6.2. Properties of Common Coagulants.[a]

Common Name	Formula	Equiv. Weight	pH at 1%	Availability (%)
Alum	$Al_2(SO_4)_3 \cdot 14H_2O$	114	3.4	Lump—17 Al_2O_3 Liquid—8.5 Al_2O_3
Lime	$Ca(OH)_2$	40	12	Lump—as CaO Powder—93–95 Slurry—15–20
Ferric Chloride	$FeCl_3 \cdot 6H_2O$	91	3–4	Lump—20 Fe Liquid—20 Fe
Ferric Sulfate	$Fe_2(SO_4)_3 \cdot 3H_2O$	51.5	3–4	Granular—18.5 Fe
Copperas	$FeSo_4 \cdot 7H_2O$	139	3–4	Granular 20 Fe
Sodium Aluminate	$Na_2Al_2O_4$	100	11–12	Flake—46 Al_2O_3 Liquid—2.6 Al_2O_3
Aluminum Chloride	$AlCl_3$	44	—	Liquid

[a] Reproduced from Kemmer,[9] courtesy of the McGraw-Hill Book Company.

term given to colloids "hating" the solvent, which in water becomes hydrophobic; such colloids are stabilized by an electrostatic repulsion between particles arising from ions that are attracted to the surface from bulk solution or dissolved out of the solid's surface. These stabilizing forces are seen in Figure 6.2.[11]

Stability of Colloids

Colloids are stable in aqueous systems, by virtue of the hydration and/or electrostatic charge on their surfaces. Both phenomena depend primarily on the chemical structure and composition of the particle at the water-solid interface (Figure 6.2). The particle presents to the water an electronic or electrostatic capacity, which in turn represents the attractive forces for molecules of water and/or various cations and anions. These stabilizing water molecules and ions are held by forming bonds with the particle. In accord with their energies (kcal/mol), these bonds are: ionic crystal bonds (150–200), covalent (50–100), hydrogen (1–10), and polar (<5). There may be some induced polarization (London–van der Waals forces) also in molecules and atoms that are neutral electrically under normal conditions. These forces of attraction are weak and have bond energies similar to the polar bonds. It is, however, the electrostatic stability of hydrophobic colloids that is of concern in coagulation of natural waters.

In natural waters, colloids are predominantly negatively charged due to a variety of negative functional groups on the surface of the particle (Figure 6.2). This negative charge was reported in 1929 from an early study of chemical coagulation.[12] Therefore, if the particle's surface has a negative charge, and the bulk of the solution is neutral electrically, a potential difference exists between this surface and a point at some distance into the bulk solution.[13] This distance can be calculated exactly from a derivation of the Boltzmann-Poisson distribution equation for the probability of finding a single electronic charge at any distance from an attracting

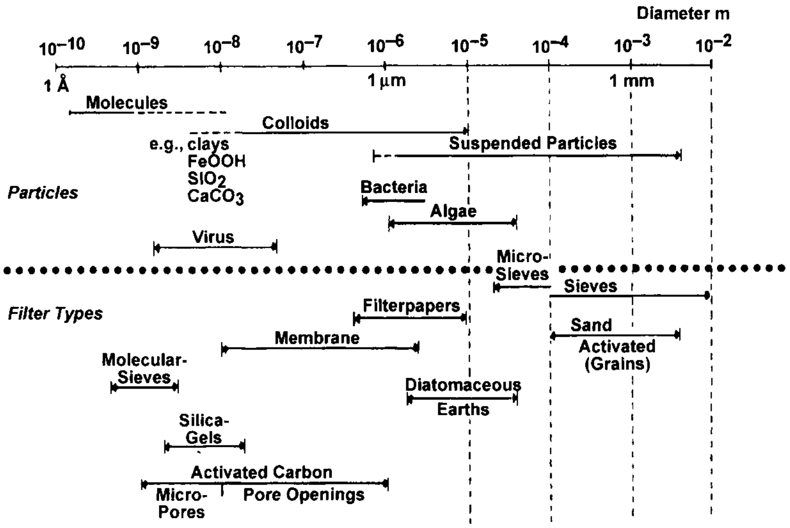


Figure 6.1. Suspended particles in natural and wastewaters varying in diameter from 0.005 to about 100 µm (5×10^{-9} to 10^{-4} m). Reproduced from Stumm,[10] courtesy of the American Chemical Society.

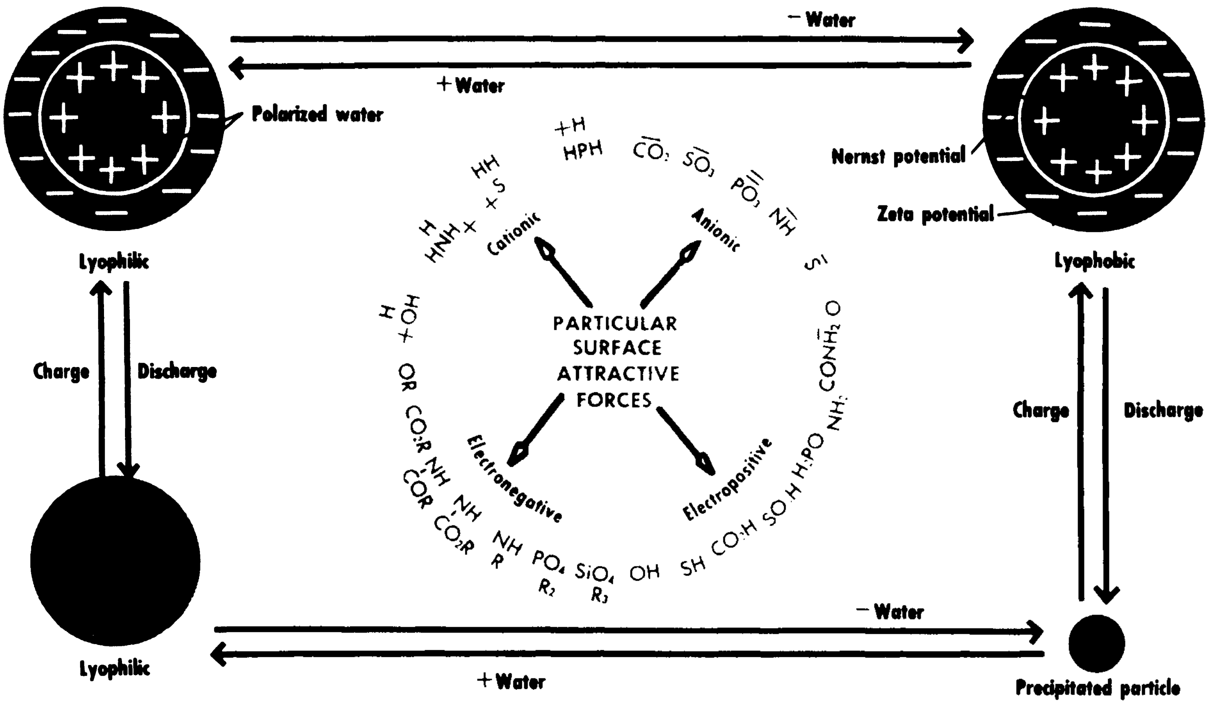


Figure 6.2. Stability of colloidal particles in aqueous suspensions depends on hydration and electrostatic charge, both of which depend on chemical composition and structure of substrate at the liquid-solid interface. Reproduced from Preising,[11] courtesy of the American Chemical Society.

plane (in this case, the particle's surface). In the presentation of electrostatic models of colloids in water, it is convenient to use a spherical shape. The Boltzmann-Poisson equation is:

$$\kappa_2 = \frac{1}{\delta^2} = \frac{8\pi\eta\varepsilon^2 z^2}{DkT} \qquad (3)$$

where κ = inverse of the thickness of the double layer δ (Figure 6.3)
η = number of ions per cm^3
z = their valence
ϵ = their electronic charge (esu)
D = dielectric constant
k = Boltzmann constant
T = absolute temperature

Equation 3 is defined for the case of equal valence of counterions (ions opposite in charge to the colloid's surface charge) and similions (ions similar in charge).[13] For example, the thickness δ of the double layer is, in the case of monovalent ions in a 0.1 M solution, approximately 10^{-7} cm or 10 Å (10^{-8} cm).

Figure 6.3 illustrates the concept of the distribution and position of counterions and similions around a spherical particle. There are two layers of ions whose potential and potential decay is of interest in colloidal stability. One layer is at the surface of the particle itself. This is the so-called Stern layer, where the positively charged counterions may have originated from the particle itself or by preferential adsorption from solution. This compact "double" layer—which measures the total potential of that layer—is given the symbol psi (ψ), which is sometimes distinguished as ψ_0, the Nernst potential. In the absence of thermal agitation (Brownian motion), the Stern layer would be formed simply by a very compact layer of counterions. However, the Brownian motion overcomes, in part, the electrostatic attractions and causes the diffusion of the double layer out into the bulk solution. Electroneutrality, therefore, is established at some finite distance into the solution.

The second layer is formed by the boundary between the Stern layer—the so-called "plane of shear"—and the bulk solution. This region is called the diffuse double layer, or the Gouy-Chapman layer. The potential gradient over this region is the zeta potential, Z. When a particle is put into motion by a direct current potential gradient (electrophoresis), the Stern layer apparently migrates with the particle in a rigid manner so that the dividing line between these two layers is called the plane of shear. There is, of course, disagreement as to the precise location of this plane of shear. For example, Mysels[13] gives a model of the distribution of counterions and similions around a particle that has these layers. It is tempting to label this model "triple layer." Mysels has a layer of bound solvent (water molecules) between the Stern and Gouy-Chapman diffuse layer. This apparently accommodates the water of hydration of the counterions. Mysels' plane of shear begins with these bound water molecules.

Concentration and valence of the counterions does affect, of course, the thickness and decay of the Nernst and zeta potentials. An increase of concentration in bulk solution leads to a corresponding and proportional increase in the concentration of counterions near the particle's surface. This gives a screening effect, which in turn causes the potential to decay more quickly in terms of distance (Figure 6.4).[14] Thus, an increase in the concentration of simple electrolytes gives a compaction of the double layer.

If the charge of the counterions is increased to di- and trivalent cations, there is a drastic effect on the double layer. The effect on the electric field is doubled and tripled, whereupon the counterions are brought closer to the particle's surface. Consequently, the thickness of the double layer is decreased with the concomitant quicker decay of potential. Figure 6.4d illustrates this point, where a trivalent cation has entered the fixed double layer. This lowers the zeta potential to such a low value that coagulation might occur.

Another consideration in determining the double-layer thickness and potential decay is the charge density σ on the particle's surface. This is usually expressed as the electronic charge per 100 Å^2, i.e., per 1 μm^2. According to Mysels,[13] a monolayer of average-sized ions corresponds to a charge density on the order of five such units. All things being equal, the potential increases as charge density is increased. Doubling the charge density does not necessarily result in a doubling of the potential. In fact, the potential is less than doubled because the double layer becomes compressed due to the attraction of more counterions. It should be noted that the charged surface and its double layer are electrically neutral when considered together. Consequently, the particle's charge density is also the charge density of the diffuse double layer.

Destabilization

Figure 2.2 depicts the destabilization of colloidal systems by removal of the solvent molecules and "neutralization" of the charged particle. In water treatment practice and research, colloidal destabilization is the aggregation of these particles for their rapid sedimentation and filtration. This is in contrast to the aggregation of colloids in research systems, where destabilization is measured by an increase rather than a decrease of turbidity. This is usually confined to silver halide hydrosols, where useful information is frequently obtained that may be applied to water treatment. In any event, at least four distinct mechanisms of destabilization exist: (1) compression of the double layer, (2) adsorption for neutralization of charges, (3) entrapment in a precipitate, and (4) adsorption for interparticle bridging.[15]

Double Layer Compression

When the addition of an electrolyte causes no specific interaction between it and the particle, these counterions enter into the double layer and determine its nature. Figure 6.5a shows that, under these conditions, the particle's charge remains constant, but the double layer thickness will decrease,

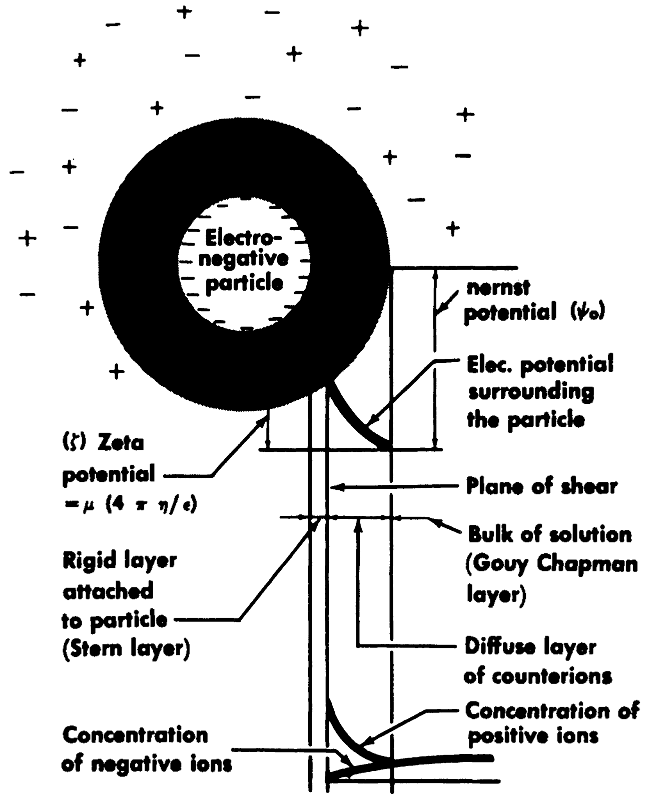


Figure 6.3. Zeta potential is the potential gradient across the diffuse double layer, which is the region between the Stern layer and the bulk of the solution. Reproduced from Preising,[11] courtesy of the American Chemical Society.

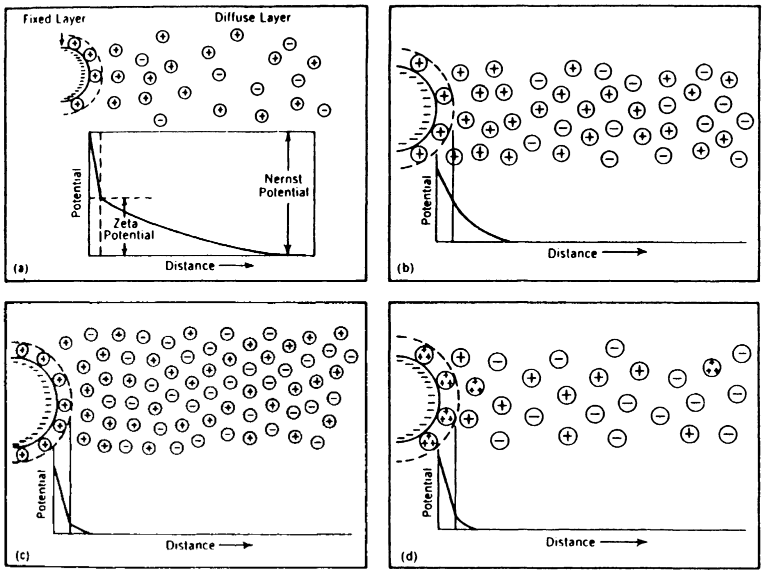


Figure 6.4. Source of zeta potential and effect of ions of opposite charge. (a) represents a negative colloidal particle in a low concentration of monovalent ions. As the ion concentration increases from that in (b) to that in (c), more positive ions enter the fixed double layer, and the zeta potential is reduced. In (d), a trivalent positive ion has entered the fixed double layer and so reduced the zeta potential that coagulation probably would result.

and the Nernst and zeta potentials will decrease. If a sufficient amount of an "indifferent" electrolyte is added, coagulation occurs. In addition, this effect increases greatly as the valence of the counterion is raised from one to two, and from two to three, etc. That is, a trivalent ion will require a lesser concentration than a divalent ion and a monovalent ion. This valence effect of the counterions on coagulation is called the Schulze-Hardy rule.[16,17]

Figure 6.5b shows the situation where the Nernst potential remains constant despite the addition of an electrolyte. In this case, the so-called potential-determining ions (whose ionization or adsorption is responsible for the charge of the particle) overcome the effects of concentration and valence of the added counterions. While the zeta potential decreases, there is a considerable effect on coagulation of these systems.

Figure 6.5c shows where counterions penetrate into the Stern layer and overcome the stabilizing effect of the potential-determining ions. As the concentration of counterions increases, more are adsorbed in the Stern layer. The Nernst potential remains constant, but the double layer is compressed, and the zeta potential is decreased. The valence of the counterion is significant here in the same way it is significant in Figure 6.7. This is the situation in water treatment practice.

Several coagulation curves are seen in Figure 6.6, where residual turbidity (%) is plotted against coagulant dose. Figure 6.6a represents the empirical Schulze-Hardy rule and the effects of indifferent electrolytes on colloidal stability. It does not, however, account for all of the mechanisms by which colloids are destabilized in the coagulation of water and wastewaters. There are many interactions of the coagulant with the particles in addition to the electrostatic effects.

Adsorption and Charge Neutralization

Researchers have recently compiled a considerable amount of information from various coagulant-colloidal systems indicating that interactions other than electrostatic are responsible for destabilization. For example, Figure 6.6b shows the reaction of dodecylammonium ions ($C_{12}H_{25}NH_3^+$) with negative silver iodide sols.[18] On the basis of electrostatic models, this monovalent cation should induce coagulation in a manner similar to Na^+ ions. Figures 6.6a and b show that a [Na^+] of about 10^{-1} *M* is needed for coagulation, whereas approximately 6×10^{-5} *M* of the organic amine was effective. This suggests a coagulation mechanism in addition to an electrostatic interaction. An additional effect can be seen in Figure 6.6b, which shows a restabilizing of the AgI sols above the coagulation concentration of the organic amine. This is accompanied by a charge reversal of the sols from negative to positive, which is explained by adsorption of excess counterions.

Another example of the effects of adsorption on colloidal stability is seen in Figure 6.6c, where residual turbidity after settling is plotted against aluminum nitrate concentration at pH 5.0.[19] This curve shows: (1) coagulation with aluminum compounds is effective at "low" dosages (6×10^{-6} *M*); (2) the colloidal system was restabilized and the charge was reversed at a higher dose of aluminum nitrate (4×10^{-5} *M*); and (3) there was another zone of coagulation at higher coagulant doses ($\sim10^{-2}$ *M*) where $Al(OH)_{3(s)}$ is precipitated. This second area of coagulation is entrapment of the colloidal particles by precipitation of $Al(OH)_{3(s)}$. The colloids in this case were AgI and AgBr.

Entrapment

In this situation, the coagulant is precipitated rapidly, floc is formed, and an interaction occurs with the colloid. This is called "frequently orthokinetic" coagulation.[20] It is the entrapment of a "low" zeta potential colloid with a precipitate with, perhaps, a net charge of zero. In this case, the coagulant [$Al(OH)_{3(s)}$, $Fe(OH)_{3(s)}$, $Ca(OH)_{2(s)}$, etc.] physically destabilizes the colloidal system.

Adsorption and Interparticle Binding

Recently there has been recently a large increase in the utilization of synthetic organic polymers in the treatment of water and wastewaters as coagulants or aids to coagulation. Optimum treatment frequently is obtained with anionic and polymeric destabilization of negatively charged particles. It is obvious that an electrostatic mechanism is not the only means of destabilization. A "bridging" theory was proposed by LaMer and Healy[21] and others[15] to account for the destabilization of colloidal systems by high-molecular-weight organic polymers. Adsorption of the polymer on specific sites of the colloid plays an important role in the "bridging" theory. This theory resembles the "binder" theory proposed for alum precipitation and coagulation.[20]

In order for a polymer molecule to be an effective destabilizer, it must contain constituents that can interact with sites on the colloidal particle. This is depicted in Reaction 1, Figure 6.7a,[15] which results in coagulation. In Reaction 2, the unattached portion of the polymer can interact with a second particle, which also leads to coagulation. Thus a "bridge" occurs between the two particles. Reaction 3 shows the possibility that bridging may not occur, resulting in little or no coagulation.

An example of anionic polymer coagulation is seen in Figure 6.6d where the curve describes aggregation of a negatively charged kaolinite suspension.[22] A comparison of Figures 6.6d and 6.6c shows that coagulation occurs at a much lower dosage than with Al^{3+}, and that restabilization occurs with excess doses. This type of restabilization cannot be

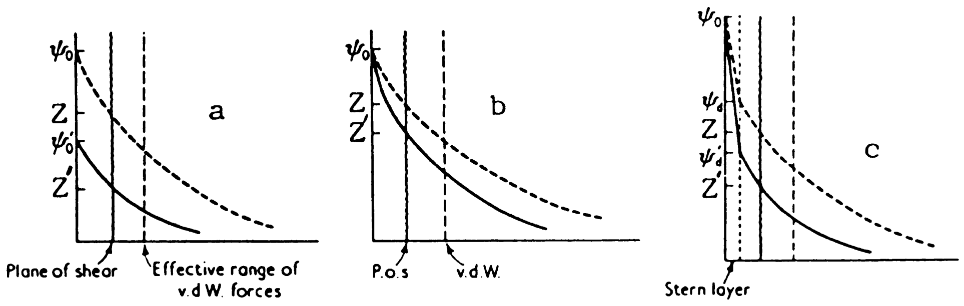


Figure 6.5. (a) In the absence of any interaction, the double layer is compressed and both ψ_0 and Z are lowered. (b) In the diffuse double layer, if ψ_0 is maintained constant, the double layer is compressed, and therefore Z is lowered. (c) In the presence of a Stern layer, and with constant ψ_0, Z is lowered by both a lower ψ_0 and a compression of the double layer. Reproduced from Mysels,[13] courtesy of John Wiley & Sons, Inc.

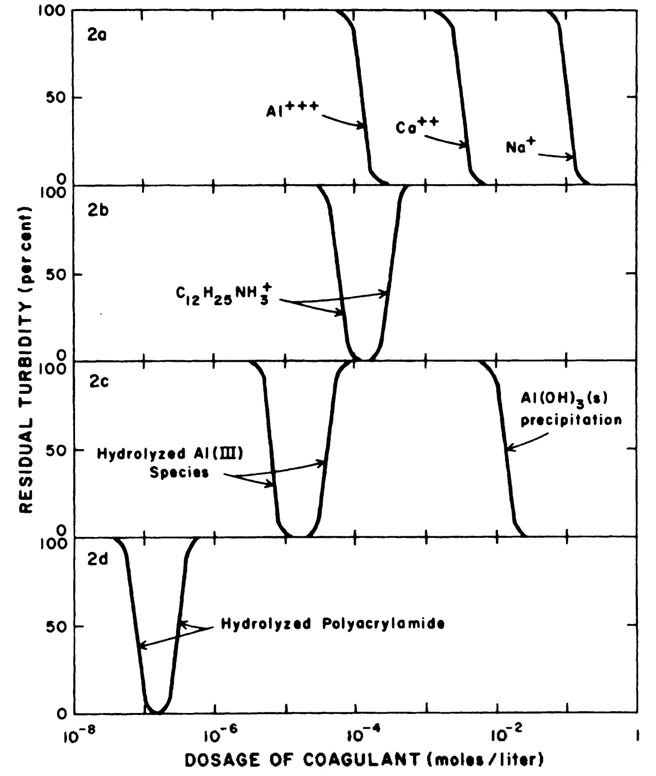


Figure 6.6. Schematic coagulation curves for several different coagulants. Reproduced from O'Melia,[15] courtesy of John Wiley & Sons, Inc.

due to charge reversal, since the colloid and polymer have the same apparent negative charge. Reaction 4 (Figure 6.7) may describe the restabilization by saturation of the particle's surface with excess polymer. Reactions 5 and 6 describe situations where systems that had been aggregated are restabilized by extended agitation.

Hydrolytic Chemistry of Silica, Aluminum, and Iron

Silica

Sodium silicate modified by acidification ("activated silica") was utilized as a coagulation aid to improve the treatability of water from Lake Michigan.[23] This was especially significant when alum was employed as the primary coagulant during the colder winter months. An explanation was provided subsequently from thermodynamic and kinetic considerations.[24]

A solubility diagram for amorphous silica in water is seen in Figure 6.8a. Equilibrium data used in construction of this diagram are given in Table 6.3. The solubility of amorphous silica is constant at 2×10^{-3} *M* (120 mg/L as SiO_2) below a pH value of approximately 8.5 where the principal species is a monomer, $Si(OH)_4$. Above this pH value, the solubility of amorphous silica is increased by the formation of anionic mono- and polymeric species. Most concentrated, commercial silicate solutions are in this pH range, which contain such stable anionic species as $Si_4O_6(OH)_6^{2-}$.

Preparation of "activated silica" is accomplished by acidification of a concentrated sodium silicate solution where it is oversaturated with respect to the precipitation of amorphous silica (point A, Figure 6.8a). This precipitation starts with polymerization reactions where monomers condense to form Si-O-Si bonds.[24] Negatively charged silica sols are formed by cross-linking and aggregation of the polysilicates. Dilution of the acidified solution can terminate or reverse these polymerization reactions at or near the insolubility limit (point B, Figure 6.8a). Many types of activated silicas, which range from anionic polysilicates to colloidal SiO_2 precipitates, are prepared by variation of this concentration and basicity of the initial stock solution, the method and extent of acidification, the time of aging, the amount of dilution, and the temperature. These activated silicas may remain active as coagulants for several weeks. These same principles apply also to the partial neutralization of $AlCl_3$ solu-

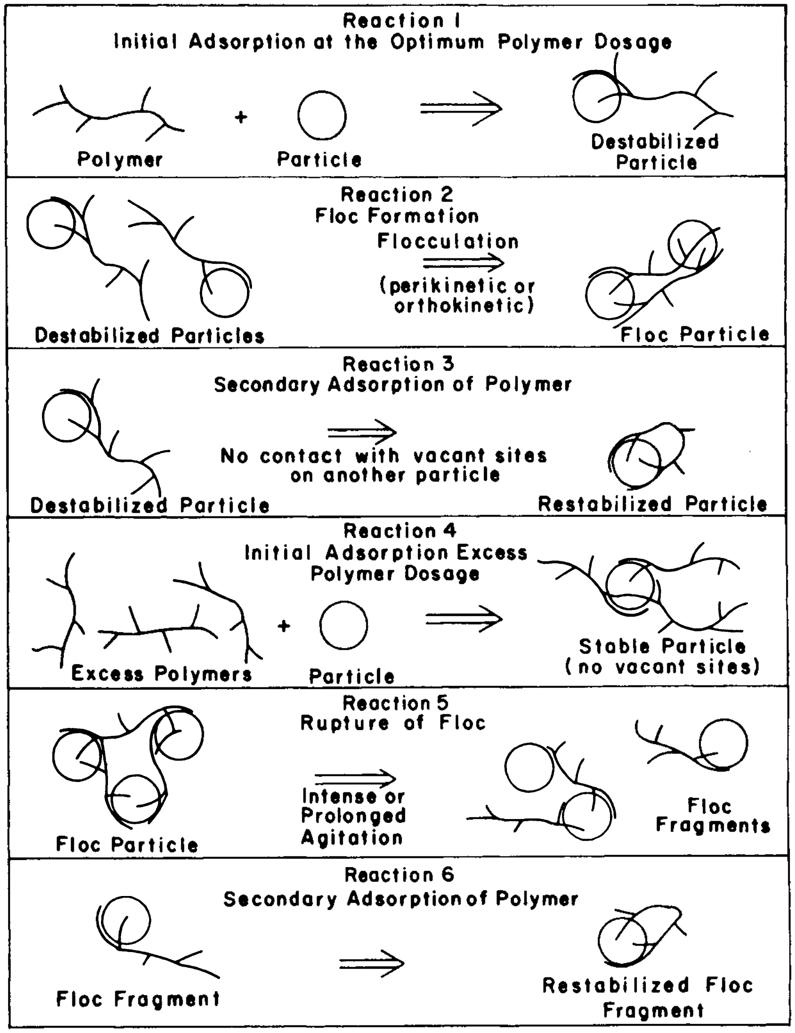


Figure 6.7. Schematic representation of the bridging model for the destabilization of colloids by polymers. Reproduced from O'Melia,[15] courtesy of John Wiley & Sons, Inc.

tions and preparation of polyaluminum chloride (PACl). PACl solutions are useful for treatment of cold, soft, and turbid waters (see below).

Aluminum and Iron

Aluminum and iron cations undergo hydration reactions in aqueous systems to an extent governed by the ligand properties of the cation, the metal ion concentration, and the $[H^+]$ concentration. That is, "naked" metal ions do not exist in water, but occur as aquocomplexes of varying degrees. The addition of Al(III) and Fe(III) salts to water at concentrations lower than the solubility product constants of their amorphous hydroxides leads to the formation of soluble monomeric, dimeric, and polymeric hydroxometal complexes. Some of these reactions and their equilibrium constants for Al and Fe (Equations 8–25) are given in Table 6.3 at 25°C.[26] It should be noted that both Al and Fe are amphoteric; that is, cationic and anionic complexes are formed. Experimental evidence confirms the existence of all complexes in Table 6.3; however, there is doubt about the significance of such "giant" cations as $Al_{13}O_4(OH)_{24}^{7+}$ in the coagulation of waters in plant practices.

Whenever the solubility product constants are exceeded for $Al(OH)_{3(s)}$ (Reaction 17) and for $Fe(OH)_{3(s)}$ (Reaction 25), a series of hydrolytic reactions occurs (Table 6.3). Amorphous forms of the metal hydroxides eventually precipitate. As depicted in Figures 6.8b and c, $[H^+]$ affects the solubility of these precipitates. The quantities of Al and Fe salts employed in treatment plant practice of coagulation

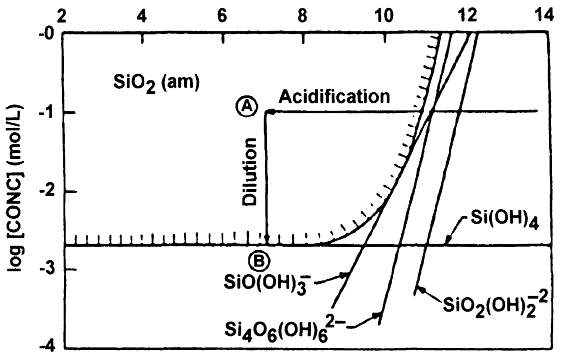


Figure 6.8a. Solubility of SiO_2(am).[25]

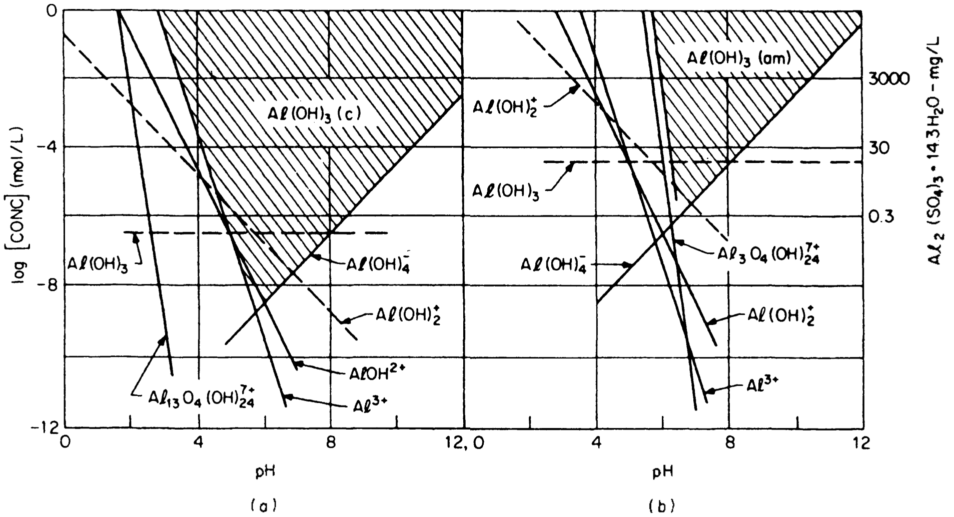


Figure 6.8b. Solubility of aluminum at equilibrium with (a) gibbsite and (b) amorphous $Al(OH)_3$. Thermodynamic data from Table 6.3.[25]

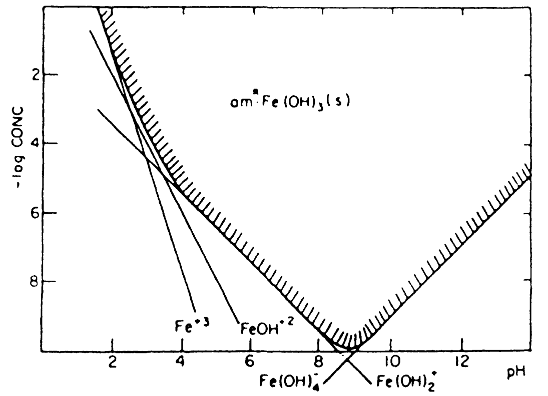


Figure 6.8c. Solubility equilibria of amorphous $Fe(OH)_{3(s)}$.[15]

are sufficient to exceed the K_s values of their hydroxides. For example, a 30 mg/L dosage of alum as $Al_2(SO_4)_3$ is approximately 10^{-4} *M*, and is well within the solid region of $Al(OH)_{3(s)}$ at pH values of 6-8.

Table 6.3. Hydrolytic Constants for Silica, Aluminum, and Iron Equillibria.[26]

Reaction No.	Reaction	Log K_{eq}[a]
4	$SiO_2(am) + 2H_2O = Si(OH)_4$	–2.7
5	$Si(OH)_4 = SiO(OH)_3^- + H^+$	–9.46
6	$SiO(OH)_3^- = SiO_2(OH)_2^- + H^+$	–12.56
7	$4Si(OH)_4 = Si_4O_6(OH)_6^- + 2H^+ + 4H_2O$	–12.57
8	$Al^{3+} + H_2O = AlOH^{2+} + H^+$	–4.97
9	$Al^{3+} + 2H_2O = Al(OH)_2^+ + 2H^+$	–9.3
10	$Al^{3+} + 3H_2O = Al(OH)_{3(aq)} + 3H^+$	–15.0
11	$Al^{3+} + 4H_2O = Al(OH)_4^- + 4H^+$	–23.0
12	$2Al^{3+} + 2H_2O = Al_2(OH)_2^{4+} + 2H^+$	–7.7
13	$3Al^{3+} + 4H_2O = Al_3(OH)_4^{5+} + 4H^+$	–13.9
14	$13Al^{3+} + 28H_2O = Al_{13}O_4(OH)_{24}{}^{7+} + 32H^+$	–98.7
15	$\alpha\text{-}Al(OH)_{3(s)} + 3H^+ = Al^{3+} + 3H_2O$	8.5
16	$Al(OH)^3 + 3H^+ = Al^{3+} + 3H_2O$ amorph.	10.5
17	$Al^{3+} + 3OH^- = Al(OH)^{3(s)}$	33.0
18	$Fe^{3+} + H_2O = FeOH^{2+} + H^+$	–2.19
19	$Fe^{3+} + 2H_2O = Fe(OH)_2^+ + 2H^+$	–5.67
20	$Fe^{3+} + 3H_2O{=}Fe(OH)_{3(aq)} + 3H^+$	<–12.0
21	$Fe^{3+} + 4H_2O = Fe(OH)_4^- + 4H^+$	–21.6
22	$2Fe^{3+} + 2H_2O = Fe_2(OH)_2^{4+} + 2H^+$	–2.95
23	$\alpha\text{-}FeOOH(s) + 3H^+ = Fe^{3+} + 2H_2O$	0.5
24	$(am)FeOOH(s) + 3H^+ = Fe^{3+} + 2H_2O$	2.5
25	$Fe^{3+} + 3OH^- = Fe(OH)_{3(s)}$	38.0

[a] At 25°C and I = 0.0.

Normally, freshly precipitated amorphous $Al(OH)_{3(am)}$ (log $K_{eq} \approx 31.5$, Reaction 17, Table 6.3) forms when aluminum salts are added to water. This is seen in the solubility diagram for aluminum in Figure 6.8b where only one polymer, $Al_3O_4(OH)_{24}{}^{7+}$, and three monomers, Al^{3+}, $Al(OH^+)_2$, and $Al(OH)_4^-$ are given. Other polymers and monomers are possible from the reactions in Table 6.3. Aluminum is the least soluble within a pH range of 5.7 to 6.2. Below a pH of 5.7, freshly precipitated $Al(OH)_{3(am)}$ is quite soluble and such polymer species as $Al_3(OH)_4^{5+}$ (not shown) and $Al_{13}O_4(OH)_{24}{}^{7+}$ can predominate. Also, this solubility diagram for Al is quite "small," which has profound implications for water treatment practice. This simply means that pH values greater than 5.7 to 6.2 and alum dosages greater than 10^{-6} M must occur for $Al(OH)_{3(am)}$ to precipitate (the dashed box in Figure 6.8b) and effect coagulation of turbid waters. Outside of the shaded area and especially under acidic conditions then, the cationic polymers and monomers may be important coagulants. In any event, such thermodynamic diagrams as seen in Figures 6.8b and c neglect the kinetics of the hydrolytic reactions and reactions with particles and natural organic matter (NOM). This point is considered again in the text below.

An example of the above comes from the use of PACl, which is prepared by combining lime or caustic with acidic Al salts. These preparations contain polymeric or colloidal forms of hydrolyzed aluminum, and are commercially available. Applications of this coagulant are given below.

The hydrolytic reactions of alum and PACl were investigated under laboratory conditions that simulated water treatment plant conditions[26a,b] at typical Al doses ($10^{-3.3}$ M, 13.5 mg Al/L). Alum showed no evidence of polymer formation, whereas PACl consists of preformed polymers that are stable upon dilution below pH 6. Solubility studies showed that alum and PACl precipitate to form different solid phases. Alum precipitates are adequately described by amorphous $Al(OH)_{3(s)}$ solubility. The polymeric structure of PACl is retained upon precipitation that yields a solid phase with different light scattering characteristics, electrophoretic mobility (EPM), and solubility than alum floc. These chemical differences between alum and PACl are noted in Figure 6.9a and b.[26a] Here, the most significant differences are seen in the positive EPM values over the range of 4.5 to 10 for PACl and the minimum effect of temperature on PACl chemistry. The second phase of this study was concerned with the coagulation of fulvic acid (FA) by alum and PACl.[26b] It is interesting to note that the dose requirements for these two coagulants for FA removal were nearly identical.

It is argued that the dosages of Al(III) and Fe(III) are always high enough to exceed the solubility product constants of their hydroxides in plant practice.[15] The significance of this is that the polymeric forms, i.e., hydrometal complexes, are adsorbed onto the colloidal particles and cause their destabilization. The quantity required for coagulation depends, of course, on the quantity of colloids in the water. This relation describes the "stoichiometry" of the coagulation reaction.[27]

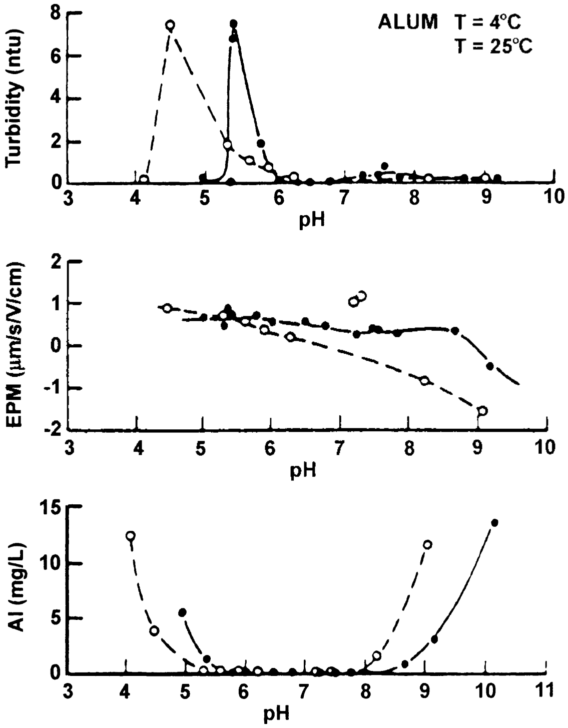


Figure 6.9a. Experimental results for alum (5×10^{-4} M Al) in deionized water at two temperatures.[26a]

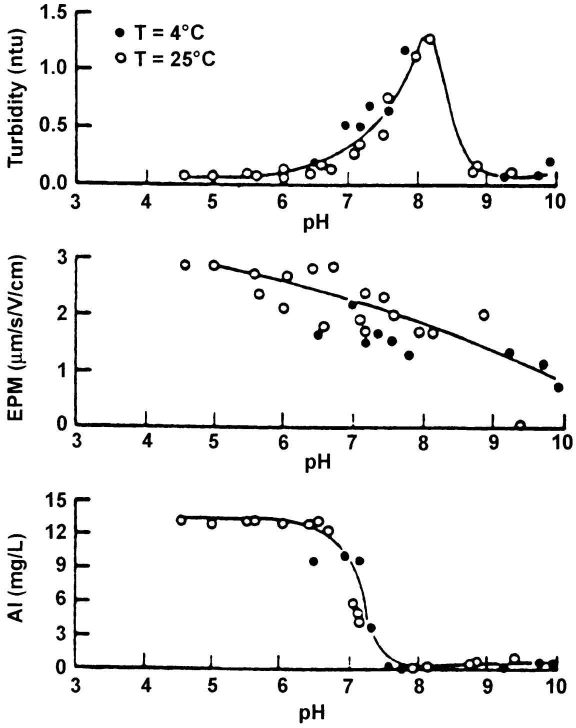


Figure 6.9b. Experimental results for PACl (5.04×10^{-4} M Al) in deionized water at two temperatures.[26a]

A solubility diagram for Fe(III) in water is seen in Figure 6.8c using the thermodynamic data in Table 6.3. Here, only freshly precipitated amorphous $Fe(OH)_{3(am)}$ (log K_{eq}=38.0, Reaction 25, Table 6.3) is considered. At pH values less than 8.0, such cationic monomers as Fe^{3+}, $Fe(OH)_2^+$, and $FeOH^{2+}$ are the dominant soluble species. Above a pH value of 8.0, the principal soluble species at equilibrium with the $Fe(OH)_{3(am)}$ is the monomeric soluble species, $Fe(OH)_4^-$. A comparison of hydrolytic equilibria in Table 6.3 and Figure 6.8b and c shows that Fe(III) is considerably less soluble than Al. For example, a 10^{-4} M solution of Fe(III) can precipitate $Fe(OH)_{3(am)}$ above a pH of about 3.0 and well into the alkaline pH range. However, the predominant use of iron salts lies with the coagulant of wastewaters.

Example Problem 6.1: A raw water supply is treated with an alum dosage of 25 mg/L. Calculate the following:

1. The amount of alum required to treat a flow of 1.0 MGD.
2. The amount of natural alkalinity required to react with the alum added.
3. The volume of $Al(OH)_3$ sludge produced per MGD if it is collected at 2.0% solids. Assume that the dry solids have a specific gravity of 2.2.

Solution:

1. The dosage of alum for a 1.0 MGD flow is

$$\frac{\text{lb}}{\text{day}} = 8.34 \, \frac{\text{lb / day}}{(\text{mg / L})\,(\text{MGD})} \times$$

$$25 \text{ mg / L} \times 1.0 \text{ MGD} = 208.5$$

2. The reaction between alum and natural alkalinity is:

$$\overset{666.43}{Al_2(SO_4)_3 \cdot 18H_2O} + \overset{3(162)}{3Ca(HCO_3)_2} \rightarrow$$

$$\overset{155.96}{2Al(OH)_3} + 3CaSO_4 + 18H_2O + 6CO_2$$

One mole of alum reacts with 3 moles of $Ca(HCO_3)_2$ as shown in Equation 1.

Expressing the reaction on a weight basis, 1 mg/L of alum will react with

$$\frac{3(162)}{666.43} = 0.729 \text{ mg / L } Ca(HCO_3)_2$$

Expressing $Ca(HCO_3)_2$ in mg/L as $CaCO_3$, mg/L as $CaCO_3$ =

$$0.729 \times \frac{\text{eq. wt. } CaCO_3}{\text{eq. wt. } Ca(HCO_3)_2} =$$

$$0.729\left(\frac{50}{81}\right) = 0.45 \text{ mg/L}$$

Amount of natural alkalinity reacting with alum

$$= 25 \text{ mg/L alum} \times 0.45 \frac{\text{mg/L alkalinity}}{\text{mg/L alum}} =$$

$$10.8 \text{ mg/L}$$

3. The volume of $Al(OH)_3$ sludge produced per day:
   (a) Referring to step 2, 1 mole of alum produces 2 moles of $Al(OH)_3$.

Expressing the reaction on a weight basis, 1 lb alum will produce

$$\frac{155.96}{666.43} = 0.234 \text{ lb } Al(OH)_3$$

Thus, 208.5 lb alum will produce

$$0.234\,(208.5) = 48.79 \text{ lb/day } Al(OH)_3$$

(b) Calculate the specific gravity of sludge at 2% solids:

$$\frac{1}{S_s} = \sum_{i=1}^{n}\left(\frac{W_i}{S_i}\right)$$

where S_s = specific gravity of sludge
W_i = weight fraction of *i*th component of sludge
S_i = specific gravity of *i*th component of sludge

$$\frac{1}{S_s} = \left(\frac{0.98}{1.0} + \frac{0.02}{2.2}\right) = 0.98 + 0.009 = 0.989$$

$$S_s = 1.011$$

(c) Calculate the volume of sludge:

$$\text{volume} = 48.79 \frac{\text{lb}}{\text{day}} \times \frac{100}{2} \times \frac{1}{8.34 \text{ lb/gal}} \times \frac{1}{1.011}$$

$$= 289.28 \text{ gal}$$

Alternatively, water in sludge

$$= 48.79 \frac{\text{lb}}{\text{day}} \times \frac{98}{2} = 2390.31 \text{ lb/day}$$

volume of wet sludge

$$= \frac{48.79 \text{ lb/day}}{8.34 \text{ lb/gal} \times 2.2} + \frac{2390.31 \text{ lb/day}}{8.34 \text{ lb/gal}}$$

$$= 2.65 \text{ gal} + 286.62$$

$$= 289.3 \text{ gal}$$

This example problem was modified from Reference 27a.

Mechanisms of Coagulation

A schematic representation of residual turbidity as a function of coagulant dosage when the pH value is held constant is seen in Figure 6.10a.[15,27] These four curves represent natural waters treated with Al(III) and Fe(III). Each water contains a different content of colloidal material where this is expressed as colloidal surface/unit volume of suspension, $\bar{S}$ (e.g., m^2/L). Four "zones" of coagulant dosages react with the colloidal matter. In zone 1, no destabilization occurs, since the coagulant dosages are "low." In zone 2, destabilization occurs because of higher dosages of the coagulant. Here, aggregation occurs and the residual turbidity is low or nil. In zone 3, restabilization of the colloidal materials occurs due to the higher coagulant contents when the pH value is appropriate. In zone 4, coagulation occurs as the result of a "large" quantity of the precipitates of Al and Fe. This is the so-called zone of "sweep floc" where the colloids are swept from solution by the coagulants. In plant practice, this type of coagulation predominates.

Figure 6.10b shows a graphic representation of the relation between coagulant dosage and colloidal surface concentration at a constant pH value. When the colloid concentration is "low," $\bar{S}_1$, it is necessary to have an excess of coagulant in solid form. This is typical of most natural surface waters that contain "low" turbidities, less than 50 JTU. It is necessary to overwhelm the widely dispersed particulates with a "large" quantity of the coagulant in the "sweep floc" zone. When colloid concentrations are higher, $\bar{S}_2$ and $\bar{S}_3$, lower coagulant doses are needed for floc formation and destabilization. There is a greater number of colloidal particles at $\bar{S}_2$ and $\bar{S}_3$, which affords a greater contact with the floc. This occurs in zone 2 and where there is a stoichiometric relation between the colloid concentration and the coagulant dosage.[27] When the colloid concentration is very "high," a "large" quantity of coagulant is needed. This is represented by S_4 in Figure 6.10b, where coagulation occurs in zone 2. An example is the destabilization of sludges accumulated at wastewater treatment plants, or the conditioning of water treatment sludges for ultimate disposal.

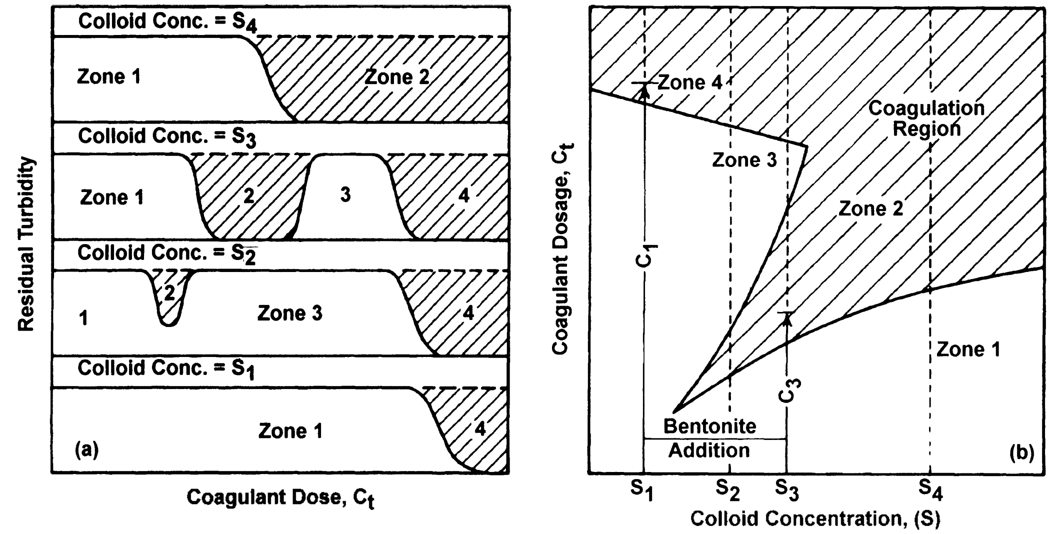


Figure 6.10. Schematic representation of coagulation observed in jar tests using Al(III) or Fe(III) slats at constant pH. Reproduced from O'Melia,[15] courtesy of John Wiley & Sons, Inc.

In general, there are two mechanisms of coagulation, both depicted in Figures 6.10a and b. One is neutralization of surface charges on the colloid by positively charged cations of Al and Fe or their hydrous oxides. In this case, it is not necessary to achieve electroneutrality. Rather, a reduction in the zeta potential frequently results in destabilization of the colloids. The second mechanism is physical entanglement of the colloid with floc. In this case, the zeta potential of the colloids is "low" or, at least, very close to the point of destabilization.

Coagulant dosage and pH value are, perhaps, the two most important variables that are controlled in water treatment plant practice for effective coagulation. Certainly the diagrams in Figure 6.10 indicate a stoichiometry between the colloid and coagulant. Another type of diagram has become available for prediction of the chemical conditions under which coagulation occurs for inorganic turbidity and NOM removal. An example is seen in Figure 6.11 that was developed by superimposition of the chemical conditions where coagulation occurs on the thermodynamic stability diagram for $Al(OH)_{3(s)}$.[25,28] This type of diagram may be useful for planning, analyzing, and interpreting laboratory and pilot plant studies.

Inorganic Turbidity

A generic alum coagulation diagram is seen in Figure 6.11 for removal of turbidity via the charge neutralization mechanism with a reduction of the zeta potential (Figure 6.3). Coagulation should occur when either a soluble hydrolytic species (e.g., Al^{3+}) or solid $Al(OH)_3$ (that may be positively charged) interacts with inorganic particulates. This interaction and the relation of the zeta potential to the coagulation diagram is seen in the lower portion of Figure 6.11. The isoelectric point (iep) of zero charge for $Al(OH)_{3(s)}$ is in the pH range of 7.0 to 9.0 [the iep for $Al(OH)_{3(s)}$ in Figure 6.11 was assumed to be 8.0]. Positively charged $Al(OH)_{3(s)}$ reacts with negatively charged colloids, which produces two points of zero zeta potential at pH values of 4.8 and 6.8 (points D and E in Figure 6.11). Between these two values, colloids can be restabilized because of an excessive adsorption of the positively charged coagulant species (see Figure 6.6c). Also, these conditions may be suitable for direct filtration.[25]

The classic research work of Black and several coworkers on the alum coagulation of turbidity artificially created by clay minerals demonstrates the principal concepts of Figure 6.11.[29-32] Kaolinite, Fuller's earth (illite), and montmorillonite are representative of the three major classes of clay minerals. That they are negatively charged in water is seen by their electrophoretic mobilities, as seen in Figure 6.12a, that are negative over the pH range of 3.3 to 10.0.[29] Figure 6.12b shows the effect of 5 mg/L of alum on residual turbidity and the electrophoretic mobility as a function of $[H^+]$. These data indicate that a "small" quantity of alum is sufficient to reverse the charge of kaolinite at a pH of about 5, whereas the floc particles formed with the other two clay minerals vary slightly in their negative charge (between points D and E on Figure 6.11). In Figure 6.12c, a dosage of 15 mg/L alum reverses the charge of kaolinite and fuller's earth, but not montmorillonite.

The curves in Figures 6.12b and c also show the pH zones within which destabilization occurs. All three clays are coagulated somewhat within the pH range of 3.5 to 4.5 where

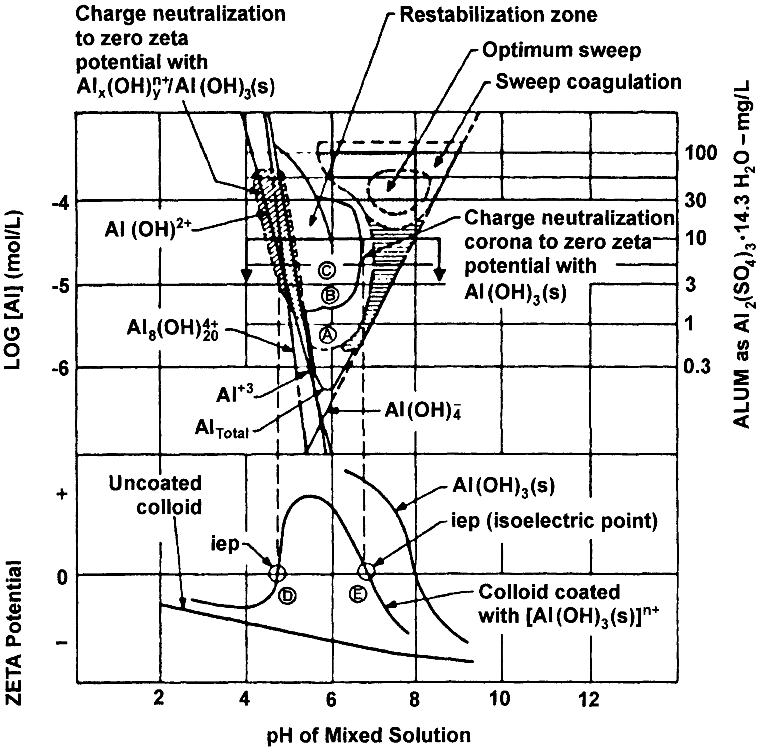


Figure 6.11. The alum coagulation diagram and its relationship to zeta potential.[28]

the particles are weakly and negatively charged. As the pH value is increased, there is a charge reversal of kaolinite and Fuller's earth over a pH range which defines a zone of no floc formation. Finally, the data indicate that all three clays are flocculated best in the pH range of 7.4 to 8.2, where the particles have a slight negative charge. The curves in Figure 6.12b show that a "sweep floc" dosage of alum, 100 mg/L, neutralizes the charge with destabilization at pH values 3.5 to 4.5. As the pH value is increased, the charge is reversed first to positive values, with restabilization occurring within 4.5 to 5.5. Finally, the three clay minerals are destabilized as the pH value is increased beyond 5.5 with the charge slowly becoming negative.

These studies do not explain that charge neutralization alone effects coagulation of the three clay minerals by alum. This is evident where the best turbidity removal occurs at pH values of 7.5 to 8.5 in a region of negative particle mobility, rather than at the point of charge reversal. A "large" alum dosage, 100 mg/L, is required to reverse the charge on montmorillonite (Figure 6.12d), but only a small amount, 15 mg/L, is needed for "good" coagulation (Figure 6.12c). Since the isoelectric point (i.e., zero net charge) of $Al(OH)_{3(s)}$ is somewhere in the pH range of 7.5 to 8.5 (see Figure 6.11), this suggests that coagulation is occurring with a neutral floc. In turn, this is explained by the "sweep" floc mechanism, or by an adsorption mechanism.

There are three important mechanistic constraints in the application of the alum coagulation diagram (Figure 6.11) to water treatment practice. First, the surface area of the particulate determines the position of the restabilization zone. This occurs for alum dosages of 2–30 mg/L and in pH ranges of 5.0 to 6.8. These domains are applicable for waters with "low" turbidities that are most frequently used as sources for drinking water. Second, "high" concentrations of such anions as phosphate (PO_4^{3-}), silicate ($HSiO_4^{3-}$), or sulfate (SO_4^{2-}) may cause suppression of charge reversal and restabilization. There is some evidence that SO_4^{2-} concentrations in raw water greater than 10 to 14 mg/L tend to eliminate charge reversal of the colloid.[33,34] Third, natural organic matter in the form of humic substances could control the alum dosages needed for effective coagulation, which would, in turn, alter the zones of coagulation, as seen in Figure 6.11.

Naturally Occurring Organic Color

Aluminum Coagulants

Considerable information is available about the chemical nature of organic color in natural waters,[35] yet the precise structure of the color molecules is still largely unknown. It is known, however, that organic color in water has the physical properties of a negatively charged colloid[36] and that their particle sizes range from 3.5 to 10 μm.[37]

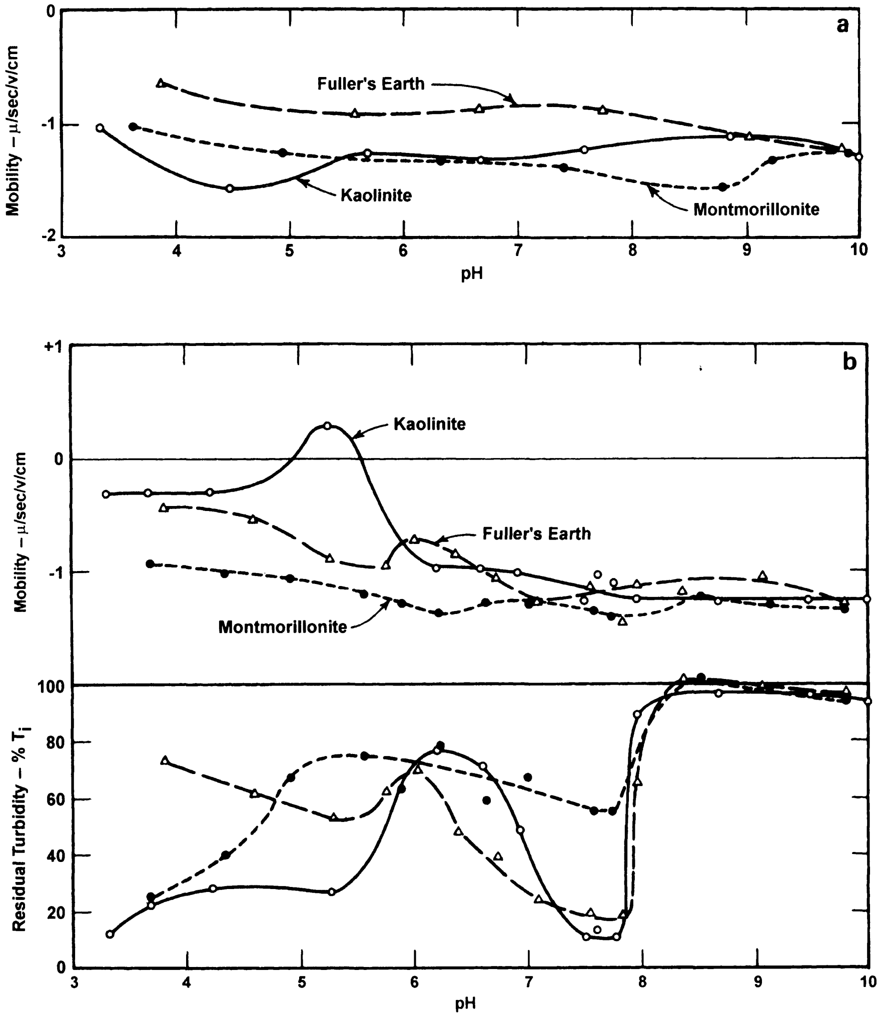


Figure 6.12. (a) Mobilities of clays without alum. (b) Coagulation of three clays with a dosage of 5 ppm alum. (c) Coagulation of three clays with a dosage of 15 ppm alum. (d) Coagulation of three clays with a dosage of 100 ppm alum. Reproduced from Black and Hannah,[29] courtesy of the American Water Works Association.

Coagulation diagrams have been constructed also for effective color removal from water. Regions where color removal occurs for humic acids (mostly laboratory studies) are seen in Figure 6.13.[38] Two distinct regions are defined that may be associated with two removal mechanisms. In the pH range of 6 to 8, removal may occur by adsorption of the humic acid on freshly precipitated $Al(OH)_{3(am)}$. On the other hand, humic acid can be precipitated by a change reversal mechanism through oppositely charged soluble or solid phase aluminum hydrolytic species in the pH range of 4.0 to 5.5. These wide generalizations on the mechanisms of color removal by alum have been suggested and validated by many investigators.[38–43] It is important to note that the color domains shown on Figure 6.13 are applicable to high-molecular-weight (>50,000) humic acids from commercial preparations. However, naturally occurring humic substances with their lower-molecular-weights (<10,000) are removed with lesser efficiency by coagulation. Consequently, such other processes as carbon adsorption should be considered for their removal. Also, it is noted that efficient color removal is favored by a lower pH range than for optimum inorganic turbidity removal.

Early research with two highly colored surface waters coagulated with Al(III) and Fe(III) sulfates gave, perhaps, the first indication that charge reversal is one of the mechanisms of removal.[41] Figure 6.14a shows the electromobility and residual color values when a highly colored water was coagulated with 60 mg/L of alum. Figure 6.14b presents similar data for coagulation of the same water with 50 mg/L of ferric sulfate. These two figures, in an almost classic man-

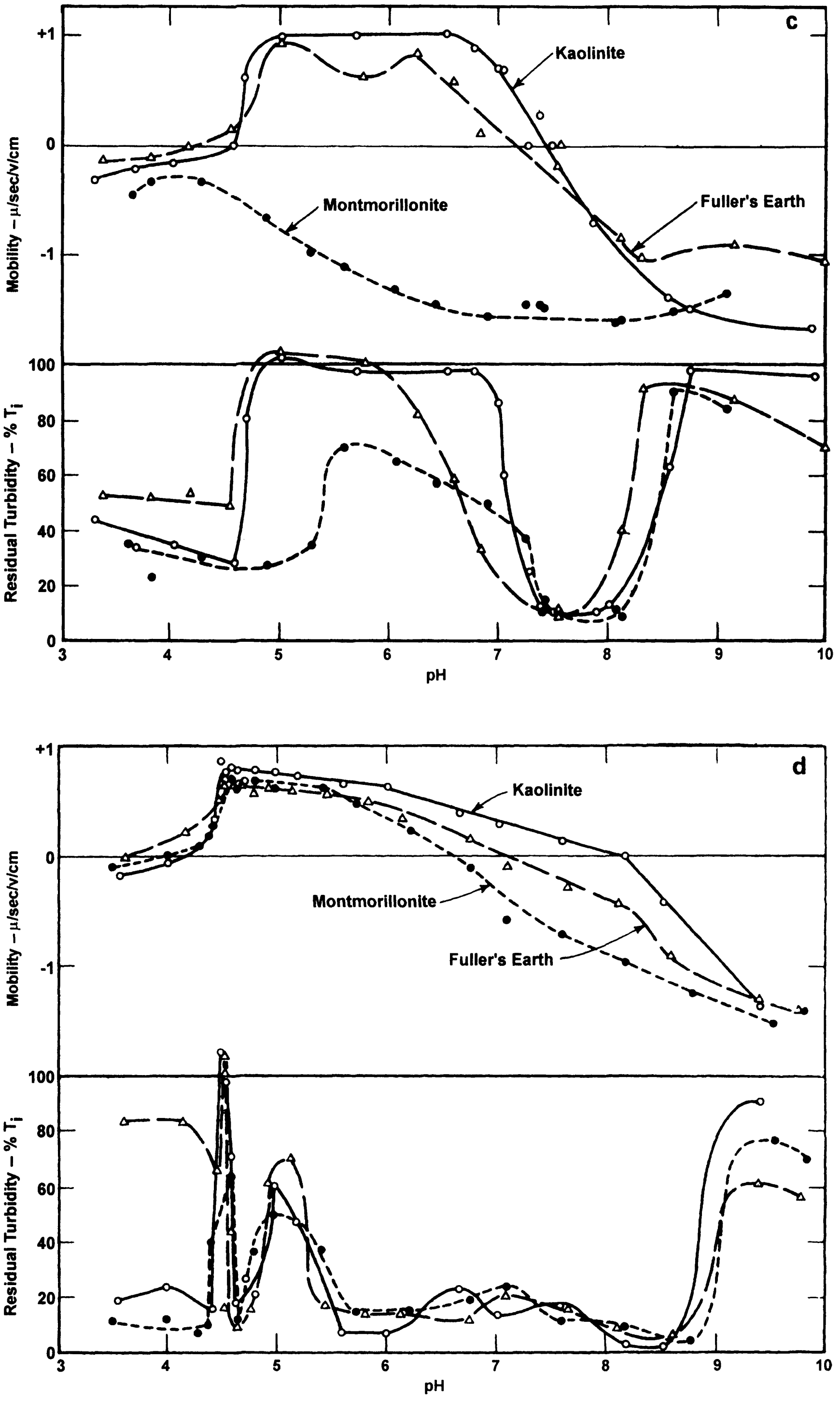


Figure 6.12 (Continued). (a) Mobilities of clays without alum. (b) Coagulation of three clays with a dosage of 5 ppm alum. (c) Coagulation of three clays with a dosage of 15 ppm alum. (d) Coagulation of three clays with a dosage of 100 ppm alum. Reproduced from Black and Hannah,[29] courtesy of the American Water Works Association.

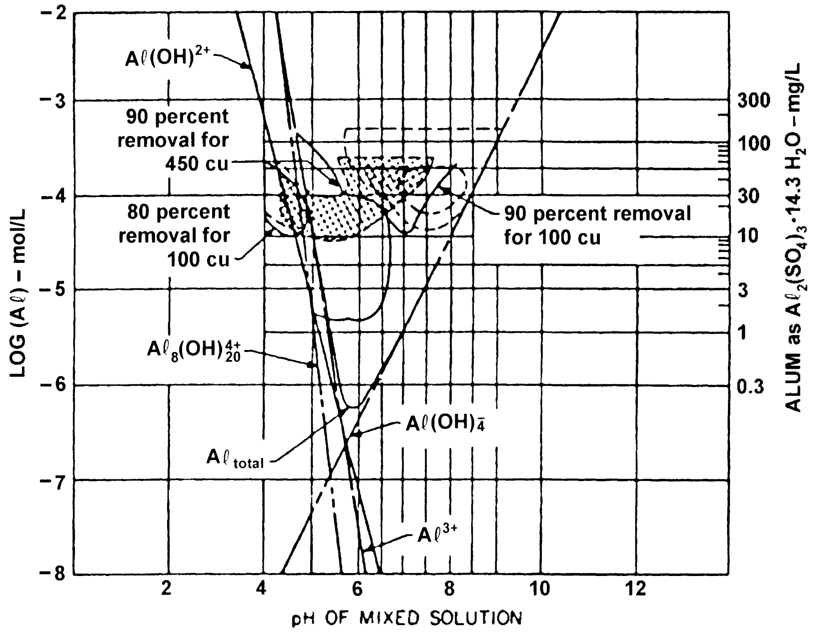


Figure 6.13. Color removal domains on the alum coagulation diagram for initial humic acid of 4 mg/L as TOC (100 cu) and 20 mg/L as TOC (450 cu) with zero turbidity.[25,38]

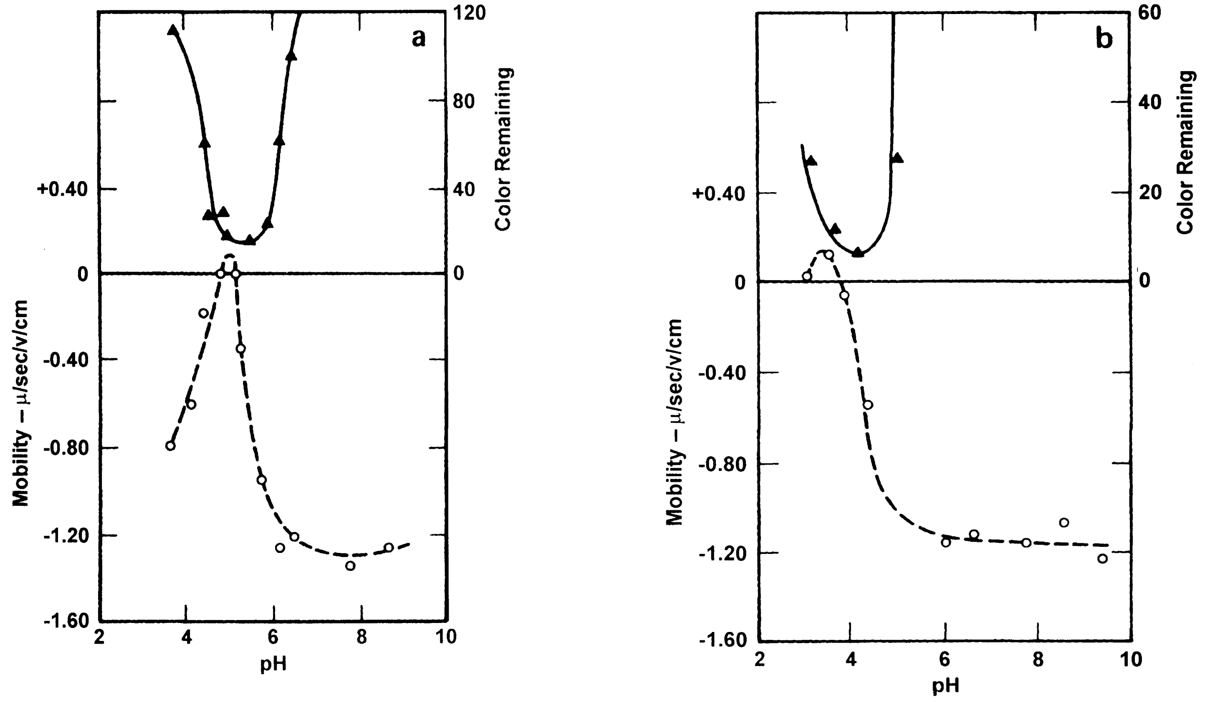


Figure 6.14. (a) Effect of pH and constant alum dosage on coagulation of water B. A constant alum dosage of 60 mg/L was used, and the pH was varied with HCl and $Ca(OH)_2$. Although the mobility curve is shown with a small positive loop, actually no definitely positive particles were found in any jar. (b) Effect of pH and constant ferric sulfate dosage on coagulation of water B. A constant $Fe_2(SO_4)_3$ dosage of 50 mg/L was used, and the pH was adjusted with HCl and $Ca(OH)_2$. Reproduced from Black and Williams,[41] courtesy of the American Water Works Association.

ner, show that charge reversal of the floc particles and optimum color removal occurs at or very near the same pH value.

Raw water supplies with "low" concentrations (i.e., less than 10 mg DOC/L) of natural organic color are difficult to coagulate. For treatment of these waters, the removal of humic substances apparently occurs by direct precipitation with monomers and small polymers of aluminum at pH values less than 5.0.[39] On the other hand, at pH values greater than 7.0, removal occurs by adsorption of humic substances on $Al(OH)_{3(s)}$. In between these pH values, both mechanisms of removal can occur. Consequently, the concentration of the organic color is significant because of the stoichiometry of the coagulation reaction. When the DOC is "low," the formation of humic-aluminum precipitates is favored. When the DOC is "high," the precipitation of $Al(OH)_{3(s)}$ is kinetically favored over the formation of humic-Al precipitates. Consequently, coagulant dosages are higher, direct filtration is eliminated as a treatment option, and sludge volume is increased.[25]

Iron Coagulants

The necessity to remove color from raw water supplies initiated the research of Black and Packham.[41–43] These waters contained relatively high concentrations of color and humic substances with dissolved organic carbon (DOC) contents greater than 25 mg/L. That ferric sulfate dosage is a function of raw water color is seen in Figure 6.15, and of pH value is seen in Figure 6.16. Also, the pH value for optimum color removal, 3.78, is related closely to the pH value at which a zero electromobility value is recorded (Figure 6.11b). The best color removal is recorded at a pH value just below the isoelectric point where mobility of the floc particles is positive, and just above the pH of the maximum positive charge.

A comprehensive study has described the coagulation of organic color with the "hydrolyzing coagulants," alum and ferric chloride, in the presence of dilute clay suspensions.[43] The characteristics of coagulation given in Table 6.4 show that there is some agreement with the stoichiometry presented by Black et al.[42] It is argued that organic color in the form of humic and fulvic acids is removed through a precipitation reaction with alum.[61] A precipitate apparently is formed "by the interaction of a partially hydrolyzed aluminum ion of empiric formula $Al(OH)_{2.5}$ and an ionic group, probably a carboxyl, on the organic molecule." This stoichiometric relation between coagulant dosage and color is explained by the formation of a soluble chelate with aluminum through secondary acidic groups on the organic molecule (probably, the phenolic-OH). These observations are slightly different than the traditional explanation of destabilization of a colloidal system by an oppositely charged particle.

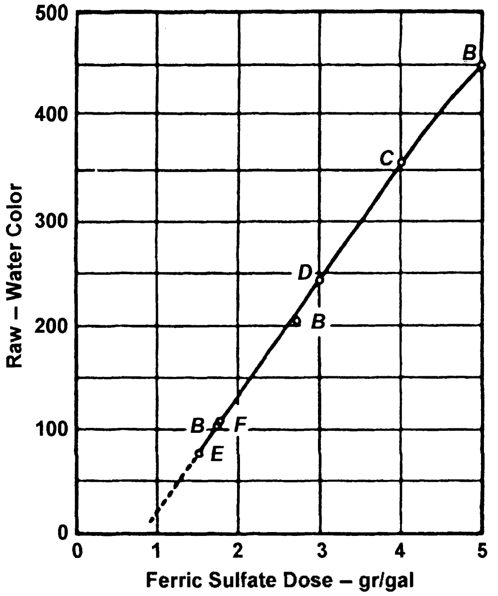


Figure 6.15. Minimum ferric sulfate dose as a function of raw water color. The data for the various waters are indicated by the point associated with the letter designation of the water. The data indicated that the minimum ferric sulfate dose necessary for good color removal is a simple function of the raw water color. Reproduced from Black et al.,[42] courtesy of the American Water Works Association.

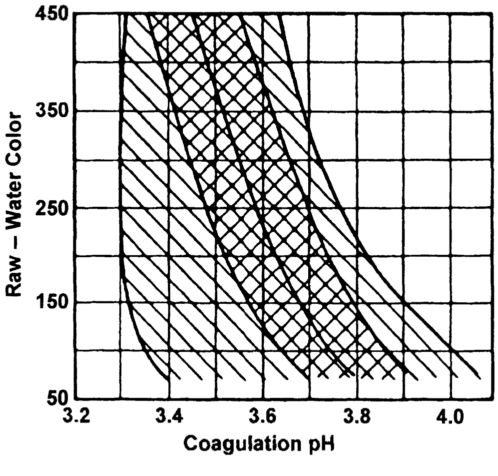


Figure 6.16. Range of optimum coagulation pH as a function of raw water color. The cross-hatched area is for best color removal, the diagonally lined area is for acceptable color removal. Reproduced from Black et al.,[42] courtesy of the American Water Works Association.

When ferric salts are used as coagulants for removal of humic substances (DOC), similar statements (to alum) can be made about the mechanisms of removal and the conditions for their occurrence. However, specific pH values and limits are somewhat lower. Other factors are molecular size, charge, and solubility of the organic compounds.[44] In some

Table 6.4. Characteristics of Coagulation of Dilute Clay Suspensions and Humic Substances with Aluminum Sulfate.[a]

Dilute Clay Suspensions	Humic Substances
Optimum pH 6.5–7.5	Optimum pH 5–6
Minimum residual turbidity independent of pH	Minimum residual color dependent on pH
Increased concentration slightly reduces coagulant doses	Increased concentration increases coagulant dose
Dose and optimum pH changed in presence of humic substances	Dose and optimum pH independent of presence of clay

[a] Reproduced from Hall and Packham,[43] courtesy of the American Water Works Association.

Table 6.5. Cationic Polyelectrolyte and Alum Required for Reaction with Humic and Fulvic Acid Solutions as a Function of the Anionic Groups.[a]

Acids	Concentration (mg/L)	Σ—COO— + —O— (μeq/L)	—COO— (μeq/L)	—O— (μeq/L)	Cationic Polyelectrolyte[b] Optimal Dose at pH 8.0 (μeq/L)	Alum Optimal Dose	
						μeq/L	pH
Humic	5	43.5	22.2	21.3	43.1	27.0	6.7
	10	87.0	44.5	42.5	79.5	45.0	6.6
	25	218.0	111.0	107.0	190.0		
	50	435.0	222.0	213.0	342.0	97.7	6.0
Fulvic	25	118.0	41.0	77.0	101.0		
	50	236.0	82.0	154.0	228.0	90.0	5.8
	100	472.0	164.0	308.0	380.0		

[a] Reproduced from Narkis and Rebhun,[45] courtesy of the American Water Works Association.

[b] Purifloc C–31. The Dow Chemical Co., Midland, Michigan.

situations, DOC removals may be as low as 70%, with the residual 30% characterized as low-molecular-weight (<1000), nonpolar, neutral compounds of low to intermediate solubility. These residual compounds were the dominant precursors for THM and TOX formations from coagulated waters.

Polyelectrolytes

Several researchers have demonstrated that humic materials are precipitated by synthetic organic cationic polyelectrolytes.[41,45–57] The stoichiometric relationship between humic and fulvic acids and alum and cationic polyelectrolytes was researched.[45] Table 6.5 shows the optimal doses of cationic polyelectrolyte required for "complete reaction" with humate and fulvate solutions as a function of their anionic groups. Reasonably good agreement is obtained between the cationic polyelectrolyte in μeq/L and the sum of carboxyl and hydroxy groups in μeq/L for optimal coagulation at a pH value of 8.0, where both functional groups are in the anionic form. This is strong evidence for a charge-neutralization reaction between the polycation and the phenolate and carboxylate groups of humic and fulvic acids. A similar relationship is found for the optimal dose of alum for its coagulation of these two naturally occurring organic acids. Agreement of 45 μeq/L alum and 44.5 μeq/L of the carboxyl groups from 10 mg/L humic acid is good at pH 6.6. At this pH value, only the carboxyl groups are dissociated. At higher concentrations of humic acid, the stoichiometry between alum dosage and the two organic acids deviates somewhat. Figure 6.17 shows the effect of the cationic polyelectrolyte on removal of humic acid. The electrophoretic mobility becomes zero at the point where the humic acid content is minimal. This is additional evidence that negatively charged color molecules are destabilized by positively charged coagulants.

Role of Adsorption

The theory of electrical double-layer interactions is, perhaps, the simplest model that describes the reactions among colloidal particles in aqueous systems. The Gouy-Chapman double-layer model assumes that an equilibrium exists between the electrostatic forces attracting counterions from

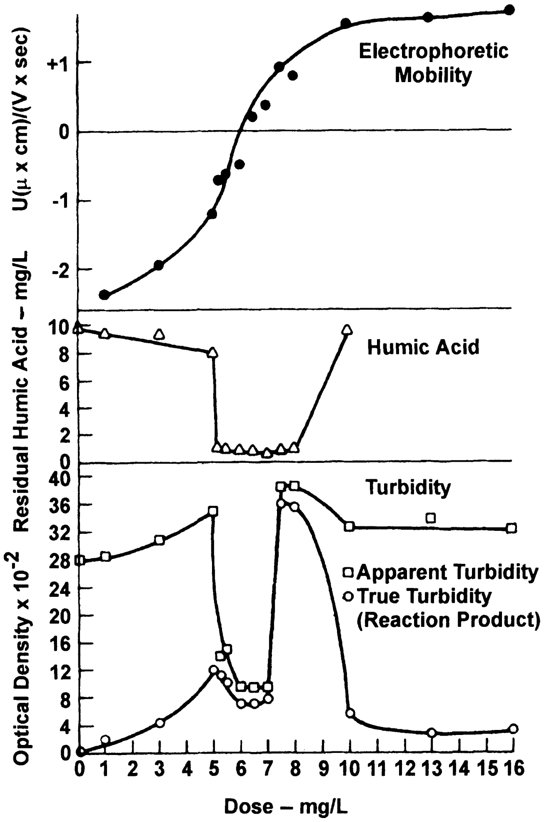


Figure 6.17. Effect of cationic polyelectrolyte on Na-humate solution; 10 mg/L humic acid; pH 8.0. Reproduced from Narkis and Rehbun,[45] courtesy of the American Water Works Association.

bulk solution to the charged surface, and diffusion that permits these ions to migrate back into bulk solution where the ionic concentration is lower. In this model, destabilization occurs when an indifferent electrolyte is added to a colloidal system. The content for destabilization depends on the valence of the indifferent electrolyte. Conformance to the Schulze-Hardy rule occurs. Also, restabilization of the colloids does not occur when the electrolyte concentration exceeds the CCC. There is considerable evidence that coagulation and restabilization of colloids occur also by noncoulombic forces; that is, coagulation by hydrolyzed metal ions (here, aluminum) and by "large" molecular species (polyelectrolytes, etc.), is greatly different than coagulation by simple ions (Na^+, Ca^{2+}, Al^{3+}, etc.). The hydrolyzed metal ions and the polyelectrolytes apparently are adsorbed on colloidal surfaces, which affects destabilization at contents considerably less than nonadsorbable coagulants.

As mentioned above, much of the adsorption phenomena in coagulation comes from using natural and synthetic macromolecules as aggregating agents. Figure 6.7 depicts the "bridging" model, which attempts to explain the destabilization of colloidal suspensions by polymers.[21,48,49] This model or theory explains such anomalies as the destabilization of negatively charged colloids with negative polymers. The optimum aggregation of colloids frequently occurs when the electromobility and/or zeta potential is not zero.

A strong argument for destabilization by adsorption is seen in Figure 6.18,[50] where it is observed that there is an inverse relation between the quantity of polymer required for saturation of the surface and the clay content. This is explained by a greater probability of interparticle collisions in the more concentrated clay suspensions than in the less concentrated suspensions. This affords a greater probability of interparticle bridging (Reaction 2, Figure 6.7) where one polymer molecule or, at least, one site on the polymer, must occupy at least one adsorption site on the clay's surface that is being bridged. Consequently, a larger saturation weight ratio of polymer to clay occurs in the lower clay suspensions. Another interpretation is that less bridging of particles occurs in dilute systems, whereas more bridging occurs in the concentrated systems.

A summary is given in Table 6.6 of several possible mechanisms for the removal of NOM by coagulation processes (see Reference 70). It is obvious that NOM is not removed by any single mechanism. The pH of coagulation determines to a large extent the monomeric or polymeric nature of the coagulant, which involves charge neutralization and colloidal destabilization. On the other hand, precipitation, coprecipitation, and/or adsorption remove NOM when it occurs in a true soluble state.

Chemical and Physical Factors Affecting Coagulation

Many factors affect the coagulation process in water treatment practice: (a) coagulant dosage, (b) [H^+], (c) turbidity, i.e., particulate concentration, (d) natural color concentration (color units, TOC, or DOC), (e) "foreign" ions in solution, (f) mixing effects, (g) electrophoretic mobility (related to zeta potential), and (h) temperature. Some of these variables have been discussed above and in Reference 51. Mixing effects are discussed below.

Foreign Ions

The effect of such anions as sulfate on suppression of the charge reversal and acceleration of the kinetics of precipitation of $Al(OH)_{3(s)}$ have been recognized for a long time.[52,53] Also, such divalent cations as Ca^{2+} and Mg^{2+}, etc., have a significant effect on the coagulation of natural colloidal particles associated with humic acids.[54] That Ca^{2+} affects the stability of anionic polymer-clay systems was suggested by Black and coworkers.[50,55] Three mechanisms are possible: (a) divalent cations compress the double layer of a negative colloid, (b) the repulsive forces between polymers and clay

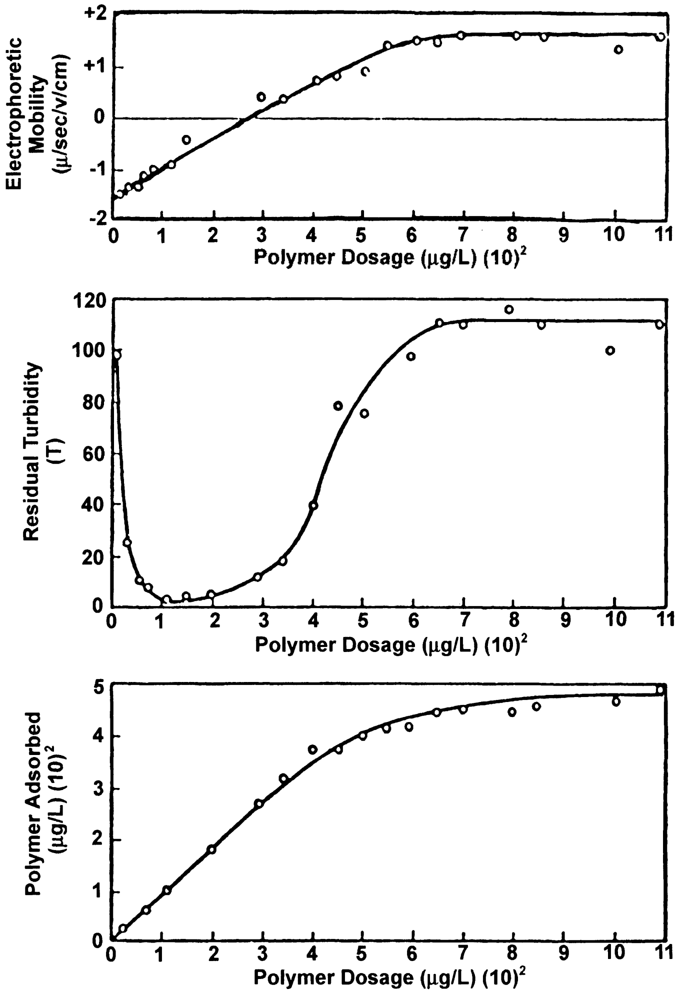


Figure 6.18. Destabilization of a kaolinite clay suspension with cationic polymer No. 4. Initial clay concentration = 73.2 mg/L. Reproduced from Black et al.,[42] courtesy of the American Water Works Association.

particles are reduced by the cations that enhance adsorption of the polymer on the clay particle, and (c) the range of repulsive barrier between adsorbed anionic polymers is probably reduced by the Ca^{2+}. This is reasonably strong evidence that indicates divalent ions are necessary for anionic polymers to flocculate negative colloids. Also, Ca^{2+} was reported to have a destabilizing effect on natural particulates, which are in turn stabilized by fulvic acids.[56,57]

Temperature

In water treatment practice, temperature has an extremely important role in turbidity removal by chemical coagulants. Normally, colder temperatures result in decreased efficiency of turbidity removal. Very little can be done operationally about temperature. Some remediation can be achieved by changing coagulants from alum to ferric chloride[58] or to polymeric iron chloride.[59] Another possibility is to switch from "sweep" for coagulation to an adsorption-charge neutralization by the addition of such solids as bentonite clay and/or the return of sludge from the coagulation process. Decreased efficiency at the colder temperatures is due to increased viscosity and its effect on particle sedimentation, and because structurally, the aggregates are smaller at the lower temperatures, and the kinetics of hydrolysis and precipitation are slower.

ASPECTS OF TREATMENT PLANT PRACTICE

Jar Test

There is an extensive use of the laboratory jar test for quality control of the in-plant coagulation process. It is an extremely useful technique for determination of such operational parameters as: (a) coagulant selection and dosage,

Table 6.6. Possible Mechanisms for the Removal of Natural Organic Matter by Coagulation.[70]

Conditions	Removal Mechanism(s) Assuming Humic Acid is Colloidal	Removal Mechanism(s) Assuming Humic Acid is in True Solution	Comments
Acid addition to pH 1.0 by	Charge neutralization by H^+, perhaps accompanied by EDL compression	Precipitation of the insoluble acid of a soluble salt	Humic acid is insoluble at pH 1.0 definition
Metal salts at low pH (5–6)	Charge neutralization by positively charged hydrolysis products	Precipitation of aluminum or iron humate	Relatively low dosage required; hydroxides may not precipitate; dosage proportional to humic acid concentration
Metal salts at high pH (7–8)	Enmeshment in a precipitate; adsorption and bridging; or perhaps charge neutralization, with higher dosages required because of competition with hydroxide or less positively charged hydrolysis species[a]	Precipitation of Al or Fe humate impeded by precipitation of hydroxide; or coprecipitation, involving adsorption of humic acid onto metal hydroxide particles	A higher dosage of coagulant is required than at low pH; dosage increases as humic acid and pH increase; metal hydroxides are precipitated
Polymers	Charge neutralization or adsorption and bridging	Precipitation of insoluble polymer-humate complexes	Dosage proportional to humic acid concentration
Lime softening pH 9.5–10.5	Enmeshment in precipitating calcite, perhaps with heterogeneous nucleation on humic particles	Precipitation of calcium humate; adsorption of humic acid onto calcite nuclei and crystals	Removal may be poor unless another coagulant is added
Lime softening pH >11	As above, aided by charge neutralization by positively charged magnesium hydroxide complexes and nuclei[a]	As above, but with adsorption onto positively charged magnesium hydroxide particles the primary mechanism	Magnesium hydroxide also precipitated; excellent removal possible

[a] Mutual coagulation (or adsorption) of positively and negatively charged colloids is also a possibility, but this can be viewed as a special case of adsorption and charge neutralization or adsorption and bridging.

(b) optimum pH, (c) alkalinity addition and control, (d) floc time, (e) optimization of mixing energy and time for rapid and slow mixing, and (f) such other measurements as zeta potential (electrophoretic mobility). However, this procedure is not particularly useful for "scaling up" information about flocculation rates from the jar test to plant operation.[15] Nonetheless, some positive results have been obtained from these tests which, in turn, are translated to more efficient and effective plant operation. Details and recent innovations in the jar test are given in References 25 and 60.

Jar and full-plant tests were conducted for an economical design and operation of a new 80-mgd water treatment facility at Phoenix, Arizona.[61] The raw water supplies for this city are the Salt and Verde Rivers. These parameters were investigated: (1) time required for good rapid mix; (2) need for rapid, uniform coagulant dispersion during rapid mix; (3) effects of diluting alum solutions upon coagulant effectiveness; (4) variances in flocculation characteristics of the two rivers supplied to Phoenix; and (5) effects of flocculation time on turbidity removal. Figure 6.19a shows that turbidity removal is affected, of course, by the basin overflow rate, but is independent of rapid mix times for a given overflow rate. In this experiment, 18 mg/L alum were applied to each jar while the rapid mix occurred at a velocity gradient of 350 sec^{-1}. This was followed by a flocculation period of 30 min at a velocity gradient of 30 sec^{-1}.

Turbidity removals are not improved by a rapid mix greater than 5 sec. Figure 6.19b shows that the rapidity and uniformity with which alum is mixed with the entire volume of water are extremely important. The turbidity removals clearly show that alum should be added "instantaneously" to the entire volume of water.

That the jar test results correlate reasonably well with plant tests is seen in Figure 6.20a.[61] The optimum flocculation velocity gradient is in the 20 to 30 sec^{-1} range. Another important operational variable is the detention time of the flocculation period. From plant operation, it was noted that basins with detention times of 55–60 min were producing water with lower turbidities than basins with 95–100 min of retention. Jar tests (Figure 6.20b) confirmed this observation where optimum turbidity removals were obtained within 30–35 min. Results from this jar test study of alum coagulation apparently were translated successfully into a more effective and efficient plant operation for the parameters reported, some of which have kinetic implications.

Jar test results are significant for a number of quality control techniques for the coagulation-filtration process. They are: "time required for appearance of first floc, visual evaluation of floc size, rate of settling of floc, visual or photometric measurement of supernatant or filtrate clarity or color, and analytical determination of residual coagulant in supernatant or filtrate."[62,63] The use of electrophoretic mobility measurements was suggested also for controlling the coagulation process. In-plant and continuous monitoring of turbidity is an extremely useful quality control for determining the optimum coagulant dosage.

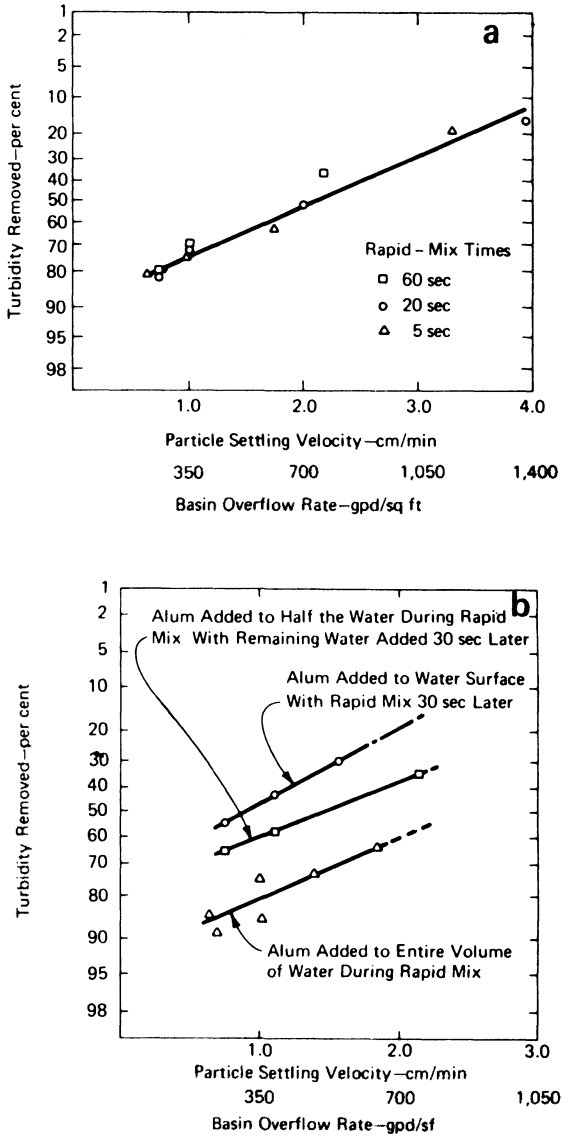


Figure 6.19. Turbidity removals vs. settling for various rapid mix (a) times and (b) conditions. Reproduced from Griffith and Williams,[61] courtesy of the American Water Works Association.

Frequently, coagulation is mandated for low turbidity water, i.e., 1 ntu or less. The conventional jar test is ineffective for determining optimal coagulant dosages for these waters. Consequently, a jar filtration test was designed to meet the water treatment plant operator's need for a simple bench-scale procedure for these waters.[64]

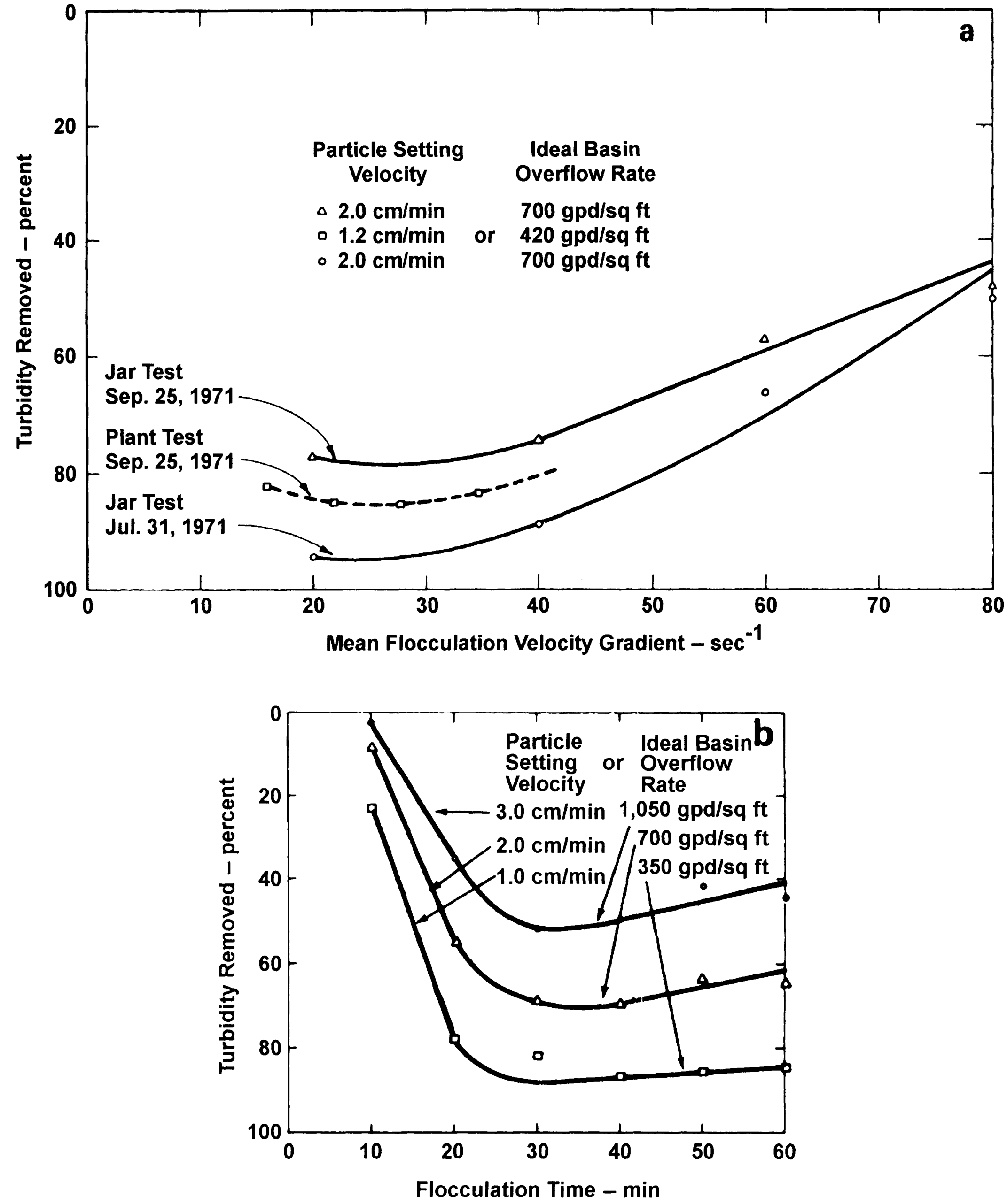


Figure 6.20. (a) Comparison of full-plant and jar test turbidity removals after flocculation and sedimentation. (b) Effect of flocculation time on turbidity removal. Reproduced from Griffith and Williams,[61] courtesy of the American Water Works Association.

Removal of Natural Organic Matter (NOM)

Considerable information was given above for the removal of naturally occurring organic matter from water by chemical coagulation with Al and Fe salts. Some of this NOM takes the form of precursors for the formation of trihalomethanes via reactions with chlorine (see Chapter 2). Subsequently, this discovery motivated several additional studies on the removal of these precursors by coagulation. While neither unique nor new, these studies provide useful operational data.

In addition to the formation of THMs and other halogenated organics during disinfection, NOM is indicative of the presence of color in the water, it utilizes adsorption capacity of activated carbon beds, exerts an oxidant demand, and may transport other contaminants via complexes through the water treatment plant. A summary is given below of the most recent and relevant research on the chemical coagulation of NOM that is applicable to water treatment plant practice.

Process Variables

Coagulant Type

Aluminum and iron salts are equally capable of reducing inorganic turbidity (see above) to an acceptable level. However, they vary significantly in their ability to remove soluble NOM. Al salts are frequently found to be more effective than iron salts, but occasionally the opposite is true. Some organics, for example, have a stronger preference for iron than for aluminum. In any event, the difference in performance is not very great, and the optimum removal is usually about the same for either salt. Selection of a coagulant for NOM removal may be based on differences in chemical costs and handling requirements.

Polymerized Al and Fe chloride salts are relatively new to the U.S. water treatment field, although polyaluminum chloride was first introduced about 25 years ago in Japan.[65] Research has been conducted to compare the more traditional coagulants to these poly coagulants for removal of both turbidity and NOM. For example, it was found that polyaluminum was likely to be a better coagulant than alum for low and moderate concentrations of humic acids and clay-fulvic acid suspensions, especially at pH values <5.5 and >7.0.[39,40] On the other hand, no difference was found between polymeric iron chloride and ferric chloride over a pH range of 5–8 for the removal of NOM.[59]

Organic, cationic polymers have received considerable investigation for the removal of NOM.[66–69] In most situations, "good" removal of humic substances and color was achieved. These polymers may be advantageous in the direct filtration of colored, low turbidity waters, but are used more often as coagulant aids in conjunction with metal salts or lime.

Coagulant Dosage

That there is a stoichiometric relation between NOM removal is seen in Figure 6.15 for the removal of color by ferric sulfate[42] and in Figure 6.21 for the removal of humic acid by alum.[67] In these situations, stoichiometry is defined as the required dosage being proportional to the NOM concentration. Of course this is generic, but it could be established for a given treatment situation. It should be noted that overdosing (i.e., exceeding the stoichiometry) may lead to restabilization of the NOM. This is possible where cationic polymers are employed as coagulant aids.[70]

Another type of "stoichiometry" is conceivable; that is where coagulation is associated with "high" pH, "low" concentrations of NOM, and NOM that may not be of humic origin. Higher coagulant dosages are required as the [NOM] increases, but the relation is not necessarily stoichiometric.[70] Overdosing is not possible, but any increase in NOM removal is marginal at best. This behavior is quite common for surface waters where turbidity and alkalinity are "moderate to high," according to Reference 70. Removal of soluble synthetic organic chemicals [SOC] is expected to follow this "stoichiometry" and mechanism of coagulation.

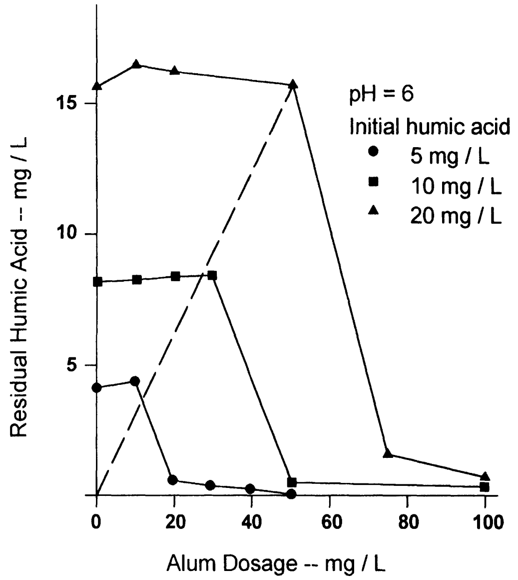


Figure 6.21. Stoichiometric relationship between alum dosage and humic acid concentration.[67]

Influence of pH

The optimum pH range of 5–6 is cited usually for removal of NOM by alum with a slightly lower value for iron salts (see above). Data in Figure 6.22 are typical for the removal of humic and fulvic acids.[43] This is an important operational variable, especially where coagulation is used as a pretreatment for activated carbon processes. Subsequently, the pH value would have to be adjusted upward before AC treatment and discharge into the distribution system.

Mixing

The removal of NOM and SOCs is influenced by rapid and slow mixing. When the particulates of NOM and SOC are removed via the charge neutralization mechanism, the type of rapid mixing greatly influences this reaction;[28] that is, it is imperative that the coagulants be dispersed into the raw water stream as rapidly as possible (<0.1 sec) so that the hydrolysis products—which develop in 0.01 to 1 sec—will destabilize the colloid. On the other hand, removal of dissolved NOM should be influenced by rapid mixing, since

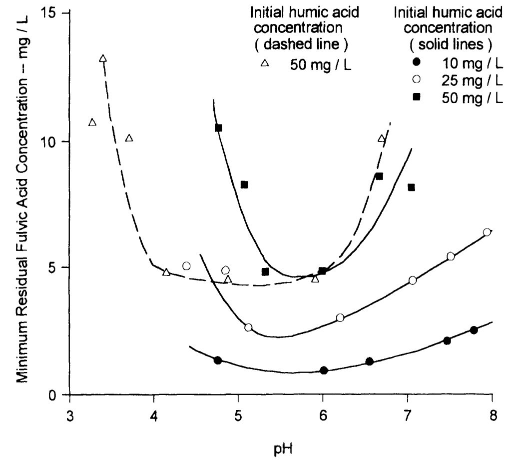


Figure 6.22. Influence of pH on the removal of fulvic acid with acid alum and humic acid with ferric chloride.[43]

it will influence the charge and distribution of the metal hydrolysis products. Here it is necessary for the metal hydroxide to have a high surface area and an amorphous structure for the coprecipitation of the soluble NOM and SOCs. Aged or recycled coagulant sludges are not very effective for dissolved organics because these solids will become more crystalline as they age.[70]

Water Quality

Several raw water quality constituents that vary temporally and seasonally in surface supplies influence the coagulation of NOM and SOCs. These include turbidity, "other" organics, divalent cations, sulfate, and alkalinity.

All particulates and "other" organics exert a demand for the coagulant. Consequently, they will compete for the hydrolysis species or adsorption sites with the targeted compounds (NOM and SOCs). This, obviously, may affect the removal of NOM and SOCs; that is, NOM can drastically influence the pH and coagulant dosage required for good turbidity removal. On the other hand, turbidity per se has little or no effect on the optimum conditions for NOM removal.[38,43,71]

That divalent cations greatly affect the dosage of coagulant necessary to remove NOM is seen in Figure 6.23 for fulvic acids derived from peat.[72] Generally, divalent cations expand the pH range for effective removal, and lower the required coagulant dosage.[73] The significance of Ca^{2+} in coagulation of NOM from algae was demonstrated in a laboratory study.[74]

It is well known that SO_4^{2-} influences the coagulation of turbidity by expanding the optimal pH range.[75,76] On the other hand, there is evidence that SO_4^{2-} inhibits the removal of color.[73] However, there is insufficient evidence to draw a firm conclusion on this latter point.

Alkalinity (mainly bicarbonate) is an extremely important variable for the coagulation process in general, as well as for the removal of NOM and SOCs. For the most part, alkalinity controls the pH value, which is achieved without using supplemental addition of acid and base. For example, the stoichiometric reaction indicates that 1.0 mg/L alum requires 0.45 mg/L of alkalinity as $CaCO_3$. Excessive alkalinity may increase the coagulant dosage beyond that required for turbidity and NOM removal. Insufficient alkalinity requires the addition of a supplemental base [i.e., $NaHCO_3$, or NaOH, or $Ca(OH)_2$]. If the latter situation prevails, the raw water's pH value may be too low for optimal removal of NOM (see above). Consequently, the coagulation process for optimal removal of NOM and SOCs may have to be adjusted frequently.[70]

Polymerized Coagulants

Solutions of aluminum and iron salts may be treated prior to their addition to water for preformation of their polymeric species (see above). For example, Al_2O_3 is reacted with HCl at elevated temperatures to form $AlCl_3$, which is then reacted with a base at an elevated temperature and pressure to form Al polymers. PACl is a coagulant that consists of partially hydrolyzed $AlCl_3$ produced by the addition of a base to a concentrated solution of $AlCl_3$.[56]

The greater effectiveness of PACl over alum in coagulation of NOM apparently is due to the greater amounts of monomers, "small," "medium," and "large" polymers that are formed over the pH range of 4.5 to 7.0. This is seen by comparison of Figure 6.24a (alum) with Figure 6.24b (PACl).[56] The employment of PACl was found to be beneficial at "low" fulvic acid (FA) concentrations and low pH. Better removals of FA were observed with PACl than with alum.[56] It was recommended that PACl should be employed with low total organic carbon (TOC) and low pH because lower dosages of PACl will be required than with other Al coagulants.

Additional evidence for the effectiveness of PACl for the removal of humic substances is seen in Figures 6.25 and 6.26.[40] Stability domains are seen in Figure 6.25 for the coagulation of fulvic acid (FA4) by alum, $AlCl_3$, and PACl. Here, two zones of removal are delineated: Zone I corresponds to the log Al_T-pH conditions where the settleable precipitate of $Al(OH)_{3(s)}$ is formed, whereas Zone II occurs where precipitation of $Al(OH)_{3(s)}$ is unlikely and where, for alum and $AlCl_3$, formation of large polymers is unlikely. For PACl, Zone II extends to low pH values. All of this suggests three mechanisms of FA removal: (a) at pH <5, removal may occur by direct precipitation of FA by monomeric species of Al, (b) between pH 5–6, "low" dosages of coagulant, FA will be precipitated by polymers of Al, and (c) at pH >7, FA is adsorbed or forms a soluble FA-Al complex on a precipitate of $Al(OH)_{3(s)}$.[40]

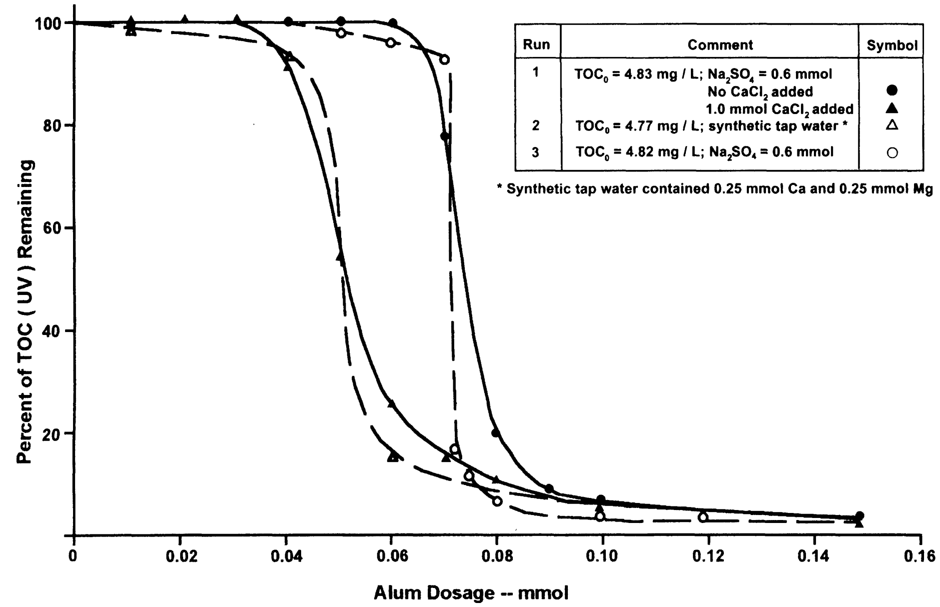


Figure 6.23. Influence of salts on the coagulation of peat fulvic acid at pH 6.0.[72]

The stoichiometry of coagulation of FA by PACl is given in Figure 6.26 where the pH value was 5.0.[40] Here, an increase in the FA concentration resulted in an increase in the required dosage of coagulant (note the "low" dosages), a broadening of the zone of removal, and an increase in the extent of removal. This demonstrates a somewhat greater efficiency of PACl for NOM removal from water than by the conventional alum. Similar results were obtained for the PACl and alum coagulation of clay mineral-FA suspensions.[39]

Softening Processes

Some NOM and SOC removal occurs, incidentally, in water softening processes where lime-soda are employed to precipitate $CaCO_{3(s)}$ and $Mg(OH)_{2(s)}$. This is not coagulation per se, but the magnesium hydroxide has similar adsorbent properties to freshly precipitated $Al(OH)_{3(s)}$ and $Fe(OH)_{3(s)}$. Numerous researchers have reported that $Mg(OH)_{2(s)}$ greatly enhances removal of colloidal and dissolved contaminants.[77-80] For example, humic substances, including FA, were removed from water by lime softening, where removal was increased by raising the pH value, increasing the precipitated solids, lowering the total organic carbon (TOC) content, and precipitating $Mg(OH)_{2(s)}$.[77,78] Removal of FA apparently was achieved by coprecipitation onto calcite crystals rather than by direct precipitation and/or colloidal destabilization. Similar results were observed for several SOCs. A more detailed discussion of NOM and SOC removal by softening processes appears in Reference 70.

Pretreatment to Other Processes

Chemical coagulation can greatly influence the removal of NOM and SOCs by such downstream processes as GAC adsorption. Also, it may be employed in conjunction with such other processes as direct filtration and PAC adsorption. On the other hand, the removal of organics by coagulation may be influenced by upstream processes such as chemical oxidation (O_3, $KMnO_4$, ClO_2, etc.). In any event, the water treatment plant must be viewed as an integrated whole when removal of organics is imperative.[70]

Treatment prior to adsorption is especially appropriate because the quantity of organic matter presented to the carbon is reduced considerably. Also, characteristics of the organic compounds may be rearranged whereby their adsorptive properties and their biological degradability are altered.[81] Several techniques are available: chemical coagulation, aeration for volatilization, and oxidation by O_3, ClO_2, and Cl_2. Most of the research on pretreatment has been on a full-scale water treatment plant. Consequently, the results are applicable immediately. An example is seen in Figure 6.27, where four adsorption isotherms are given for different pretreatments.[81] Ozonated Rhine River bank filtrate was coagulated with $FeCl_3$ and $Al_2(SO_4)_3$ prior to adsorption. The isotherm from the $FeCl_3^-$ coagulated water shows very little effect, whereas the $Al_2(SO_4)_3$ system gave a higher isotherm. This suggests a better adsorption of the remaining organic compounds after coagulation. Another example is seen in Figure 6.28 where five adsorption isotherms are given for Rhine River bank filtrate.[81] The combination of ozonation and clarification resulted in better adsorption of organics than either process alone.

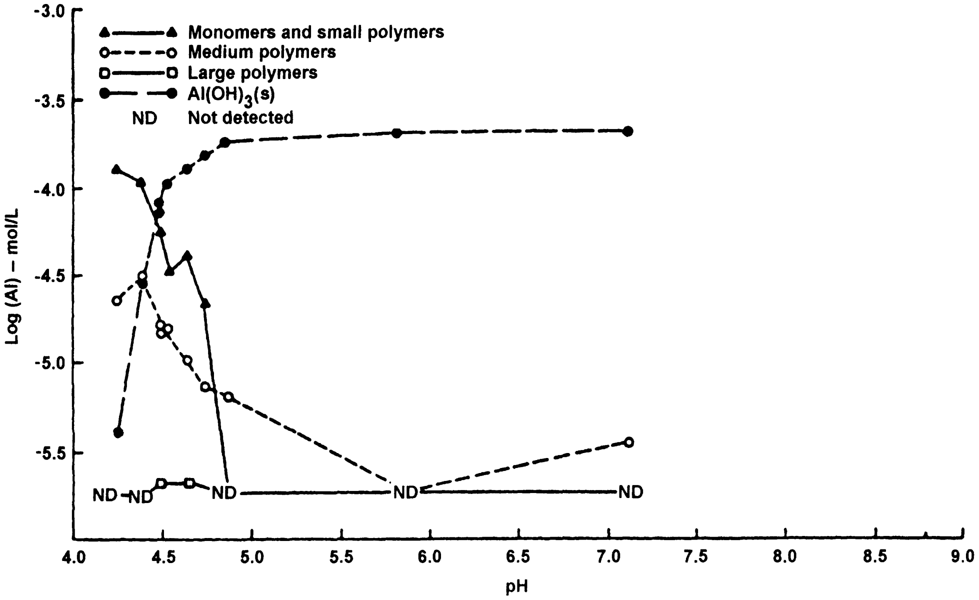


Figure 6.24a. Aluminum speciation diagram for 1.78 × 10^{-4} *M* alum.[56]

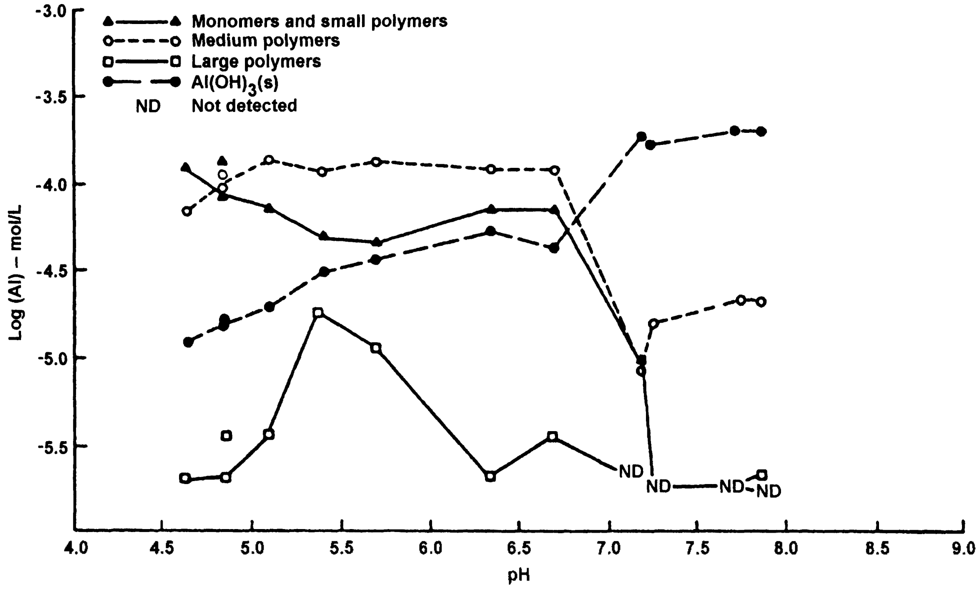


Figure 6.24b. Aluminum speciation diagram for 1.95 × 10^{-4} *M* AC100S PACl.[56]

Alum coagulation and lime softening exhibited variable effectiveness for removing the TOC associated with humic substances in Huron River water in a laboratory study.[82] For example, 50 mg/L of alum was effective in removing 80% of the TOC from the humic and fulvic acid solution. However, the river water TOC was less amenable to removal by alum, 50 mg/L, where only a 30% reduction was achieved. Lime softening, 150 to 160 mg/L, of the Huron River water produced only a 50% reduction of humic and fulvic acid TOC. Pretreatment with alum or lime also affected the subsequent adsorption of TOC by GAC (F-400, mesh size not given). Freundlich isotherm parameters for solutions before and after lime and alum treatments are given in Table 6.7.[82] These results indicate that lime and alum pretreatments yield humic and fulvic acid solutions with residual TOC components that adsorb differently than the TOC

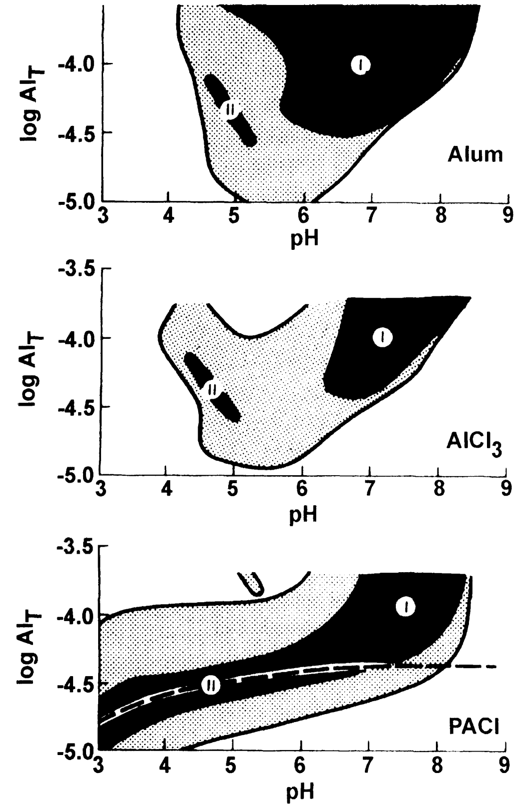


Figure 6.25. Stability domains of FA4 coagulated with alum, AlCl3, and PACl (shaded areas denote regions in which at least 20% removal occurred by coagulation and settling [black] or by membrane filtration of settled supernatants [hatched]; original TOC = 3.5 mg/L).[40]

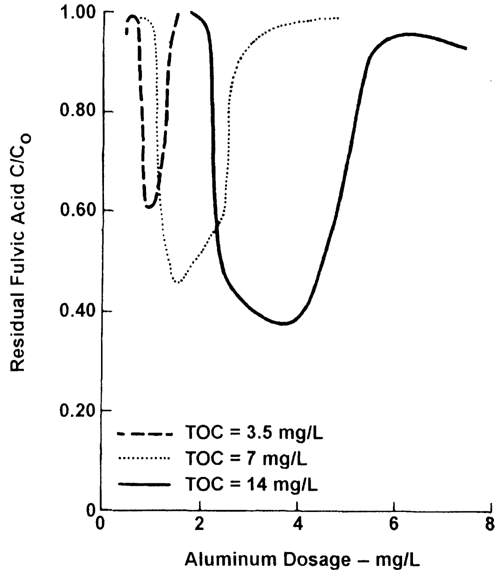


Figure 6.26. Stoichiometry of coagulation of fulvic acid by PACl.[40]

components of the same origin that were not pretreated. The effectiveness of pretreatment for removing TOC and for altering the adsorption characteristics of residual humics appears to depend on the source and type of humic material, at least for the Huron River.

In general, coagulation is an excellent pretreatment for activated carbon adsorption, as seen above. Numerous studies have shown that adsorptive capacity and bed life are increased greatly following coagulation.[70] Particulates are removed that would otherwise plug a GAC filter. Also, coagulation preferentially removes the higher-molecular-weight substances that are adsorbed to a lesser extent than low-molecular-weight materials. Removal of SOCs is generally improved by pretreatment of organic matter, which reduces competition for adsorption sites and extends the bed life of the carbon filter.

Careful attention should be given to pH value and coagulant dosage when coagulation is employed ahead of GAC. These variables will influence strongly the removal of organics by both processes. Consequently, an effort should be made to identify the most cost-efficient operating conditions for the whole plant. In general, organics removal by coagulation is optimal in the pH range of 5 to 6, and adsorption of NOM by GAC generally improves with decreasing pH. Therefore, the optimum pH value for both processes is expected to be acidic and dependent on the water's alkalinity (see Chapter 4 and Reference 83).

Treatment plant operating costs are, of course, a concern in the removal of organics. Consequently, any pretreatment by coagulation may reduce the relatively high cost of GAC adsorption. This has been demonstrated for a hypothetical system designed to maintain a TOC concentration of <1 mg/L in the treatment of Mississippi River water.[84]

Powdered activated carbon (PAC) has found reasonable success in the control of seasonal taste and odor problems (see Chapter 4). Subsequently, the use of PAC was researched for the removal of THM precursors. Generally, the results were disappointing.[70] There are several reasons why PAC used in conjunction with coagulation is ineffective for removal of NOM: "(a) PACs used for taste and odor control are not necessarily effective for removing NOM; (b) precipitation of metal hydroxides on the surface of the carbon particles may retard adsorption or block access to some of the pores; (c) PAC generally remains in contact with the water for a very short time, typically 30–45 min, and the larger-size particles may settle out even more rapidly; and (d) PAC adsorption in a continuously mixed flow reactor is inherently far less efficient than adsorption in a column."[70] On the other hand, there are several features that make the addition of PAC in conjunction with coagulation

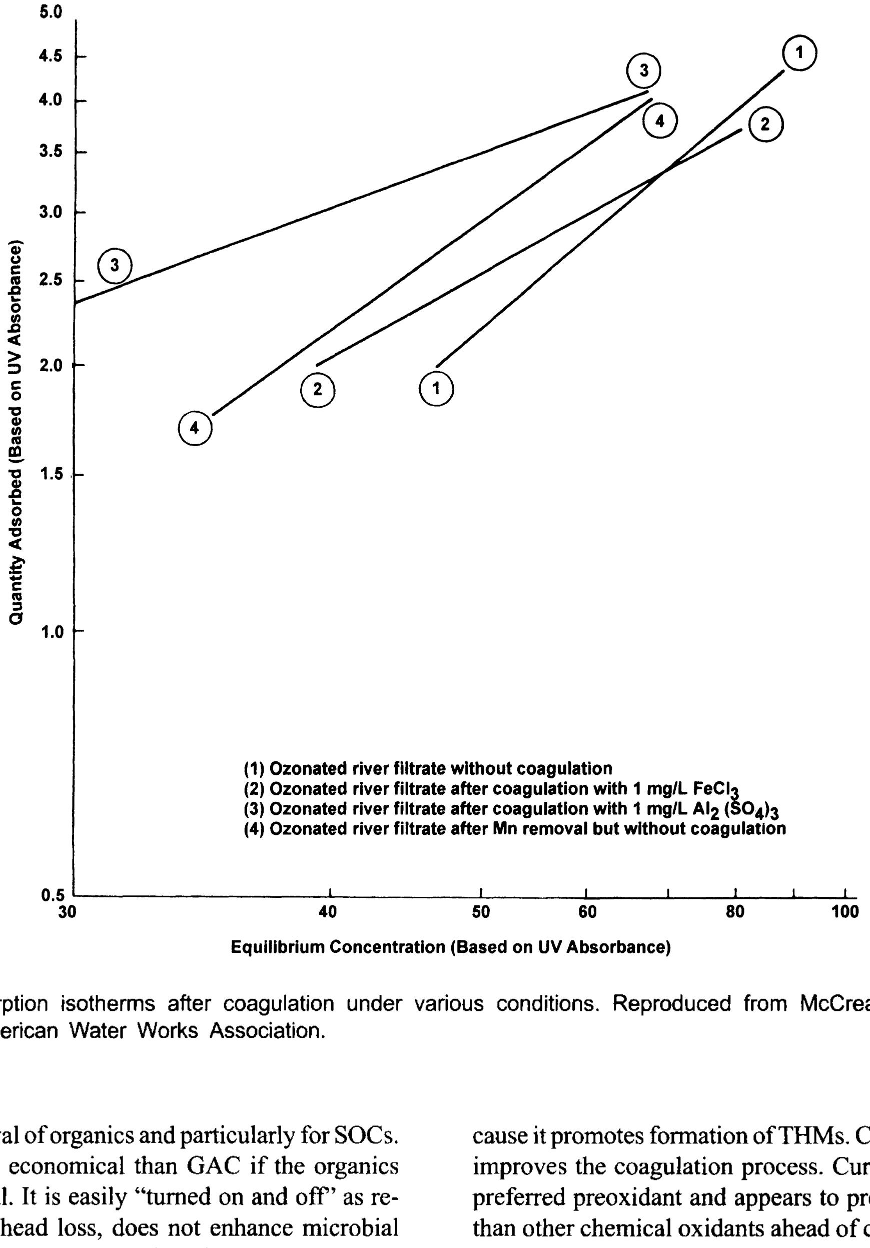


Figure 6.27. Adsorption isotherms after coagulation under various conditions. Reproduced from McCreary and Snoeyink,[81] courtesy of the American Water Works Association.

attractive for removal of organics and particularly for SOCs. PAC may be more economical than GAC if the organics problem is seasonal. It is easily "turned on and off" as required, creates no head loss, does not enhance microbial growth, and capital costs are considerably less than GAC. PAC should be applied early in the treatment process so that adsorption will occur prior to addition of the coagulant.[70]

Coagulation and chemical oxidation interact in two ways: (a) coagulation removes a substantial fraction of organic matter that would interact with an oxidant and (b) addition of an oxidant ahead of coagulation can influence the efficiency of the coagulation process.[70] Generally, coagulation of any faction of TOC, NOM, etc., reduces the oxidant demand later in the treatment process. An example is the report of a cationic polymer that reduced turbidity of a raw water and also reduced the chlorine demand by 85%.[85]

There is considerable evidence that chlorine enhances coagulation. However, prechlorination is avoided now because it promotes formation of THMs. Chlorine dioxide also improves the coagulation process. Currently, ozone is the preferred preoxidant and appears to produce better results than other chemical oxidants ahead of coagulation.[70]

There is considerable evidence that preozonation has beneficial effects on the coagulation process by enhancement of the aggregation by removing or altering the stabilizing NOM coating on particles in water.[86,87] On the other hand, several investigators have noted that ozone hinders the removal of organic matter by coagulation.[86–88] For example, the coagulant dosage, at a constant pH value, required for optimal particulate removal in the presence of NOM is increased with ozone dosage for the hydrolyzable metal salts (alum, $AlCl_3$, and $FeCl_3$). By contrast, the requirements for a cationic, organic, and polymeric coagulant in the same system were decreased upon ozonation.[89] For this polymer, the decreased coagulation requirements after ozonation were accompanied by a decrease in TOC removal in this one in-

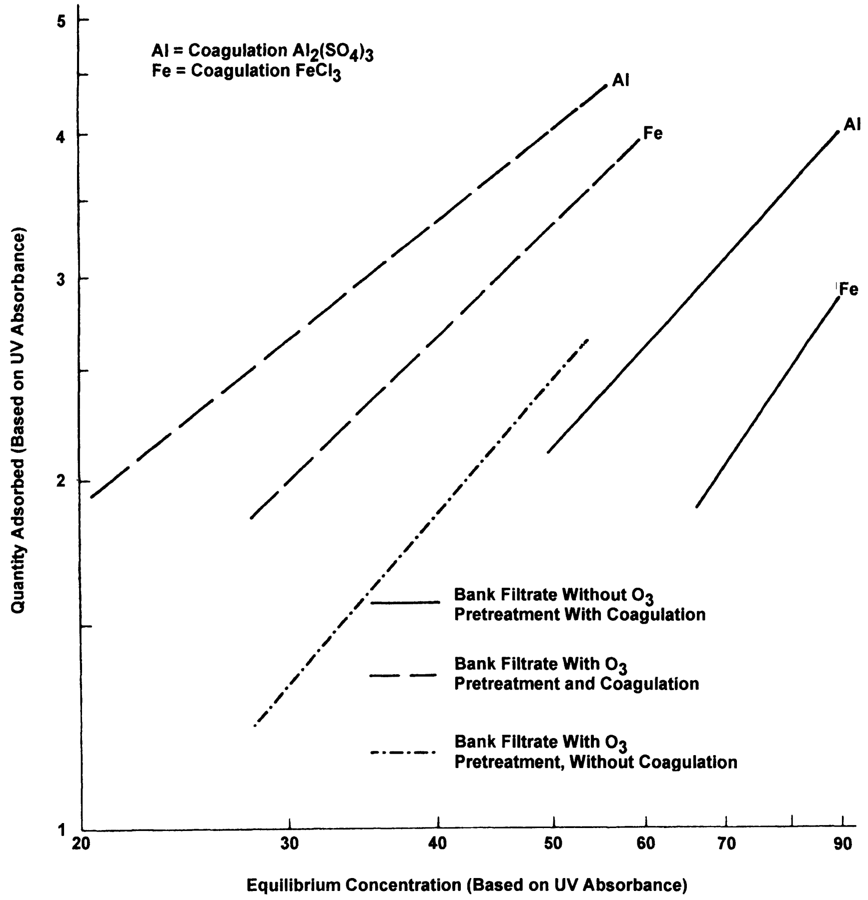


Figure 6.28. Adsorption isotherms after various pretreatments (Düisberg-Wittlaer). Reproduced from McCreary and Snoeyink,[81] courtesy of the American Water Works Association.

Table 6.7. Freundlich Isotherm Parameters for Treated and Untreated Humic Solutions.

Solution	C_o (TOC) (mg/L)	K_F[a] (mg/g)	n
Huron River water (HRW)	5.4	15.8	1.3
HRW after lime (100 mg CaO/L)	4.2	21.7	1.3
HRW after alum (150 mg alum/L)	3.2	61.0	1.3
Humic acid in DDW	5.4	0.8	2.0
Humic acid in river water IBM (HA-IBM)	3.3	34.0	0.8
HA-IBM after lime (100mg CaO/L)	3.1	37.0	0.7
HA-IBM after alum (40 mg alum/L)	3.4	27.5	5.0
Fulvic acid in river water IBM (FA-IBM)	3.1	43.5	1.1
FA-IBM after lime (70 mg CaO/L)	3.3	16.0	1.7
FA-IBM after alum (20 mg alum/L)	3.5	43.0	1.4
HRW after prechloramination and $KMnO_4$ addition[b]	6.1	14.1	1.4
HRW after lime and filtration[b]	3.9	12.2	2.0

[a] Calculated at an equilibrium solution concentration of 1.0 mg/L.

[b] Samples taken after different treatment stages at the Ann Arbor, Michigan, water plant.

Source: Reproduced from Weber and Jodellah,[82] courtesy of the American Water Works Association.

Note: $q_e = K_F C_e^n$, where q_e is the adsorbed phase concentration (mg/g), C_e is the residual solution phase concentration (mg/L) at equilibrium, and K_F and n are characteristic constants.

stance. At this point in time, any benefits of preozonation on the coagulation process must be tempered by its disadvantages. Consequently, any water utility considering the use of ozone should take a very comprehensive review of its effects on the entire treatment system, its costs and operating requirements.

Enhanced Coagulation Under the D/DBP Rule

Under the proposed D/DBP Rule (see Chapter 1), enhanced coagulation is defined as the addition of excess coagulant for the improved removal of DBP precursors by conventional filtration treatment. The rationale behind the introduction of this treatment technique was that only a very small fraction of the chlorination by-products and associated health risks have been identified. Presumably, an increase in precursor removal will reduce overall known and unknown public health risks. Conventional coagulation removes only a fraction of the NOM precursors, which leaves a fraction that reacts with chlorine to form DBPs.

A two-step process will be proposed for utilities with conventional treatment plants to demonstrate the installation of enhanced coagulation. The first step will be the use of a 3 × 3 matrix (see below), with required percentage removals based on raw water alkalinities.[89a]

Alkalinity (mg/L as $CaCO_3$)

TOC (mg/L)	<60	60–120	>120
2–4	40%	30%	20%
4–8	45%	35%	25%
>8	50%	40%	30%

Systems will be required to achieve the percentage removal of TOC between the raw water and the treated water prior to continuous disinfection. The latter is defined as the continuous addition of a disinfectant for the purpose of achieving a level of inactivation to meet the minimum requirements of the SWTR.

If a conventional treatment plant cannot achieve the TOC reduction seen above, the utility can go to a step 2 procedure to determine enhanced coagulation. This alternative enhanced coagulation procedure would require a coagulant dosage and a coagulant pH value such that an incremental addition of 10 mg/L of coagulant results in a TOC removal of 0.3 mg/L or more. Also, step 2 would require enhanced coagulation to occur at pH values less than or equal to a maximum value determined by the raw water alkalinity. The step 2 approach requires the approval of the local enforcement agency.

Several bench-scale studies have been conducted to evaluate the effectiveness of enhanced coagulation for controlling chlorination by-products and to assess the impact of coagulation pH preadjustment on TOC removal and plant operating costs.[89a] Tests were conducted on a variety of surface water sources:

Water Source	TOC (mg/L)	Turbidity (ntu)	Alkalinity (mg/L as mg/L $CaCO_3$)	pH	TOC Removal Required (%)
Lake Houston and Trinity River	6.2	25	90	8.0	35
Missouri River[a]	3–8	10–25	220	8.1	25
Sacramento River	2.0	6.0	40	7.5	40
Big Sioux River	11	24	240	8.15	30
Weiser River	8.4	14–50	150	8.0	30
Mississippi River[b]	8.3	2.5		10.9	NA[c]

[a] Presettled raw water.

[b] Softened water.

[c] Not applicable.

Ferric chloride was consistently more effective than alum in removing NOM, as measured by TOC residuals. The coagulation pH value "appeared" to be a determining factor for maximum NOM removal when $FeCl_3$ was used as a primary coagulant. Typically, preadjustment of pH at a value of 6.0 ± 0.2 increased NOM removal to as much as 65% and reduced the coagulant dose by as much as 65%. These observations are consistent with those of Black and Packham that were reported over 30 years ago.[41–43] The six case studies showed that enhanced coagulation is a valuable means of controlling DBP formation without requiring significant capital investments. The enhanced coagulation requirements of the proposed D/DBP Rule were met in all cases where sufficient TOC removal was generally achieved under simulated distribution system (SDS) chlorination conditions. The DBP standards proposed in Stage 1 of the D/DBP Rule were met. On the other hand, the anticipated long-term HAA and TTHM MCLs could not be met solely by enhanced coagulation. This was observed in two of the six case studies.

Enhanced coagulant should not be viewed as the cure-all for removal of NOM to meet the proposed D/DBP Rule. A significant assessment of this process and two alternatives, GAC adsorption and membrane filtration, were reported in an overview report.[89b] A qualitative summary of the three treatment options in terms of the efficiency of each process in removing NOM, the complexity of the process in relation to operation and maintenance, and total annualized cost of the technology is given:

Treatment Process	NOM Removal Efficiency	Process Complexity	Process Cost
Coagulation	Fair-good	Low-medium	Low[a]
GAC adsorption with regeneration	Very good	Medium-high	Medium
Nanofiltration	Excellent	Medium	Medium-high

[a] Under certain coagulation conditions, pH adjustment and site-specific sludge disposal costs may increase this ranking to medium.

At this time, many utilities hope to comply with the new regulations by using existing facilities and enhancing the coagulation process. However, there are many uncertainties in Stage 2 D/DBP regulations so that modification of existing facilities and the avoidance of construction of new facilities is attractive to utilities that wish not to make capital investments at this time. Consequently, the three options for effective removal of NOM should be considered in preparation for Stage 2 requirements.

Enhanced coagulation tests were conducted at the Metropolitan Water District of Southern California's (MWDSC) 5.5 MGD demonstration plant for three months in 1992.[89c] In this study, two diverse source waters were examined: California State Project water (SPW) and Colorado River water (CRW). TOC values were 3.54 ± 0.25 mg/L and 2.44 ± 0.04 mg/L, respectively. The objectives were to evaluate, at the demonstration level, (a) the effect of alum dosage and coagulation pH on TOC and UV_{254} removal, (b) the associated reductions in THMFP and SDSDBP levels, (c) sludge production, and (d) the additional costs of implementing enhanced coagulation. It was assumed that the final D/DBP Rule will include the MCL levels of 80 mg/L for TTHMs and 60 mg/L for HAA5, and a separate requirement for DBP precursor control. For the SPW and CRW sources, this requires 30 and 20% TOC removals, respectively. For the SPW source, treatment at either a pH of 6.3 and an alum dosage of 40 mg/L or a pH of 5.5 and 20 mg/L alum would be required. The additional costs of these two options were comparable: $0.08 to 0.10/1000 gal. However, the higher pH of 6.3 is more desirable because of neutralization costs with the lower pH value. For the CRW source, the enhanced coagulation requirements would be a pH value of 6.3 and an alum dose of 20 mg/L with an additional cost of $0.08/1000 gal. Enhanced coagulation and postchloramination in SPW will lower the TTHMs to below the 80 mg/L Stage 1 standard. HAA5/6 levels in SPW can be met without enhanced coagulation. Both the TTHM and HAA5/6 levels in CRW will meet the proposed standards without enhanced coagulation; partially because of postchloramination. This study certainly does demonstrate the complexities of a treatment protocol to meet the proposed D/DBP rule. It appears that some source waters can meet these standards without enhanced coagulation and/or other treatment options.

Coagulation by Polyelectrolytes and Coagulant Aids

A number of methods and/or chemicals are used either as "aids" to coagulation or as the primary coagulant. Many difficulties with alum coagulation of natural waters have been cited above. An additional problem is posed by the small and slow-settling flocs from low-temperature coagulation and/or those in "soft" colored waters. Fragmentation of "fragile" flocs under hydraulic forces in basins and sand filters and the inability to obtain clear water in the presence of interfering substances also are problems.[8] It is necessary, therefore, to overcome these difficulties and to improve the settleability and "toughness" of the flocs. This will increase the production of potable water without requiring expansion of the plant's physical facility. The materials that find utilization as "coagulant aids," i.e., any substance that improves the floc's quality, are, for the most part, polyelectrolytes or activated silica.

Polyelectrolytes

These compounds are mostly synthetic organic compounds of high-molecular-weight. They are polymers composed of a chain of monomers. In turn, these monomers are varied frequently within a given polymer, which results in compounds with different molecular weights. These polymers are linear or branched. If the monomer contains an ionizable group, such as carboxyl, amino, or sulfonic, then the polymer is called a polyelectrolyte. There are cationic, anionic, or ampholytic (has both positive and negative) groups which, of course, depends on the nature of the functional groups within the monomer. Nonionic polymers are those compounds without any ionizable groups. Some examples of polymers and polyelectrolytes are seen in Table 6.8 that have been approved for use in drinking water treatment.[90] As mentioned above, these polymers and polyelectrolytes are able to flocculate colloidal particles due to adsorption. In most cases, the bonding mechanism between a functional group on the polymer and a site on the colloid's surface is quite specific. In addition, molecular weight and degree of branching of the polymer play a mechanistic role in their ability to flocculate. Some case histories follow.

Estimates have been made that more than half of the water treatment plants in the United States use one or more polyelectrolytes to improve treatment efficiency.[94] Other studies have shown that, of 23 treatment plants with very high quality filtered water, 20 were using one or more polyelectrolytes as coagulant aids.[90] Filtered water quality requirements from the 1986 amendments to the Safe Drinking Water Act may

Table 6.8. Polymers Accepted for Use in Drinking Water Treatment.[90]

Common Name and Abbreviation	CAS Registry Number	Chemical Name	References Indicating Approval for Drinking Water
Acrylamide polymers			
Polyacrylamide (nonionic polyacrylamide, PAM)	9003–05–8	2–Propenamide, homopolymer $(C_3H_5NO)_n$	91–93
Acrylamide–acrylic acid copolymer (PAM–PAA)	9003–06–9	2–Propenoic acid, polymer with 2–propenamide $(C_3H_5NO \cdot C_3H_4O_2)_n$	91–93
PAM–PAA (Na salt)	25085–02–3	2-Propenic acid, sodium salt, polymer with 2-propenamide $(C_6H_4O_2 \cdot C_3H_5NO \cdot Na)_n$	91–93
Poly (DADMAC) (Diallyldimethyl ammonium chloride, homopolymer)	26062–79–3	N,N-Dimethyl-N-2-propenyl-2-propen-1-ammonium chloride, homopolymer $(C_8H_{16}N \cdot Cl)_n$	91–93
Epi–DMA polymer Epichlorohydrin–dimethylamine, polymer	25988–97–0	N-Methyl methanamine, polymer with (chloromethyl) oxirane $(C_2H_7N \cdot C_3H_5ClO)_n$	91–93
Epi–DMA[a]	39660–17–8	Poly [(dimethylimino)(2-hydroxy-1,3-propanediyl)chloride]$(C_5H_{12}NO \cdot Cl)_n$	91–93
Epi–DMA with ethylenediamine[b]	42751–79–1	1,2-Ethanediamine polymer with (chloromethyl) oxirane and N-methyl methanamine $(C_2H_5N \cdot C_3H_5ClO \cdot C_2H_7N)_n$	91–93
Additional epichlorohydrin–based polyamine polymers			
Epichlorohydrin with monomethylamine	31568–35–1	Methanamine, polymer with (chloromethyl) oxirane $(CH_5N \cdot C_3H_5ClO)_n$	92
Epichlorohydrin with a polyamine	27029–41–0	N,N-dimethyl-1,3-propanediamine polymer with (chloromethyl) oxirane $(C_5H_{14}N_2 \cdot C_3H_5ClO)_n$	92
Polyethylenimine			
Polyethylenimine	9002–98–6	Aziridine, homopolymer $(C_5H_5N)_n$	91,92
PEI[a]	25988–99–2	Ethanimine, homopolymer $(C_2H_5N)_n$	91,92
PEI[a]	26913–06–4	Poly(imino-1,2-ethanediyl)$(C_2H_5N)_n$	91,92
Polyethylene polyamine polymers			
Polyethylene polyamine (polyalkyleneamine)[c]	8660–40–1	1,2-Dichloroethane polymer with ammonia $(C_2H_4Cl_2 \cdot H_3N)_n$	91–93
Polyethylene polyamine[c]	29320–38–5	1,2-Dichloroethane polymer with ammonia $(C_2H_4Cl_2 \cdot H_3N)_n$	91–93
Polyethylene polyamine[d]	49553–92–6	1,2-Ethanediamine polymer with 1,2-dichloroethane $(C_2H_8N_2 \cdot C_2H_4Cl)_n$	91–93
Melamine–formaldehyde polymers	9003–08–1	1,3,5-Triazine-2,4,6-triamino polymer with formaldehyde $(C_6H_6N_6 \cdot CH_2O)_n$	91–93
Mannich reaction-modified polyacrylamide (AMPAM)	25765–48–4	N,N-[dimethyl(amino)methyl] 2-propenamide, homopolymer $(C_6H_{12}N_2O)_n$	92,93
Poly (DMAEMA) (N,N-dimethylaminoethyl methacrylate, homopolymer)	25154–86–3	2-Methyl-2-propenoic acid, 2-(dimethylamino) ethyl ester, homopolymer $(C_8H_{15}NO_2)_n$	91,93

[a] The compound is identified by its repeating structural units or by the use of a different monomer nomenclature.

[b] This compound contains the monomer ethylenediamine in addition to the monomer formed from epichlorohydrin and dimethylamine.

[c] The reason for a multiple listing by Chemical Abstract Service is not known.

[d] This compound is structurally similar to the preceding compound but is produced using different starting materials.

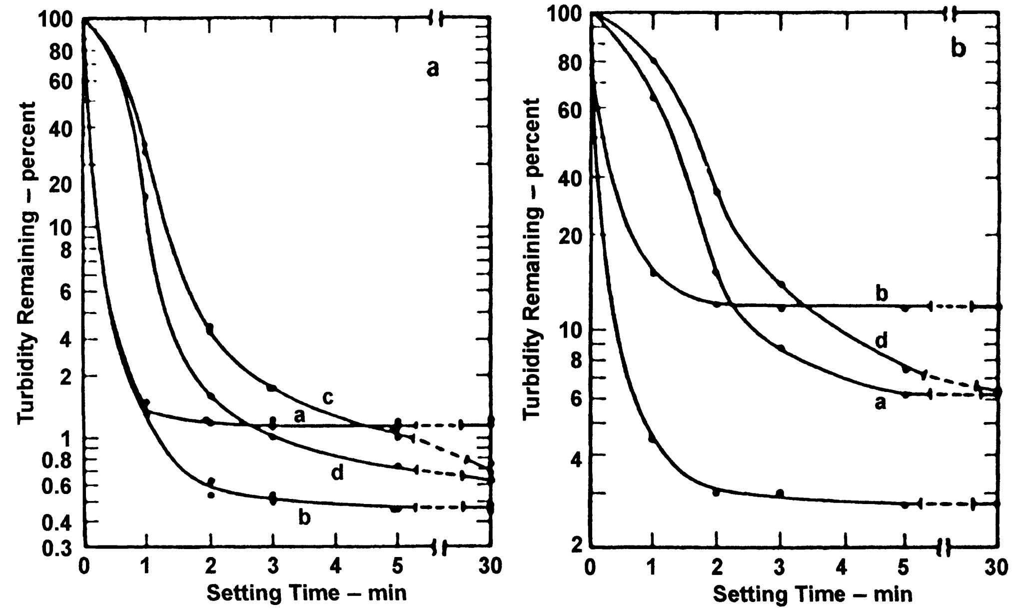


Figure 6.29. (a) Effect of coagulant aids on Ohio River water; 40 mg/L alum was added to each test. Curves—each one an average of duplicate tests—represent coagulants made with aids added in optimum amounts, as follows: a = 1 mg/L anionic A; b = 6 mg/L cationic B; c = 20 mg/L nonionic C; d = alum alone. (b) Effect of coagulant aids on pond water. Each solution contained 20 mg/L alum. Curves represent coagulations obtained with: a, alum alone; b, 0.5 mg/L.

lead to the greater use of polyelectrolytes for water treatment in the United States (see Chapter 1).

Early Research

An "anionic A" polymer (acrylamide), a "cationic B" polymer (organic cation), and a "nonionic C" (natural cellulose derivative) were used in the laboratory coagulation of five natural waters.[95] Representative results from the jar test are seen in Figure 6.29 for Ohio River Water (initial turbidity = 1000 units) and for a pond water (initial turbidity = 300 units), respectively. It is apparent that greater turbidity removals are effected in less settling time with the cationic B polyelectrolyte than with alum alone or with the anionic A and the nonionic C. Similar results were obtained by Black et al.,[96] who investigated 17 polyelectrolytes and polymers for their ability under laboratory conditions to flocculate suspensions of two clay minerals: kaolinite and illite.

A Georgia kaolinite suspension (CEC = 12.2 meq/100 g, surface area of 15.8 m^2/g) was flocculated by a cationic polymer (PDADMA) and two anionic polymers that were partially hydrolyzed polyacrylamides (4% HPAM 4 and 30% HPAM 30).[97] It was noted that flocculation of the negatively charged kaolinite was effected by the two anionic polymers where electrophoretic mobility values remained negative. These studies also included the calcium content as a variable, where 250 mg/L was a factor in the flocculation mechanism.

Late Research

In the 1970s, '80s, and '90s, polymer research focused upon coagulation of NOM, notably the precursors of THMs. For example, four cationic polymers were tested as sole coagulants for removing THM precursors from synthetic and natural waters.[69] Waters synthesized from humic acid were more amenable to polymer coagulation than those synthesized from fulvic acid. The presence of kaolinite appeared to improve removal of trihalomethane formation potential (THMFP) from these waters. For natural waters, the effectiveness of polymer coagulation in THMFP reduction varied as a function of raw water source.

In another study, the removal of THM precursors by coagulation was studied with low turbidity, low alkalinity waters containing high levels of humic materials.[98] Jar tests were conducted with synthetic and natural waters using alum, high-molecular-weight (HMW) polymers, cationic polymers, and various combinations of these coagulants. Cationic polymers alone were less effective than alum in the coagulation of humic substances. HMW polymers used with alum improved turbidity removal but not precursor removal. However, high charge density cationic polymers with alum provided good precursor removal at low alum dosages. Also, cationic polymers with alum are promising for direct filtration of low TOC waters because solids production can be minimized and good precursor removals are realized.

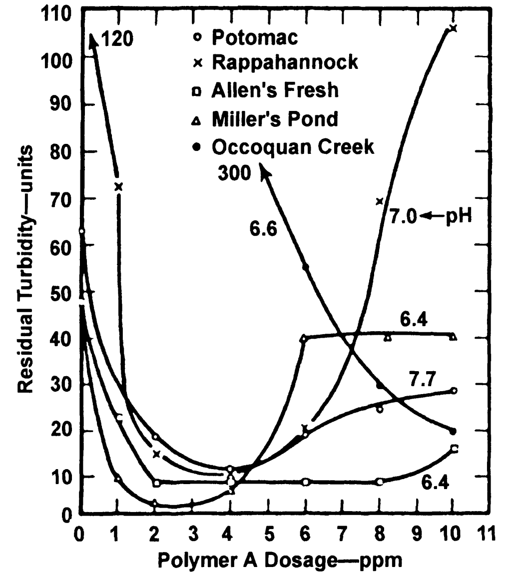


Figure 6.30. Flocculation of various waters treated with Polymer A. Reproduced from Pressman,[101] courtesy of the American Water Works Association.

Several researchers have demonstrated that humic materials are precipitated by synthetic organic cationic polyelectrolytes used alone as coagulants.[41,45–47] In many situations, the composite solids formed from the humic materials and polyelectrolytes were not settleable but, when the proper polymer dosage was applied, they were always filterable. All of these researchers demonstrated a stoichiometry between the concentration of humic substances and the subsequent sedimentation and filtration. Good removals occurred at or near zero electrophoretic mobilities of the precipitates. Poor removals occurred at lower and higher polymer dosages. Overdosing produced restabilization of the precipitates by forming positively charged particles. pH value is also a factor affecting the stoichiometry of polymer coagulation of humic substances.[45] Since the anionic charge on humics becomes less negative as the pH value is decreased, and the positive charge on many organic polyelectrolytes increases with decreasing pH, polymer dosages may decrease with lower pH values.

Also, it has been demonstrated that cationic polyelectrolytes can be used in the direct filtration of waters containing humic substances, which produces small destabilized particles that are filterable.[68] On the other hand, a coagulant is required for particle growth in flocculation when sedimentation is employed for removal.

Other important considerations in the selection and use of polyelectrolytes are floc size and strength, and polymer molecular weight and charge density. These factors have been researched and results reported in references.[99,100]

Case Studies

Eight cationic polyelectrolytes were evaluated as primary coagulants in Potomac River water and five other natural waters by means of the jar test.[104] It was concluded that these compounds can serve effectively as prime coagulants for the treatment of natural water in a solids-contact clarifier and pressure diatomite filter system. Figure 6.30 shows that the optimum polymer dosage indicated by the minima of the turbidity curves is on the order of 2–4 ppm. These quantities are somewhat higher than those for similar synthetic suspensions with comparable turbidities.[50,79]

The cationic polyelectrolyte, poly-4-vinyl-N-methyl pyridonium iodide (PVMPI), flocculated various mixtures of clay minerals and fulvic and humic acids in laboratory studies.[102] Figure 6.31 shows the effectiveness of PVMPI on removal of humate, the clay mineral montmorillonite, and mixtures of the two. It appears that this cationic polyelectrolyte requires 1 mg/L or less for removal of the clay mineral, 2–6 mg/L for an organoclay complex (humate adsorbed on the clay), 12–14 mg/L for a suspension of the clay mineral in a 10 mg/L solution of humate, and 16–20 mg/L for the organoclay complex in a 7 mg/L solution of humate. All of these mixtures were designed to simulate natural water quality. In each system, a zero electrophoretic mobility is recorded at optimum removal.

Impurities in Polyelectrolytes

Polyelectrolyte formulations contain contaminants from the manufacturing process, such as residual monomers, other reactants, and reaction by-products that could potentially affect human health.[90] Also, these polymers and their contaminants may react with chlorine in the disinfection process. Because of this concern, Switzerland and Japan do not permit the use of polyelectrolytes in drinking water treatment, whereas West Germany and France have established strict limits on application dates. In the United States, the USPHS and USEPA have been the primary agencies responsible for the safety of polyelectrolytes since 1957. However, in 1984 the USEPA began to deregulate the use of water treatment additives, and moved the product evaluation to the private sector. Much of its responsibility was transferred to a consortium of organizations led by the National Sanitation Foundation (NSF).[103] Table 6.9 is a list of various contaminants that are definitely found in commercial polyelectrolytes and some that are speculative contaminants.[90] Details of the health significance of these products and their contaminants are given in Reference 90.

Coagulation of Carbon Suspensions

Some circumstances require the employment of slurries of powdered activated carbon for taste and odor control, rapid removal of organics, etc., in the overall treatment pro-

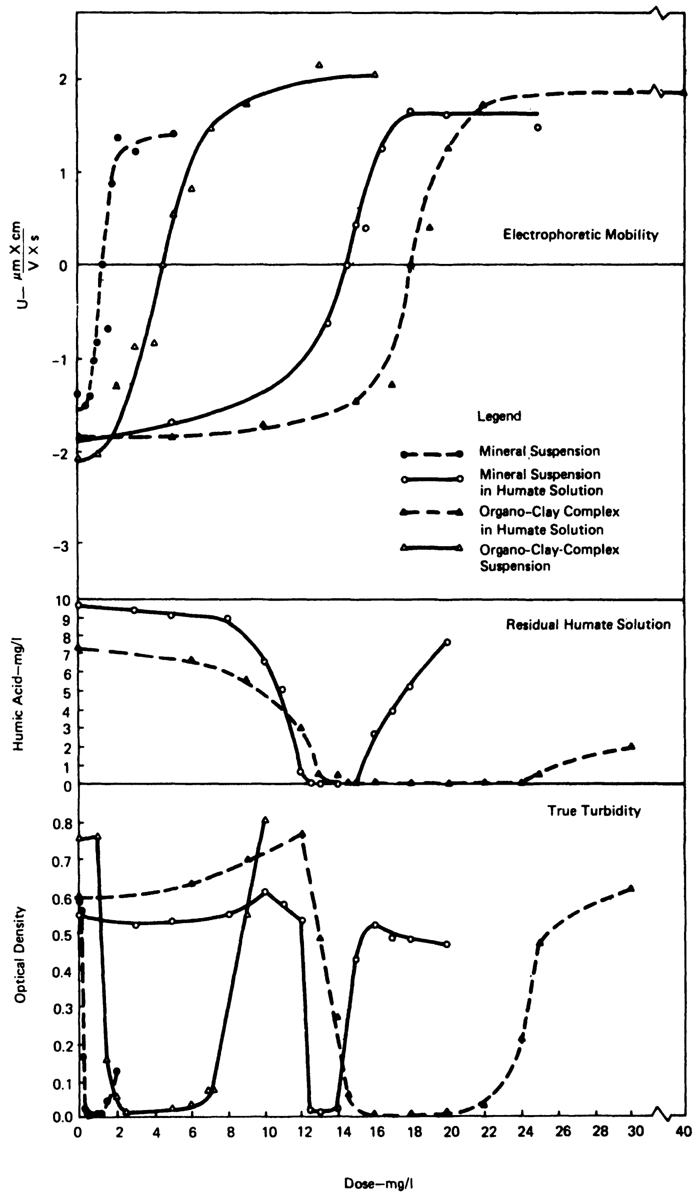


Figure 6.31. Flocculation curves of various systems of montmorillonite using PVPMI. Reproduced from Narkis and Rebhun,[102] courtesy of the American Water Works Association.

cess (see Chapter 4). It is frequently necessary to improve the sedimentation and filtration characteristics of this carbon by alum coagulation. Data summarizing laboratory study of this operational problem appear in Table 6.10.[104] The initial residual turbidities were measured after pH adjustment and the subsequent rapid-mix, slow-mix, and sedimentation periods. The percentage turbidity reductions refer to reductions in the initial residual turbidities (~6 turbidity units with carbon content >25 mg/L). Effective coagulation occurred over a broad range of alum doses.

Control of Residual Aluminum in Filtered Waters

Questions have been asked about the human health implications of elevated levels of aluminum in drinking water that may affect persons with Alzheimer's disease and dialysis patients. However, no conclusions have been reached, to date, about this health concern. There is also the postprecipitation of aluminum residuals in distribution systems where significant decreases in carrying capacity may

Table 6.9. Contaminants That May be Found in Polyelectrolyte Products.[90]

Contaminant	Polyelectrolytes[a]
Direct evidence	
Acrylamide	PAM, PAM-PAA, AMPAM, copolymers of acrylamide and DMAEMA
Hydroxypropionitrile	See acrylamide
Isobutyronitrile	See acrylamide
Diallyldimethylammonium chloride	Poly(DADMAC)
Epichlorohydrin	Epi-DMA, epi-DMA-EDA, epi-MMA, epi-DMPDA
Glycidol	See epichlorohydrin
1,3-Dichloro-2-propanol	See epichlorohydrin
3-Chloro-1,2-propanediol	See epichlorohydrin
2,3-Dichloro-1-propanol	See epichlorohydrin
Indirect or inconclusive evidence	
Melamine	Melamine-formaldehyde polymer
Methylolmelamines	Melamine-formaldehyde polymer
Formaldehyde	Melamine-formaldehyde polymer, AMPAM
Dimethylamine	Poly(DADMAC), epi-DMA, epi-DMA-EDA
Ethylenimine	PEI
Methylamine	Epi-MMA
Low-molecular-weight oligomers of polyethylene polyamines	EDC-NH_3, EDC-EDA
N,N-dimethyl-1,3-propanediamine	Epi-DMPDA
Dimethylaminoethyl-methacrylate	Poly(DMAEMA)
Speculative	
Ethylene dichloride	EDC-NH_3, EDC-EDA
Vinyl chloride	EDC-NH_3, EDC-EDA
Allyl chloride	Poly(DADMAC)
Diallyl ether	Poly(DADMAC)
5-Hexenal	Poly(DADMAC)
2-Hydroxy-3-dimethyl-aminopropyl chloride	Epi-DMA
1,3-*Bis*(dimethylamino)-2-propanol	Epi-DMA
Methyl chloride	Compounds quaternized with methyl chloride
Dimethyl sulfate	Compounds quaternized with dimethyl sulfate

[a] PAM—polyacrylamide; PAM-PAA—copolymer of acrylamide and acrylic acid; poly(DADMAC)—polydiallyldimethylammonium chloride; epi-DMA—epichlorohydrin with monomethylamine; epi-DMPDA—epichlorohydrin with N,N-dimethyl-1,3-propanediamine; PEI—polyethylenimine; ECD-NH_3—ethylene dichloride with ammonia; EDC-EDA—ethylene dichloride with ethylenediamine; AMPAM—Mannich reaction-modified polyacrylamide; poly(DMAEMA)—N,N-dimethylaminoethyl methacrylate homopolymer.

Table 6.10. Coagulation of Carbon Suspensions (pH 7.0, Alkalinity 2 meq/L).[a]

		Alum Dose to Achieve			
Concentration of Carbon (mg/L)	Initial Residual Turbidity (units)	50% Turbidity Reduction	Residual Turbidity of One	Minimum Residual Turbidity (units)	Minimum Residual Turbidity (units)
2	0.36	7.2		25	0.04
5	1.3	7.0	5.8	30	0.06
25	5.6	6.8	8.0	25	0.14
50	5.5	3.9	7.8	30	0.27
100	5.9	3.9	7.6	25	0.22
150	6.0	2.8	9.0	25	0.21
300	6.2	2.9	10.2	35	0.45
500	5.9		12.2	25	0.75

[a] Reproduced from Letterman et al.,[104] courtesy of the American Water Works Association.

occur. The USEPA has proposed an SMCL of 0.05 mg/L to ensure removal of coagulated material ahead of the distribution system (see Chapter 1 and Reference 105).

A survey of over 100 water utilities indicated that nearly 60% of those reporting had total Al contents higher than the guideline level of 0.05 mg/L.[106] These "high" total Al contents in treated water apparently are associated with: (a) high [Al] in raw water source waters, (b) high treated water turbidity, (c) the use of atomic absorption spectrometry to measure Al (uses an acidic digestion as a pretreatment), and (d) Al is a contaminant in lime used for postfiltration pH adjustment.

Residual Al levels in treated water can be reduced by adjustment of pH to circa 6.0, which is close to its minimum solubility (see Figure 6.9). Whether or not pH control can significantly affect total residual Al contents has been questioned because changes in pH value affects speciation of the soluble Al, but not the total Al content.[106] Alternative strategies for reduction of Al residuals are: (a) use of alternative coagulants such as iron,[107] (b) reduction of alum dosage by alum-polymer combinations, and (c) effective removal of particulate matter including $Al(OH)_{3(s)}$ during filtration.

Disposal of Coagulation Sludges

In recent years, disposal of sludges from the coagulation process is becoming more and more difficult because the most expedient method, direct discharge to surface waters, is forbidden by federal and state legislation. Two statistics indicate the magnitude of this sludge disposal problem.[107,108] First, there are 3600 or more water treatment plants in the United States. Second, there is an estimated quantity of solids from these plants in excess of 10^6 ton/yr.[109]

Alum sludge is a non-Newtonian, bulky gelatinous material composed of hydrous aluminum oxide and such other inorganic particles as clay, sand, or carbon, and such organics as color colloids, wastewater particulates, and various types of microorganisms.[107] In addition, the sludge consists of other sediments from the clarifiers, filter wash water, and sludge from wash water recovery. The total solids content is, of course, variable, but is in the range of 1000–20,000 mg/L, of which 75–90% are suspended solids. Volatile solids are 20–35% of the total solids. Alum sludges tend to have neutral pH values. These sludges are readily settleable, but the resulting sludge volume and low solids content make them inconvenient to handle and subsequently to place in a landfill.

Few data have been published concerning the inorganic and organic contents of alum sludge and filter backwash water. These data undoubtedly exist, since permits are required for the discharge of these wastes to the environment. Table 6.11 gives the elemental (primary and secondary drinking water constituents) contents of alum sludge and filter backwash water from the water treatment plant at Oak Ridge, Tennessee.[110] These contents are neither unusual nor exceedingly "high."

Table 6.11. Contents of Some Elements in Alum Sludge and Filter Backwash Water.[110]

Constituent	Alum Sludge Average (ppm)	Backwash Water Average (ppm)
As	13.0	15.0
Ba	333.0	450.0
Cd	<1.0	1.0
Cr	200.0	7,260.0
Pb	47.0	50.0
Hg	<2.0	<2.0
Se	1.0	1.0
Ag		
Cu	7.0	120.0
Fe[a]		42,733.0
Mn	983.0	1,800.0
Zn	167.0	467.0

[a] "Too high."

The metallic contents of commercial alum and recovered alum were reported from a solids reduction study.[111] These values appear in Table 6.12 for a 2.5% solids concentration sludge. The numbers are shown in terms of total metal present (mg/L of sludge, presumably) and are normalized to micrograms of metal per milligram of Al. There are, indeed, significant quantities of chromium, lead, and arsenic that would be eluted into the finished water.

Considerable treatment of the alum sludge and the filter backwash water is required before ultimate disposal. To the extent that these two wastes are "low" in solids or "high" in water contents, it is necessary to dewater the sludge to achieve at least 20% solids (dry weight) prior to any subsequent handling.[108] The traditional methods of sludge dewatering are: sand drying beds, lagooning, centrifugation, vacuum filtration, pressure-filter presses, and bed-filter presses. Other methods of disposal and/or treatment are alum recovery discharge to sewerage system and "pellet" flocculation.

An innovative process that combines sludge dewatering and alum recovery was developed and patented by Fulton.[112] It can be utilized with or without recovery of the alum. A flow diagram of the Fulton process is seen in Figure 6.32.[111] Recovery of the alum should be close to 100%.

Figure 6.33 shows the flow diagram of a pellet flocculation process that was developed in Japan.[111] It involves multistage thickening of the sludge, treatment with sodium silicate and a polymer, and subsequent dewatering on a large horizontal rotating drum called the "dehydrum." Following addition of the sodium silicate, a polymer is added to the sludge just before it enters the dehydrum. This drum is compartmented into a settling chamber or pelletizing section at the

Table 6.12. Recovered Alum Quality.[111]

	Commercial Alum		Recovered Alum Test 1	
Metal	**mg/L**	**µg metal/mg Al**	**mg/L**	**µg metal/mg Al**
Cadmium	[a]	0	[a]	0
Chromium	9.5	0.2	0.6	0.3
Copper	0.1	0.002	0.6	0.3
Iron	1160.0	18.4	292.0	146.0
Sodium	57.0	0.9	6.5	3.3
Potassium	5.6	0.1	6.1	3.0
Manganese	1.7	0.03	255.0	127.0
Nickel	0.1	0.002	0.06	0.03
Lead	1.5	0.02	0.03	0.02
Zinc	1.1	0.02	1.7	0.90
Calcium	6.3	0.1	2.8	1.4
Magnesium	12.5	0.2	5.5	2.7
Aluminum	63,000.0		1970	
Silicon	14.2	0.2	8.5	4.2
Barium	0.5	0.01	0.3	0.1
Silver	0.4	0.01	[a]	0
Arsenic	3.0	0.05	1.1	0.05
Selenium	[a]	0	[a]	0
Mercury	0.001	0	0.002	0

[a] Below detection limit.

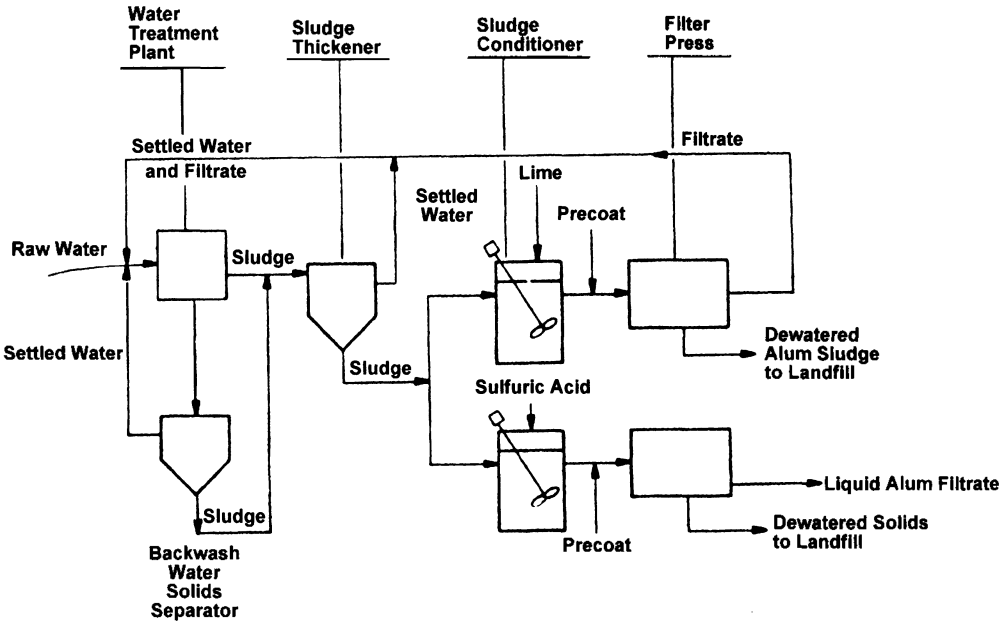


Figure 6.32. Sludge treatment system. Fulton process. Reproduced from Bishop et al.,[111] courtesy of the American Water Works Association.

inlet end. The decanting section is in the center of the drum. A sludge with 25–30% dry solids is discharged onto a conveyor. Additional drying to 65–70% solids may be accomplished in oil-fired dryers.

In 1976 the Passaic Valley Water Commission began operating an alum sludge and filter backwash water treatment and disposal process.[113] Figure 6.34 shows the complex flow diagram of these two wastes from the water

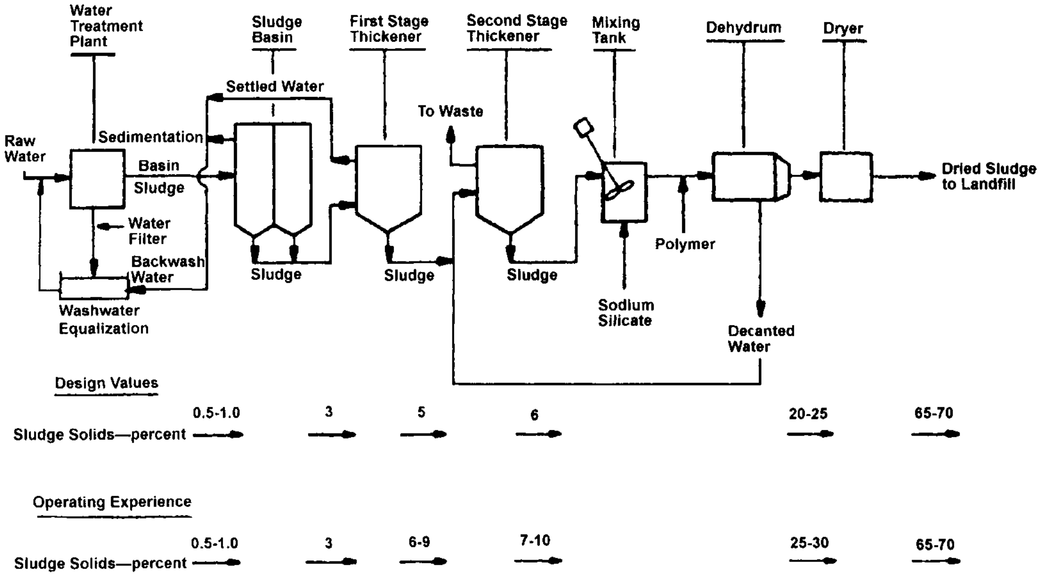


Figure 6.33. Sludge treatment system for Nishi-Nagasawa purification plant, Kanagawa Prefecture, Japan. Reproduced from Bishop et al.,[111] courtesy of the American Water Works Association.

treatment portion of the plant to the sludge facility. After the sludge is collected (storage tanks 1 and 2) from the coagulation process and from the filter backwash water settling tank, a polyelectrolyte is added to the sludge, which is thickened by centrifugation. At this point, lime and precoat are added to the thickened sludge, which then is concentrated further by an automatic filter press consisting of several septa. The conditioned sludge, 70% dry solids, is ready for ultimate disposal.

Several laboratory studies have been conducted to investigate variables affecting sludge thickening and dewatering characteristics. These must be viewed within the framework of overall treatment efficiency within such other issues as concurrent organics removal, solids separation characteristics, and minimization of residual alum concentrations.[115] The thickening and dewatering characteristics of aluminum and ferric sludges were affected by increases in the rate and extent of dewatering that occurred when: (a) the pH of coagulation was reduced, (b) the coagulant-to-influent turbidity ratio was reduced, and (c) the coagulation mechanism was adjusted from enmeshment to adsorption-charge neutralization. Enmeshment coagulation tended to yield a larger floc with significantly greater amounts of incorporated water. On the other hand, adsorption-charge neutralization produced smaller and denser floc that yielded improved sludge properties. However, this mechanism of coagulation gave higher effluent turbidities because it is less efficient at removing extremely fine particles from the water. These studies were followed by an evaluation of the effect of incorporated natural organic matter (NOM) on the dewatering characteristics of $Al(OH)_{3(s)}$ sludges.[116] Here, sludge dewatering characteristics became worse when the amount of NOM incorporated into the sludge floc matrix was increased. The addition of $KMn0_4$ as a preoxidant to alum coagulation of NOM produced improvements in sludge dewatering rates. In a third study, an investigation was made of the procedures for evaluation of polymer performance and selection in coagulation, sedimentation, filtration, and sludge conditioning.[117]

KINETICS OF PARTICLE AGGREGATION

Flocculation and coagulation of colloids, by whatever mechanism, depend on the frequency of collisions and on the efficiency of particle contacts. Whenever suspended particles collide, there are at least three mechanisms of transport:[118]

1. Particles are in motion because of their thermal energy (Brownian motion). Any coagulation occurring by this means is called "perikinetic."
2. When the particles are large enough, or when the fluid shear rate is high enough, the relative motion from velocity gradients exceeds that by thermal effects. This is called "orthokinetic" coagulation.
3. In the sedimentation process, particles with different gravitational settling velocities may collide and aggregate.

Perikinetic Coagulation

In a monodisperse system, the decrease of the concentration of particles, N, with time due to collisions by Brownian motion is:[15,119]

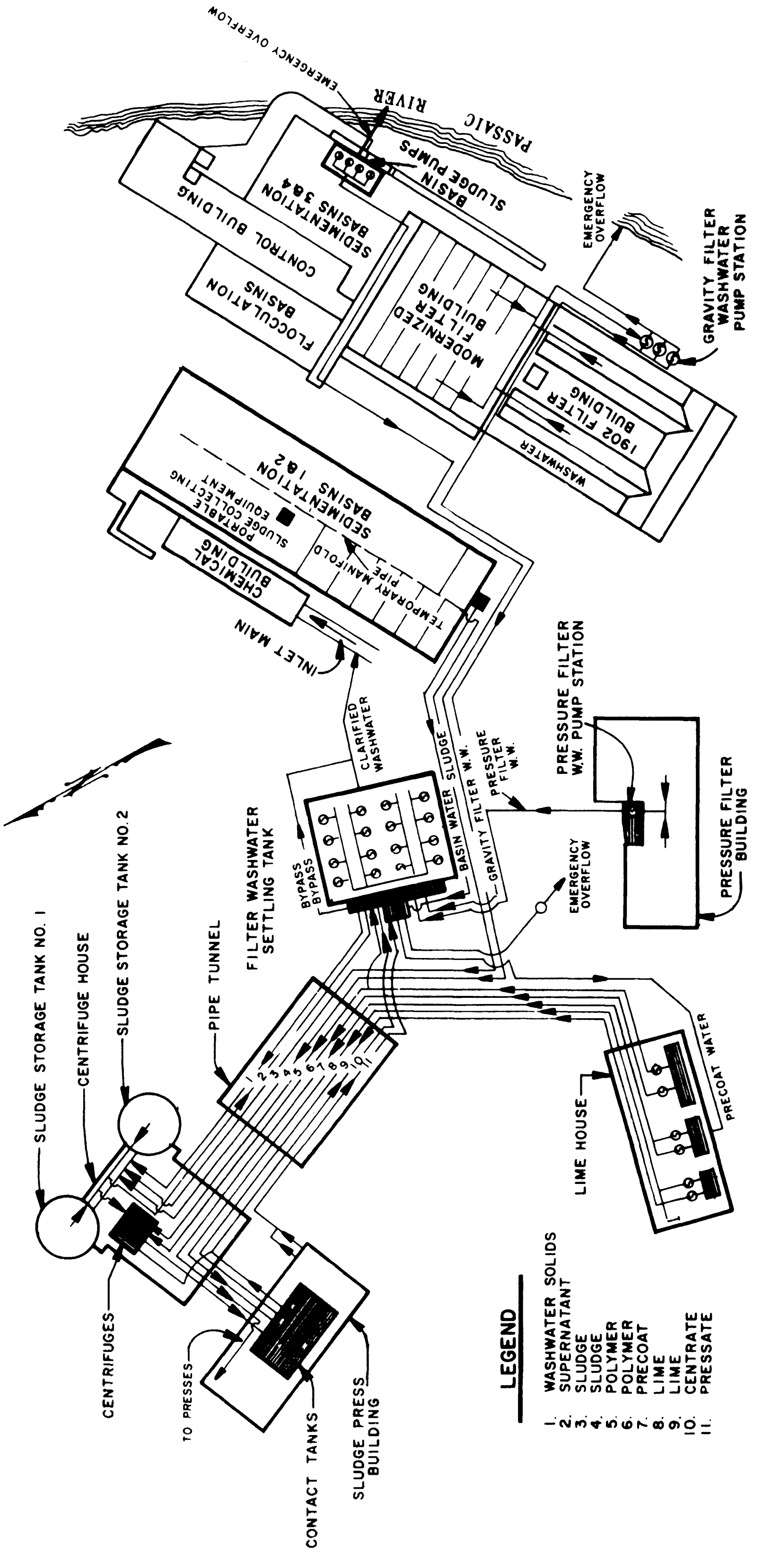


Figure 6.34. Plant schematic of sludge treatment at the Passaic Valley Water Commission, Little Falls, New Jersey.

$$\frac{dN_o}{dt} = -k_p N_o^2 \tag{26}$$

where N_o = total concentration of particles at time, t
k_p = the second-order rate constant

or,

$$\frac{1}{N_o} - \frac{1}{N_o^o} = k_p t \tag{27}$$

where N_o^o = the total particle concentration at t=0.

For k_p, the Smoluchowski[120] equation is:

$$k_p = \alpha_p 4D\pi d \tag{28}$$

where α_p = the fraction of collisions leading to permanent aggregation
d = diameter of particle
D = Brownian diffusion coefficient, which can be expressed from the Einstein-Stokes equation:

$$D = \frac{kT}{3\pi\eta d} \tag{29}$$

where k = the Boltzmann constant
T = the absolute temperature
η = the absolute viscosity

Substituting Equations 28 and 29 into Equation 27:

$$\frac{dN_o}{dt} = -\alpha_p \frac{4kTN_o^2}{3\eta} \tag{30}$$

k_p is on the order of 2×10^{-12} cm^3/sec for water at 20°C when α_p=1.[81] For a turbid water with 10^6 particles/cm^3, this concentration would be reduced by about one-half in approximately six days due to Brownian motion.

Integration of Equation 30 yields [15]:

$$N_o = \frac{N_o^o}{1 + (4\alpha_p kTN_o^o / 3\eta)t} \tag{31}$$

When the quantity $(4\alpha_p kTN/3\eta)=1/t_{1/2}$, Equation 31 becomes:

$$N_o = \frac{N_o^o}{1 + (t/t_{1/2})} \tag{32}$$

where $t_{1/2}$ = time necessary to reduce the concentration of particles by one-half

For water at 25°C, the equation for $t_{1/2}$ is:[15]

$$t_{1/2} = \frac{1.6 \times 10^{11}}{\alpha_p N_o^o} \tag{33}$$

where $t_{1/2}$ has units of seconds, N, particles/mL and α_p is dimensionless. In Equation 33, $t_{1/2}$ is dependent on the initial particle content and the collision efficiency.

Orthokinetic Coagulation

Agitation, of course, accelerates aggregation of particles in a moving fluid. Any spatial change in the fluid's velocity causes a velocity gradient, and, since particles follow the fluid, there will be opportunities for interparticle contact. The rate of decrease in numbers of particles due to their aggregation under the effect of a mean velocity gradient G (time^{-1}) is:[119]

$$\frac{dN_o}{dt} = -2/3\alpha_o \bar{G} d^3 N_o^2 \tag{34}$$

where α_o = the fraction of collisions resulting in permanent aggregation (α_o is similar to α_p)
d = the diameter of particles

Equation 34 describes the aggregation of particles in motion as orthokinetic coagulation. The respective rates of orthokinetic and perikinetic coagulations may be ratioed:

$$\frac{(dN/dt)ok}{(dN/dt)pk} = \frac{\bar{G}d^3\eta}{2kT} \tag{35}$$

This assumes $\alpha_o = \alpha_p$. This ratio is unity when the velocity gradient is 10 sec^{-1}, 25°C, and the colloidal particles have uniform diameters of 1 µm.[20] In a similar manner, when particle diameters are uniformly 10 µm, a velocity gradient of 0.01 sec^{-1} offers sufficient orthokinetic flocculation to equal the contacts resulting from diffusion. Mean velocity gradients of 10–100 sec^{-1} are common in water treatment plants.[15]

The volume fraction of colloidal particles ϕ (volume per unit volume of suspension) is:

$$\phi = \frac{\pi}{6} d_o^3 N_o \tag{36}$$

where d_o = diameter of the particles at time=0.

Substitution of Equation 36 into Equation 34 yields:

$$\frac{dN_o}{dt} = -\frac{4}{\pi}\alpha_o\bar{G}\phi N_o \qquad (37)$$

Integration of Equation 37 for the boundary conditions $N_o = N_o^o$ at $t=0$ and $N_o = N_o$ at time t yields:

$$\ln\frac{N_o}{N_o^o} = -\frac{4}{\pi}\alpha_o\phi\bar{G}t \qquad (38)$$

Thus, the rate of orthokinetic flocculation is apparently first-order with respect to N_o, $\bar{G}$, and ϕ, the floc volume fraction.

In any system, the mean velocity gradient depends on the power dissipated within the water. Camp and Stein[121] gave this equation:

$$\bar{G} = \left(\frac{\bar{P}}{V\mu}\right)^{1/2} \qquad (39)$$

where $\bar{P}$ = the power input to the fluid
V = the volume of the reactor or, in this case, flocculator
μ = the viscosity of the fluid

When flocculation chambers are baffled, interparticle collisions are accomplished by hydraulic mixing within the fluid as it flows through the tank. An equation from Camp[122] is:

$$\bar{P} = Q\rho_l g h_f \qquad (40)$$

where Q = flowrate
ρ_l = fluid density
g = gravity acceleration constant
h_f = head loss in the tank

Substitution of Equation 40 into 39 yields:

$$\bar{G} = \left(\frac{Q\rho_l g h_f}{V\mu}\right)^{1/2} = \left(\frac{g h_f}{\nu\bar{t}}\right)^{1/2} \qquad (41)$$

where ν = kinematic viscosity of the fluid
$\bar{t}$ = mean detention time of the fluid in the tank

The intent of the foregoing discussion is to apply the theories of particle transport to the design of flocculation units. O'Melia provides an excellent discussion of particle transport processes.[15,25] Equations that describe perikinetic and orthokinetic coagulation are corrected for electrostatic effects, hydrodynamic retardation, and other factors.[25] In any event, treatment plant design involves the selection of a velocity gradient $\bar{G}$, a reactor configuration and a contact time sufficient for aggregation of colloidal particles for subsequent removal by an appropriate treatment unit (e.g., settling tank, vacuum filter, and sand filter).

Example Problem 6.2: Flocculation is achieved in a batch system by stirring a destabilized suspension at a velocity gradient of 10/sec for 60 min. The number of particles in suspension is reduced by 90% ($N_o/N_o^o = 0.1$).

a. Determine the product of the collision efficiency factor and the floc volume fraction ($\alpha_o\phi$) for the water being treated. Neglect floc breakup due to high and/or extended agitation.
b. To produce the same degree of aggregation using the same velocity gradient, what detention time is required if a single completely mixed, continuous-flow flocculation tank is used?
c. What total detention time is required if three continuous stirred-tank reactors (CMF), each having the same volume, are used in series?
d. If a single CMF reactor with a detention time of 60 min and a velocity gradient of 10/sec is used, what degree of aggregation would you expect?
e. If three CMF reactors, each having the same volume, were used in series to provide a total detention time of 60 min, what degree of aggregation would you expect if a mean velocity gradient of 10/sec were used in each tank?

a. We begin by rearranging Equation 38:

$$\alpha_o\phi = \frac{\pi}{4\bar{G}T}\ln\frac{N_o^o}{N^o}$$

$$\alpha_o\phi = \frac{(3.14)(2.3)}{4(10)(60)(60)}\log 10$$

$$\alpha_o\phi = 5 \times 10^{-5}$$

b. The required detention time, $\bar{t}$, can be estimated from the following equation when m (the number of CMF reactors) = 1.0:

$$m\bar{t}_{CMF} = \frac{\pi m}{4\alpha_o\bar{G}\phi}\left[\left(\frac{N_o^o}{N_m^o}\right)^{1/m} - 1\right] \qquad (42)$$

Here N_o^o is the concentration of colloidal particles in the influent to the first tank and N_m^o is the concentration of particles in the effluent from the last of the series.

$$\bar{t} = \frac{(3.14)(1)}{4(5\times10^{-5})(10)}[10-1]$$

$$\bar{t} = 1.4\times10^{4}\text{ sec} = 234\text{ min}$$

c. For a value of m=3, Equation 42 yields a value for $\bar{t}$ of

$$\bar{t} = \frac{3.14(3)}{4(5\times10^{-5})(10)}[(10)^{1/3}-1]$$

$$\bar{t} = 5.4\times10^{3}\text{ sec} = 90\text{ min}$$

d. Rearranging Equation 42, and using m=1,

$$\frac{N_o^o}{\bar{N}_m^o} = 1 + \frac{4(5\times10^{-5})(10)(60)(60)}{3.14}$$

$$\frac{N_o^o}{\bar{N}_m^o} = 3.29 \text{ or } \frac{\bar{N}_m^o}{N_o^o} = 0.3$$

Thus, the number of particles is reduced by 70% in this single CMF reactor compared with a 90% reduction in a batch system of equal detention time.

e. Again rearranging Equation 42 for m=3

$$\frac{N_o^o}{\bar{N}_m^o} = \left[1 + \frac{4(5\times10^{-5})(10)(60)(60)}{(3.14)(3)}\right]^3$$

$$\frac{N_o^o}{\bar{N}_m^o} = 5.5 \text{ or } \frac{\bar{N}_m^o}{N_o^o} = 0.18$$

Thus the number of particles in suspension is reduced by 82% in this series of 3 CMF reactors compared with a 90% reduction in a batch system of equal total detention time.

This example problem was modified from material in Reference 15.

Initial Mixing and Coagulation Mechanisms

It was cited above that coagulation of turbidity in water treatment by Al and Fe salts is effected, essentially, by two mechanisms: (a) adsorption of hydrolysis species on the particulate that causes charge neutralization, and (b) sweep coagulation where the colloid interacts with the precipitated hydroxide. These mechanisms are summarized in Figure 6.35 using alum as an example. Reactions that precede charge neutralization with alum are extremely rapid and occur within microseconds without formation of Al polymers, and within 1 second if polymers are formed.[15,123] The formation of $Al(OH)_{3(s)}$ before sweep coagulation is slower and occurs in the range of 1 to 7 seconds.[124] This suggests that rapid dispersion (less than 0.1 second) of the coagulants into the water is required in order for the hydrolysis products to develop in 0.01 to 1 second and destabilize the colloid. Since sweep coagulation flocs form within 1 to 7 seconds, extremely short dispersion times and high intensities of mixing are not as critical as in charge neutralization.

Turbulent Rapid Mixing for Charge Neutralization

Destabilization of colloids by charge neutralization requires collisions between the colloids and the incipiently forming products of the hydrolysis reactions. At low doses of chemicals, this type of coagulation often produces small, destabilized pinpoint floc that are ideal for direct or in-line filtration. This concept of transport during the destabilization step was employed to develop a theory for analyzing the required turbulent energy for initial mixing.[125] This model assumes that eddies of the dimensions of the Kolmogaroff microscale of turbulence (η) interact with colloidal particles (diameter d_i) and cause their destabilization. This theory uses turbulence transport equations (not given here, see Reference 125) for the viscous subrange ($\eta > d_i$) and the inertial subrange ($\eta < d_i$). The simple result was, that for particle destabilization in the charge neutralization mechanism under all conditions of the universal equilibrium range of turbulence, rapid mixing should avoid the range of energy dissipation where $\eta = 1.33\ d_i$ to $2.00\ d_i$. That is, rapid mixing should avoid mixing conditions that would produce a Kolmogaroff microscale of the same order as the size of the particulates to be destabilized. There is some experimental evidence to support the above theory. For a suspension of 3 μm colloidal particles, the theory indicated that the range of average velocity gradients $\bar{G}$ of 1500 to 3500 sec^{-1} should be avoided for effective destabilization. Also, the experimental results provided a theoretical rationale for two types of rapid mixing units to be used in practice: (a) backmix reactors having mean $\bar{G}$ values of 700 to 1000 sec^{-1} and in line blenders having values of 3000 to 5000 sec^{-1} (see Figure 6.39).

Rapid Mixing for Sweep Coagulation

In sweep coagulation conditions, the water is supersaturated by 3 to 4 orders of magnitude with coagulant, whereupon the hydroxide is precipitated very rapidly. Here, the chemical conditions for rapid precipitation and subsequent flocculation of the particulates are significantly more important than the transport interactions between the two. Therefore, the chemical aspects of the destabilization step

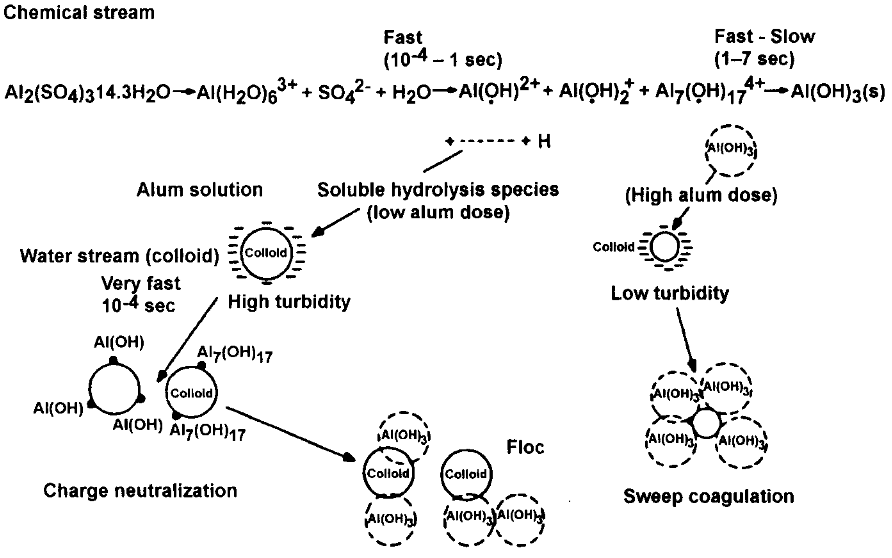


Figure 6.35. Reaction schematics of coagulation.[125]

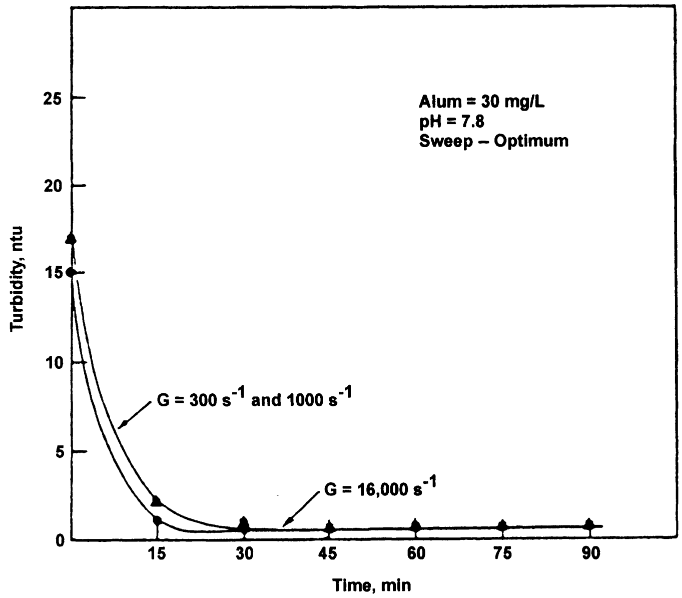


Figure 6.36. Response of sweep coagulation to variations in rapid mixing.[128]

and the transport aspects of flocculation are the significant factors (see Figure 6.35). When sweep coagulation is practiced, the results are indifferent to rapid mixing energy inputs. This is seen in Figure 6.36, where rapid mixing with values from 300 to 16,000 sec^{-1} produced the same settled water turbidities after 30 minutes.[28]

Rapid Mixing with Polymers

The mechanisms of coagulation with organic polymers are charge neutralization and interparticle bridging. The high intensities of mixing may not be necessary for organic polymers because these mechanisms are slightly different than those for inorganic coagulants.

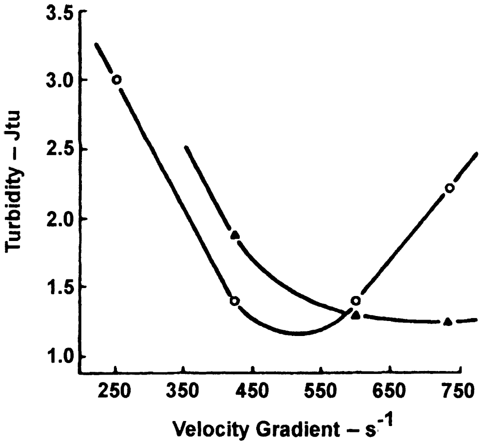


Figure 6.37. Results of application of velocity gradients greater than 400 sec^{-1}. ○ = 2.0 mg/L; ▲ = 1.0 mg/L. Reproduced from Morrow and Rausch,[126] courtesy of the American Water Works Association.

Table 6.13. Beaver River Study: Polyelectrolyte and Inorganic Coagulant Results.[a]

Coagulant Treatment	Velocity Gradient (sec^{-1})	Coagulant Dosage (mg/L)	Raw Water Turbidity (JTU)	Average Settled Water Turbidity: Pilot Unit (JTU)	Average Settled Water Turbidity: Plant (JTU)
Alum	250	24.0	6–14	1.5	2.5
Alum/polymer[b] A	250	12.0/0.2	4–8	1.9	1.6
Polymer A	425	1.0	5–7	1.85	1.8
Polymer A	425	2.0	4–6	1.4	1.25
Polymer A	600	1.0	5–6	1.3	1.25
Polymer A	600	2.0	4–7	1.4	1.65
Polymer A	730	1.0	4–6	1.25	1.45
Polymer A	730	2.0	4–6	2.2	1.45
Polymer A	250	2.0	4–6	3.0	2.3

[a] Reproduced from Morrow and Rausch,[126] courtesy of the American Water Works Association.
[b] Cat-Floc B, polyquaternary ammonium compound.

Some data from pilot-plant studies suggest that cationic polyelectrolytes can effectively destabilize colloidal and particulate matter without inorganic salts by the application of increased mixing energy.[126] Mechanical rapid mixing units at water treatment plants are designed to provide 10–60 sec of detention time by intense mixing, and to yield velocity gradients on the order of 300 sec^{-1} or more. Flocculation basins that follow the rapid mix have a velocity gradient range of 5–100 sec^{-1}, wherein the destabilized particles coalesce and compact.

Pilot-plant studies were conducted at three sites in the United States:[126] (1) Beaver River, Pennsylvania, (2) Missouri River, Missouri, and (3) Mississippi River, Illinois. Figure 6.37 and Table 6.13 show the effect of velocity gradient on the cationic polyelectrolyte (Cat-Floc B, Calgon Corporation) flocculation of a low turbidity water. The polyelectrolyte apparently can replace alum as the primary coagulant for low and high turbidity (data not shown) waters when $\bar{G}$ values of greater than 400 sec^{-1} are applied. There is an additional advantage to this process: sludge produced by polyelectrolyte treatment is heavier and denser than the alum sludge and has better compaction and sedimentation characteristics.

A bench-scale batch reactor was used to evaluate rapid mixing velocity gradients and time effects on flocculation characteristics.[127,128] A rapid mix of 650 sec^{-1} for 0.5–8 sec is optimum for various water turbidities coagulated with 3 mg/L alum, pH 6.4, and 0.15 mg/L anionic polyelectrolyte.

The kinetics of particle aggregation suggests that the total particle concentration rate of decrease can be represented by a first-order rate equation of the form:[127]

$$\frac{dN_t}{dt} = -K_E N_t \qquad (42)$$

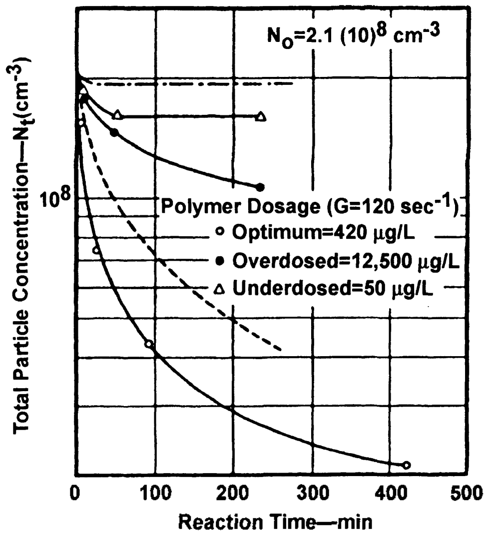


Figure 6.38. Effect of mixing intensity and polymer dosage on the flocculation kinetics of latex suspensions. --- = Brownian motion destabilization at the optimum polymer dosage; —•—•— = Brownian motion destabilization at under- and overdosed polymer conditions; — = turbulent flocculation destabilization. Reproduced from Birkner and Morgan,[129] courtesy of the American Water Works Association.

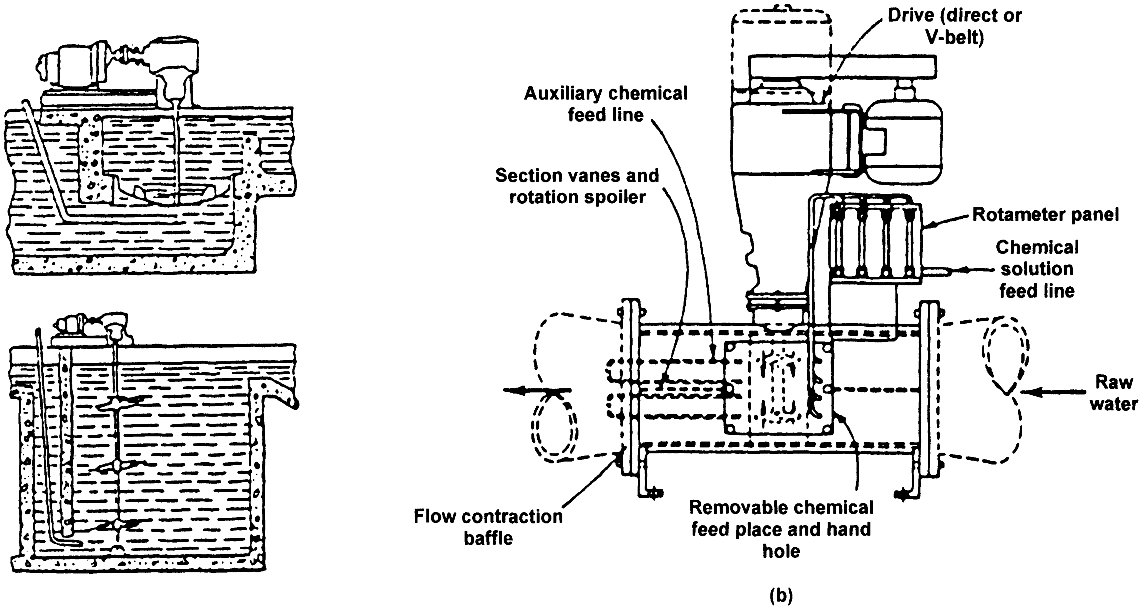
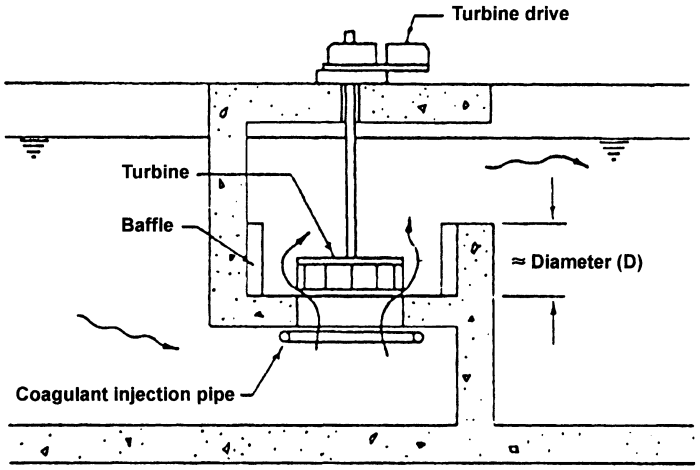


Figure 6.39a and b. Rapid mixers used in practice. (a) Mechanical backmix type mixers; (b) inline blenders.[25]

where K_E= experimental first-order rate constant comparable to the $K(4/\pi\alpha_0\bar{G}\phi)$ in Equation 37.

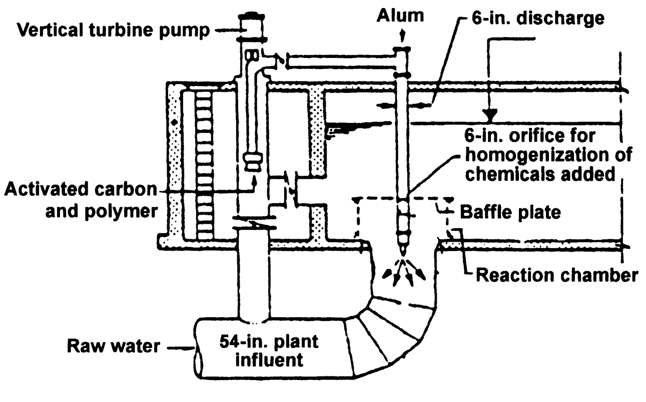
This first-order rate expression is applicable only at the optimum polymer dosage, and only during the initial phase of the flocculation process (Figure 6.38). When the flocculent is insufficient or in excess, the reaction is definitely not first-order. K_E values of 1.06×10^{-3} to 9.53×10^{-4} are observed for the optimum system when five $\bar{G}$ values ranged from 11 to 120 sec^{-1}. Furthermore, a 90% reduction in the initial particle concentration occurred after a reaction time of 424 min (7 hr).

These observations apply, of course, to the experimental systems of Birkner and Morgan.[129] It is assumed that simi-



Flash mixer section

(c)



(d)

Figure 6.39c and d. Rapid mixers used in practice. (Continued) (c) Radial turbine flash mixer; (d) pump injection mixer.[25]

lar kinetics occur under optimum conditions at water treatment plants.

COAGULATION UNITS

There are several alternative initial mixing devices available for use in water treatment plants: (a) backmix reactors, (b) inline blenders, (c) hydraulic pumps, (d) diffusers and injection devices, and (e) motionless static devices, as seen in Figure 6.39. These devices have been evaluated comparatively for use in design.[130] Design considerations for these initial mixing units are given elsewhere.[25,131]

Initial mixing is followed by flocculation in the baffled portion. Sedimentation follows in a rectangular tank, as seen in Figure 6.40a, after which the water is filtered. In cases where space is limited or a higher rate of treatment is required, the solids-contact clarifiers frequently are used. These are seen in Figure 6.40b, along with the intimate mixing and recycling of the sludge with the incoming water. Automatic and selective recycling of the sludge occurs, as well as its removal for additional treatment. These clarifiers can be operated at an upflow rate of 1 gpm/ft^2, which permits a higher rate of filtration to follow. Other types of upflow solids contact clarifiers are described elsewhere.[25,130,131]

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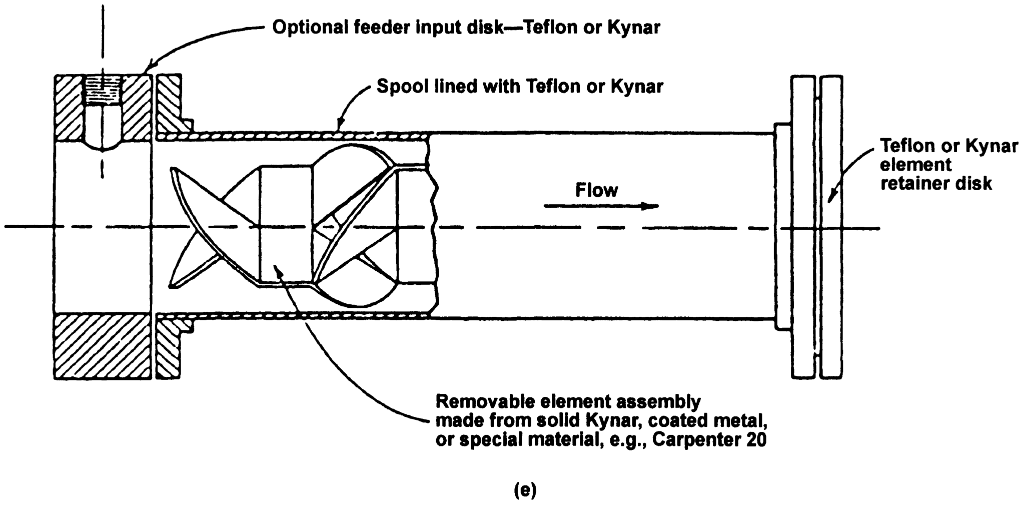

Figure 6.39e. Rapid mixers used in practice. (Continued) (e) Static (motionless) mixer.[25]

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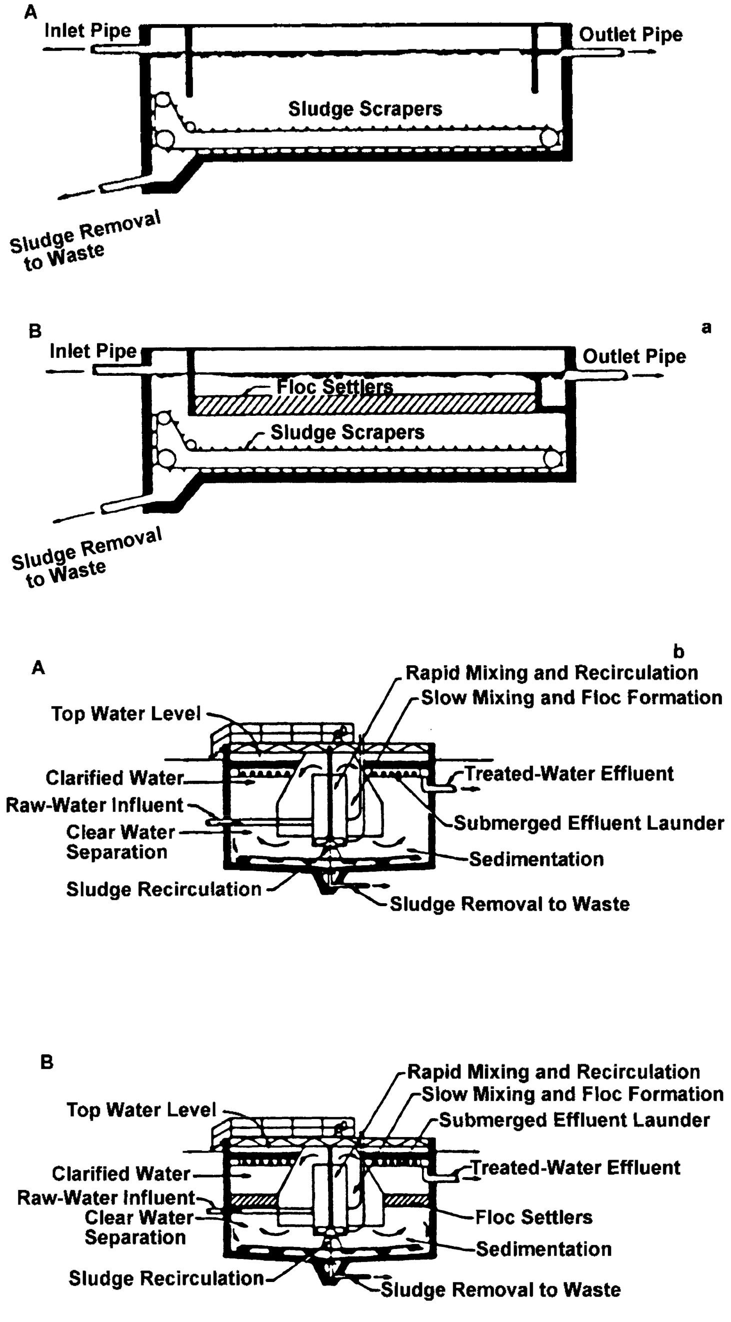

Figure 6.40. (a) Rectangular steeling tank: A = standard; B = modified. (b) Clarifier: A = standard; B = modified. Reproduced from LaFontaine,[114] courtesy of the American Water Works Association.

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Chapter 7

Removal of Particulate Matter by Filtration and Sedimentation

7

Removal of Particulate Matter by Filtration and Sedimentation

HISTORY OF THE FILTRATION PROCESS

Filtration is the process of removing solids from a fluid by passing it through a porous medium. It is widely used in water treatment to remove solids, including bacteria present in surface waters, precipitated hardness from lime-softened waters, and precipitated iron and manganese. Filtration is employed in wastewater treatment as a finishing process beyond secondary biological treatment or to remove solids remaining after precipitation or chemical coagulation in physicochemical processing. This chapter will focus primarily on deep granular filters (sand, dual-media, and multimedia), although some attention will be given to precoat filters (diatomaceous earth).

The use of filtration in water treatment dates back to the slow sand filters used in London, England, as early as 1829. Filters of this type were operated at a rate of 2–4 mgad (million gallons per acre per day) through a bed depth of 3 ft and served as the sole treatment device. The famous Broad Street (London) well epidemic in the early 1850s generated an international movement to require the filtration of all potable water. Rapid sand filters operating at rates of 1–4 gpm/ft^2 were subsequently designed in the United States in the late nineteenth century to minimize the required surface area and capital cost to achieve the desired capacity. Today's deep-bed (18–30 in.) granular filters utilize sand, or sand in combination with other materials, as the filter medium.

The use of precoat filters is quite limited. Diatomaceous earth filters are commonly used for swimming pool filtration and some industrial applications. Other applications have used various media, including perlite and powdered activated carbon.

SIGNIFICANCE OF THE FILTRATION PROCESS

In the 1986 amendments to the Safe Drinking Water Act of 1974 (Public Law 99-399), it was stated that:

> Not later than 18 months after the enactment of the Safe Drinking Water Act Amendments of 1986 the Administrator shall propose and promulgate national primary drinking water regulations specifying criteria under which filtration (including coagulation and sedimentation, as appropriate) is required as a treatment technique for public water systems supplied by surface water sources.
>
> In promulgating such rules, the administrator shall consider the quality of source waters, protection afforded by watershed management, treatment practices (such as disinfection and length of water storage) and other factors relevant to public health.

The regulation that the U.S. Environmental Protection Agency (USEPA) developed in response to this section of the amendments is known as the Surface Water Treatment Rule (SWTR). The final version of the SWTR was published on June 29, 1989, and the rule became effective December 31, 1990. The SWTR includes criteria that the states (those with primacy) are to use in determining which public water systems supplied by a surface water source (surface water source includes groundwater "under the direct influence of surface water." States are required to establish criteria to be used to determine whether a groundwater source is under the direct influence of surface water), are to install filtration and, for those systems with filtration, in determining if treatment is adequate. The states with primacy are also required to specify enforceable design and operating criteria for filtration on a statewide or system-by-system basis. See Chapter 1 for additional information on the SWTR and the appropriate references.

In the early 1990s, the USEPA estimated that implementing the SWTR will affect approximately 2800 water systems that are currently unfiltered and 6900 systems that are currently filtered. According to a USEPA cost analysis of the 6900 filtered supplies, approximately 5100 systems will incur total annualized costs of $113 million per year to up-grade to meet the new requirements. For the 2800 unfiltered supplies, the estimated annualized costs of installing (or avoiding) filtration is $337 million per year. A large proportion of the total costs for unfiltered supplies is attributable to 15 large systems, each serving over 100,000 people. However, communities with populations less than 10,000 represent over 90 percent of unfiltered supplies, and it is likely that the per capita cost of implementing the rule will be greatest in these locations.[1]

The SWTR is concerned with the filtration of surface water supplies to protect against microbiological contaminants. All the requirements in the rule pertain to this treatment objective. Some of the other purposes for which filtration is used in water treatment are described at the end of the chapter.

"Filtration" in the SWTR refers to the entire system used to remove microbial contaminants, including the pretreatment processes that prepare the suspension for separation (coagulation and flocculation); pretreatment separation processes that might precede the filters (e.g., sedimentation, flotation, and coarse-bed filtration); and the filtration process (e.g., granular-bed and diatomaceous earth filters). This chapter is concerned only with the processes of filtration and sedimentation.

FILTRATION MECHANISMS

Filtration involves a complex variety of mechanisms, which includes transport, attachment, and detachment. Transport mechanisms bring a small particle from the bulk fluid to the surface of the filter medium. Important transport mechanisms include screening, interception, inertial forces, gravitational settling, diffusion, and hydrodynamic conditions. These mechanisms and the efficiency of the removal of suspended solids depend on such physical characteristics as the size distribution of the filter medium, filtration rate, temperature, and density and size of the suspended particles. Mathematical models for these transport mechanisms are presented below.

An attachment mechanism is required to retain the suspended particle once it has approached the surface of the filter medium or previously attached solids. Attachment mechanisms include straining, van der Waals forces, electrostatic interactions, chemical bridging, and specific adsorption. The efficiency of the attachment mechanisms can be affected by coagulants applied in pretreatment and the chemical characteristics of the water and the filter medium.

The role of detachment as a filtration mechanism is also important. During deep granular filtration, sediments build in the filter, removed by the aforementioned mechanisms. The particles held in the filter are thus in equilibrium with hydraulic shearing forces that tend to tear them away and wash them deeper or through the filter. Since the presence of solids causes the interstitial volume to decrease, this causes an increase in the interstitial velocity, and the clogged layers become less efficient at removing solids, which then pass on to the lower, less clogged, portion of the media.

The transport, attachment, and detachment mechanisms were introduced, perhaps, in the 1960s by several investigators.[2–7] O'Melia and Stumm outlined the framework for a conceptual model for the filtration process that is considered to include both physical and chemical phenomena. These authors first considered particle transport as a physical-hydraulic process that is principally affected by those parameters that govern mass transfer. On the other hand, particle attachment is basically a chemical process that is influenced by both physical and chemical parameters.

Three transport mechanisms, considered to be the most important in particle transport, are: sedimentation, interception, and diffusion.[8] These models are essentially extensions of air filtration theories. They are useful in indicating the various parameters that are important in the transport of particles of different size and density in granular bed filters of various grain sizes, water velocity, and temperature. Each mechanism is expressed in terms of an ideal single spherical collector efficiency, η, which is the ratio of the number of successful collisions to the total number of potential collisions in the cross-sectional area of the collector. Mathematical models that describe these transport steps are found in References 7, 8, and 9, of which some are presented below.

The attachment of a suspended particle at the solid-liquid interface presented by the filter (either to a sand grain or to another particle previously retained in the bed) is controlled by the surface properties of these materials.[7] Two models that describe particle attachment and that have theoretical interest and practical significance are the double layer theory and the bridging theory. The first model is based upon the interactions of electric double layers. Application of this theory assumes that the net interaction between a suspended particle and the filter surface can be described by a quantitative combination of van der Waals attraction with the coulumbic repulsion or attraction of the two double layers (see Chapter 6 for a fuller description of this theory). It seems reasonable to extend the experimental information obtained from chemical coagulation research to filtration by granular media. However, the double-layer model is restricted in its application to lyophobic surfaces and simple electrolytes. This restriction arises primarily from the observation that this model neglects the dominating role that chemical forces may play in particle attachment. When the suspended particle and the filter particle have opposite charges, coulumbic attraction is often invoked as the basis for attachment. In some situations, specific chemical forces can outweigh electrostatic forces. For example, adsorption of anionic polymers on negative surfaces is common.[10] This and other situations led LaMer and coworkers[10] to develop a chemical bridging theory. In this theory, the destabilizing agent, usually a precipitated Al and Fe coagulant, a polyelectrolyte, or a natural macromolecule, forms a "bridge" between two particles that effects their removal. This bridge is usually explained by chemical and physical adsorption. It is conceivable that bridges can be constructed in granular filters. There is some experimental evidence to support this conjecture.[7]

There have been other attempts to model the particle removal mechanisms of transport, attachment, and detachment.[9] Phenomenological and trajectory theories coupled with empirical evidence to stress the importance of chemical destabilization, initial degradation and filter ripening, minimization of rate changes, and the use of polymers for producing high quality water have been tried to explain filtration mechanisms. However, the proponents of these theories state: "phenomenological theories—are not generally applicable but require pilot-scale experimental determination of coefficients for a particular raw water and trajectory theories are elegant and mathematically rigorous but are unable to model results when double layer repulsive conditions occur."[9] All of these theories are interesting and initiate academic inquiry. However, the main concern in filtration remains its efficiency to remove the various impurities from water. The effects of different parameters on particle removal efficiency are summarized in Table 7.1.[11]

FILTRATION HYDRAULICS

Head loss (i.e., pressure drop) occurs when clean water flows through a bed of clean filter medium. Water flow through a clean filter of ordinary grain size (0.5 to 1.0 mm) at ordinary filtration rates (2–5 gpm/ft^2 or 4.9 to 12.2 m/h) is in the laminar range of [illegible]. This is in accord with the Kozeny equation, which is dimensionally homogeneous:

$$\frac{h}{L} = \frac{k\mu}{\rho g}\,\frac{(1-\varepsilon)^2}{\varepsilon^3}\left(\frac{a}{\upsilon}\right)^2 V \qquad (1)$$

where h = head loss in depth of bed L
g = acceleration of gravity
ε = porosity
a/v = grain surface area per unit of grain volume = specific surface $S_v = 6/d$ for spheres and $6/(\psi d_{eq})$ for irregular grains
d_{eq} = grain diameter of sphere of equal volume
V = superficial velocity above bed = flow rate/bed area
μ = absolute viscosity of fluid
ρ = mass density of fluid
k = dimensionless Kozeny constant commonly found close to 5 under most filtration conditions

This equation is generally acceptable for most filtration calculations because the Reynolds number, R_e, which is based on superficial velocity, is usually less than 3 under these conditions:

$$Re = d_{eq}\frac{Vp}{\mu} \qquad (2)$$

The Kozeny equation can be derived from the Darcy-Weisbach equation for flow through circular pipes:

$$h = f\frac{LU^2}{D(2g)} \qquad (3)$$

where f = friction factor, a function of pipe Reynolds number
D = pipe diameter
U = mean flow velocity in pipe

Initial head losses in clean filters commonly range from less than 1 ft to 2.5 ft, depending on the particle size distribution of the media and the overflow rate (flow/filter surface area). The pressure distribution within the media of a typical gravity filter is displayed in Figure 7.1. Negative head (less than atmospheric pressure) occurs in a gravity filter when the summation of head loss from the media surface downward exceeds the available pressure. Air pockets reduce the effective filtering area and increase the filtration rate and head loss through the remaining filter area. This results in a degradation of filter effluent quality. Negative head conditions can be eliminated by the use of pressure filters.

It is important to calculate head loss through a clean fixed bed because provision for this head must be made in the filter design. Also, head must be provided in the plant design for an increase in loss caused by clogging during the filtration cycle. An example calculation follows for head loss that was provided by Reference 14.

Example 7.1: Calculate the head loss for the 3-ft-deep (0.91-m) bed of the filter sand shown in Figure 7.2 at a filtration rate of 6 gpm/ft^2 (14.6 m/hr) and a water temperature of 20°C, using a grain sphericity of 0.75 and a porosity of 0.42, estimated from Table 7.2.

Solution: Because the sand covers a range of sizes and will be stratified during backwashing, divide the bed into five equal segments and use the middle sieve opening size for the diameter term in the solution.

Table 7.1. Effects of Different Parameters on Particle Removal Efficiency.[11]

Parameter	Change in Parameter	Change in Particle Removal Efficiency
Influent particle concentration	Increase	No change
Particle density	Increase	Increase
Interstitial velocity (filtration rate)	Increase	Decrease
Filter pore diameter (medium-grain diameter)	Increase	Decrease
Length of the filter pore (depth of the medium)	Increase	Increase
Particle attachment efficiency (degree of destabilization)	Increase	Increase

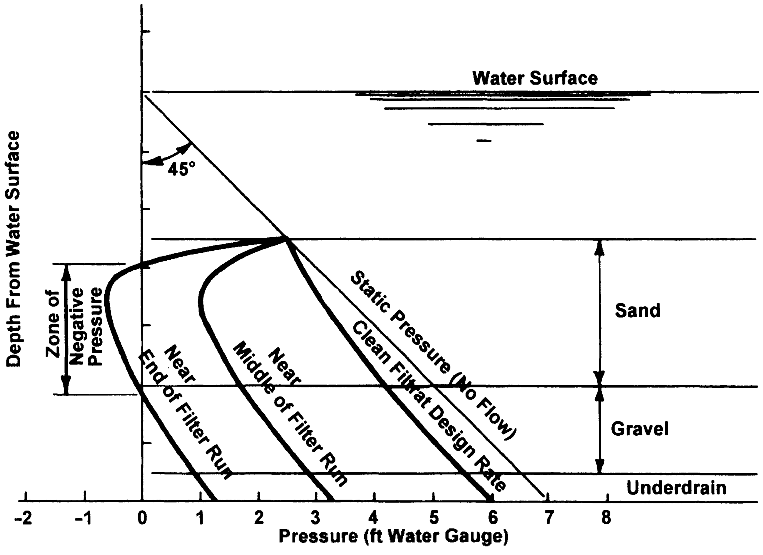

Figure 7.1. Pressure vs. depth in a gravity filter at various times during a filter run. Reproduced from Weber,[13] courtesy John Wiley & Sons, Inc.

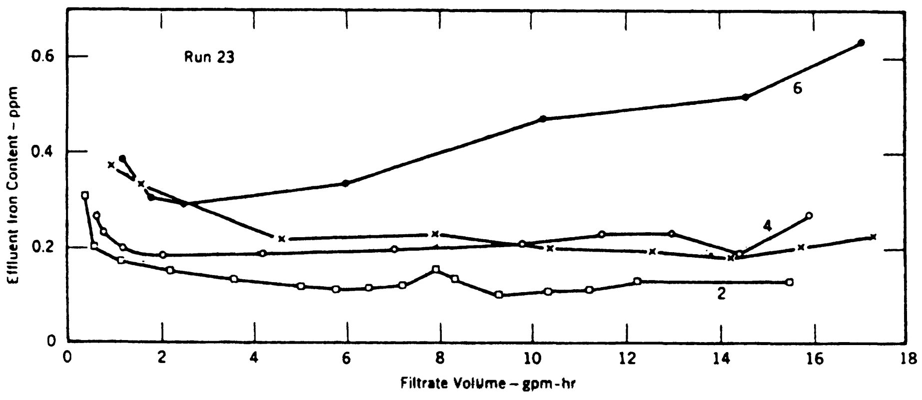

Figure 7.2. Effluent iron content and filtrate volume. Numbers on curves indicate filtration rate. Numbers on curves indicate filtration rate. Curve X indicates constant pressure. Initial rate was 6 gpm/ft^2, which decreased as head loss increased. Reproduced from Baumann.[15]

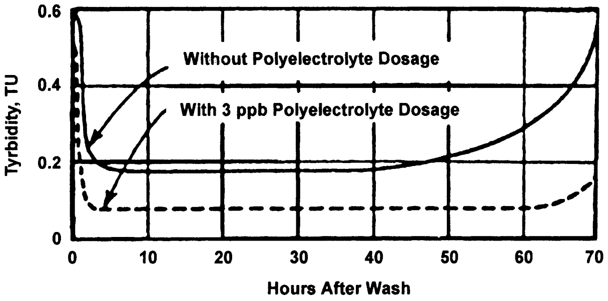

Figure 7.3. Effluent turbidity with constant filtration rate of 3.5 gpm/ft^2. Reproduced from Baumann.[15]

Kozeny equation:

$$\frac{h}{L} = \frac{k\mu}{\rho g} \frac{(1-\varepsilon)^2}{\varepsilon^3} \left(\frac{a}{\upsilon}\right)^2 V \qquad \text{cm·g·s}$$

where a/v = $6/\psi d = 6/0.75\ d$
μ/ρ = $v = 0.01003\ \text{cm}^2/\text{s}$ at 20°C
g = 981 cm/s^2
k = Kozeny's constant, typically 5 for filter media
V = 6 gpm/ft^2 = 0.408 cm/s

$$h/L = \frac{5 \bullet \frac{0.01003}{981} \bullet \frac{(1-0.42)^2}{0.42^3} - \frac{6^2}{0.75^2 d^2} - 0.408 =}{\frac{0.00606}{d^2}}$$

From Figure 7.2 select mid-diameters and calculate h/L for each.

Size	Mid-diameter (cm)	h/L	Layer depth (ft)	h (ft)
d_{10}	0.054	2.08	0.6	1.25
d_{30}	0.066	1.39	0.6	0.83
d_{50}	0.073	1.14	0.6	0.68
d_{70}	0.080	0.95	0.6	0.57
d_{90}	0.087	0.80	0.6	0.48
		1.27 average		3.81

Alternatively, because each layer was the same depth, the average h/L can be used to calculate the head loss for a 3-ft (0.91-m) bed of sand:

L = 3 ft (0.91 m)
average h/L = 1.27
h = 1.27 × 3 = 3.81 ft (1.16 m) of water

FILTRATION RATE PATTERNS

The efficiency of a filter is more sensitive to changes in rate rather than the actual rate itself. With pretreatment and proper design, Baumann[15] showed that there is little difference in water quality from filters operated at rates between 2 and 6 gpm/ft^2 (0.08 to 0.24 m^3/m^2-min), as displayed in Figures 7.2 and 7.3. Cleasby et al.,[6] however, investigated the effect of rate disturbances on quality. A representative run from their work is displayed in Figure 7.4. Tuepker and Buescher[5] evaluated the effect on performance by the severity of rate changes. An example of their work, displayed in Figures 7.5 and 7.6, shows that gradual rate changes did not affect performance as severely as rapid changes, and that the addition of a coagulant virtually damped out all effects. These characteristics are considered in the methods for filter operation. The three basic methods are constant-pressure filtration, constant-rate filtration, and variable declining-rate filtration.[16]

True constant-pressure filtration effectually provides declining-rate filtration. At the beginning of a filter run, the filter resistance is small. As the filter medium begins to clog, the flowrate decreases. Current practice does not employ such a method, since it requires the storage of a large volume of water.[13] This method is represented by trace A in Figure 7.7.

Constant- and declining-rate filtration are more commonly employed in current practice. A constant pressure is maintained across the filter system, and the filtration rate is then held constant by means of a flow control valve. Trace B in Figure 7.7 represents this method. As the filter resistance increases during operation (due to solids clogging), the flow control valve is gradually opened to maintain a constant flow. Several disadvantages have commonly been associated with this method, including high capital and maintenance costs, a poorer effluent quality than that obtained using declining-rate filtration[18,19] and frequency of equipment failure.[17] Alternative methods of flow control include flow splitting and declining-rate filtration.

Flow splitting usually involves the use of an influent weir box on each filter to split the flow nearly equally among the operating filters. Beside the obvious benefit of achieving constant-rate filtration without rate controllers, other benefits include gradual rate changes when bringing filters into

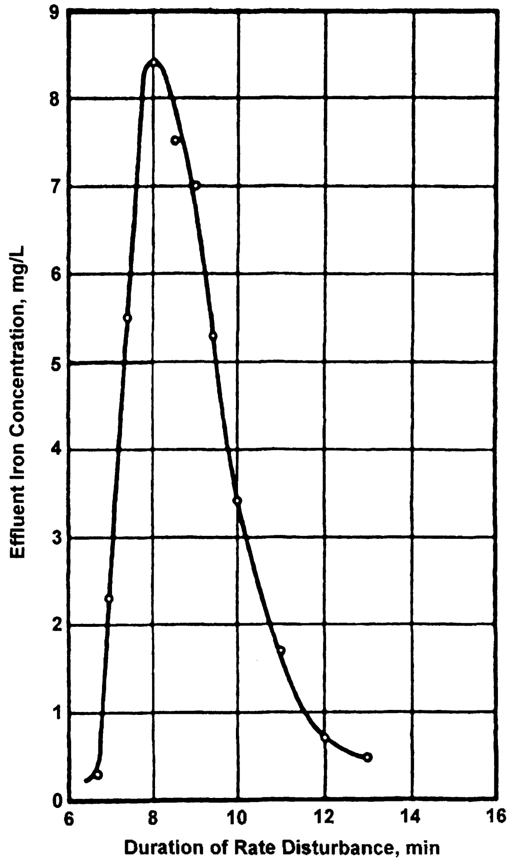

Figure 7.4. Effect of typical rate disturbance on effluent quality. This run had an instantaneous rate change from 2.0 to 2.5 gpm/ft^2. Reproduced from Cleasby et al.,[6] courtesy of the American Water Works Association.

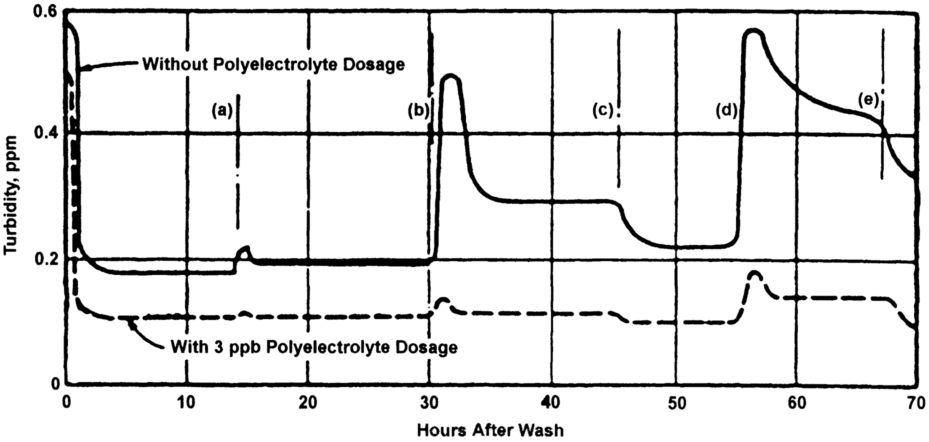

Figure 7.5. Effluent turbidity with rapid rate changes. (a) Rate increased to 2.5 gpm/ft^2 within 10 sec. (b) Rate increased to 3.5 gpm/ft^2 within 10 sec. (c) Rate decreased to 2.5 gpm/ft^2. (d) Rate increased to 3.5 gpm/ft^2 within 10 sec. (e) Rate decreased to 2.5 gpm/ft^2. Reproduced from Tuepker and Buescher,[5] courtesy of the American Water Works Association.

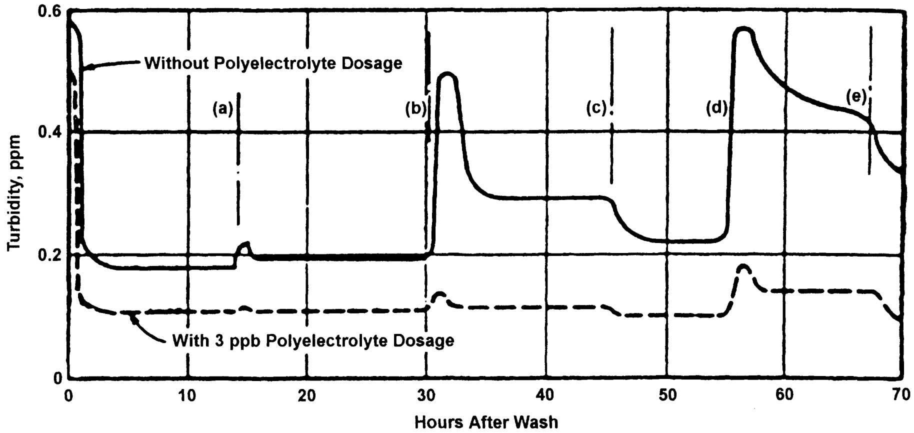

Figure 7.6. Effluent turbidity with gradual rate changes (over a 10-minute period). Reproduced from Tuepker and Buescher,[5] courtesy of the American Water Works Association.

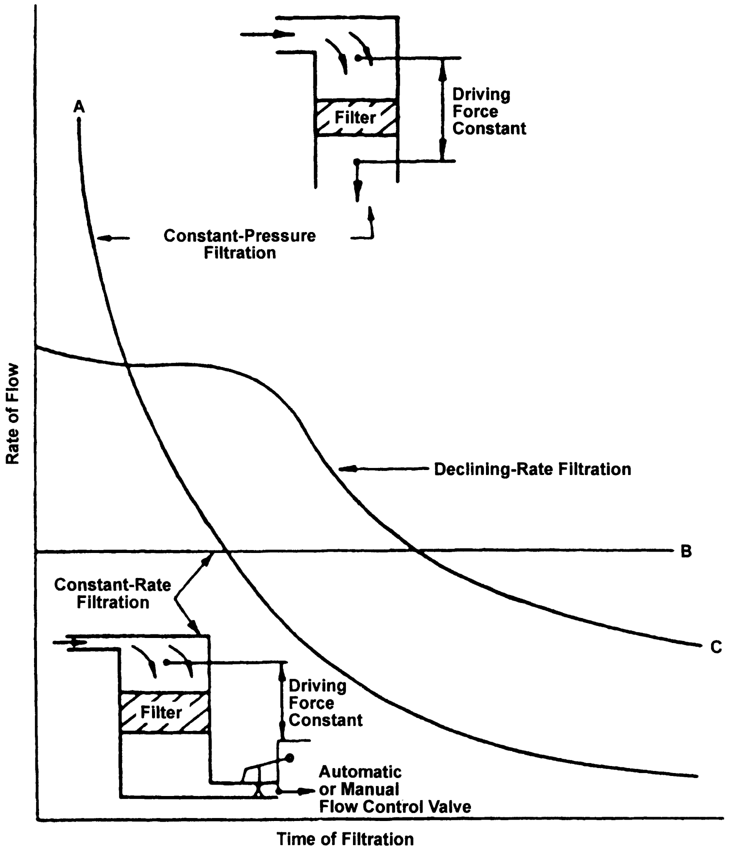

Figure 7.7. Typical rate of filtration patterns during a filter run. Reproduced from Baumann and Oulman,[17] courtesy of the University of Texas Press.

or out of service[5,6] and head loss in the filter evidenced by the water level in the filter box. In addition, since the effluent control weir must be located above the sand to prevent dewatering of the bed, the possibility of a negative head in the filter is eliminated. The only disadvantage of this system is the additional depth required of the filter box to accommodate raising of the effluent outlet to a position above the filter media surface. A schematic of this method is displayed in Figure 7.8.

Variable declining-rate filtration is currently the most widely designed method of operation for gravity filters.[15] Its operation is similar to influent flow splitting, as a comparison of its schematic (Figure 7.9) with Figure 7.8 will show. The principal differences involve the location and type of influent arrangement and the provision of less available head. The filter influent enters below the low water level (wash trough level) of the filters. The water level is essentially the same in all filters at the same time, except during backwashing. This is provided by a large influent header with large influent valves to each filter, thus resulting in small head losses. As a filter accumulates solids, consequently restricting its flow, the cleaner filters automatically pick up the lost capacity. The additional head required to accomplish this is provided by a rise in the water level of each filter. Typical water level variations in potable water plants range from 1.5 to 2 ft.[20] Trace C in Figure 7.7 illustrates this method's rate pattern. Advantages of this method include a better effluent water quality toward the end of a run than that achieved by the constant-rate method, and a lesser head requirement due to the decrease in rate as the run progresses and head losses increase.

FILTER MEDIA

Silica sand, anthracite coal, garnet, and ilmenite are the most common types of medium used in granular bed filters. Use may be alone or in dual- or triple-media combinations. Garnet (SG 3.6 to 4.2) and ilmenite (SG 4.2 to 4.6) are naturally occurring, high-density minerals. Garnet is a generic term that refers to many different minerals (i.e. almandite, andiadite, and grossularite) composed of silicates of iron, aluminum, and calcium. Ilmenite is an iron titanium ore that is associated usually with hematite and magnetite (iron oxides). Other types of media include granular activated carbon (GAC), which serves both as a filter and an adsorber (see Chapter 4). Occasionally, it is used as a filter alone following an adsorption unit.

Diatomaceous earth (DE, fossilized skeletons of microscopic diatoms) or perlite (a "glassy" rock of rhyolite) are used on precoat filters. Grades of DE used in potable water filtration have a mean pore size of the cake ranging from about 5 to 17 μm. Perlite is employed less frequently than DE. Some of its particulates remain as small glassy spheres that may float and render the medium ineffective as a filter.

Significant Granular Medium Properties

Grain Size and Size Distribution

This important property is determined by sieve analyses using the American Society for Testing and Materials (ASTM) Standard Test C136-84a, Sieve Analyses of Fine and Coarse Aggregates.[21] Figure 7.10 shows a log-probability plot of a typical sieve analysis where most plot linearly for most filter materials.

Effective size (ES) and the uniformity coefficient (UC) are employed in the United States to describe the filter medium. When 10% of the grain size is smaller by weight, this fraction is called the ES. It is read from the sieve analysis curve at the 10% passing point on the curve, and is frequently abbreviated by d_{10}. The UC measures the size range of the medium. It is the ratio of d_{60}/d_{10} sizes, read from the sieve analysis curve with d_{60}, that size for which 60% of the grains are smaller by weight. Also, the d_{90} size is recommended for calculation of the required backwash rate for a filter medium.[14]

Other Medium Properties

The *shape* and *roundness* of the filter grains are significant because they affect the backwash flow requirements, the fixed-bed porosity, head loss for flow through the medium, filtration efficiency, and the ease of sieving. There are different measures of grain shape that have evolved in the geological and chemical engineering literature, as well as confusion in terminology.[14] The chemical engineering literature defines the sphericity, ψ, as the ratio of the surface area of an equal volume sphere (diameter of d_{eq}) to the surface of the grain. In turn, this is influenced by both shape and roundness of the grain.[22] The sphericity of the filter medium can be determined indirectly by measurement of the pressure drop for flow of water or air through a bed of uniformly sized grains.[14]

Grain density (or specific gravity), the mass per unit grain volume, affects the backwash flow requirements for the medium. Grain density is determined from the specific gravity that follows the ASTM Standard Test C28-84, "Specific Gravity and Absorption of Fine Aggregate."[21]

The *hardness* of filter grains is significant in the durability of grains during long-term service as a filter medium. The rather crude Mohs hardness test involves a scale of hardness based on the ability of various minerals to be scratched by another harder object.[14]

Fixed-bed porosity is the ratio of void volume to total bed volume and is expressed as a decimal fraction or a percentage. It affects the backwash flow required, the fixed-bed head loss, and the solids-holding capacity of the medium. It is determined by placing a sample of known mass and density in a transparent tube of known internal diameter.[14]

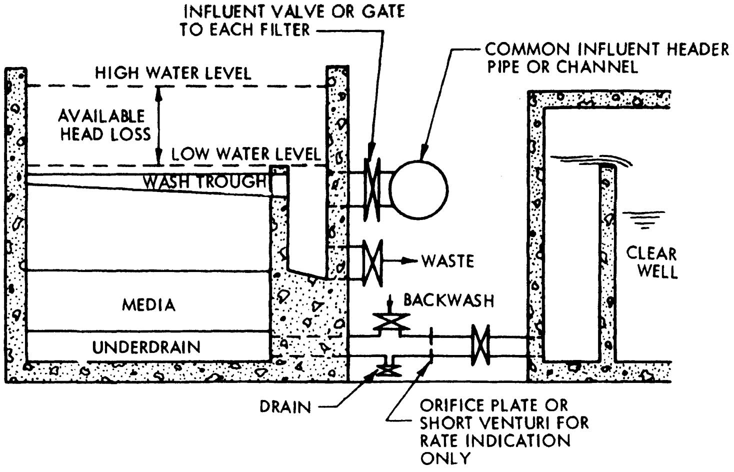

Figure 7.8. Gravity filter arrangement for rate control by influent flow splitting. Reproduced from Weber,[13] courtesy of John Wiley & Sons, Inc.

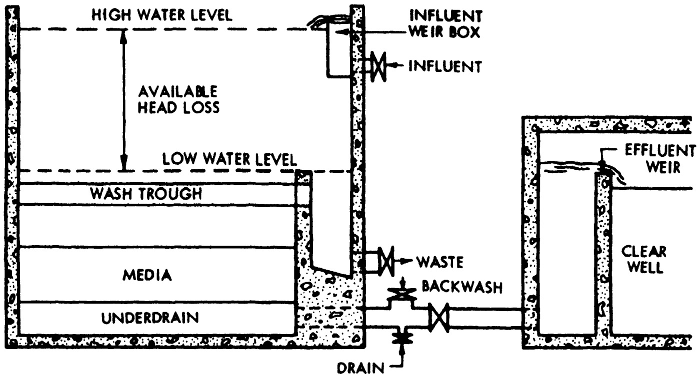

Figure 7.9. Gravity filter arranged for variable declining-rate of filtration. Reproduced from Weber,[13] courtesy of John Wiley & Sons, Inc.

Typical Properties of Filter Media

Table 7.2 shows some typically measured values for properties of fine filter media. Construction of dual- and triple-media filters is possible due to large differences in grain densities. Coarse grains of low density are on top, with finer grains of higher density material underneath. Alluvial sands have the highest sphericity, whereas such crushed materials as anthracite, ilmenite, and some garnet have lower sphericities.

TYPES OF FILTERS

Slow Sand Filters

A slow sand filter generally consists of a watertight basin containing a layer of sand over a layer of gravel. Common thicknesses for the sand are 3–5 ft, and 0.5 to 1 ft for the gravel. The filter is operated with a water depth of 3–5 ft above the sand surface. A *schmutzdecke* forms, in which most of the solids are removed. The *schmutzdecke* is a layer of microorganisms that facilitate removal of particles. When the head lost through the filter becomes excessive (commonly 305 ft), the filter is removed from service, drained and cleaned. Filter runs can range from 1 to 6 months (see below).

Rapid Sand Filters

Rapid sand filters generally consist of a 2 to 2.5 ft layer of sand over a layer of gravel. Filter depths usually range from 8 to 9 ft. Multiple, rectangular units are generally used with a length/width ratio of 1.25. Individual units usually range in size from 450 to 4500 ft^2. Units are run until head losses become excessive (generally 8–9 ft), and are then backwashed.

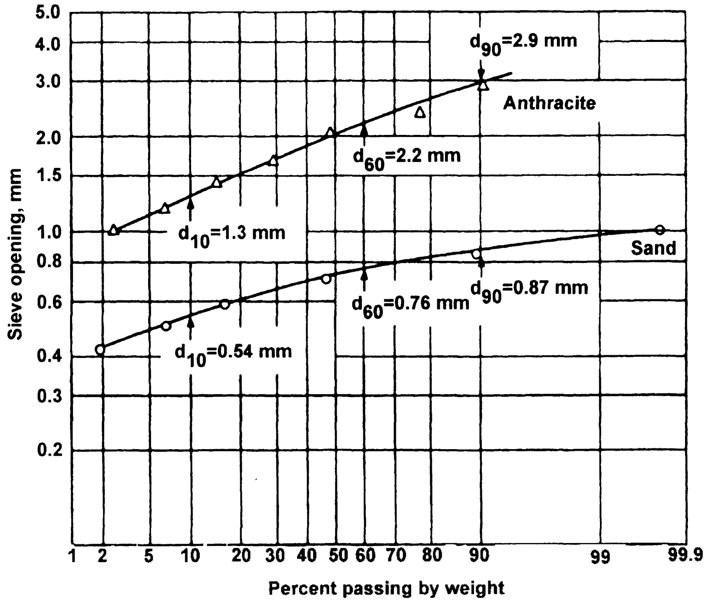

Figure 7.10. Typical sieve analysis of two filter media.[14]

Table 7.2. Typical Properties of Common Filter Media for Granular-Bed Filters.[14]

	Silica Sand	Anthracite Coal	Granular Activated Carbon	Garnet	Ilmenite
Grain density, ρ_s, g/cm^3	2.65	1.45–1.73	1.3–1.5[a]	3.6–4.2	4.2–4.6
Loose-bed porosity, ε_0	0.42–0.47	0.56–0.60	0.50	0.45–0.55	[a]
Sphericity, ψ	0.7–0.8	0.46–0.60	0.75	0.60	[b]

[a] For virgin carbon, pores filled with water, density increases when organics are adsorbed.
[b] Not available.

Precoat Filters

Precoat filters generally consist of a septum (which supports the filter medium), the filter medium, a housing, and a pump for operation in either pressure or vacuum mode. The filter medium is generally either diatomaceous earth or perlite. Diatomaceous earth (diatomite) is composed of fossil skeletons of diatoms, which have been subjected to crushing, calcining, air classification, and other processes. The resultant medium is a fine, porous, multishaped medium ranging in size from 5 to 50 μm.

Perlite is a siliceous rock, similar in outward appearance to diatomaceous earth. Perlite has a bulk dry density of 10–15 lb/ft, as compared to 18–20 lb/ft for diatomite. Precoat filter applications include industrial and swimming pool filtration. It has been employed in some small-scale municipal applications.

FILTER BACKWASHING—RAPID FILTERS

When the media become so clogged during filtration that head losses become excessive (generally about 8–9 ft), the unit must be removed from service and the media must be cleaned. This may be accomplished by scouring the clogged portion of the bed or by reversing the flow through the bed. This procedure of expanding the bed and washing out the trapped particles is called backwashing.

A schematic of a filter during backwashing is shown in Figure 7.11. Fluidization of a bed occurs when the upward or backwash velocity equals the critical velocity of the particles. Increasing the backwash velocity causes a concomitant expansion of the bed, which can allow open space for the trapped particles to be washed away. As the critical velocity, V_c, of the particles is reached, the frictional resis-

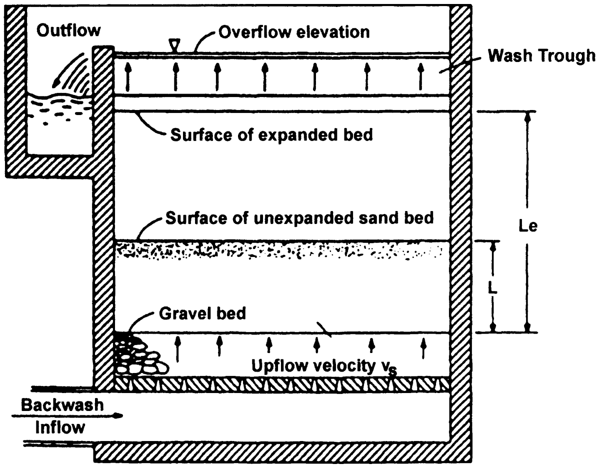

Figure 7.11. Expansion of a filter bed during backwashing. Reproduced from Clark and Viessman,[23] courtesy of the International Textbook Co.

tance of the particles will balance the head loss of the fluid expanding the bed, such that:

$$h_f \rho g = (\rho_s - \rho)\, g(1-\varepsilon_e)D_e \qquad (4)$$

where h_f = head loss incurred during filter expansion (L)
ρ_s = density of media particles (M/L^3)
D_e = depth of expanded bed (L)
ε_e = porosity of expanded bed (dimensionless)

For a uniform bed of sand, Fair et al.[24] determined that:

$$\varepsilon_e = (V_s / \upsilon_s)^{0.20} \qquad (5)$$

where V_s = backwash velocity (L/t)
υ_s = terminal fall velocity of media particles (L/t).

Therefore, a uniform bed of sand will expand when:

$$V_s = \upsilon_s {\varepsilon_e}^{5.0} \qquad (6)$$

Since the volume of sand particles of the expanded bed equals the volume of sand particles of the unexpanded bed:

$$D(1-\varepsilon)A_s = D_e(1-\varepsilon)A_s \qquad (7)$$

where D = depth of unexpanded bed (L)
A_s = surface area of filter (L^2)

Therefore:

$$\frac{D_e}{D} = \frac{(1-\varepsilon)}{(1-\varepsilon_r)} \qquad (8)$$

For multimedia beds, expansion occurs successively for each different layer. The upper layers will be expanded at lower backwash rates than the lower layers. Full expansion will be obtained when Equation 6 is satisfied for particles with the greatest size. The relative expansion of the bed is given by:

$$\frac{D_e}{D} = (1-\varepsilon)\sum_{i=1}^{n} \frac{P_i}{(1-\varepsilon_{ei})} \qquad (9)$$

where i = layer number (dimensionless)
n = number of layers (dimensionless)
P_i = weight fraction of particles in layer (dimensionless)
ε_{ei} = expanded porosity of particles in layer (dimensionless)

Rapid Filters

Effective and frequent backwashing of rapid filters is essential for long-term successful service. There should be no progressive evidence of the development of such dirty filter problems as mudballs, filter cracks, etc. There are several methods of backwashing currently in use.[25]

Upflow Wash with Full Fluidization

Traditionally, the backwash system in the United States uses an upflow water wash with fluidization of the full bed. Backwash water is introduced into the bottom of the bed through an underdrain system. In order not to disturb the gravel layers or subject the underdrain to sudden increases in pressure, the backwash water should be turned on gradually. As the backwash flow rate is increased and as the bed expands, the filter medium gradually assumes a fluidized state. Typical backwash rates are 15 to 20 gpm/ft^2 for the media sizes used in U.S. practice. The bed expansion is in the 15 to 30% range. Backwash flow continues with full fluidization until the wastewater is reasonably clear, with an approximate turbidity of about 10 ntu, whereupon the supply valve is shut off.

Backwashing by water fluidization alone does not solve all dirty filter problems[26] that are attributed to the lack of complete abrasion of the medium grains in a fluidized bed. Consequently, backwashing is assisted frequently by a surface wash or an air scour. Details of the surface wash and air scour are given in Reference 14. The most effective backwash is achieved by simultaneous air scour and subfluidization water backwash, which have been evaluated by several studies.[25]

GAC Filter-Adsorbers

Since the properties of GAC (see Chapter 4) are somewhat different than those of conventional anthracite or sand, some special precautions are required to backwash GAC filter-adsorbers. The lower density of GAC dictates that lower backwash rates are required to fluidize the common particle sizes in current use. Lower wash rates mean lower hydraulic shear and less effective upflow wash. A common problem in GAC filter-adsorbers is the formation of mudballs. Consequently, a surface wash or auxiliary air scour is essential for GAC backwashing.

The higher uniformity coefficient of typical GAC size gradations results in a greater percentage of expansion if the bed is fluidized fully. Here, there is a greater potential for loss of GAC media into the backwash troughs. If existing filters are retrofitted into GAC filter-adsorbers, raising the backwash troughs may be necessary to reduce this loss of carbon media.

Metals in GAC filter-adsorbers should be abrasion- and corrosion-resistant. Coats of corrosion-resistant substances can be applied to the metals of these filters.

Problems in Rapid Filters

Rapid filters are not without operational problems. These include such difficulties as: dirty filter media, mudballs, and mineral deposits. These are described in great detail in Reference 14 as well as their remedies.

Most filters have layers of graded gravel to support the filter medium. Conventional gravel layers are graded from coarse on the bottom to fine at the top. With this arrangement, some have reported mounding of the gravel caused by lateral movement of the fine gravel. In severe situations, the finest gravel layers may be completely removed from some areas of the filter bed. This leads to leakage of the filter medium into the underdrain system, and eventually to the necessity to clean the underdrains and to rebuild the filter's gravel and medium. Mechanisms of gravel movement have been thoroughly discussed in Reference 27 and summarized in Reference 14.

The filter underdrain is an extremely vital component of the rapid filter. It collects the filtered water, supports the filter gravel and filter medium, and distributes backwash water. Needless to say, proper design and construction of the underdrain is essential for a successful filter installation. If underdrain systems are designed improperly, uneven distribution of the backwash water may result. In turn, this can lead to many of the filter problems described above. The remedy to improperly designed underdrains is obvious and expensive.

PRESSURE FILTERS

Frequently, the filter medium is housed in a steel pressure vessel that is used for rapid filtration. Water enters the filter under pressure and leaves at a slightly reduced pressure due to head loss encountered in the filter medium, underdrain, and piping connection. A typical pressure filter is seen in Figure 7.12.

Operation of pressure filters is identical to rapid gravity filters. Operational difficulties are also the same as gravity filters, and are compounded by the inability to observe the operation visually.[14] Outbreaks of waterborne diseases have been attributed to failure of pressure filters.[28,29] Consequently, some state regulatory agencies have excluded the use of pressure filters in certain situations.[14]

Small water systems tend to use pressure filters, since water can be delivered to the point of use without repumping. Pressure filters are employed in industrial, wastewater, and swimming pool operations. Pressurized systems are frequently used for groundwaters containing iron.[14]

SLOW SAND FILTERS

There has been a recent renewed interest in slow sand filtration due to outbreaks of giardiasis in communities using unfiltered or poorly filtered water. Also, slow sand filters can assist in meeting the disinfection requirements of the SWTR (see Chapters 1 and 11).

Effective sizes of the sand grains range from 0.15 to 0.40 mm, uniformity coefficients from 1.5 to 3.6, and initial bed depths from 1.5 to 5.0 ft. The sand is supported on 6 to 36 in. graded gravel. Filtration rates range from 0.016 to 0.16 gpm/ft^2 (0.04 to 0.40 m/hr) and 0.03 to 0.05 gpm/ft^2 (0.07 to 0.12 m/hr) which are most common for source waters that receive no pretreatment by coagulation. Head loss through these filters ranges from 2.5 to 14 ft, with 3 to 5 ft the most common. A recent survey of slow sand filters in operation in the United States indicated that the sand descriptions and filtration rates fell within the above ranges.[30]

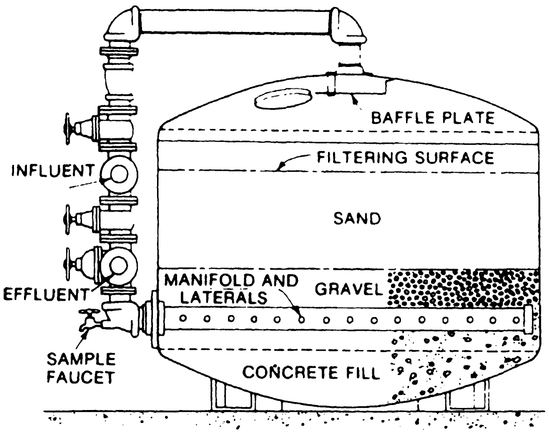

Figure 7.12. Cross section of a typical pressure filter.

Particulates are removed on slow sand filters by the dirty skin (*schmutzdecke*) that develops on the surface. A "ripening" period occurs at the beginning of each filtration cycle after the *schmutzdecke* has been removed. This ripening period varies from 6 hours to 2 weeks.[31] Frequently, the filtered water from this period is wasted where cysts of *G. lamblia* may be present.[14] Slow sand filters are extremely effective in the removal of total bacteria, salmonella, coliforms, viruses, and organic and inorganic contaminants, including turbidity.[14,32]

Slow sand filters are cleaned by scraping the *schmutzdecke* and a small amount of the sand depth. This sand is cleaned hydraulically and stockpiled for later reuse. Usually the scraping and resanding are accomplished by manual labor that is rather intensive. Various techniques have been studied to reduce labor costs.[14] Slow sand filters in London, England are scraped mechanically.[14]

Studies and surveys have been conducted to determine the "ideal" source water for slow sand filtration.[14] A 1984 survey of 27 plants in the United States found that 74% used lakes or reservoirs as their source water, 22% used rivers or streams, and 4% used groundwater.[30] The mean source water turbidity was about 2 ntu, with a peak of about 10 ntu. Filtration cycles varied from 42 days in the spring to 60 days in the winter. Cycles up to one year were reported by some operators.[30]

PRECOAT FILTRATION

Precoat filters use a thin layer of a very fine material—such as diatomaceous earth—as the filter medium. In turn, this medium is precoated on a septum, a permeable material that is supported by a rigid structure called a filter element. Particles are, of course, mostly removed by the filter medium. As the filter cycle continues, the filter medium, called body feed, is added regularly into the influent water flow in proportion to the solids that are being removed. This body feed is necessary to avoid an increase of head loss across the precoat layer. Eventually, the pressure drop through the filter system increases to a point where continued filtration becomes impractical. Consequently, the filtration process is stopped and the dirty filter medium is washed off the septum and a new precoat is applied. The thickness of the initial layer of precoat material is normally 1/16 to 1/8 in., wherein very fine particles (as small as 1 μm) are retained.

Precoat filters are widely used in industrial filtration situations and in swimming pool operation. They have been used in municipal potable water treatment, mostly for direct inline filtration of high quality surface water (turbidity <10 ntu) and in the filtration of iron and manganese from pretreated groundwaters. Currently there may be more than 150 treatment plants in the United States using precoat filtration.[14] The largest of these plants is the 20 MGD operation at San Gabriel, California.

Advantages and disadvantages of precoat filters have been summarized in Reference 14 and are reproduced here:

1. "Capital cost savings may be possible because of smaller land and plant building requirements.
2. Treatment costs may be 40 to 60% less than for conventional coagulation, sedimentation, and granular media filtration when filterable solids are low, although sedimentation would not usually be needed for such high-quality source water.
3. The process is entirely a physical and mechanical operation, and does not require operator expertise in water chemistry relating to coagulation.
4. The waste filter medium is easily dewatered, and in some cases it may be reclaimed for other uses, including soil conditioning and land reclamation.
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 the turbidity of the finished water within acceptable limits.
6. Terminal turbidity breakthrough is not generally observed because it is dominantly a surface filtration process.

The disadvantages of precoat filtration are as follows:

1. There is continued cost of filter medium, usually discarded at the end of each filter cycle.
2. It is less cost-effective for water that requires pretreatment for algae, color, or taste and odor problems. Water containing only larger plankton such as diatoms can sometimes be treated economically by microstraining prior to the precoat filtration.
3. Proper design, construction, and operation are absolutely essential to prevent the dropping or crack-

ing of the filter cake during operation, which might result in failure to remove the target particulates.

4. Mechanical devices require maintenance and can fail."

Details of the filter element and septum, filter vessel, filter media, filter operation, body feeding, and spent cake removal are also given in Reference 14.

FILTRATION MATHEMATICAL MODELS

Several investigators have attempted to mathematically model deep-bed filtration processes. In general, two approaches have been tried, one of which employs measurable macroscopic variables of filtration, including filtration rate, grain size, and water viscosity, to model head loss and filtrate quality as a function of time. The other approach uses a more deterministic, microscale approach, which, at the outset, employs submodels describing the mechanics of removal. Each is discussed briefly.

Iwasaki[33] originally noted that the rate of solids removal per unit depth of filter was proportional to the local concentration of solids, mathematically:

$$-\frac{\partial C}{\partial L} = \lambda C \qquad (10)$$

where C = suspended solids concentration (M/L^3)
L = depth of filter (L)
λ = filter coefficient ($1/L$).

The filter coefficient, λ, is a function of both time and position in the filter.

Since filtration results in an accumulation of solids in the filter pores, the decrease of suspended solids in a filter lamina must balance the increase in solids depositing, or:

$$\upsilon \frac{\partial C}{\partial L} = \frac{\partial \Omega_d}{\partial t} + (\varepsilon - \Omega_d)\frac{\partial C}{\partial t} \qquad (11)$$

where Ω_d = volume of specific deposit per unit filter volume (dimensionless)
υ, C, L, and ε are as before

The term $(\varepsilon - \Omega_d)\, \partial C/\partial t$ is generally considered significant, since it represents the change in the amount of material in suspension within the pores with time.

Ives[3] proposed specific surface models for spherical particles and cylindrical capillaries, incorporating them into a general relationship between λ and Ω:

$$\lambda = \lambda_o \left[1 + \frac{\beta_p \Omega_d}{\varepsilon}\right]^y \left[1 - \frac{\Omega_d}{\varepsilon}\right]^2 \left[1 - \frac{\Omega_d}{(\Omega)_\mu}\right]^x \qquad (12)$$

where λ_o = filter coefficient for a clean filter ($1/L$)
β_p = packing constant of media (dimensionless)
$(\Omega_d)_i$ = ultimate volume of specific deposit per unit filter volume (dimensionless)
x,y,z = coefficients (dimensionless)

The coefficients x, y, and z enable this model to accommodate the work performed by other investigators. A value of unity for each leads to Ives' original[34] equation.

Substituting Equation 12 into Equation 10:

$$-\frac{\partial C}{\partial t} = \lambda_o \left[1 + \frac{\beta_p \Omega_d}{\varepsilon}\right]^y \left[1 - \frac{\Omega_d}{\varepsilon}\right]^z \left[1 - \frac{\Omega_d}{(\Omega_d)_\mu}\right]^x \qquad (13)$$

yields an equation for filtrate quality as a function of time. Ives[3] also developed an expression for head loss:

$$\frac{\partial h_f}{\partial L} = \left(\frac{\partial h_f}{\partial L}\right)_o \left[1 + (2\beta_p + 1)\frac{\Omega_d}{\varepsilon} + (\beta_p + 1)^2\left(\frac{\Omega_d}{\varepsilon}\right)^2 + (\beta_p + 1)^3\left(\frac{\Omega_d}{\varepsilon}\right)^3 + \cdots\right] \qquad (14)$$

Several investigators, including O'Melia[7] and Yao et al.,[8] have attempted more deterministic models. Filtration is considered to be primarily dependent on particle transport and attachment. An analogy is drawn between filtration and coagulation/flocculation. The attachment mechanism involves particle destabilization, as in coagulation. The transport mechanism is similar to flocculation, where the particles must be moved from the bulk fluid to near the vicinity of the solid-liquid interface.

These models result in a single collector efficiency η_c which accounts for Brownian diffusion (for smaller particles about 1 μm in size), settling, and interception (both for larger particles). The equation for diffusional efficiency is given by:

$$(\eta_c)_D = 4.04\, Pe^{-2/3} \qquad (15)$$

where Pe = Péclet number (dimensionless), given by:

$$Pe = \frac{\upsilon' d_c}{D_p} \qquad (16)$$

where υ' = velocity at an infinite distance from the collector (L/T)
d_c = collector diameter (L)
D_p = particle diffusivity (L^2/t) given by:

$$D_p = \frac{\bar{k}T}{3\pi\mu d_p} \tag{17}$$

where $\bar{k}$ = Boltzmann's constant (ML^2/t^2)
T = absolute temperature (°K)
μ = absolute viscosity (M/Lt)
d_p = particle diameter (L)

The interception efficiency is:

$$(\eta_c)_I = -\frac{3}{2}\left(\frac{d_p}{d_c}\right)^2 \tag{18}$$

The gravitational efficiency is based on Stokes' law:

$$(\eta_c)_o = \frac{(\rho_2 - \rho_1)gd_p^2}{18\mu\upsilon} \tag{19}$$

where r_s and r_l are the respective densities of the particle and the liquid.

The overall efficiency is then given by:

$$\eta_c = (\eta_c)_D + (\eta_c)_I + (\eta_c)_G \tag{20}$$

Iwasaki's equation (Equation 10) can be modified to:

$$\frac{\partial C}{\partial L} = -\frac{3}{2}\left[\frac{(1-\varepsilon)}{d_c}\right]\eta\eta_c C \tag{21}$$

where η = collision efficiency factor (0 for no adhesion, 1 for total adhesion).

Integration of Equation 21 yields:

$$C = C_0 \exp\left[-\frac{3}{2}(1-\varepsilon)\eta\eta_c\frac{L}{d_c}\right] \tag{22}$$

Yao et al.[8] used this model to demonstrate the relative efficiencies with respect to particle size. Figure 7.13 shows some of their results.

These mathematical models and others have been reviewed in Reference 35. Attempts were made to test these models experimentally by the effects of changes in solution chemistry on the deposition of relatively large or non-Brownian particles.

RECENT DEVELOPMENTS IN FILTRATION

Direct Filtration

In the 1970s, direct filtration received considerable attention in the treatment of drinking water.[36–38] This treatment is defined as filtration that is not preceded by sedimentation. This definition includes flow sheets that utilize either flocculation basins or contact basins without sludge collection equipment. Figure 7.14a shows a flowsheet typical of older rapid sand filter plants, whereas Figure 7.14b shows design trends in recent years for conventional filter plants.

Figures 7.14a and 7.14b show two options available for direct filtration. One flowsheet shows the addition of alum to a rapid mix influent, which is followed by an application of a nonionic polymer or activated silica to the influent of dual- or mixed-media filters. The other flowsheet is a direct filtration scheme that uses a flocculation basin without sludge collection.

Direct filtration offers several advantages over conventional treatment of "good-quality" surface water. No sedimentation tank is required because lower coagulant (if needed) dosages are directed to form pinpoint-sized floc that is filterable, rather than the larger, settleable floc. This results in lower chemical and capital costs compared to conventional treatment. Sludge volumes are lower; that results in lower costs for sludge treatment and disposal.[14]

Some disadvantages of direct filtration are: it cannot effectively treat waters high in turbidity and/or color, less response time is available for sudden changes in source water quality, and there is less detention time for seasonal taste and odor control efforts.[14]

There have been a number of efforts to define acceptable qualities of source water for direct filtration. Key issues are the type and dosage of coagulants needed to achieve a desirable filtrate quality. For example, one study suggested that 12 mg/L of alum (the primary coagulant) on a continuous basis would yield 16- to 20-hour filter runs at 5 gpm/ft^2.[39] Another study found that waters requiring 6 to 7 mg/L alum and a small dose of polymer were favorable candidates for direct filtration.[40] Bench-scale (jar) and pilot-plant tests are recommended to determine full-scale design parameters.

An attempt was made to define criteria for source water quality for direct filtration:[41] color <40 cu, turbidity <5 ntu, algae <2000 asu/mL, iron <0.3 mg/L, and manganese <0.05 mg/L. These are, of course, guidelines for which there are exceptions. Others have suggested turbidity limits of 12 ntu when alum is used alone or 16 ntu when a cationic polymer is used alone during "low algae" seasons.[14] During "high algae" seasons, the suggested limits were 7 ntu and 11 ntu, respectively. Best performance was achieved during low algae seasons with alum dosages between 5 and 10 mg/L. Lesser results were obtained with alum dosages up to 20 mg/L during high algae seasons.

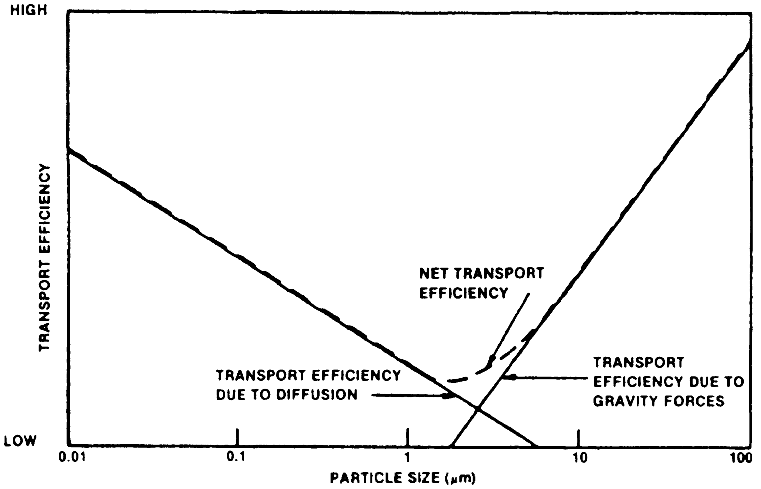

Figure 7.13. Relationship between transport efficiency and particle size. Reproduced from Yao,[8] courtesy of the American Chemical Society.

Some chemical pretreatment may be necessary for direct filtration of source waters in order to meet the desirable qualities cited above. Usually, this chemical pretreatment consists of coagulation with alum or iron compounds that may be supplemented with a cationic polymer.[14] Studies from pilot- and plant-scale operations have reported typical dosages of 2 to 10 mg/L of alum plus a cationic polymer in the 0.2 to 2 mg/L range.[42] Inasmuch as sedimentation does not precede direct filtration, small "pinpoint" floc must be formed in the chemical pretreatment.

In the direct filtration process, the rapid mix usually does not differ from conventional plants. A hydraulic jump in a Parshall flume may be used for the rapid mix.[36] Field experience has been good. Some designs extend the time for this type of mixing up to as much as five minutes, which is longer than conventional plants.

Filter media designs are basically the same for direct filtration as they are for conventional plants, with the important exception that sand should not be used as the medium. Rather, dual- and mixed-media beds are employed because they provide the space for storing solids removed from the water. Operating experiences have shown that a high quality of water is produced in direct filtration rates of 1–8 gpm/ft^2 ($0.7\text{–}5\times10^{-3}$ m/sec). The design rate usually is 5 gpm/ft^2 (3.3×10^{-3} m/sec).

Fine filter media are supported on a gravel bed, which is preferred over direct support on bottoms equipped with mechanical strainers or nozzles. The latter are not recommended.[36] Surface wash or an air scour is necessity in direct filtration. Backwash rates of 15 gpm/ft^2 (0.01 m/sec) are adequate.

Culp[36] argues for a mixed-media bed over a dual-media bed. The former has the advantage of providing more filter grains and more surface area of grains for a given head loss across the bed than dual-media beds. This is seen from these data:

Type of Filter Bed	Total Surface Area of Grains/ mm^2 of Bed Surface Area	Total Number of Grains/ mm^2 of Bed Surface Area
Dual-Media, 76 cm (30 in.)	2090	1200
Mixed-Media, 76 cm (30 in.)	2680	2770

It is essential, however, to use a polymer that increases the shearing strength of floc and its adherence to the surface of filter grains. An excellent 36 in. (91 cm) deep mixed-media filter would consist of:

1. 16 in. (41 cm) of –4 to +14 mesh coal, SG of 1.48
2. 8 in. (20 cm) of –9 to +18 mesh coal, SG of 1.62
3. 9 in. (23 cm) of –30 to +40 mesh sand, SG of 2.4
4. 3 in. (8 cm) of 40 to 80 mesh garnet, SG of 4.2

A typical 36 in. (91 cm) deep dual-media bed would consist of:

1. 25 in. (64 cm) of –4 to +20 mesh coal, SG of 1.55
2. 11 in. (28 cm) of –20 to +50 mesh sand, SG of 2.4

According to Culp,[36] this dual-media bed produces the same quality of water as a mixed-media bed, but the chemical dosages will be higher and the filter runs shorter. The key for successful operation of direct filtration apparently lies in optimum coagulant and polymer dosages.

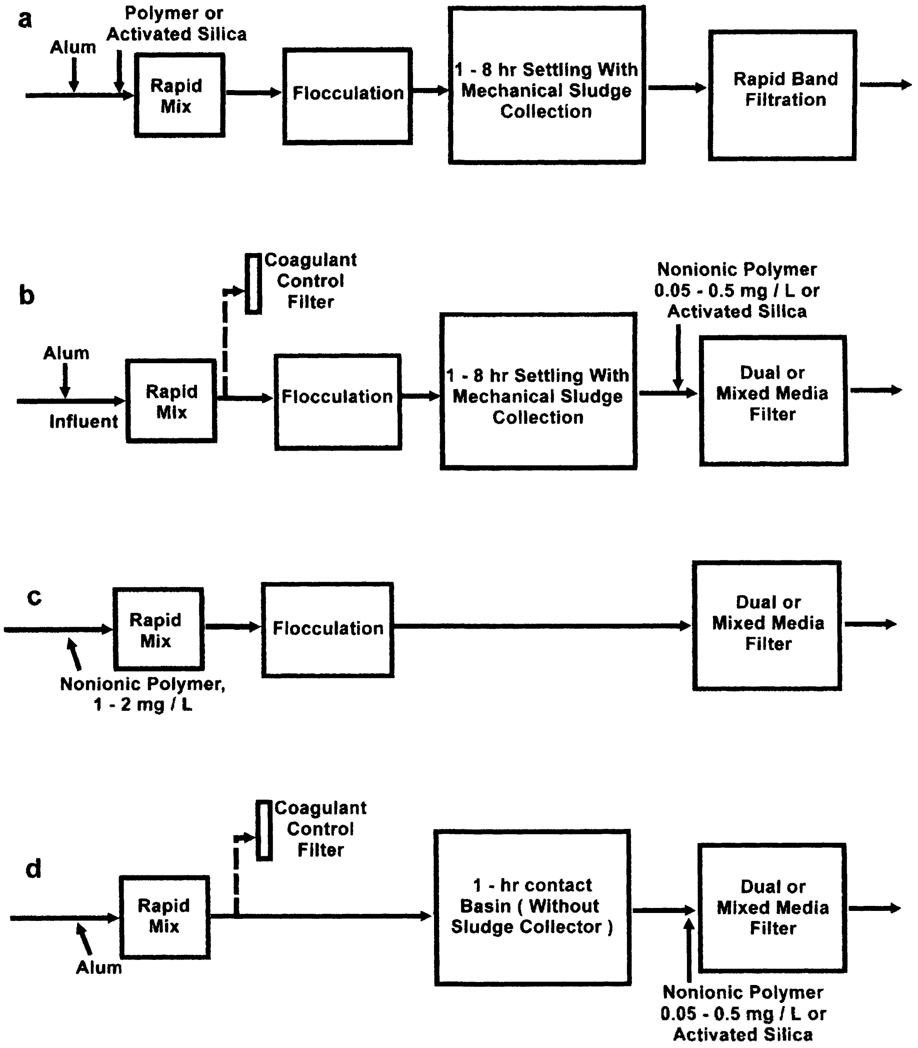

Figure 7.14. Flowsheets for (a) typical older conventional filter plants; (b) typical recent design trends for conventional filter plants; (c) typical direct filtration using a flocculation basin; (d) typical direct filtration using a contact basin. Reproduced from Culp,[36] courtesy of the American Water Works Association.

Some recent studies have addressed important issues in the direct filtration of source water. Pilot-scale constant-rate and declining-rate direct filtration systems were evaluated that used two flow rates and alum or cationic polymer as the primary coagulant.[43] Turbidity, particle count, and total coliform count were used to compare filtrate qualities. Effluent qualities for the two filtration schemes were the same. These results indicate a measure of flexibility in the direct filtration of source waters.

Direct filtration of "high turbidity" waters (>10 ntu) was investigated in a pilot plant study by the greater Vancouver (B.C.) Water District (GVWD).[44] Their water is obtained from three surface water impoundments located in the Coast Mountains north of Greater Vancouver. There were episodes of high turbidity from these reservoirs. Two pilot plants, a 5 gpm (19 L/min) and an 8 gpm (30 L/min) were installed at two locations. The process trains included chemical feed (soda ash, Al and Fe salts, cationic polymer, and a nonionic polymer), two-stage rapid mixing, variable speed flocculation, and mixed media filtration. An ozone generator was added for application to raw or flocculated water. Filter runs were terminated when the filtered turbidity increased to 0.2 ntu or exceeded 1% of the raw water turbidity.

In the GVWD study, the factors that were most important in the performance of direct filtration were the chemical pretreatment (alum dose between 5.9 and 7.0 mg/L) filter media design (1.2 and 1.5 mm-es medium). A significant aspect of pretreatment was selection of the appropriate filter and dosage (cationic polymer, 0.22 to 0.27 mg/L). This and other studies indicated the need for polymers for the production of low turbidity waters. It was concluded: "The ability of the pilot plant to repeatedly treat water in the 20–30 ntu and 40–60 ntu range is very encouraging and suggests that direct filtration is appropriate for treatment of a wider range of raw water turbidities than would have been possible with dual-media filters."[44]

Color Removal by Direct Filtration

Removal of naturally occurring color by direct filtration is an important concern and has been the subject of several studies.[37,45–50] For example, color was removed effectively from a raw water supply in Australia by coagulation with alum (10 mg/L) and cationic polymer (1 mg/L), and with a direct filtration rate of 6 gpm/ft^2 (4 mm/sec).[39] A typical removal was from 40 to 5 acu in a pilot plant operation. Also, turbidity was reduced from 2.5 turbidity units to values of 0.2 turbidity units, and iron (0.8 mg/L) and manganese (0.13 mg/L) were reduced to less than 0.05 mg/L by direct filtration. In a related study using Owens River water for the city of Los Angeles, pretreatment with ozone (1–2 mg/L) improved the turbidity quality of direct filtered water.

That naturally occurring color and other $CHCl_3$ precursors are removed by direction filtration was reported by Scheuch and Edzwald.[48] Synthetic and natural waters from the Raquette River (New York) were utilized in a bench-scale pilot plant operation. For the natural water, turbidity values ranged from 0.68 to 1.4 turbidity units, whereas color values ranged from 40 to 70 color units (cu). The experimental filter was 2.54 cm (i.d.) × 14 cm deep. Sieved and washed Ottawa sand was the filter medium, with a geometric mean grain size of 0.6 mm and a bed porosity of 0.4. The filtration rate was 2 gpm/ft^2 (1.3 mm/sec). A cationic polymer was used as the only coagulant.

Typical results from the Raquette River study are seen in Figure 7.15.[48] The residual turbidity and color after filtration were within drinking water standards. A 75–80% color removal was achieved by direct filtration. However, head losses reached 60–100 in. within a relatively short period of time—4 hr. Chloroform formation was monitored also in the direct filtration experiments. There was a concurrent reduction in $CHCl_3$ with color removal.

An extensive comparative study was conducted on the performance of dual- and mixed-media filters at the treatment plant in Minneapolis, Minnesota.[49] Other sites throughout the United States were examined also, as seen in Table 7.3. The filtration rate was held constant at 2 gpm/ft^2 (1.3 mm/sec). The raw water supply was obtained from the Mississippi River, which had a turbidity of 1.9 to 2.0 turbidity units in the experimental time frame. However, the water was softened by the addition of lime, followed by alum coagulation and direct filtration.

Typical results for two runs using dual- and mixed-media filters at the Fridley Filter Plant (FFP) at Minneapolis were evaluated.[47] In the initial stages, the mixed-media produced a filtered water turbidity equal to or slightly less than the dual-media. After 24 hr, a breakeven point was reached, after which the dual-media produced a more consistent effluent quality than the mixed-media. The gradual increase in the water's turbidity from the dual-media beyond the breakpoint indicated a progressive saturation of the interstitial pore spaces and deep penetration into the bed. For the mixed-media, the rapid increase in turbidity after the breakpoint indicates a breakthrough condition. Head losses were about the same for both media. Since the shapes of the head loss curves are linear, this signifies filtration with depth. According to Qureshi, the performance of the dual-media was superior to mixed-media in terms of head loss, filter effluent turbidity, and unit filter run.[49]

Slow Sand Filtration

Small water systems in the United States face immense difficulties in meeting requirements of the SWTR. Herein, some recent developments and case studies in slow sand filtration are described.

An excellent example of the small system situation is found in Oregon, where many communities are using (circa 1990) unfiltered surface water.[51] Conventional filtration processes of coagulation, sedimentation, and rapid sand filtration in the form of package plants were unable to provide proper operation and maintenance due to a variety of reasons. Consequently, alternative filtration techniques were sought. This led to slow sand filtration, since two large water systems had successfully operated prior to 1980 with this technology.

A typical case study is found in Westfir, Oregon, a small community of 310 or so persons.[51] Recurring violations of the turbidity MCL prompted the Oregon Drinking Water Program (DWP) to recommend alternative filtration options for their surface water supply. This led, first, to a pilot study of slow sand filtration. Success of this study was measured by total coliform removal (95–100%) and turbidity removal (50%, 1.3 to 0.7 ntu). Consequently, a full-scale plant was designed from a number of conditions and assumptions:

- The filters should operate continuously to provide the most effective and efficient removal of bacteria and *Giardia*.
- Intake pumps were to run continuously to keep the filters operating; peak flows were to be provided from system storage.
- At least two filters were needed to allow uninterrupted operation during scraping and subsequent

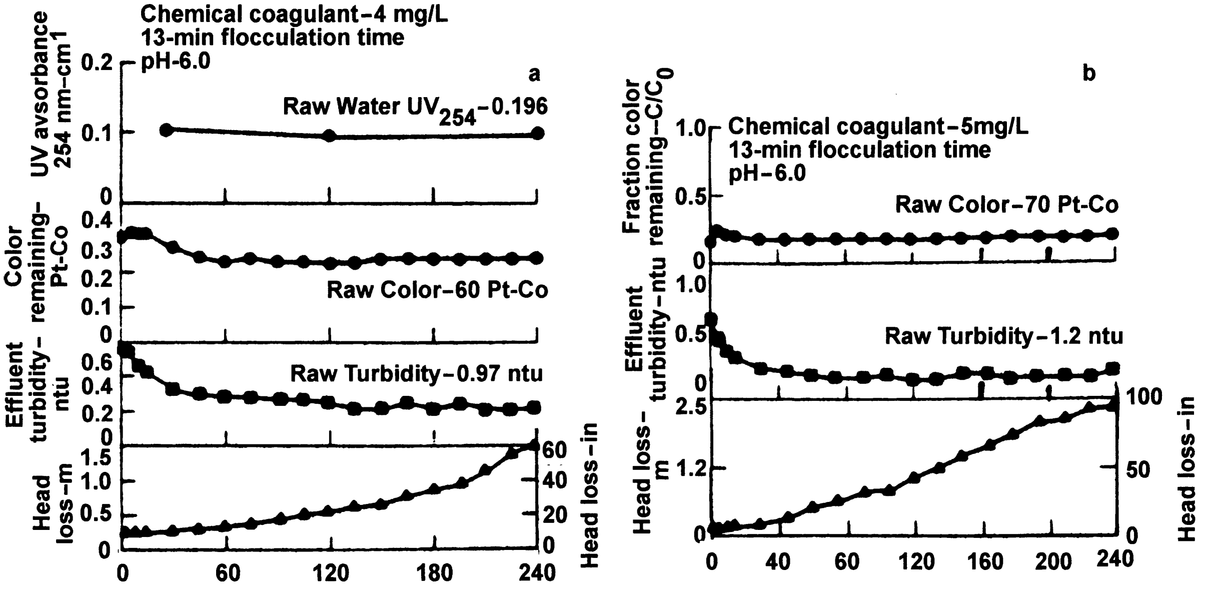

Figure 7.15. Filtration performance for Raquette River. Head loss data are in meters (in.) of water. Reproduced from Scheuch and Edzwald,[30] courtesy of the American Water Works Association.

Table 7.3. Media Design Specifications.[a]

Plant	Filter Design	Media	Depth		Effective Size (mm)	Uniformity Coefficient
			(mm)	(in.)		
Duluth Plant[b]	Mixed	Coal	41.25	16.5	1.0–1.1	1.7 max.
		Sand	22.5	9.0	0.42–0.45	1.35–1.7
		HDS[c]	11.25	4.5	0.21–0.32	1.8 max.
	Dual	Coal	52.5	21.0	1.0–1.1	1.7 max.
		Sand	22.5	9.0	0.42–0.45	1.35–1.7 max.
Minneapolis Plant[b]	Mixed	Coal	48.75	19.5	1.03–1.05	1.6
		Sand	22.5	9.0	0.50	1.6
		HDS	3.75	1.5	0.20	1.8
	Dual	Coal	50.0	20.0	1.00	1.5
		Sand	30.0	12.0	0.4	1.6
Clinton, Connecticut, Pilot Plant	Mixed	Coal	41.25	16.5	1.0–1.2	<1.7
		Sand	22.5	9.0	0.45–0.50	1.5
		HDS	3.75	1.5	0.2–0.3	<2.0
	Dual	Coal	65.0	26.0	0.95	<1.5
		Sand	25.0	10.0	0.45	<1.35
New York (Croton) Pilot Plant	Mixed	Coal	45.0	18.0	1.05–1.15	1.6–1.8
		Sand	22.5	9.0	0.5–0.6	1.4–1.6
		HDS	7.5	3.0		
	Dual	Coal	45.0	18.0	1.05–1.15	1.6–1.8
		Sand	30.0	12.0	0.5–0.6	1.4–1.6
Seattle, Washington, Pilot Plant	Mixed	Coal	45.0	18.0	1.0–1.1	1.7
		Sand	22.5	9.0	0.42–0.55	1.8
		HDS	7.5	3.0	0.18–0.32	2.2
	Dual	Coal	50.0	20.0	0.92	1.28
		Sand	25.0	10.0	0.40	1.3

[a] Reproduced from Burns et al.,[50] courtesy of the American Water Works Association.
[b] Surface wash was provided for all filters.
[c] HDS=high-density sand.

reripening periods. Scraping was to be scheduled to avoid periods of peak demand.

- The design could only provide for existing domestic flows under grant rules. Future capacity needs or fire flows could not be funded by the grant.
- A $294,000 block grant budget was available for the pilot study, design, and construction of the filtration plant and chlorination facility, and replacement of leaking water lines.
- Thirty minutes of chlorine contact time was to be provided; use of CT (concentration × time) analysis was not yet in practice.
- The city of Westfir did not want to raise rates excessively as a result of the construction of these facilities.

A schematic of the full-scale plant is seen in Figure 7.16, where the 70 gpd/ft^2 filtration rate should be noted. It was placed into service in November 1986. Quality of the treated water has averaged: <1/100 mL for total coliform, <1/100 mL for fecal coliform, and 0.7 ntu for turbidity. The filter consisted of a 3-ft layer of sand (0.315-mm es and a 2.32 uc), which was supported by three layers of appropriately sized gravel layers. This treatment plant can serve as a model for small water systems in similar situations.

Another case study was reported from the small mountain town of Empire, Colorado, where 110 cases of waterborne giardiasis were reported in 1981.[52] At this time, the only treatment of the surface supply was chlorination. Budget constraints prevented a pilot plant study. Consequently, a full-scale plant was designed and constructed, primarily, on previous research.[53] A summary of the design of the sand filters is seen in Table 7.4. They were placed into operation in January 1985. Operational results were excellent: no *Giardia* cysts were detected in the filter's effluent, turbidities averaged <1.0 ntu, and free-living nematodes were also obtained by three slow sand filters operating in northern Idaho, where removals of turbidity, total and fecal coliforms, heterotrophic plate count, and *Giardia* cysts were monitored.[54]

The capacities of three municipal slow sand filters to remove natural organic matter (NOM) and organic precursors (measured by dissolved organic carbon, UV absorbance, and THM formation potential) were evaluated in New England.[55] Operating conditions for each slow sand filter are summarized in Table 7.5, where the filtration rates ranged from 0.021 to 0.250 m/h. The overall levels of treatment achieved at the three municipal plants are given in Table 7.6, where NPDOC, UV absorbance, and THMFP reductions ranged from 13 to 33%, 17 to 33%, and 9 to 27%, respectively, during winter conditions, and from 12 to 31%, 15 to 43%, and 14 to 27%, respectively, during fall conditions. Presumably, these filters were more effective during spring and summer conditions, which were not reported. Two pilot plant studies were conducted, however, at two sites in New Hampshire during the spring and summer months of 1987. Average NOM and organic precursor removals were 15±5%. It would appear that slow sand filters, based on this study, are not very effective in removing NOM from raw water. This is an important consideration where slow sand filters may be the only alternative treatment for small municipal supplies that are disinfected by chlorination. THM formation is a distinct possibility in these situations.

The inability of conventional slow sand filters to remove NOM effectively has been noted by others.[56–58] Reductions of 15–25% were frequently observed, which led to a recommendation of color levels of 10 to 30 cu as upper acceptability limits.[56] The techniques of preozonation and surface amendment have been explored for improving NOM removals. For example, pilot- and full-scale evaluations of the effect of preozonation on slow sand filtration were conducted in England.[56] Doses of 3 mg/L O_3 benefited the run lengths of pilot slow sand filters and presumably were related to the reduction in UV absorbance (254 and 400 nm) to 70 and 90%, respectively, compared to 15 and 25% reductions, respectively, for the control filters. Other effects of preozonation on NOM removal by slow sand filters are described in Reference 56.

The effects of preozonation and water column biofilm support media on slow sand filtration were compared in pilot-scale studies to the performance of the full-scale facility at Andover, Massachusetts.[59] Preozonation and biofilm support were observed to have a positive influence on filter performance, transformation of NOM, microbiology, and removal of biodegradable dissolved organic carbon (BDOC). Presumably, ozone was beneficial with regard to NPDOC, THMFP, and BDOC removal by enhancing conditions for promoting biodegradative processes in the filter water columns and filter media. Ozone increased the BDOC content of the NOM. A dose of 2.0 mg O_3 consumed/mg NPDOC was effective for removing NPDOC, UV, and THMFP from the raw water source. On the other hand, ozone also reduced filter runs, presumably through increased clogging of the filter media via biofilm development. This increased head loss was reduced through the use of a biofilm support structure located in the water column. The slow sand filter with its larger effective size (0.80 mm), media (sand), and a biofilm support structure, which operated at 0.08 gpm/ft^2 (0.2 m/h) and was dosed with ozone (see above), provided a performance that was compared to that of the full-scale ozone—conventional treatment—GAC (0.6 mm es) system. The authors are quite optimistic about the potential of this enhanced slow filter system as an effective treatment for compliance with the SWTR.

ALTERNATIVE FILTRATION STRATEGIES

Pretreatment

All of the unit operations that precede filtration and affect the overall system's particle removal efficiency are con-

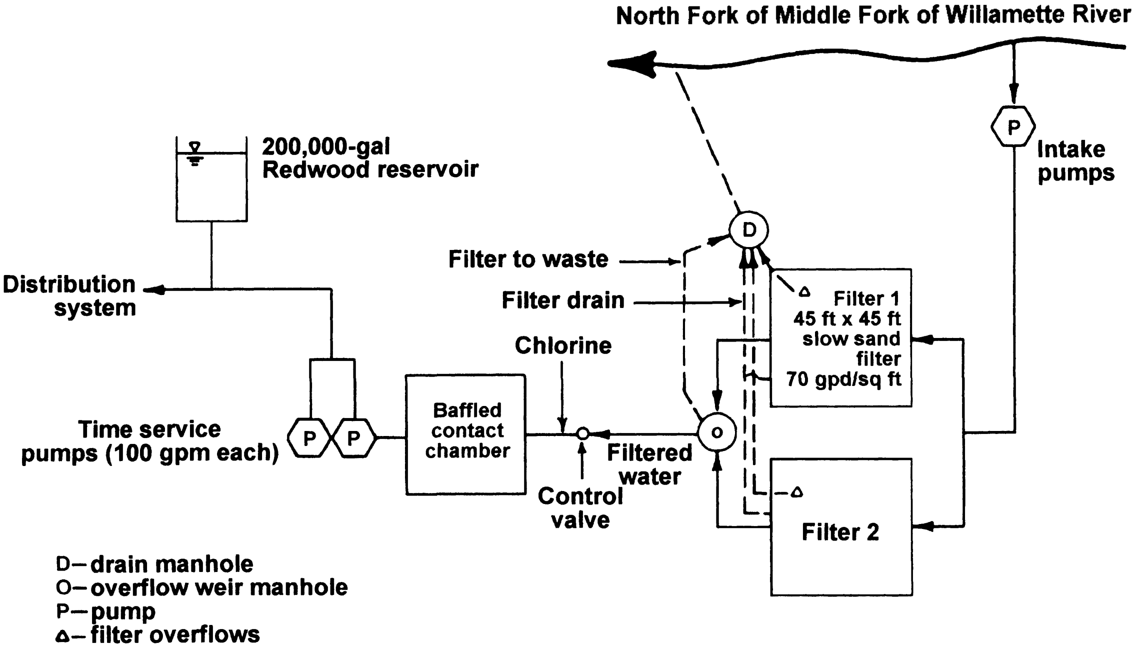

Figure 7.16. Westfir slow sand filtration plant schematic plan.[51]

Table 7.4. Design Summary of the Slow Sand Filter at Empire, Colorado.[53]

Flow—250,000 gpd (946,000 L/d)
Hydraulic loading rate—0.10 gpm/ft^2 (0.26 m/h)
Total filter area—1650 ft^2 (153 m^2)
Number of filters—two
Pretreatment—presedimentation
Operating head above outlet pipe—5 ft (1.5 m)
Sand depth—4 ft (1.2 m)
Gravel support—2 ft (0.6 m)
Underdrains—4 in. (0.1 m) diameter perforated polyethylene tubing spaced at 5 ft (1.5 m)
Sand media—effective size: 0.15–0.35 mm specified, 0.24 actual: uniformity coefficient: 0.75 specified, 2.67 actual
Support gravel—
    1.5–2.5 in.—9 in. (0.23m)
    0.75–1.5 in.—5 in. (0.13m)
    0.5–0.75 in.—4 in. (0.1m)
    0.25–0.5 in.—4 in. (0.1m)
    0.125–0.25 in.—2 in. (0.05m)
Rate of flow controller—manually operated 3 in. (0.08 m) diaphragm valves

sidered pretreatment processes.[1] These are, usually, chemical coagulation and preoxidation with ozone. Generally, the pretreatment system starts with a short period of high intensity mixing for coagulant dispersal, followed by a longer period of low intensity mixing to promote the formation of flocs (see Chapter 6 for details and the chemistry of coagulation). These flocs, then, are separated from the flow by sedimentation, air flotation, or filtration through a bed of coarse granular material. Frequently, a coagulant aid, usually an organic polyelectrolyte, is applied to treat the remaining particles before they pass to the filter. Pretreatment processes are described earlier in this chapter for slow sand filters, and in Chapter 4 for GAC adsorption processes.

Many authors stress the significance and importance of pretreatment—especially chemical coagulation—for filtration processes.[1,11] For example, it was concluded that "Chemical pretreatment prior to filtration is more critical to success than the physical facilities at the plant."[60] This is especially important for raw waters of variable quality and with slow sand filtration.[31]

Table 7.5. Operating Conditions of Municipal Slow Sand Filters at the Time of Sample Collection.[55]

Facility	Date	Water Temperature (°C)	Time from Last Cleaning (days)	Filter Depth (m)	Head Loss (m)	Filtration Rate (m/h)	Filter Media Contact Time (h)	Typical Effective Size of Sand (mm)	Typical Uniformity Coefficient of Sand (d_{50}/d_{10})
Winter visit									
Springfield	1/23/87	2.5	200	0.79		0.040	19.8	0.30	2.3
West Hartford	2/11/87	2.5		0.67	1.0	0.131	5.1	0.27	2.0
New Haven	2/11/87	2.0	30	0.46	0.2	0.021	21.9	0.30	2.7
Fall visit									
Springfield	9/24/87	17.0	90	0.70		0.049	14.3	0.30	2.3
West Hartford	9/24/87	16.0	25	0.64	1.7	0.250	2.6	0.27	2.0
New Haven	9/24/87	20.0		0.46	1.2	0.061	7.5	0.30	2.7

Table 7.6. Treatment Performance Achieved by the Slow Sand Filter.[55]

	Winter Visit (1/23/87)			Fall Visit (9/24/87)		
Parameter	**Raw Water**	**Filtered Water**	**Decrease[a] percent**	**Raw Water**	**Filtered Water**	**Decrease[a] percent**
Springfield						
Color—cu	16.0	9.0	44	12.0	7.0	42
NPDOC—mg/L	2.34	2.00	15	0.093	0.073	22
UV absorbance (254 nm, pH7)—cm^{-1}	0.081	0.054	33	0.093	0.073	22
THMFP—µg/L	152.0	138.0	9	88.0	76.0	14
West Hartford						
Color—cu	13.0	3.0	77	3.0	1.0	67
NPDOC—mg/L	1.82	1.22	33	2.26	1.56	31
UV—absorbance (254 nm, pH 7)—cm^{-1}	0.042	0.032	24	0.056	0.032	43
THMFP—mg/L	180.0	132.0	27	62.0	45.0	27
New Haven						
Color—cu	15.0	6.0	60	25.0	5.0	80
NPDOC—mg/L	1.16	1.01	13	3.56	2.56	28
UV absorbance (254 nm, pH7)—cm^{-1}	0.042	0.035	17	0.079	0.067	15
THMFP—µg/L	108.0	98.0	9	101.0	85.0	16

[a] Rounded to the nearest whole number; a negative value indicates a percentage increase.

Research examples of pretreatment processes follow:

Pilot studies showed that, with water temperatures <37°F (3°C) and raw water turbidities <2 ntu, $FeCl_3$ removed turbidity more efficiently than did $Al_2(SO_4)_3$, but the latter caused slower head loss development.[61] Other studies are cited above for chemical pretreatment prior to direct filtration. The effects of preoxidation with ozone and Peroxone (H_2O_2 and O_3) on inline filtration were examined by conducting pilot-scale experiments and comparing results with full-scale plant operation.[62] Preozonation (0.5 to 0.75 mg/L O_3) did not indicate that coagulation dosages could be lowered by preoxidation. However, ozone provided some performance benefits when filter runs were increased by more than 30%. The results of ozone and Peroxone showed little difference in filter performance. However, there was a reduction in odor formation following disinfectant addition.[62] Significantly different results were obtained from a pilot study of the effect of four preoxidants—O_3, Cl_2, ClO_2—and $KMnO_4$, on particle removal by two clarification-filtration processes.[63] Ozonation (1.0 to 2.8 mg/L O_3) dramatically improved the removal of particles (actual count) on the filters (anthracite-sand) when compared with the other three oxidants. Preoxidation did not have any observable effect on filter maturation time or the head-loss buildup rate across the filter media. The particle removal data was employed to demonstrate the level of *Giardia* removal provided by the treatment system.

Haberer Process

Two new technologies—the refiltration flocculation (REFIFLOC) process and the powdered activated carbon (PAC)-embedding filtration (PACEFILT) process for the removal of particulates and organic micropollutants were introduced to the potable water treatment industry in Germany in the 1970s.[64,65] These processes may be operated separately or combined to treat heavily polluted water that requires high dosages of chemicals. Upflow filtration is a unique feature of both processes. Figure 7.17 shows the flow diagram of a full-scale plant that was installed in 1979 for the treatment of artificially recharged groundwater (Weisbaden-Schierstein), and in 1982 for the treatment of reservoir water (Aachen-Hitfeld).

The principal advantages of the REFIFLOC and PACELIFT processes are:

- the simplicity and security of the operation
- the high capacity of the upflow filters for solids and floc
- the effective use of highly reactive powdered activated carbon
- the ability to remove poorly adsorbable organic micropollutants, even in small-scale plants
- the simultaneous use of flocculants together with carbon
- the short filter run between two backwashes in the PACELIFT process, compared with granular activated carbon filters[64]

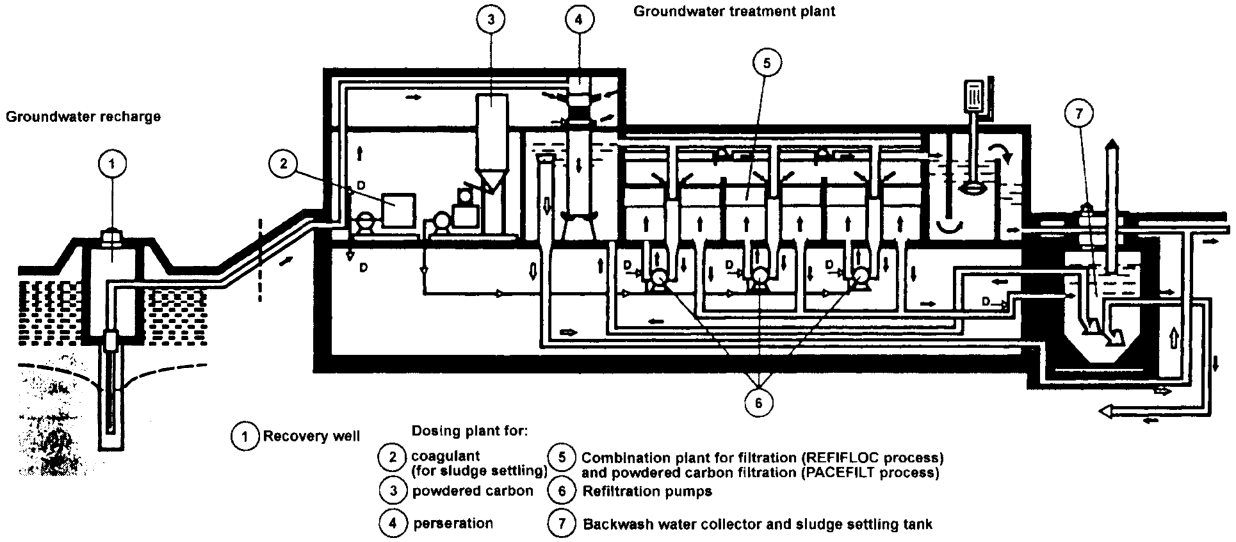

Figure 7.17. Full-scale water treatment plant with REFIFLOC and PACEFILT in Wiesbaden-Schierstein, Germany.[64]

Design details of the Haberer process are given in Reference 64, and the operational results of a pilot plant at Shreveport, Louisiana are found in Reference 65.

Dual-Stage and Mixed-Media Filtration

Dual-stage filtration (DSF), in packaged form, is a good alternative to conventional rapid rate filtration for small systems. The effectiveness of DSF for removing *Giardia* cysts from low turbidity waters (<1 to 4 ntu) and low temperature (~32°F) water was evaluated.[66] Removals of total coliform bacteria and turbidity were determined also. The filter assembly is composed of two filtration tanks, the depth clarifier and the depth filter, and a single raw water pump that pressurizes the system (Figure 7.18). This system can be operated in the hydraulic loading rate range of 7 gpm/ft^2 (4.7 mm/s) to 10 gpm/ft^2 (6.8 mm/s). Removals of >99% of *Giardia* cysts were observed from waters with a turbidity <1 ntu and a temperature of <46°F when proper chemical treatment (alum and polymers) was applied, and at a hydraulic rate of 10 gpm/ft^2 or less. Removals of total coliform bacteria exceeded 98% and turbidity exceeded 90%.

Full-scale dual- and mixed-media filters were compared side by side at nominal loadings of 3,4,5, and 6 gpm/ft^2 for eight months using flocculation and sedimentation pretreatment at Knoxville, Tennessee.[67] Raw water turbidities averaged 11 ntu. This *in situ* study compared media at several filtration rates and with more turbid surface waters and identical pretreatment—alum flocculation. This study also tested a hypothesis that turbidity would be dislodged in dual-media but not mixed-media during flow surges.[68] Table 7.7 shows the dual- and mixed-media specifications. Both media produced an effluent of <0.5 ntu at all loadings. However, the mixed-media filter was more successful than the dual-media filter for attainment of a 0.1 ntu effluent standard using the alum pretreatment. Neither media showed a turbidity breakthrough when subjected to a 33% flow surge and did not show any significant media loss.

Granular Activated Carbon Filter-Adsorber Systems

Chapter 4 describes the use of GAC as an adsorber for the removal of soluble organic and inorganic contaminants. These adsorption units are located usually after the pretreatments of chemical coagulation, sedimentation, and sand filtration. This use is designated as second-stage GAC filtration. Also, GAC can be used as the filtration medium in an otherwise conventional deep-bed filter. This combines the removal of dissolved organics and of turbidity in a single filtration step. This second alternative, often called the sand replacement option, is labeled the first-stage GAC filtration.

A full-scale study of the conversion of rapid sand filters to GAC filter adsorbers was conducted at the Church Wilne water treatment plant near Nottingham, England.[69] The primary purposes of this study were to identify the engineering problems associated with the change and to compare the effectiveness of the GAC system with the rapid sand system. The original filter medium was the typical layers of fine sand (0.65 es) on fine and coarse gravel. The sand was replaced with GAC (0.6 es), but the gravel was left undisturbed. There was an empty bed contact time of 7.2 min at a filtration rate of 2 gpm/ft^2 (5 m/h). Figure 7.19 shows the comparative effectiveness of the sand and GAC filter units for turbidity removal. There appears to be no significant difference between the two units. Figure 7.20 shows the re-

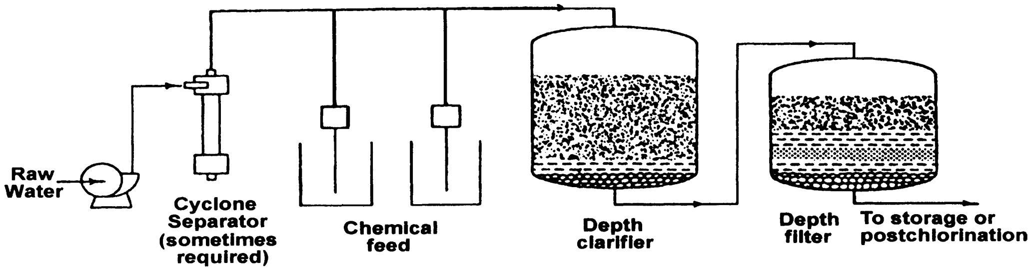

Figure 7.18. Schematic of dual-stage filtration system.[66]

Table 7.7. Media Specifications.[67]

Media	Layer	Depth (in.)	Specific Gravity	Effective Size (mm)	Uniformity Coefficient
Dual	Anthracite	20	1.70	0.98	1.37
	Filter sand	10	2.65	0.52	1.30
Mixed	Anthracite	18	1.70	1.07	1.63
	Filter sand	9	2.65	0.53	1.30
	Fine garnet	3	4.00	0.28	1.61
	Large garnet	3	3.91	1.60	1.19

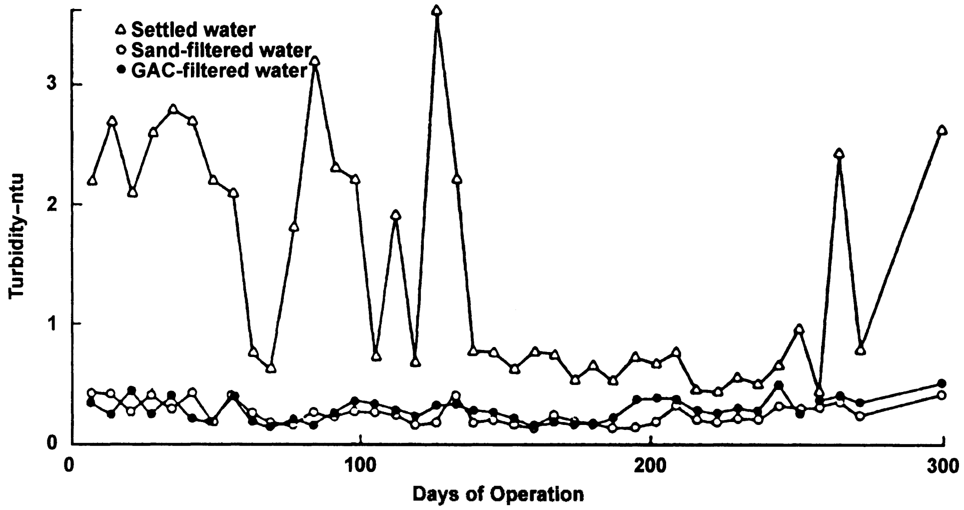

Figure 7.19. Comparison of sand and GAC filtration for turbidity removal.[69]

sults of TOC removal by the two units. The GAC filter did remove more TOC than the sand unit, but left a residual of 1.0 to 2.5 mg/L TOC. On the average, 60% longer filter runs were obtained with the GAC filter (72 hours) compared with the sand filter (44 hours). The microorganisms of sanitary significance—37°C plate counts, coliforms, and *E. Coli*—were effectively removed by chlorine after the GAC filter. However, this study did not address the question of THM formation from the chlorination of the residual TOC in the GAC filter effluents.

An interesting study was conducted when the costs of GAC filter-adsorbers (second-stage GAC filtration) were compared with those of the sand replacement option (first-stage GAC filtration).[70] Simulation models of TOC adsorption and particle removal were used to describe filter performance. First-stage filtration was found to be the most cost-effective treatment option when TOC removals of <55% are sufficient. When raw waters have "low" TOC values (<5 mg/L), a large number of adsorbers is usually used in parallel, and the GAC is regenerated offsite. In this situa-

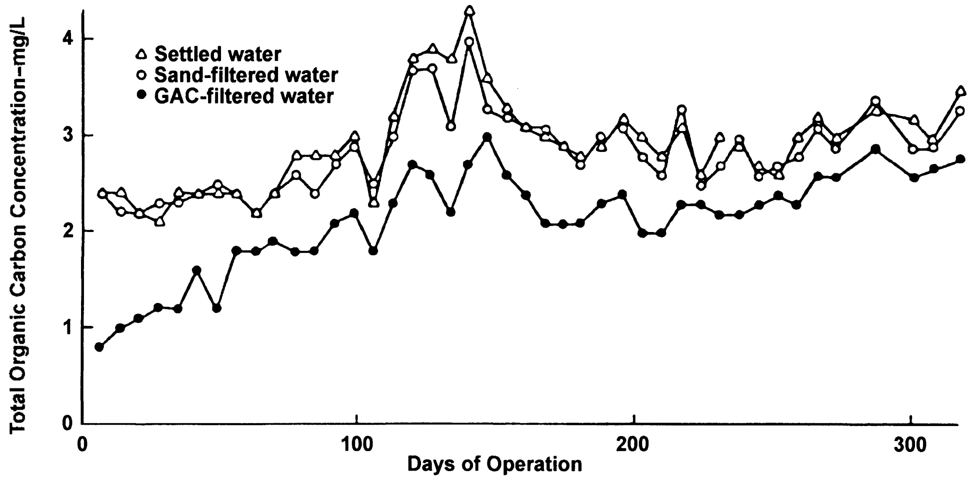

Figure 7.20. Comparison of sand and GAC filtration for total organic carbon removal.[69]

Table 7.8. Advantages and Disadvantages of First- and Second-Stage GAC Filtration.[70]

Type of GAC Filtration	Advantages	Disadvantages
First-stage	Low capital cost	Carbon loss during backwashing
	Uncomplicated sand replacement	Possible coagulant-GAC interaction
	More compact installation	
Second-stage	Better adsorption as a result of:	Possible problems with biologi-
cal		
	Possible use of smaller grain size	growth
	More flexibility in choice of EBCT	High capital cost
	Undisturbed adsorption	

tion, first-stage filtration was found to be cost-effective for TOC removals as high as 75%. Some frequently cited advantages of first- and second-stage GAC filtration are given in Table 7.8.[70]

The design, operation, and performance of GAC filter-adsorbers were documented and some potential problems were identified by means of a survey of operating plants and other sources.[71] GAC, as a total or partial replacement for sand, was found to be as effective as conventional filtration media for removing turbidity, provided an appropriate medium size is selected (Table 7.9). These filter-adsorbers, however, do not function well for removing such less strongly adsorbed compounds as THMs, volatile organics, and certain fractions of TOC. In this case, the short EBCTs for the sand replacement systems, typically 9 minutes, would require very frequent regeneration or replacement of the GAC. This would represent a significant operational cost.

High-Rate Filtration

The conventional rates for rapid filtration, about 2 to 4 gpm/ft^2 (5–10 m/h), have been traced to the historic study of G.W. Fuller in the late 1890s.[92] Later studies in the 1950s and 1960s, however, led to the widespread use of the higher rate of 4 gpm/ft^2 with the conventional sand filter medium (see above), and with pretreatment by aluminum and iron compounds for coagulation.

An increase in the filtration rate decreases the filter cycle inversely (approximately) with the rate. The use of dual or triple media filters (see above) has minimized this problem since their common installation in the 1950s.[14] These multimedia provide for better penetration of solids into the anthracite layer, which has a larger grain size than the traditional sand filter. This better utilizes the medium for storage of solids during the filter cycle. The relatively recent use of synthetic polyelectrolytes to aid coagulation and filtration has permitted higher rates without degradation of filtrate quality. Consequently, the high-rate filter plant in the 1990s may use rates up to 6 gpm/ft^2 (15 m/h) and higher that incorporate the use of multi-media and coagulation aids. However, state regulatory agencies must approve these higher rates and may require plant- or pilot-scale studies before acceptance.

There are a few reports in the literature since the 1970s where much higher filtration rates have been employed. For example, 10 gpm/ft^2 (24 m/h) was reported from Contra

Table 7.9. Characteristics of Filtration Media.[71]

	Granular Activated Carbon[a]			
Characteristic	**8 x 30**	**12 x 40**	**Sand**	**Anthracite**
Effective size (mm)	0.80–1.05	0.55–0.75	0.38–0.65	0.45–1.6
Uniformity coefficient	<1.9	<1.9	1.2–1.7	<1.8
Particle density, wetted in water (g/mL)	1.30–1.55	1.30–1.55	2.65	1.57

[a] Manufacturer's data.

Costa, California,[73] and 13.5 gpm/ft^2 (33 m/h) for the new Los Angeles direct filtration plant.[74,75] The latter rate was chosen and approved by California after 5–6 years of extensive pilot plant studies. These two case studies may be the exception, for treatment of high quality surface water in large plants with exceptionally skilled personnel. In situations where there is poorer quality water and less skillful operation, lower filtration rates may be more appropriate.

A comprehensive survey of 21 successful high-rate filtration plants throughout the United States was reported in the late 1980s.[76] The filtration rate was defined as 4 gpm/ft^2 or higher that produced a low turbidity water defined as <0.2 ntu. The major objective was to identify design features and operational practices of these 21 plants that contributed to successful production of the low turbidity water. Most of the 21 plants treat relatively high quality water with peak turbidities less than 200 ntu and daily turbidities generally less than 20 ntu. Some of the major factors that contribute to the successful high-rate filtration are reproduced from Reference 76:

a. Chemical pretreatment prior to filtration is more critical to success than the physical facilities at the plant. However, good physical facilities may make achievement of the goal easier and more economical.
b. Polymeric flocculation aids and/or filter aids are generally required at high-rate filtration plants. Cationic polymers are most commonly used as flocculation aids added ahead of the flocculation tanks, where they serve to augment the primary coagulant. Nonionic polymers are most commonly used as filter aids. High-rate plants should be equipped to feed both polymers and as a primary coagulant.
c. The operating staff must use a well defined chemical control strategy that has been verified at that particular plant for the varying raw water qualities. The chemical control strategies are quite variable in different plants. Thirteen of the 23 visited plants use control devices such as streaming current detectors, zeta potential, pilot filters, and particle counting in their control strategy. However, half of the visited plants use more traditional schemes such as jar testing, observing turbidity and pH of settled and filtered water, and filter head loss versus turbidity breakthrough performance.
d. Most conventional plants consider settled water turbidity to be important in their control strategy, but the key issue should be the filterability of the solids reaching the filter and the resulting filtrate quality.
e. Dual- or triple-media filters were utilized at all of the visited high-rate plants, except for one plant that used a deep bed of coarse anthracite. There is considerable interest in the applicability of the latter option to other raw water sources.
f. Triple-media is considered superior to dual-media under stressful filtration conditions (e.g., high rates and sudden rate increases).
However, the benefits to the filtered water quality are not well documented in published literature and additional work is needed on this issue. Triple-media causes higher clean bed head losses, and this detriment may prevent its use in upgrading existing plants with limited available filter head loss.
g. To produce the best filtrate quality, attention should be paid to minimizing periods when filtered water quality may be degraded, such as: (1) during the initial improvement period of the filter cycle (ripening period),[77] and (2) during plant startup or increases in plant load. Filtering to waste, bringing filters slowly up to rate, and leaving some residual solids above the filter at the end of the backwash operation were some of the methods being used to reduce impact of the ripening period.
h. Individual continuous turbidity monitors on each filter are desirable to optimize filtrate quality. They are useful in detecting detrimental filtrate quality changes during the ripening period and at the end of the filter cycle, and in studying the effectiveness of corrective actions.
i. Good operator training and the building of operator pride in quality of the treated water are important steps in producing the best filtered water. Some plants utilize 12-hour operating shifts to give more continuity to plant operation, and a short period of shift overlap to provide for intershift communication related to the current treatment strategy.

This report is recommended highly to any reader that has or may be considering high-rate filtration in their plant. There is a considerable amount of design, opera-

Table 7.10. Raw-Water Criteria Used by Systems not Filtering Surface Sources[a],[80]

Raw-Water Criteria	Monitoring Requirements
Total Coliforms or	<100/100mL (90% of samples over six months)
Fecal Coliforms	<20/100mL (90% of samples over six months)
Turbidity	<5 ntu over any 12 consecutive months with two periods >5 ntu permitted per year, provided a boil water order is issued
Utility Size	**Bacterial Sampling Frequency**
<501 people served	1/week
501–3,300 people served	2/week
3,301–10.000 people served	3/week
10,001–25,000 people served	4/week
>25,000 people served	5/week

[a] U.S. Environmental Protection Agency regulation; initial compliance based on at least six months of historical data augmented by a daily sampling for a three-day period following a storm.

tional, and pragmatic information on the advantages of this filtration strategy.

MISCELLANEOUS OPERATIONAL ASPECTS

There are several design options for water filtration.[78] These include such design options as: the media, underdrain systems, backwash systems, auxiliary scour, mode of filter operational control, backwash troughs, filtration rates, depth of filter box, filter conditioning, number of filters, filter configuration, and monitoring of performance. The reader is referred to Reference 78, which explains a number of alternatives, advantages and disadvantages of these alternatives, and reviews the interrelationship of the components of a filtration system. It is an excellent article for purveyors to consult about their systems already in operation and/or for design purposes.

Another evaluative article is given in Reference 79, in which the objective is to decrease turbidity of the finished water where chemical coagulation is part of the pretreatment process prior to filtration. Factors that affect turbidity removal are: physical condition of the facilities, hydraulics of treatment processes, quality of water, and operator performance. In Reference 79, descriptions of the proper operation of each component in the process train and pragmatic remedies to improve performance are given.

Certainly there may be some surface waters that may not require filtration. There are some relatively clean raw surface waters that are amenable to disinfection as the only treatment process.[80] The essential criteria and associated standards are: fecal coliforms—20 organisms/100 mL; turbidity—1.0 ntu; color—15 acu (apparent color units); and chlorine demand—2 mg/L. These criteria were selected from a study of a variety of data gathered from 34 raw waters used by purveyors with full-scale application of disinfection as the only treatment. An essential aspect of this situation is watershed management to control water quality variations and to prevent progressive deterioration of the raw water. Another essential point is the necessity of daily monitoring of the raw water and the finished water entering the distribution system at a point near the first customer. Monitoring requirements are given in Table 7.10 for these types of surface water supplies. Since disinfection is the only protection by treatment, there must be redundancy in the equipment to address emergency situations. Finished water storage capacity must be available also for at least 48 hours when the primary source characteristics are temporarily beyond the minimum quality for disinfection.

MEMBRANE PROCESSES

A brief description of the various membrane processes is offered here because of their abilities to remove contaminants from water by filtration processes under specialized conditions. The reader is directed to Chapter 11 in Reference 81 for a more detailed explanation of these membrane processes.

Types of Membrane Processes

There are various types and sizes of membranes. The membrane spectrum is given in Figure 7.21, where the relationships between micrometer size, molecular weight, and angstrom units are seen.[82]

Reverse osmosis (RO) is a pressure-driven process that retains virtually all ions and transmits water. Pressure is applied that exceeds the osmotic pressure of the salt solution against a semipermeable membrane. This forces pure water through the membrane, which leaves the salts behind.

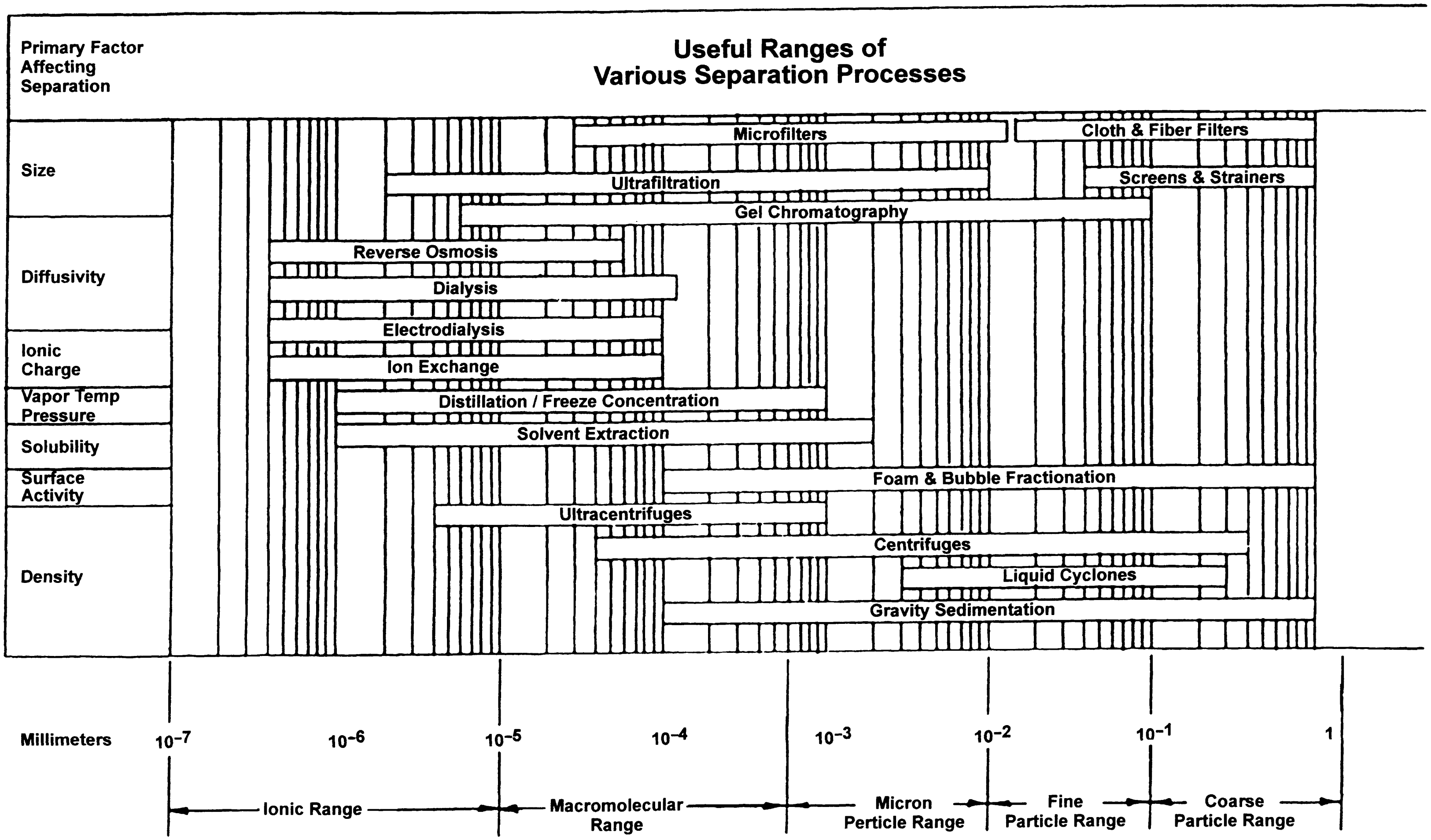

Figure 7.21. Useful ranges of separation processes.[82]

Electrodialysis (ED) involves the transfer of ions through membranes from a lower concentration to a more concentrated solution that results from the passage of direct electric current. Water flows tangentially to the membrane, while the flow of ions is perpendicular to the membrane.

Ultrafiltration (UF) is a pressurized process for fractionating and concentrating solutions containing colloids and high-molecular-weight materials (i.e., macromolecules).[83,84] Generally, UF retains nonionic matter and passes most ionic matter. This depends on the molecular weight cutoff (MWC) of the membrane. The MWC is a specification of the membrane that describes the nominal rejection of a known solute or the molecular weight above which most substances are retained by that membrane.

Membrane materials are manufactured from a variety of materials, such as cellulose acetate (CA), cellulose diacetate (CDA), cellulose triacetate, polyamide (PA), other aromatic polyamides, polyetheramides, polyetheramines, and polyetherurea. In CA membrane chemistry, the higher the acetyl content, the higher is the scale rejection, and the lower is the water flux. Cellulosic membranes are usually inexpensive and can tolerate some chlorine (<1.0 mg/L). However, there are several disadvantages: CA membranes are subject to biological attack and to hydrolysis that reverts CA to cellulose and acetic acid. This reversion occurs very rapidly at very low or high pH values.[81] PA and thin-film composite (TFC) membranes may be degraded by oxidants (i.e., Cl_2), but they are not susceptible to biological attack, and resist hydrolysis.

Membrane fouling can occur from scale, colloidal deposition, silt, metal oxides, organics, silica, and other substances in the feedwater. Pretreatment (see below) may be required to prevent fouling. These systems would contain all the necessary particulate-removal filtration units and the chemicals needed to prevent fouling and hydrolysis.

Membrane configurations are manufactured currently in four types: spiral-wound, hollow fine-fiber, tubular, and plate and frame. Only the spiral-wound (Figure 7.22) and hollow fine-fiber types (Figure 7.23) are employed for municipal water treatment. The reader is directed to Reference 81 for greater detail on the configurations of these units.

Applications of Ultrafiltration to Potable Water Treatment

System Components

Figure 7.24 shows a flow diagram of the components of a typical UF system. Pretreatment is necessary for surface waters that contain turbidity, etc., and for groundwaters that contain iron and manganese and other potential particulates (see below). The typical UF membrane system employment is a high recovery system with multiple low-pressure fiberglass vessels in parallel. Posttreatment may consist of degasification, chlorination, and stabilization of the finished water wherever required.

System Applications

There have been several pilot programs in Florida at municipal water treatment plants where organics were removed from surface and groundwaters.[86,87] A pilot-scale study was conducted for THM control using membrane processes for two groundwaters that contained excessive THM precursors.[88] These waters were treated by seven different membranes with MWCs that ranged from 400 to 40,000. Table 7.11 shows that a NF membrane with a MWC of 400 controlled the THMFP to less than the 0.10 mg/L MCL for THM. This NF membrane was designed to produce 20 gpd/ft^2 at 100 psi (689 kPa). Removals are given also in Table 7.11 for DOC, color, and total hardness (TH). It appears that, in this situation, NF and UF membranes with MWCs above 400 were not effective for THMFP at a loading of 961 mg/L.

A survey was conducted to determine the number of membrane plants currently operating in North America.[88a] By December 1993, more than 190 membrane plants with capacities greater than 25,000 gpd had been constructed for the provision of drinking water to various municipalities where the combined capacity is >215 MGD. Approximately 80% of these plants are reverse osmosis (RO), and 20% are electrodialysis reversal (EDR). Spiral-wound (SW) membranes are more widely used than hollow fiber (HF) membranes for brackish water treatment. This practice is expected to continue as a result of the significantly lower pressure required by the SW membranes. The average product water quality for all plants was 170 mg/L total dissolved solids (TDS) at an average feedwater TDS of 2223 mg/L. Recovery rates as high as 85% for RO systems and 94% for EDR systems are being used for normal operation.

A membrane filtration pilot plant in Orange County, California was operated for one year to evaluate the removal of natural organic matter (NOM) and disinfection by-product (DBP) precursors from a highly colored groundwater.[88b] Two nanofiltration (NF) membranes—a traditional softening membrane and a high-permeability, charged membrane—were selected from previous bench-scale tests of eight NF and ultrafiltration membranes. The essential raw water quality parameters were: TOC, 11.1 mg/L, DOC, 11.0 mg/L, and color, 180 cu. The latter NF membrane was operated successfully for this groundwater under conditions of higher-than-normal recovery (90%), and a flux rate of 34 L/m^2•hr (20 gpd/ft^2). This membrane produced an effluent quality of TOC, 0.6 mg/L and color of <5 cu.

A pilot-plant study was conducted to evaluate the efficacy of powdered activated carbon (PAC) as a UF pretreatment (see below also) to provide enhanced removal of

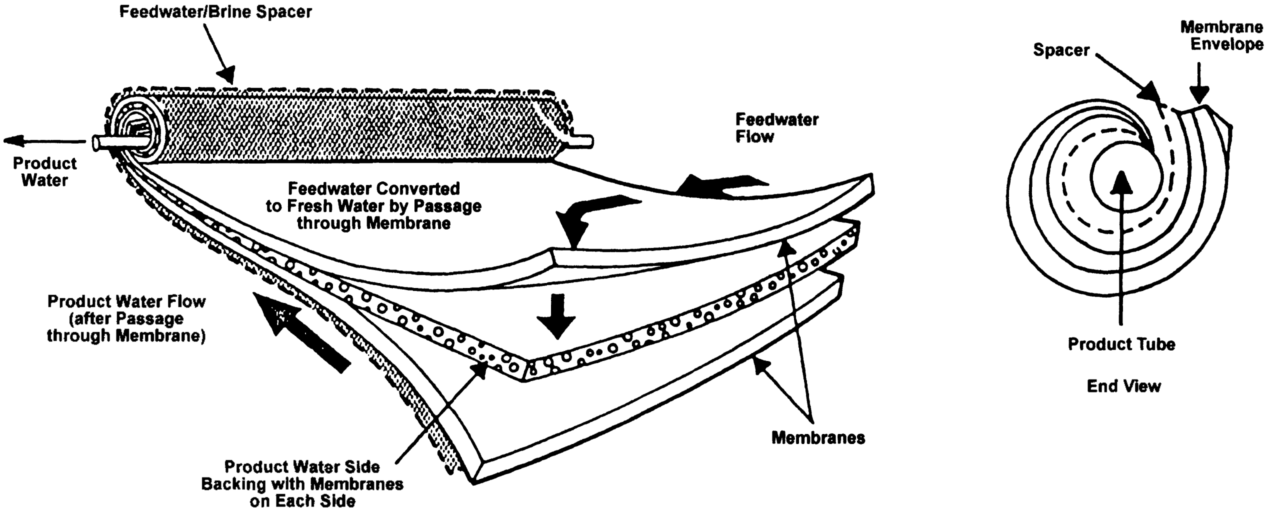

Figure 7.22. Spiral wound reverse-osmosis cartridge.[81]

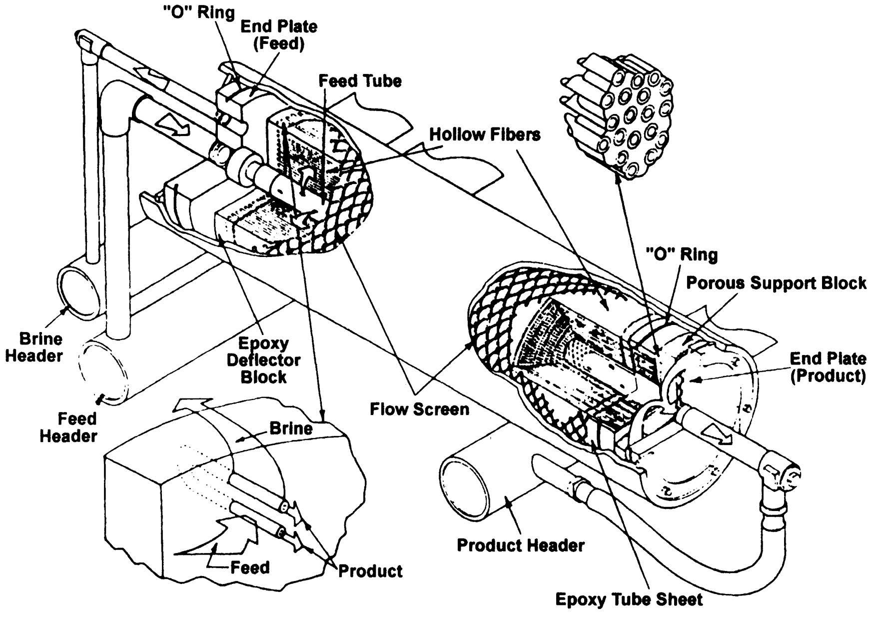

Figure 7.23. Hollow fiber permeator construction and hookup.[81]

trihalomethane and haloacetic acid precursors.[88c] Three source waters were studied: the Mokelumne River and the Sacramento-San Joaquin Delta in northern California and the Ottawa River in Canada. TOC contents of these three waters were 1.4, 5.2, and 7.4 mg/L, respectively. The UF membrane was composed of a cellulosic derivative and had an internal fiber diameter of 0.037 in. and a MWCO of 100,000 daltons, and a membrane area of 77.5 ft^2. One of the conclusions from this study was that both TOC and DBP precursors were removed "poorly" by the UF process. Pretreatment becomes necessary to this membrane process if it is to be employed for residual disinfection and to remove DBP precursors. This study showed that the addition of PAC, 30 mg/L, as a pretreatment did not cause fouling in any of the three waters when a crossflow fiber velocity (CFV) of 3.0 fps was used. As expected, TOC, SDSTHM, and SDSTOX precursor removals for the three source waters generally increased with higher PAC dosages. Removals as high as 97% of the SDSTHM and 85% of the SDSTOX precursors were achieved for one water with PAC doses of

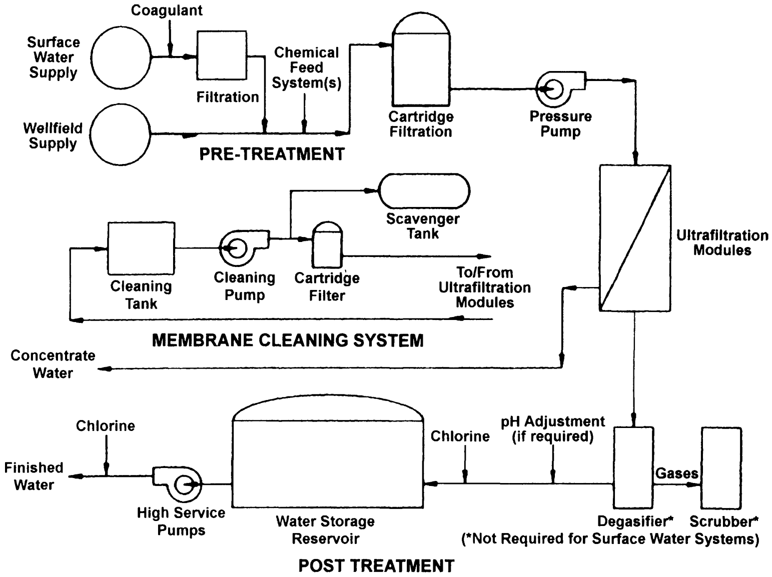

Figure 7.24. Ultrafiltration process flow schematic.[81]

90 mg/L. Some difficulties were experienced with removal of the SDSTHM precursors.

Several methods for monitoring the integrity of low-pressure membranes were identified and evaluated.[88d] Two pilot-scale membrane systems were operated in this study to treat Lake Elsman water (San Jose, California) that used two UF and two MF commercially available hollow fiber membranes. The techniques either monitor membrane integrity directly or indirectly. Direct monitoring techniques include air-pressure-hold testing, bubble-point testing, and sonic sensing. Indirect monitoring techniques include online turbidity monitoring, online particle monitoring, and online and batch particle counting.

Microfiltration (MF) and ultrafiltration (UF) have been studied for the removal of protozoan cysts and viruses.[88e] Six MF and UF membranes were evaluated at bench- and pilot-scale for the removal of *Giardia muris* cysts and *Cryptosporidium paruum* oocysts from three source waters. The nominal pore sizes of the MF membranes were in the range of 0.1 to 0.2 μm, and the nominal MWCOs of the UF membranes were in the range of 100,000 to 500,000 daltons. All four of the HF membranes removed the cysts and oocysts to below detection limits. None of these microorganisms were detected in the permeate as long as the membrane remained intact. Physical straining of these organisms from the feedwater appeared to be a primary mechanism of action. The extent of virus removal was membrane-specific, with removals ranging from <0.5 log to >6 logs. Three phenomena appeared to contribute to virus removal: physical sieving or adsorption, cake layer formation, and fouling state of the membrane.

Pretreatment Systems

Raw water sources, in most cases, must be pretreated in order to prevent membrane fouling. This is extremely important since fouling may be irreversible and result in permanent loss of flux. Backflushing and chemical treatment may restore some of the flux, but not all of the original design. Several studies have been conducted on the employment of conventional pretreatment schemes for surface and groundwaters in the United States and France: chemical coagulation,[89] coagulation-flocculation and PAC,[90] and PAC.[91]

Pretreatment with polyaluminum or ferric chloride of Seine River (France) water slowed short-term, reversible fouling of polysulfone membranes (MWC of 1000), but did not reduce the extent or the rate of irreversible fouling.[89] It was speculated that the latter was the result of selective coagulation and removal of humic materials of a relatively high MW. Apparently, polysacchacides—lower-molecular-weight substances—remain in solution and cause the irreversible fouling. No suggestions were offered to circumvent this operational difficulty.

Various combinations of coagulation-flocculation (poly aluminum) and PAC were evaluated for utilization in the UF (MWC of 100,000) of a lake water in Illinois.[90] For UF to be effective in removing NPOC and THM precursors, pretreatment with PAC is required and was more efficient than coagulation-flocculation alone. The latter pretreatment, however, did increase membrane flux through conditioning of the filter cake. The authors were encouraged by this research "because it demonstrates that, with proper pretreatment, low-pressure membrane processes like UF can remove not only the majority of particulate matter from a natural

Table 7.11. THMFP, DOC, Color, and TH Concentrations and Percent Removals by Membrane[a].[88]

					THMFP		DOC		Color		TH	
Source	Membrane	MWC	Pressure psi (kPa)	Recovery (%)	(mg/L)	Removal (%)	(mg/L)	Removal (%)	(cpu)	Removal (%)	(mg/L)	Removal (%)
AID–raw water					961	0	15.0	0	35	0	332	0
AID	A	100	190 (1310)	60	32	97	0.6	96	1	97	14	96
AID	B	400	60 (41)	65	39	96	1.4	90	1	97	97	70
AID	C	2000	100 (689)	80	326	56	7.4	40	14	60	302	13
AID	D	10000	50 (345)	73	780	19	12.6	16	32	9	334	0
AID	E	200000	50 (345)	77	605	37	12.5	16	22	37	310	7
AID	F	20000	50 (345)	85	929	3	14.2	5	33	6	320	1
AID	G	40000	50 (345)	83	947	2	14.2	5	32	9	331	0
VOG–raw water							14.7	0	52	0	246	0
VOG	A	100	190 (1310)	60	28		0.3	98	0	99	20	92
VOG	B	400	60 (414)	65	31		1.0	93	1	98	78	67
VOG	C	2000	100 (689)	80	430		6.3	57	21	65	223	5

water but also a large fraction of dissolved organic matter and THMFP."

A modeling procedure was developed to predict TOC removal from Seine River water and a central Illinois groundwater by PAC pretreatment in a UF (MWC of 100,000) pilot plant situation.[91] Briefly, this model was developed from batch TOC adsorption isotherms to obtain the Freundlich constants (1/n and K_a) and from kinetic studies to obtain the surface diffusion coefficient (D_s). In turn, these equilibrium and kinetic parameters were employed in plug-flow and CSTR (continuously stirred tank reactor) models to predict TOC concentrations from the first reactor effluent (pretreatment) and from the UF loop of the UF-PAC system. Experiments were conducted using different water sources (organic matter represented by TOC, PAC dosages, and backwashing frequencies. Predicted TOC concentrations in plant effluents were compared, of course, to actual plant values. These studies are useful for the specific situation from which the models were developed. They may have application to other water sources; however, pilot plant studies would have to be conducted for site-specific data.

SEDIMENTATION

Gravity separation of suspended particulates from the aquatic medium is, perhaps, the oldest and most widely used process in water treatment. Suspensions in which particulate matter is heavier than water tend to settle to the bottom as a result of gravity forces in this process of sedimentation. Conversely, particles lighter than the density of water tend to float in a process designated flotation. Since nearly all particulate matter in natural water is as heavy or heavier than water itself, the most widespread process is sedimentation. A brief discussion is given herein to theories of sedimentation, types of sedimentation tanks, and basic design considerations.

Theories of Sedimentation

A wide variety of suspensions—ranging from a very low concentration of nearly discrete particles to a high concentration of flocculent solids—are treatable by the sedimentation process for raw and partially treated waters. The settling characteristics of aqueous suspensions of particulates have been categorized into three general classes:[92]

> *Class 1.* Discrete particles that will not readily flocculate predominate in relatively low concentrations. An example of this type of suspension is encountered in wastewater grit chamber design and in clarification of certain industrial wastes (e.g., sand and gravel washings).
>
> *Class 2.* Relatively low solids concentrations of flocculent material. An example of this type of material is found in water subjected to flocculation by chemical addition.
>
> *Class 3.* Relatively high concentrations of material. This material may be flocculent, but not necessarily so. The term *hindered settling* is generally used to describe separation of this type of solids. Examples of this type of separation are found in sludge thickening.

These classes are illustrated in Figure 7.25. Only the settling of discrete particles is considered herein. The reader is directed to References 93 and 94 for more intensive discussions of the various mathematical models of sedimentation.

In aqueous suspensions, particles with densities greater than water will be accelerated downward under the influence of gravity until the resistance of the liquid equals the effective weight of the particle. Eventually, the gravity forces are balanced by particle drag forces, whereupon the particle will reach an equilibrium settling velocity that is relatively constant. This velocity depends upon the size, shape, and density of the particle and the density and viscosity of the water.

Classical settling theories are based on the assumption that particles are spherical; that is, of course, not always the situation. Nonspherical particles are handled by the application of coefficients relating their shapes to spherical particles. The general equation that relates these variables for spheres is:[93]

$$V = \sqrt{\frac{4}{3}\,\frac{g}{C_D}\,\frac{(\rho_l - \rho)^D}{\rho}} \tag{23}$$

where C_D = drag coefficient
g = gravity constant
ρ_l = mass density of particles
ρ = density of water
D = diameter of particle (spherical shape)
V = velocity of settling particle

The drag coefficient, C_D, varies as a function of density, relative velocity, particle diameter, and fluid viscosity. This is expressed by the dimensionless Reynolds number, R:

$$R = \frac{\rho V D}{\mu} \tag{24}$$

where ρ = density of fluid
μ = viscosity of fluid
D = diameter of particle
V = relative velocity

Reynolds numbers and C_D can be related by a series of equations and/or diagrams.[93] For Reynolds numbers less than 2, the relationship is approximately linear:

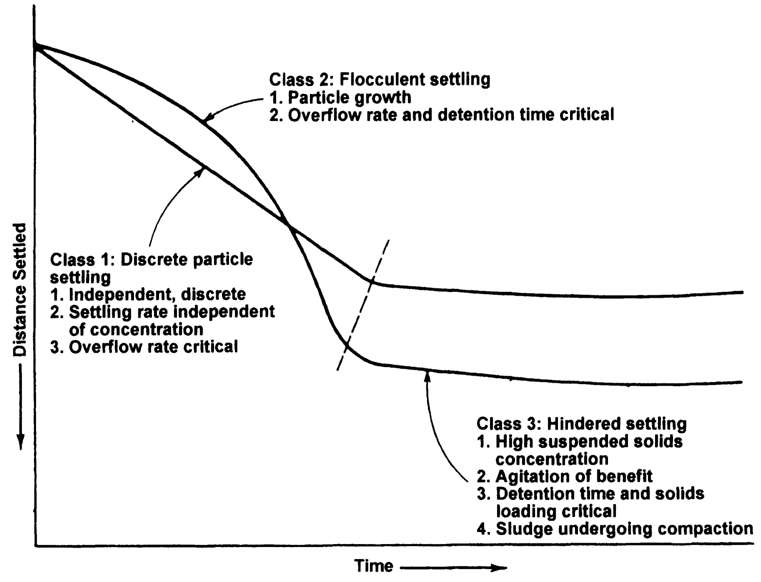

Figure 7.25. Settling characteristics of solids in water.[92]

$$C_D = \frac{24}{R} \tag{25}$$

At higher Reynolds numbers, the relationship is nonlinear, but can be approximated by:

$$C_D = \frac{24}{R} + \frac{3}{\sqrt{R}} + 0.34 \tag{26}$$

As R becomes larger in Equation 26, C_D approaches the constant value of 0.34. When R is in the range of 10^3–$10^{5.2}$, C_D is approximately 0.4 and then decreases to 0.2 for higher values. Equation 26 can be considered to be an overall relationship for a broad range of R values, but not necessarily exact for all R values.

At low velocities where Equation 25 applies, it can be substituted into Equation 24, which yields:

$$V = \frac{g(\rho_l - \rho)D^2}{18\mu} \tag{27}$$

This expression is known as Stokes' law for laminar flow conditions.[93] At higher Reynolds numbers where C_D=0.4, the velocity relationship becomes:

$$V = \sqrt{\frac{10}{3} g \frac{\rho_l - \rho}{\rho} D} \tag{28}$$

Reynolds numbers are useful, of course, in an attempt to describe the sedimentation velocity of discrete particles (spherical and nonspherical) as influenced by their diameter and the density and viscosity of water. Mathematical models are available in References 93 and 94 for sedimentation of particles under conditions described by Classes 2 and 3 above.

Types of Sedimentation Tanks

Horizontal-Flow Rectangular Tanks

In rectangular tanks with horizontal flow, water containing the particulates enters at one end and clarified water flows out the other end (Figure 7.26a). The inlet configuration must provide good flow distribution, which maximizes the opportunity for particles to settle. If coagulation/flocculation has been conducted to maximize particle size, then the flow distribution system must be as nondestructive as possible. This is accomplished by minimizing head loss between the distribution channel and the main body of the tank. However, there is a certain amount of head loss necessary to achieve the flow distribution.

In rectangular tanks, the length and cross-sectional shape of the tank must not encourage the development of counterproductive circulatory flow patterns and scour. The major differences between tanks relate to inlet and outlet arrangements; length, width, and depth ratios; and the method of sludge removal. Details of the design considerations are given in References 93 to 95.

Alternative configurations to rectangular basins are seen in Figure 7.26b, c, and d. Square clarifiers were developed in an effort to combine the advantages of common-wall construction of a rectangular basis with the simplicity of circular sludge collectors. However, square tanks suffer from poor

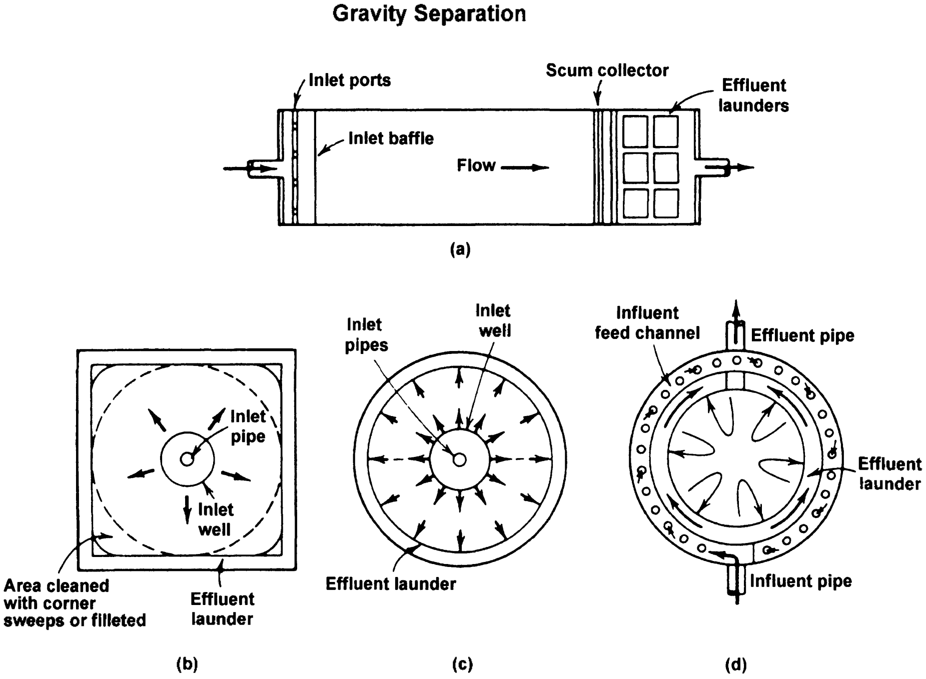

Figure 7.26. Types of sedimentation basins. (a) Rectangular. (b) Square, center feed. (c) Circular, center feed. (d) Circular, peripheral feed.[93]

flow distribution and sludge collection. Consequently, very few square basins are constructed for potable water treatment. Circular sedimentation tanks are employed frequently for small plants because they provide relatively trouble-free circular sludge removal mechanisms. Capital construction costs are lower on a unit surface area basis. Diameters are calculated on the basis of overflow rates using approximately the same criteria in common with rectangular tanks. Flow patterns for circular tanks are seen in Figure 7.26b and c.

Multi-Story Tanks

Multi-story or tray tanks recognize the importance of the settling area to the settling efficiency. There are two basic flow arrangements with these tanks: (a) the trays are coupled in parallel with the flow divided between them (Figure 7.27), or (b) they are coupled in series with the flow passing from one to the next. The water filtration plant of the Passaic Valley Water Commission at Little Falls, New Jersey uses two-pass tanks constructed on top of two-pass tanks.[94] Coagulated water enters the bottom pass and returns on the level above. Clarified water is removed by use of submerged launders. Sludge collectors move in the direction of flow with the sludge scraped into hoppers at the far end of the first pass. Each collector flight is trapped at the effluent and on the return pass, whereupon the collected material drops down into the path of the influent to the bottom pass. Multi-story tanks are attractive where the land value is high.

Inclined (Plate and Tube) Settlers

Sedimentation of aqueous suspensions can be accelerated by increasing particle size (by coagulation and flocculation) or decreasing the distance a particle must settle before removal. The latter is achieved by making the tank shallower. However, the clarification in shallow compartments must be separated from the process of sludge removal and surface current effects. Inclined parallel plates provide the short distance for the particulates to settle and permit the sludge to flow in a direction opposite to that of the liquid flow. All of this led to the development of parallel-plate and tube settlers (Figure 7.28).

The angle of inclination of tube settlers is important in their design and operation. Early tests indicated that, for alum-coagulated sludge, the solids would remain deposited in the tubes until the angle of inclination was increased to 60° or more from horizontal. Figure 7.28 shows an essentially horizontal orientation and a steeply inclined design.

The nearly horizontal tube settlers require less volume because the depth of particle fall is smaller, since it varies inversely with the cosine of the inclination angle. Consequently, an angle of 60° inclination would effectively double the maximum fall distance for particles entering the tube. On the other hand, the nearly horizontal tubes offer the advantage of lower construction costs. However, special cleaning procedures are required to remove suspended material that settles in the tubes. This restricts their use to relatively small plants of less than 1 MGD.

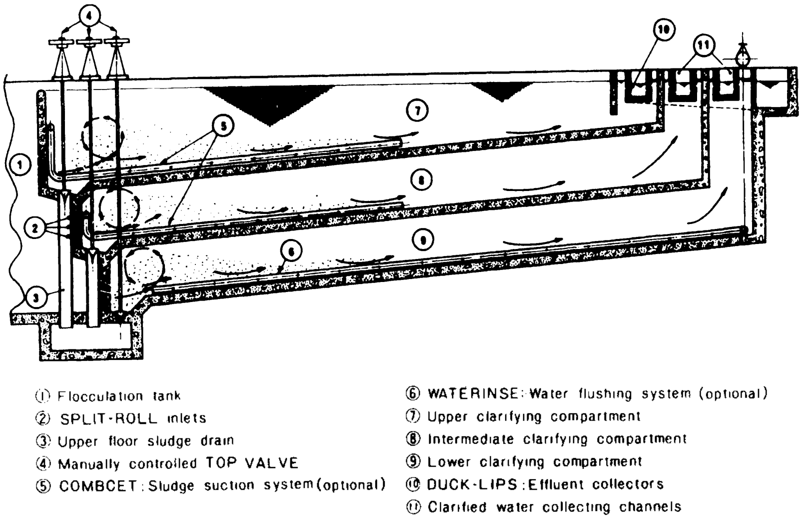

Figure 7.27. Multi-story horizontal tank with parallel flow on three levels.[94]

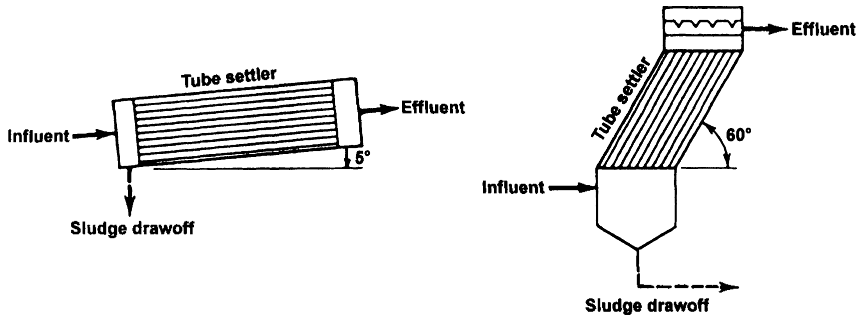

Figure 7.28. Microfloc tube settler system alternatives.[93]

The steeply inclined tube settler is, perhaps, the most widely used configuration for this type of sedimentation. The angle of inclination is steep enough to enable the sludge to flow in a countercurrent direction from the water passing upward through the tube. Consequently, the solids drop to the bottom of the clarifier and are removed by conventional sludge removal mechanisms. An example of this type of tube settler is the Lamella separator.[93]

Solids-Contact Clarifiers

Consideration is given to the solids-contact type of clarifier in Chapter 8, where it is predominantly applied to the softening of hard waters.

Design Considerations

Surface Loading Rates

The flow rate per unit of surface area of that part of the tank in which sedimentation occurs is the so-called surface loading of a sedimentation tank. The performance of all sedimentation processes is influenced by surface loading. Normally, settled water quality deteriorates when surface loading is increased; i.e., turbidity of the effluent water may increase, floc may be resuspended or not settle at all, etc. The point at which a performance curve crosses the limit of acceptable quality defines the maximum reliable surface loading.[94] There is a wide range of factors that affect reliable surface loading rates. Among these are temperature and chemical quality of the raw water supply. For example, in the wintertime, for a highly colored, low alkalinity water treated by floc-blanket sedimentation, the loading may be only 3 ft/hr (1 m/hr). Conversely, for a minerally turbid, high alkalinity water treated in the summertime with a flocculent aid, the surface loading rate could be greater than 23 ft/hr (7 m/hr)[94] (1 ft/hr = 0.125 gpm/ft^2).

Residence Time

The theoretical mean residence time of a process is the volume of the sedimentation tank divided by the flow-through rate. In horizontal sedimentation, the volume of the entire tank is important in assessment of its settling efficiency. For inclined settlers, it is the volume within the inclined surfaces that is important. Flow-through curves are a measure of the distribution in residence time (Figure 7.29). In turn, these curves can be analyzed to produce estimates of efficiency of flow distribution and volumetric utilization of a tank.[94] On the other hand, some designers consider residence time to be relatively unimportant as a design parameter and to serve only as an approximate guideline.[95] Residence times of sedimentation tanks (horizontal flow) tend to be designed around four hours.

Size and Number

The number of tanks do, indeed, affect the flexibility of plant operation. Occasionally, operation approaches the limit of acceptable quality. Obviously, if the plant contains only one tank, then plant production is affected. No fewer than two tanks should be available for reliable and consistent operation.

The size of tanks may be constrained by available site or other constructional factors. Consequently, this will determine the minimum number of tanks. One consideration is the use of "extra large" tanks. Large surface area tanks will be vulnerable to such environmental effects as wind-induced circulation.

Depth

Hazen's law states that the settling efficiency is dependent on the tank area, A, and is independent of the depth, H; (Q = flow):

$$T = \frac{AH}{Q} \qquad (29)$$

In practice, however, depth is interrelated with width, since it influences sedimentation efficiency of horizontal and inclined settlers. A minimum depth may be required to limit scour, for example.

On the other hand, tank performance is controlled by the surface loading rate. However, in the case of "large" sedimentation tanks, center depth for circular, center-fed tanks and sidewater depth for long rectangular tanks are important parameters. "It is far better to design a basin several feet too deep than too shallow. The cost of the additional depth is typically low and may improve the basin's performance for a long time under a great many variables."[95]

Miscellaneous Factors

The reader is directed to References 93 to 95 for several important factors that affect sedimentation tank design and operation. These include: flow arrangements (inlet and outlet configuration, baffling), seasonal water quality, coagulation chemistry, flocculation (solids-contact units), climate and density currents, etc.

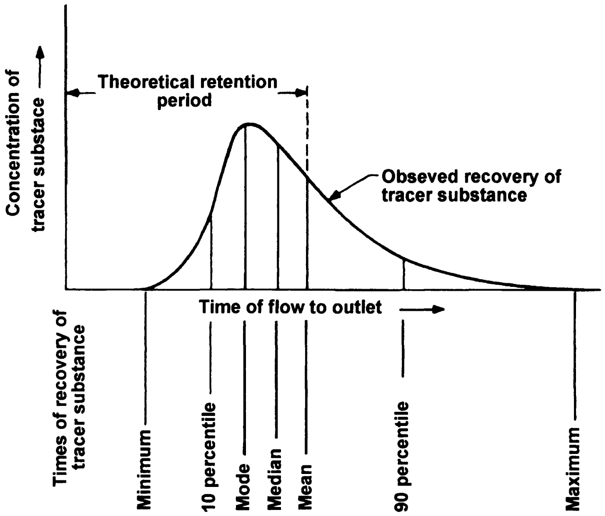

Figure 7.29. Typical plot of flow-through curve for a tracer dosed as a slug.[94]

Flotation processes have become important solids separation processes in potable water treatment. Here again, the reader is directed to References 93 to 95 for this topic.

ACKNOWLEDGMENT

Dr. Christopher Uchrin, Department of Environmental Sciences, Rutgers, The State University, New Brunswick, New Jersey prepared portions of this chapter from the book's first edition.

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Chapter 8

Removal of Hardness and Other Scale-Forming Substances

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8

Removal of Hardness and Scale-Forming Substances

SCALES AND THEIR FORMATION

Types of Scale

Hardness of natural waters results from dissolution of geologic formations (minerals) containing calcium, magnesium, and silica. In turn, these waters may be supersaturated with respect to one or more of the original minerals, whereupon "scale" is formed in a distribution system, hot water heater, boiler, etc. Hardness has been explained traditionally by the occurrence of calcium and magnesium compounds: bicarbonates, carbonates, sulfates, chlorides and nitrates in water. Silica originates in the dissolution or chemical weathering of amorphous or crystalline $SiO_{2(s)}$ and the major clay minerals: kaolinite, illite, and montmorillonite. Some typical dissolution reactions at 25°C are:

$$\underset{\text{Calcite}}{CaCO_{3(s)}} + H^+ = Ca^{2+} + HCO_3^- \qquad K_1 = 10^{1.856} \tag{1}$$

$$\underset{\text{Magnesite}}{MgCO_{3(s)}} + H^+ = Mg^{2+} + HCO_3^- \qquad K_2 = 10^{2.235} \tag{2}$$

$$\underset{\text{Gypsum}}{CaSO_4 \cdot 2H_2O_{(s)}} = Ca^{2+} + SO_4^{2-} + 2H_2O \qquad K_3 = 10^{-5.3} \tag{3}$$

$$\underset{\text{Amorphous}}{SiO_{2(s)}} + 2H_2O = H_4SiO_4 \qquad K_4 = 10^{-2.77} \tag{4}$$

$$\underset{\text{Kaolinite}}{Al_2Si_2O_5(OH)_{4(s)}} + 5H_2O = \underset{\text{Gibbsite}}{2Al(OH)_{3(s)}} + 2H_4SiO_4 \qquad K_5 = 10^{-9.93} \tag{5}$$

$$\underset{\text{Brucite}}{Mg(OH)_{2(s)}} = Mg^{2+} + 2OH^- \qquad K_6 = 10^{-10.74} \tag{6}$$

A more comprehensive list of natural chemical weathering reactions has been compiled.[1]

That there are regional variations in the hardness of ground and surface waters is seen in Figures 8.1a and b.[2] There may be locally hard waters within the generalized soft water areas. To date, no primary potable water standards exist at the federal level; however, some states, e.g., New Jersey (50–250 mg/L as $CaCO_3$) may have secondary standards for hard water.

The semantics of water hardness is confusing, to say the least. The terms "carbonate and noncarbonate" hardness attempt to distinguish sources of hardness:

Classification	Carbonate Hardness (CH)	Noncarbonate Hardness (NCH)
Calcium hardness	$Ca(HCO_3)_2$	$CaSO_4$
	$CaCO_3$	$CaCl_2$
Magnesium hardness	$Mg(HCO_3)_2$	$MgSO_4$
	$MgCO_3$	$MgCl_2$

It is somewhat difficult to assign anions exclusively to the Ca^{2+} and Mg^{2+} cations. The compounds listed above distinguish carbonate and noncarbonate hardnesses.

There are four essential types of scales: calcium carbonate, magnesium hydroxide, calcium sulfate, and silica. Each

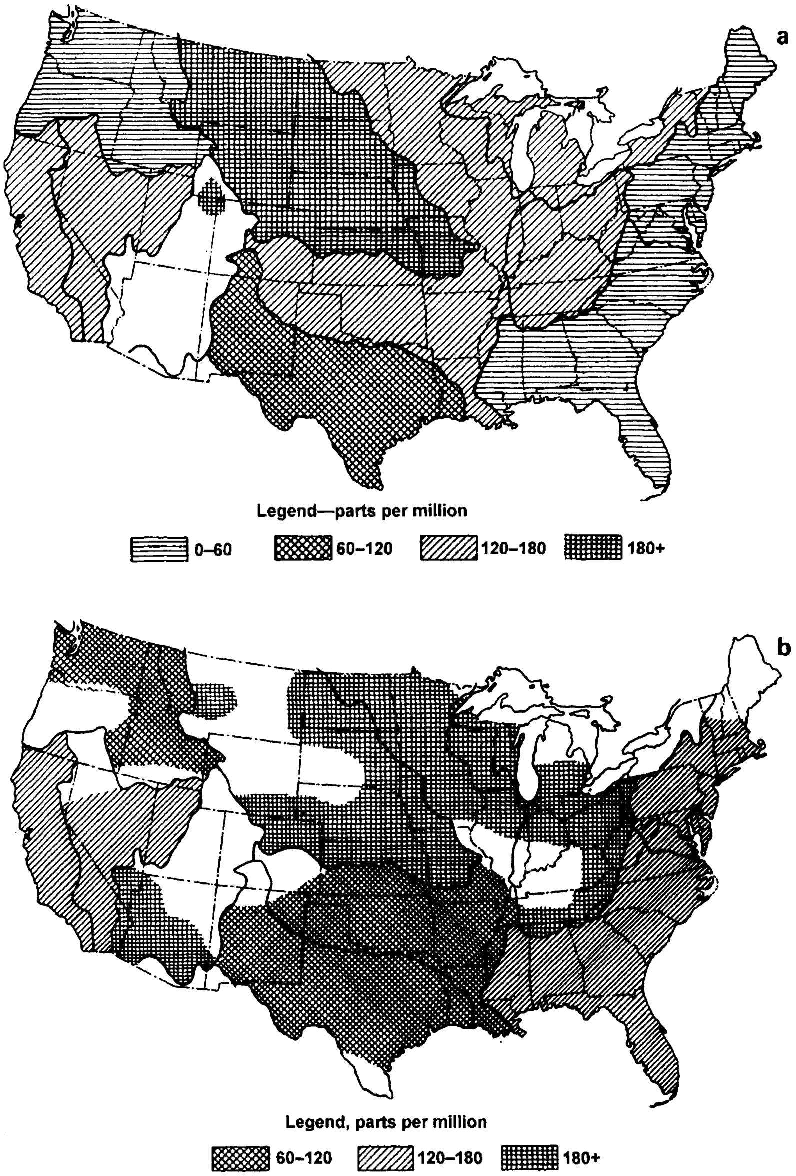


Figure 8.1. Map showing average hardness of (a) surface water and (b) groundwater weighted against population served in major drainage areas. Reproduced from Powell,[2] courtesy of the McGraw-Hill Book Company.

is formed through precipitation reactions with their solubilities at ordinary surface and groundwater temperatures, regulated by dissolution Reactions 1–6. Whenever water is heated, e.g., in domestic hot water heaters or boilers, the tendency to form scales becomes more severe because of their inverse solubility relation with temperature (Table 8.1). On the other hand, solubility of silica increases at higher temperatures:[3]

Temp. (°C)	Solubility (mg/L)	
	Quartz	Amorphous
0		60–80
25	6.0	115.0
84	26.0	
100		370.0

Table 8.1. Solubilities of Hard Water Scales.

		$CaCO_{3(s)}$		$Mg(OH)_{2(s)}$		$MgCO_{3(s)}$		$CaSO_{4(s)}$	
Temperature		$[CA^{2+}]$		$[Mg^{2+}]$		$[Mg^{2+}]$		$[Ca^{2+}]$	
°C	**°F**	**$-\log K_s$[a]**	**(mg/L)**	**$-\log K_s$**	**(mg/L)**	**$-\log K_s$**	**(mg/L)**	**$-\log K_s$**	**(mg/L)**
0	32	8.023	3.90		1.21		24.5[b]		409.0[c]
5	41	8.087							
10	50	8.150							
15	59	8.215							
20	68	8.280	2.90						
25	77	8.342		11.6[d]	2.67	7.46[d]	4.52	5.3	89.8
30	86	8.395							
40	104	8.515							
50	122	8.625	1.95						
80	176	8.975	1.30						
100	212				1.75		18.2		362.0

[a] Harned and coworkers.[4,5]
[b] Stumm and Morgan.[6]
[c] Nordell.[7] Values may be in error.
[d] *Lange's Handbook of Chemistry.*[8]

In waters where HCO_3^- and CO_3^{2-} anions predominate over Cl^-, SO_4^{2-} and NO_3^-, $CaCO_{3(s)}$ (calcite) is the principal scale-former in condensers and other water-jacketed equipment, water heaters, hot water piping and fixtures, etc. Where there is a sufficient quantity of Mg^{2+} cations, $Mg(OH)_{2(s)}$ (brucite) will form a scale rather than $MgCO_{3(s)}$, because the former is more insoluble than the latter (see Table 8.1). In waters where SO_4^{2-} predominates over Cl^-, NO_3^-, HCO_3^-, and CO_3^{2-}, $CaSO_{4(s)}$ (gypsum) will form a scale. It too has an inverse solubility-temperature relation. $CaSO_{4(s)}$ is somewhat more soluble than $CaCO_{3(s)}$, so that NCH waters have lesser scale-forming tendencies than CH waters. Silica is rather objectionable in high-pressure boilers, where it has pronounced scale-forming tendencies.[7] If calcium hardness is present, the scale may be a calcium silicate; if aluminum is present, an aluminosilicate scale may be formed (for example, Reaction 5), or the scale may consist almost entirely of silica (SiO_2). These silica scales are usually very hard, glassy, adherent, and difficult to remove. Silica is frequently carried over with the steam and forms a scale in superheater tubes and on turbine blades. Since the solubility of silica increases with temperature, it may be soluble to a certain extent in high-pressure steam. Normally, silica scale is not a problem in a domestic hot water heater. Some waters with substantial quantities of iron and manganese will form scales. Removal of these two constituents is discussed in Chapter 9.

Calculation of Potential Scale Formation

The calcium and magnesium contents of natural waters do, of course, vary considerably.[1] Consequently, scale-forming tendencies also vary. A water is considered to be hard whenever one or more of the solubility product constants cited above is exceeded. Furthermore, Reactions 1 and 2 show the $[H^+]$ dependence of the solubility of calcium and magnesium carbonate scales. In this case, stability and/or solubility diagrams may be employed to ascertain the hardness of water.[1]

The solubility product constant for $CaCO_{3(s)}$ is:

$$K_s = [Ca^{2+}][CO_3^{2-}] \qquad K_s = 10^{-8.342},\ 25°C \qquad (7)$$

Substituting for $[CO^-]$:

$$K_s = [Ca^{2+}]C_t\alpha_c^{2-} \qquad (8)$$

where $C_t = [H_2CO_3] + [HCO_3^-]+[CO_3^{2-}]$
$\alpha^{2-} = [CO_3^{2-}]/C_t$

Since $[Ca^{2+}] = C_t$:

$$K_s = [Ca^{2+}]^2\alpha_c^{2-} \qquad (9)$$

To construct a stability diagram for $CaCO_{3(s)}$, it is convenient to divide the pH scale into three regions: 0.00 to 6.35 (I); 6.35 to 10.33 (II); and 10.33 to 14.0. In region I, $\alpha_c^{2-} = K_1K_2/[H^+]^2$ (see Faust and Aly[1] for full derivation of the alpha equations for the carbonate system), whereupon:

$$K_s = \frac{[Ca^{2+}]^2\ K_1K_2}{[H^+]^2} \qquad (10)$$

where K_1 and K_2 are the primary and secondary dissociation constants for H_2CO_3, respectively. Taking logs of Equation 10 and rearranging:

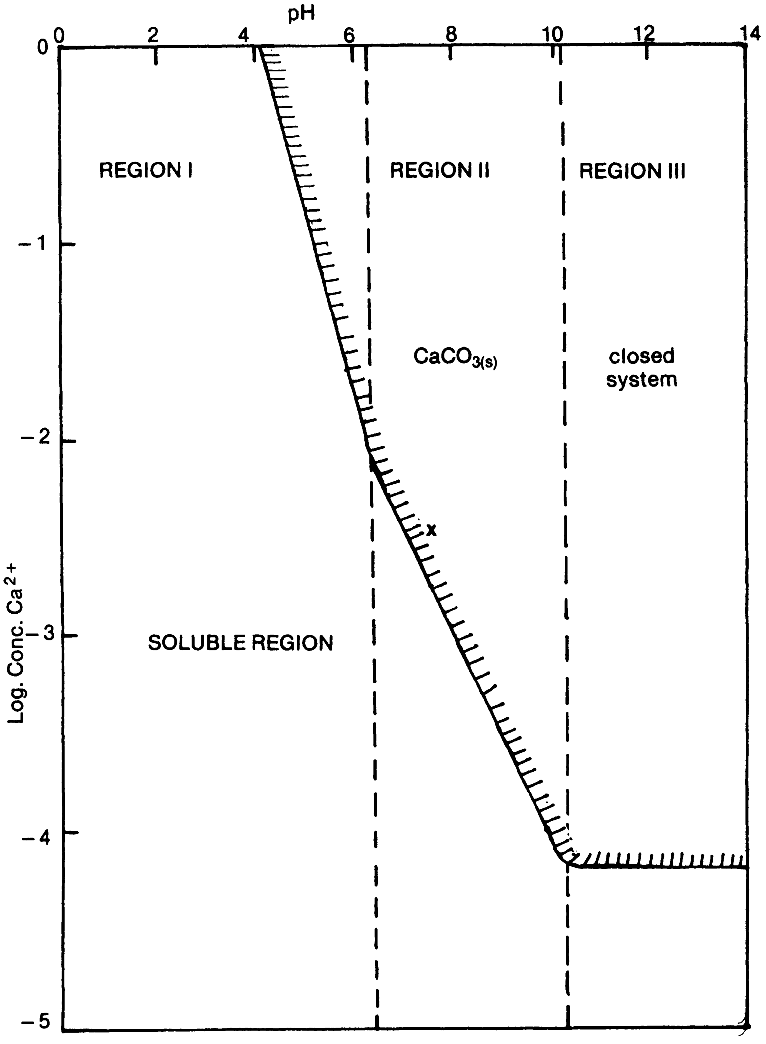


Figure 8.2. Solubility diagram for calcium carbonate in a closed system at 25°C.

$$\log[Ca^{2+}]\,eq = -pH + 0.5(pK_1 + pK_2 - pK_s) \qquad (11)$$

This equation represents the equilibrium boundary line for $CaCO_{3(s)}$ solubility in region I (Figure 8.2). In region II, $\alpha_c^{2-} = K_2/[H^+]$, whereupon:

$$K_s = \frac{[Ca^{2+}]^2\,K_2}{[H^+]} \qquad (12)$$

or

$$\log[Ca^{2+}]\,eq = 0.5\,pH + 0.5(pK_2 - pK_s) \qquad (13)$$

In region III, $\alpha_c^{2-} = K_1K_2/K_1K_2\ 1.0$, whereupon:

$$K_s = [Ca^{2+}]^2 \qquad (14)$$

or

$$\log[Ca^{2+}]\,eq = -0.5\,pK_s$$

Equations 11, 13, and 15 are the linear relations between the equilibrium concentrations of $[Ca^{2+}]$ and pH, which represent the boundary conditions between soluble and insoluble $CaCO_{3(s)}$.

Three examples shall suffice to demonstrate the use of Figure 8.2 to predict the scale-forming tendencies of natural waters.

Example Problem 8.1: A natural groundwater has a pH value of 7.8 and a $[Ca^{2+}]$ of 96.0 mg/L.[1] This is a region II water. A plot of pH 7.8 and $\log[Ca^{2+}] = -2.62$ places this water (x on Figure 8.2 in the solid region. Therefore, this water should form a $CaCO_{3(s)}$ scale at 25°C.

Table 8.2. Protolysis Constants of Carbonic Acid.[4,5]

Temperature			
°C	°F	pK_1	pK_2
0	32	6.577	10.625
5	41	6.517	10.557
10	50	6.465	10.490
15	59	6.420	10.430
20	68	6.382	10.377
25	77	6.351	10.329
30	86	6.327	10.290
40	104	6.296	10.220
50	122	6.287	10.172
80	176	(6.315)	(10.122)

Table 8.3. Reactions of the Lime–Soda Softening Process.

Equation	No.
$H_2CO_3 + Ca(OH)_2 = CaCO_{3(s)} + H_2O$	16
$Ca^{2+} + 2HCO_3^- + Ca(OH)_2 = 2CaCO_{3(s)} + H_2O$	17
$Ca^{2+} + Na_2CO_3 = CaCO_{3(s)} + 2Na^+$	18
$HCO_3^- + Ca(OH)_2 = CaCO_{3(s)} + OH^- + H_2O$	19
$Mg^{2+} + 2HCO_3^- + 2Ca(OH)_2 = 2CaCO_{3(s)} + Mg(OH)_{2(s)} + 2H_2O$	20
$Mg^{2+} + Ca(OH)_2 + Na_2CO_3 = CaCO_{3(s)} + Mg(OH)_{2(s)} - 2Na^+$	21

Example Problem 8.2: A natural groundwater has a pH value of 7.3 and a $[Ca^{2+}]$ of 79.0 mg/L.[9] This is a region II water. At 15°C the $[Ca^{2+}]eq$ is calculated from Equation 13:

$$\log[Ca^{2+}]eq = -0.5 \times 7.3 + 0.5(10.43 - 8.215)$$

$$[Ca^{2+}]eq = 2.87 \times 10^{-3} M, \ 115 \text{ mg/L}$$

Example Problem 8.3: Raise the temperature of the water in Example 8.2 to 50°C (122°F). In this case, $[Ca^{2+}]eq$ is:

The equilibrium content of $CaCO_{3(s)}$ is exceeded at 50°C (simulating a hot water heater), and the water is a potential scale-former.

Similar calculations may be performed for $Mg(OH)_{2(s)}$, $MgCO_{3(s)}$, and $CaSO_{4(s)}$. Equilibrium constants are given above and elsewhere[1] for these solid phases. The protolysis constants for carbonic acid are given in Table 8.2 for temperatures 0–80°C.[4,5]

CHEMISTRY OF SOFTENING PROCESSES

Lime–Soda Ash

In the lime–soda ash process of softening hard waters, Ca^{2+} is precipitated as $CaCO_{3(s)}$ and Mg^{2+} as $Mg(OH)_{2(s)}$. Lime, $Ca(OH)_2$, and soda ash, Na_2CO_3, are employed for reduction of the $[Ca^{2+}]$ and $[Mg^{2+}]$. Consequently, the solubility product constants of $CaCO_{3(s)}$ and $Mg(OH)_{3(s)}$ control the softening reactions; that is, stoichiometric quantities of lime and soda ash raise the pH value of the water so that $CaCO_{3(s)}$ (see Figure 8.2) and $Mg(OH)_{2(s)}$ are at their minimum solubilities.

Stoichiometric chemical reactions of the lime–soda process (Equations 16–21) are given in Table 8.3. These reactions are essentially a pH adjustment whereupon:

$$[Ca^{2+}] = C_t = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] \quad (22)$$

and

$$[Mg^{2+}] = 2[OH^-] \quad (23)$$

At a pH value of 10.3, Equation 22 becomes:

$$[Ca^{2+}] = C_t = [CO_3^{2-}] = 10^{-4.171} M, \ 2.7 \text{ mg/L} \quad (24)$$

and

$$[Mg^{2+}] = 2 \times 10^{-3.7} \text{ or } 4 \times 10^{-4} M, \ 9.72 \text{ mg/L}$$

Equations 16–21 also show that the following must be achieved after addition of lime and soda ash:

$$[Ca^{2+}]_{original} + [Ca^{2+}]_{added} = C_{t_{original}} + [CO_3^{2-}]_{added} \qquad (25)$$

Equation 16 shows the neutralization of carbonic acid (CO_2 acidity) in the natural water. If an analytical value of H_2CO_3 is not available, then it should be calculated, because one equivalent of lime is required.[1] Equation 17 is the removal of the CaCH, whereas Equation 18 is removal of the CaNCH. Equation 20 is the removal of the MgCH, whereas Equation 21 is removal of the MgNCH. These reactions are assumed to become complete in plant practice.

Throughout the lime-soda softening reactions, electroneutrality conditions must be maintained:

$$2[Ca^{2+}] + 2[Mg^{2+}] + [H^+] = [HCO_3^-] + 2[CO_3^{2-}] + 2[SO_4^{2-}] + [Cl^-] + [OH^-] \qquad (26)$$

From Equations 25 and 26, it is convenient to calculate the quantities of lime and soda ash required for softening, as well as to sort out the CH from the NCH.

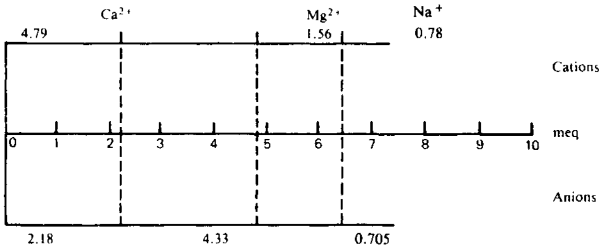
Example Problem 8.4 contains two examples of calculations for the lime-soda softening of natural groundwater cited above. First, it is necessary to calculate the milliequivalents and millimolar quantities of the major cations and anions. Second, the C_t for the carbonate species is calculated from the $[HCO_3^-]$ and the appropriate alpha value.[1] Third, the $[H_2CO_3]$ is taken as the difference between C_t and $[HCO_3^-]$. The $[CO_3^{2-}]$ is assumed to be negligible. Fourth, a meq scale is drawn above and below, on which the meq of cations and anions is drawn. It is convenient to represent the cations in this order: Ca^{2+}, Mg^{2+}, Na^+, and K^+ (if necessary), and the anions in this order: HCO_3^-, SO_4^{2-}, Cl^-, and NO_3^- (if necessary). Consequently, CaCH and MgCH take precedence over CaNCH and MgNCH. If there is no MgCH, then the order is CaCH, CaNCH, and MgNCH. There are occasionally waters with only noncarbonate hardness. For water A there are 2.18 meq CaCH, 2.61 meq CaNCH, and 1.56 meq MgNCH. The appropriate lime and soda ash quantities are given. It is not necessary to draw a scale for H_2CO_3; just make certain that its lime requirements are included with the others. For water B there are 3.94 meq CaCH, 0.44 meq MgCH, and 1.86 meq MgNCH. Both examples satisfy the conditions of Equation 26.

Example Problem 8.4: Calculation of carbonate hardness, noncarbonate hardness and lime-soda quantities.

Water A:

From Example 8.1, a natural water contains:

Constituent	mg/L	meq	m*M*
pH	7.8		
Ca^{2+}	96	4.79	2.395
Mg^{2+}	19	1.56	0.78
Na^+	18	0.78	0.78
K^+	1.5	0.04	0.04
HCO_3^-	133	2.18	2.18
SO_4^{2-}	208	4.33	2.165
Cl^-	25	0.705	0.705
H_2CO_3	5.2	0.17	0.084



Type Hardness	meq	Equation	$Ca(OH)_2$ meq	$Ca(OH)_2$ m*M*	Na_2CO_3 meq	Na_2CO_3 m*M*
H_2CO_3	0.19	16	0.17	0.84		
CaCH	2.18	17	2.18	1.09		
CaNCH	2.61	18			2.61	1.305
MgCH						
MgNCH	1.56	21	1.56	0.78	1.56	0.78
	6.52		3.91	1.945	4.17	2.085

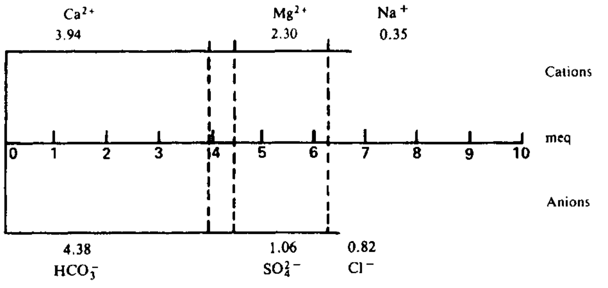
From Equation 25: 2.395 m*M* $Ca^{2+}_{original}$ + 1.954 m*M* lime = 2.264 m*M* Ct + 2.085 m*M* soda ash added

4.349 = 4.349

Water B:

From Example 8.2 a natural water contains:

Constituent	mg/L	meq	m*M*
pH	7.3		
Ca^{2+}	79	3.94	1.97
Mg^{2+}	28	2.30	1.15
Na^+	8.1	0.35	0.35
K^+	5.7	0.146	0.146
HCO_3^-	267	4.38	4.38
SO_4^{2-}	51	1.06	0.53
Cl^-	29	0.82	0.82
H_2CO_3	30.8	1.0	0.50



Type Hardness	meq	Equation	$Ca(OH)_2$ meq	$Ca(OH)_2$ m*M*	Na_2CO_3 meq	Na_2CO_3 m*M*
H_2CO_3	1.0	16	1.0	0.50		
CaCH	3.94	17	3.94	1.97		
CaNCH						
MgCH	0.44	20	0.88	0.44		
MgNCH	1.86	21	1.86	0.93	1.86	0.93
	7.24		7.68	3.84	1.86	0.93

From Equation 25:

$$1.97\ \text{m}M\ Ca^{2+}_{\text{original}} + 3.84\ \text{m}M_{\text{lime}} = 4.88\ \text{m}M\ C_t + 0.93\ \text{m}M_{\text{soda ash}}\ \text{added}$$

$$5.81 = 5.81$$

The calculations below assume, of course, that Reactions 16–21 satisfy the stoichiometric requirements. This is frequently not the case because of an insufficient contact time allotted in plant reactors to allow the completion of these reactions. In order to increase the rates of precipitation, lime and soda ash are added in excess of the calculated values. Whatever this excess, it may be added to the examples below. Higher water temperatures increase the rates of precipitation and also provide lower residual contents of Ca and Mg. This is the "hot" lime-soda process, which is employed for boiler waters. There are also occasions when it is not necessary to utilize the full quantities of lime and soda ash. For example, municipal drinking water does not need softening to $[Ca^{2+}]$=2.7 mg/L and $[Mg^{2+}]$=9.72 mg/L. The quantities of lime and soda ash could be lowered, or the technique of split treatment could be instituted (see below).

Sodium Hydroxide

Occasionally, sodium hydroxide is used instead of lime to remove carbonate and noncarbonate hardness as well as to substitute for part or all of the soda ash requirement. The appropriate reactions are seen in Table 8.4 for waters containing both CH and NCH when it is desired to use NaOH in the softening process. Equation 27 shows the reaction of carbonic acid with NaOH. It is necessary to include this reaction because it creates a chemical demand for NaOH. This reaction indicates that 1 mole (2 equivalents) of H_2CO_3 reacts with 2 moles (2 equivalents) of NaOH to form one mole (2 equivalents) of Na_2CO_3. Equation 28 represents the removal of CaCH. This reaction shows that 1 mole (2 equivalents) of Ca^{2+} reacts with 2 moles (2 equivalents) of NaOH to form 1 mole (2 equivalents) of $CaCO_{3(s)}$ and 1 mole (2 equivalents) of Na_2CO_3. Equations 29, 30, and 31 show the removal of MgCH. The net reaction (Equation 31) indicates that 1 mole (2 equivalents) of Mg^{2+} requires 4 moles (4 equivalents) of NaOH to produce 1 mole (2 equivalents) of $Mg(OH)_{2(s)}$ and 2 moles (4 equivalents) of Na_2CO_3. Equation 32 gives the removal of MgNCH by NaOH. This reaction shows that 1 mole (2 equivalents) of Mg^{2+} requires 2 moles (2 equivalents) of NaOH to form 1 mole (2 equivalents) of $Mg(OH)_{2(s)}$. It should be noted that Na_2CO_3 generated from Reactions 27, 28, and 31 will react with CaNCH according to Reaction 18. This may be an advantage in some treatment situations. An example problem is given below to demonstrate the substitution of NaOH for $Ca(OH)_2$ in the softening process.

Example Problem 8.5: Calculation of the caustic soda (NaOH) requirements in removal of carbonate and noncarbonate hardness. Determine the caustic soda dosages required to soften the natural water B given above in Example Problem 8.4. The appropriate calculations yield:

Type Hardness	meq	Equation	NaOH meq	NaOH mm	Na_2CO_3[a] meq	Na_2CO_3[a] mm
H_2CO_3	1.0	27	1.0	1.0	—	—
CaCH	3.94	28	3.94	3.94	3.94	1.97
MgCH	0.44	29,30,31	0.88	0.88	0.88	0.44
MgNCH	1.86	32	1.86	1.86	—	—
Totals	7.24		7.68	7.68	4.82	2.41

[a] Produced from CH removal.

Several advantages may be cited for the use of caustic soda in the softening process: (a) frequently only one chemical feed system will be required, (b) NaOH is easier to handle and feed than lime, (c) it does not deteriorate in storage, and (d) less $CaCO_{3(s)}$ sludge is produced. In any event, the choice of chemicals for the softening process should be based on an economic basis that considers the delivered costs of three chemicals, cost of equipment for chemical feed, and the cost of sludge handling and disposal.

Example Problem 8.6: Comparison of the amount of $CaCO_{3(s)}$ sludge formed in the lime–soda ash softening process from water B in Example Problem 8.4 to the amount of sludge produced in the caustic soda softening process from water B in Example Problem 8.5.

Table 8.4. Reactions of the NaOH-Soda Softening Process.

Equation	No.
$H_2CO_3 + 2NaOH = Na_2CO_3 + 2H_2O$	27
$Ca^{2+} + 2HCO_3^- + 2NaOH = CaCO_{3(s)} + Na_2CO_3 + 2H_2O$	28
$Mg^{2+} + 2HCO_3^- + 2NaOH = Na_2CO_3 + MgCO_3 + 2H_2O$	29
$MgCO_3 + 2NaOH = Mg(OH)_{2(s)} + Na_2CO_3$	30
Combine Equations 29 and 30:	
$Mg^{2+} + 2HCO_3^- + 4NaOH = Mg(OH)_{2(s)} + 2Na_2CO_3 + 2H_2O$	31
$Mg^{2+} + SO_4^{2-} + 2NaOH = Mg(OH)_{2(s)} + Na_2SO_4$	32

1. Tabulate the amounts of $CaCO_3$ sludge produced by the softening reactions.

	Lime-Soda Ash Softening		Caustic Soda Softening	
Type Hardness	**Reaction**	**$CaCO_{3(s)}$ meq/L**	**Reaction**	**$CaCO_{3(s)}$ meq/L**
H_2CO_3	16	1.0	—	—
CaCH	17	2 × 3.94	28	3.94
MgCH	20	2 × 0.44	31	0
MgNCH	21	1.86	32	0
Total Sludge		11.62		3.94

2. Convert the $CaCO_{3(s)}$ sludge into lb/MG of treated water.

a. Convert $CaCO_{3(s)}$ from meq/L to mg/L:
Lime–soda ash

$$CaCO_{3(s)} = 11.62\ \mathrm{meq/L} \times 50 = 581\ \mathrm{mg/L}$$

mg / L

Caustic soda

$$CaCO_{3(s)} = 3.94\ \mathrm{meq/L} \times 50 = 197\ \mathrm{mg/L}$$

mg / L

b. Convert the $CaCO_{3(s)}$ from mg/L to lb/MG:
Lime–soda ash

$$CaCO_{3(s)} = 581\ \mathrm{mg/L} \times 8.34 = 4846\ \mathrm{lb/MG}$$

lb / MG

Caustic Soda

$$CaCO_{3(s)} = 197\ \mathrm{mg/L} \times 8.34 = 1643\ \mathrm{lb/MG}$$

lb / MG

Alkalinity of the Lime–Soda Ash Process

In the operation of water softening treatment units, guidelines for quality control are based upon the total alkalinity (TALK) and phenolphthalein alkalinity (PhPhALK). For the purpose of this discussion, TALK is defined as the quantity of 0.02 *N* H_2SO_4 required for titration to the mixed indicator[11] or fixed pH endpoint. It is expressed mathematically as:

$$\frac{\mathrm{TALK}}{50{,}000} = [CO_3^{2-}] + [OH^-] - [H^+] \qquad (33)$$

where the brackets indicate mol/L. The coefficient before each term converts the mol/L to eq/L. TALK has units of mg/L as $CaCO_3$, which are converted to eq/L by the factor 50,000. In turn, PhPhALK is defined as the quantity of 0.02 *N* H_2SO_4 required for titration to the phenolphthalein endpoint (pH 8.5 to 9.0). It is approximated by:

$$\frac{\mathrm{PhPhALK}}{50{,}000} = [CO_3^{2-}] + [OH^-] - [H^+] \qquad (34)$$

Since the pH values of the lime-soda process are in the range of 10–11 from addition of $Ca(OH)_2$ and Na_2CO_3, it is necessary to have reasonably accurate values of TALK and PhPhALK for quality control. Optimum removal of Ca^{2+} occurs, apparently, when TALK/PhPhALK (as $CaCO_3$)=2.0.[10] This has been a traditional "rule-of-thumb" in water softening.[2,7]

Several methods are available for estimating the various kinds of alkalinity and the concomitant $[Ca^{2+}]$. For example, an older edition of *Standard Methods*[11] uses the alkalinity relationships shown in Table 8.5. Also, the nomographs of Dye[12] are utilized frequently. There are, however, easier and less confusing mathematical methods for calculating the three major types of alkalinity and $[Ca^{2+}]$ in Equation 33.[1,10]

The appropriate equilibrium equations are:

$$K_s = [Ca^{2+}][CO_3^{2-}],\ 10^{-8.342}\ (25°C) \qquad (7)$$

Table 8.5. Alkalinity Relationships[a].[11]

Result of Titration	Hydroxide Alkalinity as $CaCO_3$	Carbonate Alkalinity as $CaCO_3$	Bicarbonate Concentration as $CaCO_3$
P=0	0	0	T
P<1/2T	0	2P	T–2P
P=1/2T	0	2P	0
P>1/2T	2P–T	2(T–P)	0
P=T	T	0	0

[a] P: phenolphthalein alkalinity; T: total alkalinity.

$$K_W = [H^+][OH^-],\ 10^{-14}\ (25°C) \tag{35}$$

$$K_{2H_2CO_3} = \frac{[H+][CO_3^{2-}]}{[HCO_3^-]},\ 10^{-10.329}\ (25°C) \tag{36}$$

In these and subsequent equations, calcium reduction is the only objective. This is frequently the situation because either the raw water $[Mg^{2+}]$ is acceptable, or chemical costs can be saved where Mg removal is not necessary. In any event, Schierholz et al.[10] derived, by combining Equations 7, 33, 35, and 36, expressions for calculating $[HCO_3^-]$, $[CO_3^{2-}]$, and $[Ca^{2+}]$ at appropriate pH and TALK values:

$$[HCO_3^-] = \frac{TALK/50{,}000 + [H^+] - K_w/[H^+]}{1 + 2K_2/[H^+]} \tag{37}$$

$$[CO_3^{2-}] = \frac{TALK/50{,}000 + [H^+] - K_w/[H^+]}{2(1 + [H^+]/2K_2)} \tag{38}$$

$$[Ca^{2+}] = \frac{K_s}{[CO_3^{2-}]} = \frac{2K_s(1 + [H^+]/2K_2)}{TALK/50{,}000 + [H^+] - K_w/[H^+]} \tag{39}$$

By measurement of pH, TALK, temperature, and total dissolved solids (TDS), each ion concentration and the three types of alkalinity can be calculated. These values, for example, are given in Table 8.6 for a temperature of 20°C and a TDS of 200 mg/L. (It is noted that "maximum carbonate" apparently means the $[HCO_3^-]+[CO_3^{2-}]$ for a given pH value and $[Ca^{2+}]$; i.e., maximum $CaCO_{3(s)}$ precipitation.) These concentrations are, of course, those that should occur for the specified conditions from the thermodynamic equations. There may be differences between the calculated values and those observed at water softening plants due to analytical errors, "slow" kinetics of precipitation, etc. Schierholz et al.[10] give TALK ionic concentrations at 5, 10, and 15°C.

Cadena et al.[13] argue that formation of the ion pair, $CaCO_3^0$, limits the reduction of $[Ca^{2+}]$ to 13.5 mg/L as $CaCO_3$ (5.41 mg/L as Ca^{2+}) in the lime-soda softening process. This $[Ca^{2+}]$ is twice the quantity calculated from the K_s value of $10^{-8.342}$. The ion pair is formed:

$$Ca^{2+} + CO_3^{2-} = CaCO_3^0,\ K_{40} = 10^{4.467}\ 25°C \tag{40}$$

Combination of Equation 40 with Equation 7 leads to:[13]

$$CaCO_3^0 = \frac{K_sCaCO_3}{K_{40}} = \frac{4.58 \times 10^{-9}}{3.41 \times 10^{-5}} = 13.4\ mg/L\ as\ CaCO_3$$

This revelation may be important in the treatment of boiler-fed waters where $[Ca^{2+}]$ must be as low as possible.

Kinetics of $CaCO_{3(s)}$ Precipitation

Large (i.e., several MGD) water softening plants using the lime-soda process are designed around a chemical reaction time of 40–60 min;[14] that is, hydraulic design of the flocculating basins is of this order of magnitude of time. Consequently, the chemical kinetics of the $CaCO_{3(s)}$ and $Mg(OH)_{2(s)}$ precipitation must "fit" into this time frame. Kinetic studies have indicated that 25 min are required to reach equilibrium levels of the Ca^{2+} in the precipitation of $CaCO_{3(s)}$.[14] In addition, the initial pH value in the range of 9 to 12 appeared to be a factor affecting the kinetics of precipitation. The higher the pH value, the quicker is the attainment of the equilibrium content of Ca^{2+}. It was concluded that this 25-min reaction time is compatible with the traditional hydraulic design of 40–60 min.[14]

A kinetic study was conducted[15] on the precipitation and crystallization of $CaCO_{3(s)}$ under typical water softening practice conditions; i.e., a high degree of oversaturation, a "moderately high" concentration of seed crystals, and a

Table 8.6. pH and Concentration (as Calcium Carbonate) of Carbonate, Bicarbonate and Hydroxyl Alkalinity at the pH of Maximum Carbonate Concentration; Total Dissolved Solids=200 mg/L. Temperature=20°C.[a]

Alkalinity (mg/L)	pH	Carbonate (mg/L)	Bicarbonate (mg/L)	Hydroxyl (mg/L)	Calcium (mg/L)
20	10.15	8.8	5.6	5.6	10.0
22	10.18	10.1	6.0	6.0	8.7
24	10.20	11.4	6.3	6.3	7.8
26	10.22	12.7	6.7	6.7	7.0
28	10.25	14.0	7.0	7.0	6.3
30	10.27	15.3	7.3	7.3	5.8
32	10.28	16.7	7.7	7.7	5.3
34	10.30	18.1	8.0	8.0	4.9
36	10.32	19.5	8.3	8.3	4.5
38	10.33	20.9	8.6	8.6	4.2
40	10.35	22.3	8.9	8.9	4.0
42	10.36	23.7	9.1	9.1	3.7
44	10.37	25.2	9.4	9.4	3.5
46	10.39	26.6	9.7	9.7	3.3
49	10.40	28.1	9.9	9.9	3.1
50	10.41	29.6	10.2	10.2	3.0
52	10.42	31.1	10.5	10.5	2.8
54	10.43	32.6	10.7	10.7	2.7
56	10.44	34.1	11.0	11.0	2.6
58	10.45	35.6	11.2	11.2	2.5
60	10.46	37.1	11.4	11.4	2.4
62	10.47	38.7	11.7	11.7	2.3
64	10.48	40.2	11.9	11.9	2.2
66	10.48	41.8	12.1	12.1	2.1
68	10.49	43.3	12.3	12.3	2.0
70	10.50	44.9	12.6	12.6	2.0
72	10.51	46.4	12.8	12.8	1.9
74	10.51	48.0	13.0	13.0	1.8
76	10.52	49.6	13.2	13.2	1.8
79	10.53	51.2	13.4	13.4	1.7
80	10.53	52.8	13.6	13.6	1.7
82	10.54	54.3	13.8	13.8	1.6
84	10.55	55.9	14.0	14.0	1.6
86	10.55	57.5	14.2	14.2	1.5
88	10.56	59.1	14.4	14.4	1.5
90	10.57	60.8	14.6	14.6	1.5
92	10.57	62.4	14.8	14.8	1.4
94	10.58	64.0	15.0	15.0	1.4
96	10.58	65.6	15.2	15.2	1.3
98	10.59	67.2	15.4	15.4	1.3
100	10.59	68.9	15.6	15.6	1.3

[a] Reproduced from Schierholz et al.,[10] courtesy of the American Water Works Association.

pH range of 8 to 10. Data were obtained first to establish a model for Ca^{2+} removal that had been proposed previously:[16]

$$-\frac{d[Ca^{2+}]}{dt} = K \cdot [CaCO_{3(s)}] \cdot ([Ca^{2+}][CO_3^{2-}]) - \frac{K_s}{\gamma_D^2} \qquad (41)$$

where K = rate constant for calcite crystallization (l/mol/min/mg/L seed)

$[CaCO_{3(s)}]$ = crystal concentration mg/L at any time, t

K_s = solubility product constant for $CaCO_{3(s)}$

γ_D^2 = activity coefficient for divalent ions

Typical kinetic data are seen in Figure 8.3, where the reaction was followed by pH measurements with time and subsequent calculation of [Ca^{2+}], [$CaCO_{3(s)}$], and [$CaCO_3^\circ$]. Equation 41 was verified as the mathematical model for the crystallization and precipitation process. Data were obtained to evaluate factors influencing the value of K, of which [H^+] is an important component (Figure 8.4). The value of K, the apparent rate constant, was dependent on, or, at least, varied with, the initial pH value. No explanation was offered for this observation. Temperature is also a variable influencing K, for which a typical Arrhenius plot was obtained in the 10 to 40°C range. An activation energy of 10.3 ± 0.9 kcal/mol was computed. In summary, Equation 41 appears to be valid for Ca^{2+} and CO_3^{2-} concentrations ranging from 1.4 to 3.29×10^{-4} *M* and 1.83 to 5.29×10^{-4} *M*, respectively, and [$CaCO_{3(s)}$] ranging from 100 to 1000 mg/L. An important consequence of this study is the close fit of experimentally derived and theoretically calculated kinetic plots. Thus, the K value is reliable and will be useful in designing chemical reactors for water softening.

pH Control

Lime-soda softened waters usually have pH values of approximately 10.4 and are supersaturated with $CaCO_{3(s)}$ and $Mg(OH)_{2(s)}$. Consequently, it is necessary to acidify these waters to prevent postprecipitation of these two substances in filters following the softening or in the water distribution system. Adjustment of the pH value toward neutrality is accomplished either by addition of $CO_{2(g)}$ (i.e., recarbonation) or by sulfuric acid. The former process may be preferred over the latter because it is less hazardous to use than H_2SO_4.

In the recarbonation process, $CO_{2(g)}$ is bubbled into the water in order to effect these reactions:

$$CaCO_{3(s)} + CO_{2(g)} + H_2O = Ca(HCO_3)_2 \qquad (42)$$

$$Ca(OH)_2 + 2CO_{2(g)} = Ca(HCO_3)_2 \qquad (43)$$

Liquid CO_2 is the most common source, with onsite generation as an alternative process. Economy ultimately dictates the choice. A detailed description of the recarbonation process is available in Haney and Hamann.[17] Figure 8.5 shows typical $CO_{2(g)}$ feed systems.

Recarbonation is especially important where substantial quantities of $Mg(OH)_{2(s)}$ have been precipitated.[18] This occurs because $Ca(OH)_2$ must be employed to reach pH values in the range of 10 to 11, according to Equation 21 and Figure 8.6. Larson et al.[18] recommended a saturation pH value of 8.5 for 77°F water and 9.5 for 33°F water.

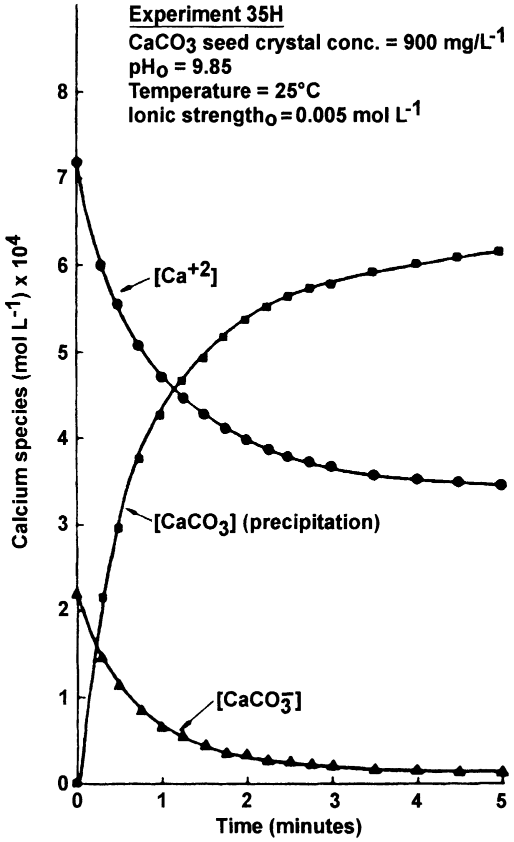


Figure 8.3. Plot of derived calcium species vs. time, from experimentally measured pH values. Reproduced from Wiechers et al.,[15] courtesy of the International Association on Water Pollution Research.

In the reduction of excessive pH values and alkalinities, sulfuric acid is also utilized:

$$H_2SO_4 + 2CaCO_{3(s)} = Ca(HCO_3)_2 + CaSO_4 \qquad (44)$$

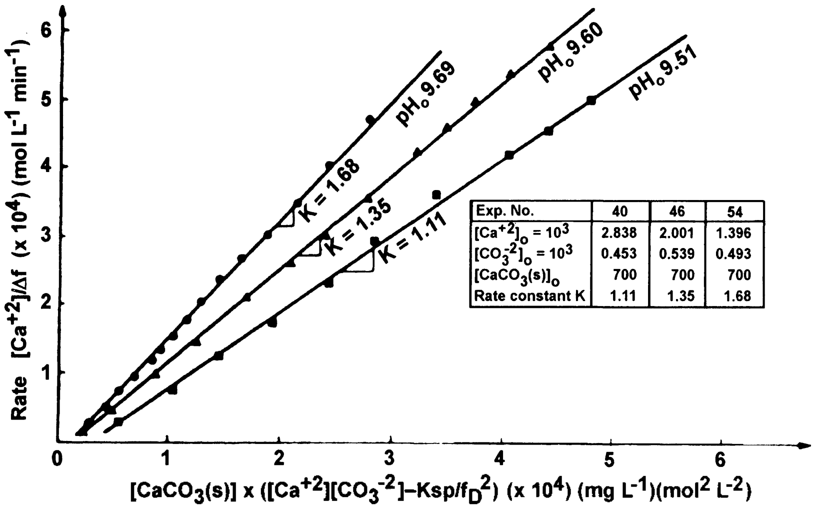
$$H_2SO_4 + Ca(OH)_2 = CaSO_4 + 2H_2O \qquad (45)$$

Needless to say, extreme caution must be utilized in handling and adding concentrated sulfuric acid to water. Powell[2] and Nordell[7] describe many kinds of acid-feeding equipment.

Silica Removal

Briefly, the aqueous chemistry of silica is:

$$\underset{\text{Amorphous}}{SiO_{2(s)}} + 2H_2O = H_4SiO_4 \qquad K_4 = 10^{-2.77} \qquad (4)$$



Exp. No.	40	46	54
$[Ca^{+2}]_o = 10^3$	2.838	2.001	1.396
$[CO_3^{-2}]_o = 10^3$	0.453	0.539	0.493
$[CaCO_3(s)]_o$	700	700	700
Rate constant K	1.11	1.35	1.68

Figure 8.4. Effect of initial pH (pH_0) on rate constant K. Reproduced from Wiechers et al.,[15] courtesy of the International Association on Water Pollution Research.

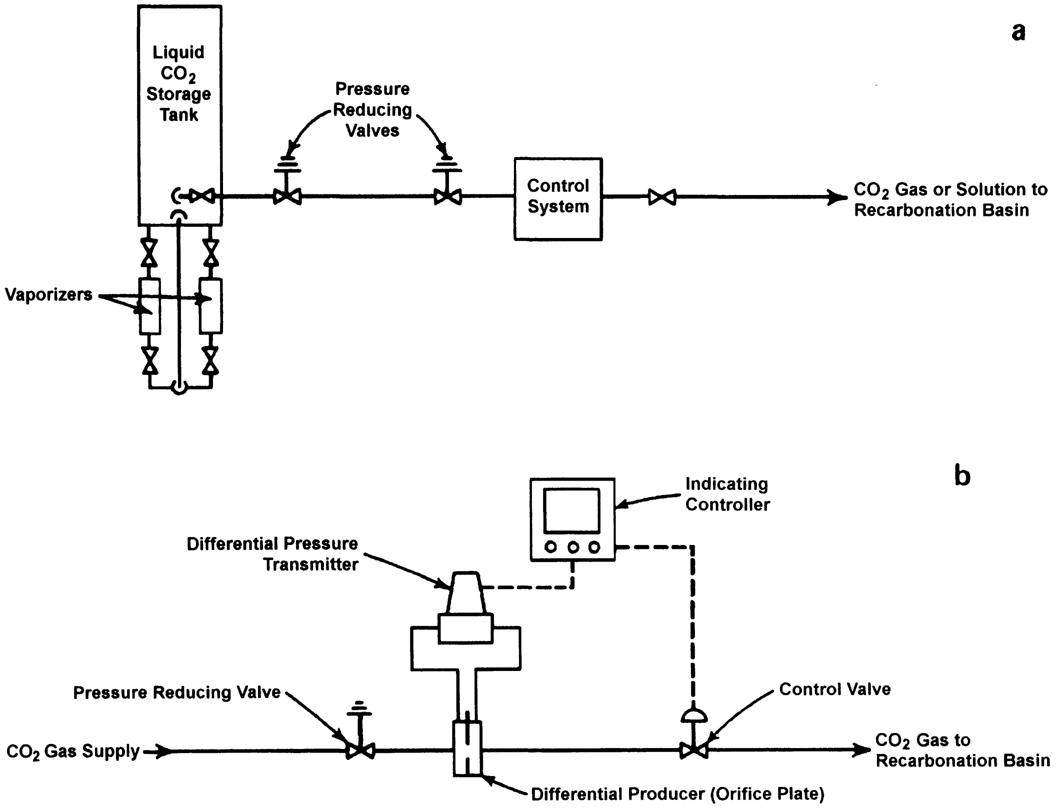


Figure 8.5. Schematics of (a) typical carbon dioxide feed system and (b) typical control system for carbon dioxide gas feed. Reproduced from Haney and Hamann,[17] courtesy of the American Water Works Association.

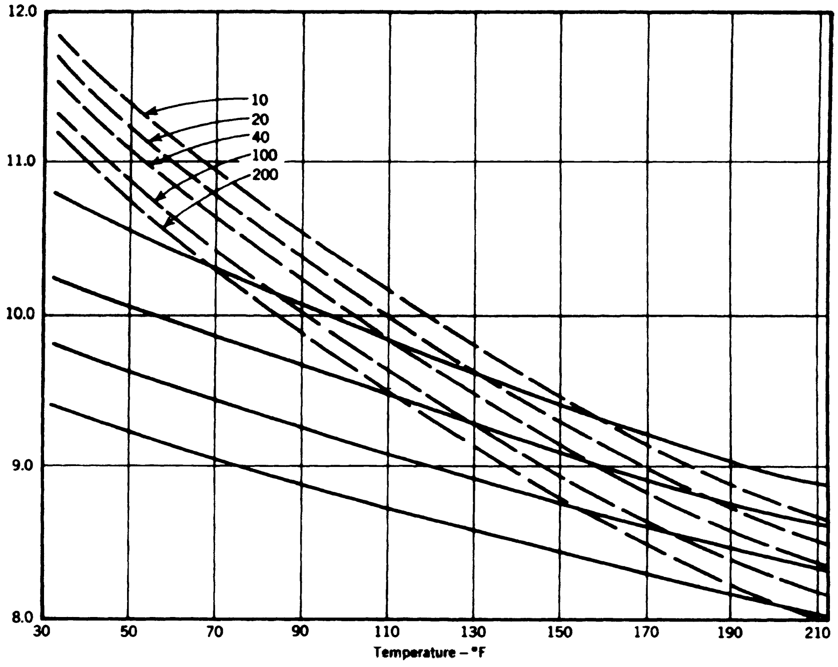


Figure 8.6. Influence of temperature on magnesium solubility at 200 ppm TDS. Dashed curves represent magnesium solubility (as $CaCO_3$), and the solid curves represent pH variation. Reproduced from Larson et al.,[18] courtesy of the American Water Works Association.

$$\underset{\text{Quartz}}{SiO_{2(s)}} + 2H_2O = H_4SiO_4 \qquad K46 = 10^{-3.76} \tag{46}$$

$$\underset{\text{Silicic acid}}{H_4SiO_4} = H^+ + H_3SiO_4^- \qquad K_{47} = 10^{-9.46} \tag{47}$$

$$H_3SiO_4^- = H^+ + H_2SiO_4^{2-} \qquad K_{48} = 10^{-12.56} \tag{48}$$

For the most part, dissolved silica is a neutral molecule [H_4SiO_4 or $Si(OH)_4$].[5] Consequently, a removal method involves adsorption of silica onto a surface such as ferric hydroxide, rather than precipitation as a discrete compound. Also, silica can be removed by a highly basic anion exchange unit.[2]

Ferric hydroxide (or ferric oxides) is precipitated from ferric sulfate by sodium or calcium hydroxide for silica removal. In this case, a pH value of 9.0 or greater is required. Dosages of ferric hydroxide are somewhat empirical[2] for waters with less than 10 ppm of silica removed. At higher silica contents, this ratio may be lowered to 10:1. According to plant experience, a residual of about 2 ppm silica is obtainable, and the process is suitable mainly for normal water temperatures.

An alternative and, perhaps, the most efficient process for silica removal is adsorption by an insoluble magnesium compound; i.e., $Mg(OH)_{2(s)}$ or $MgCO_{3(s)}$. If a natural water contains a considerable portion of Mg hardness, then silica will be removed to a certain extent with the concurrent precipitation of $Mg(OH)_2$. The efficiency of silica removal is influenced to a large degree by the water temperature. At 50°F (10°C), the removal of 1 ppm silica requires the precipitation of 30 ppm of magnesium hardness. This empirical ratio applies when the initial silica content is greater than 15 ppm. At 70°F (21.1°C), the ratio is 7 ppm Mg hardness to 1 ppm silica. In the event that there is an insufficient quantity of magnesium, dolomitic lime [$CaMg(CO_3)_2$] or MgO is added to the process.

The most efficient technique for silica removal is the "hot-process" softening.[2] In this method, the water is heated to 100°C (212°F), where the rate of hydration of MgO to $Mg(OH)_{2(s)}$ increases greatly, and the solubility of $Mg(OH)_2$ is also lower. This is appropriate for boiler feed waters and for steam generators. Figure 8.7 shows a family of curves depicting silica removal for initial contents up to 50 ppm, and for various quantities of Mg hardness removed or MgO added. The chemistry of silica removal by $Mg(OH)_{2(s)}$ is unclear. Magnesium silicate [e.g., Mg_2SiO_4 (forsterite)], may be formed, but the most probable mechanism is simple adsorption of H_4SiO_4 onto the surface of $Mg(OH)_{2(s)}$.

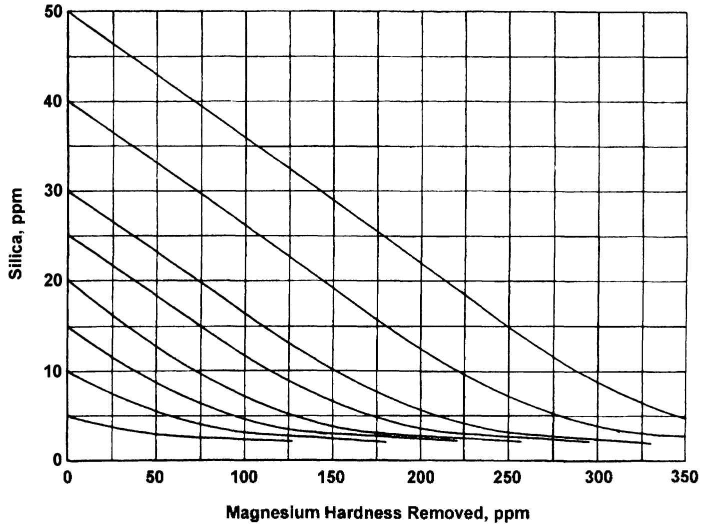


Figure 8.7. Silica removed by precipitation of magnesium in hot-process softening. Reproduced from Powell,[2] courtesy of the McGraw-Hill Book Company.

DESCRIPTIVE WATER SOFTENING PROCESSES

Cold Lime–Soda Ash

Current water softening processes by the lime–soda ash method are traced to Thomas Clark, a Scottish professor of chemistry at Aberdeen University.[2,7] In 1841, Clark found that hard waters could be softened by the addition of lime. Later, John Henderson Porter used soda ash in addition to lime. Thus, water softening by this method becomes, essentially, a process of handling the considerable quantities of $CaCO_{3(s)}$ and $Mg(OH)_{2(s)}$ "sludge" from the precipitation reactions. The "cold" process refers to the natural, ambient water temperatures. The "hot" process refers to situations where the water is heated to 100°C or so. Following softening, these waters are employed for boilers or steam generators.

There are four basic types of cold lime–soda ash processes: the sludge blanket, "conventional," "catalyst," and intermittent or batch process. The first three are continuous-flow, whereas the fourth is as the name indicates.

Sludge Blanket Type

There are a number of different designs, but the basic difference between this and the older "conventional" type of process is that this type filters the treated water upward through a suspended sludge blanket of previously formed precipitate.[2,7,19] One of the most common of this type of unit is the Spaulding precipitator (Figure 8.8). In size it may range from capacities of a few thousand to 10 million gal/day per unit. The raw water and treating chemicals are introduced into the top of the inner chamber, where they are thoroughly mixed by means of a centrally disposed, motor-driven, mechanical agitator. Either wet or dry types of feeders may be used. If the wet type is used, the hydrated or slaked lime is fed as a 5% slurry. Where soda ash is also required with the wet type of feeders, it is usually dissolved in and fed with the lime suspension rather than being fed separately. The coagulant is dissolved in and fed from a separate chemical feeder. When dry feeders are employed, separate feeders are used for the lime, soda ash, and coagulant.

The hardness constituents in water react with the added chemicals, and the precipitates are kept in suspension by the agitator. The treated water with the suspended precipitates flows to the bottom of the inner chamber and then rises in the outer chamber. At some point in the outer chamber, a given flowrate prevents the further expansion of the sludge blanket. A sludge blanket level is kept by bleeding off sludge at the same rate as that at which new sludge is formed. The bleeding-off operation is usually performed through a sludge concentrator. The density of the sludge in the blanket ranges about 1–2% solids; however, it will range about 10–15% solids in the concentrator.

Another type of tank based upon the rapid-flow principle is seen in Figure 8.9. It differs in design and operation from the Spaulding precipitator in that the chemicals are added directly to a relatively thick concentration of "sludge" near the bottom of the tank. The raw water is treated with this mixture and is stirred at a velocity higher than, for example, a coagulation tank (see Chapter 6). The purpose of this design is to introduce precipitated material that acts as a "seed." Consequently, larger-sized particles result, with a higher dry solids content.

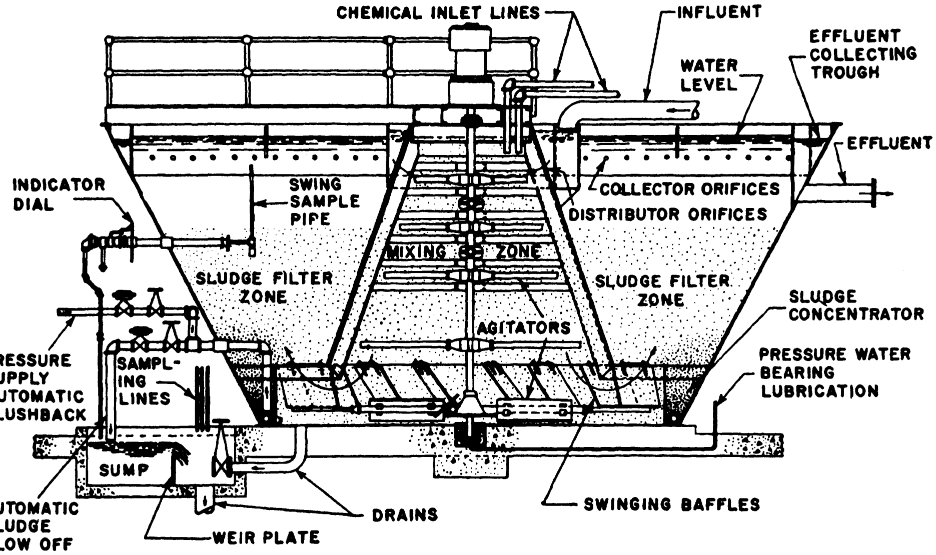


Figure 8.8. Spaulding upward-flow coagulating and clarification tank. Reproduced from Powell,[2] courtesy of the McGraw-Hill Book Company.

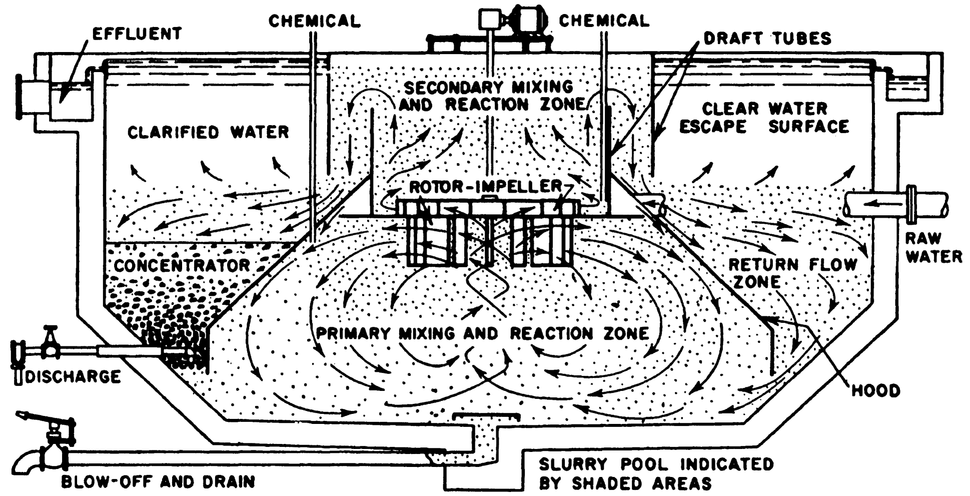


Figure 8.9. Rapid-flow slurry-pool tank. Reproduced from Powell,[2] courtesy of the McGraw-Hill Book Company.

The advantages of the "sludge blanket type" over the "conventional" type include: (1) more intimate and thorough mixing of the lime suspension with the raw water, thereby increasing the rates of chemical reaction and decreasing the waste lime; (2) elimination of "after-precipitation" due to supersaturation and/or incomplete reactions due to the intimate contact of the treated water with a large mass of the solid phase; (3) absence of "after-precipitates," resulting in the production of an effluent clear enough (turbidity usually under 10 ppm) for many industrial applications, often eliminating the use of subsequent filtration equipment; and (4) a briefer detention period (1 hr) than that required by the "conventional" type of equipment (2–4 hr), resulting in a more compact plant occupying less space.

Conventional Type

The term "conventional type" is commonly used to designate a continuous cold lime–soda water softener that does not employ a sludge blanket, but allows sludge to settle to the bottom of a softener. In the design of the "conventional" type, the raw water and chemicals are mixed in a chamber usually provided with a mechanical type of agitator. From the mixing chamber, the treated water with its precipitates flows into a settling basin or basins by gravity. The sludge settles to a solids concentration of 3–7%.

In general, the detention period is 4 hr. Dry chemical feeders are usually employed. Filters are generally used to remove turbidity. Recarbonation with flue gas is generally used to reduce after-precipitation of the carbonates.

Catalyst Type—"Spiractor"

As seen in Figure 8.10, the Spiractor consists of a conical tank which is about two-thirds filled with a finely divided, granular "catalyst." This so-called "catalyst" may be almost any finely granular (0.3 to 0.6 mm diameter) insoluble mineral substance. Crushed and graded calcite was originally employed, but waste greensands are now often used in place of calcite. The tank may be closed, to operate under pressure, or it may be of the open type for gravity operation. In either case, the raw water and chemicals—lime or lime and soda ash—enter near the bottom of the cone and spiral upward through the suspended catalyst bed.

Calcium carbonate formed by the reactions then deposits on the catalyst grains in an adherent form, so that these granules increase greatly in size. Magnesium hydroxide, however, does not form adherent deposits, nor are coagulants of any value in making magnesium deposits adhere. The Spiractor process is, therefore, largely limited to the removal of calcium hardness.

The detention period in a Spiractor is very much less than in any other type of equipment—8–12 min, as compared with 2–4 hr for the conventional type and 1 hr for the sludge blanket type. Also, the by-product is a granular material that drains rapidly to less than 5% moisture. Consequently, its disposal is a much simpler matter than that of the usual lime-soda sludge, which is a pasty material composed of about 90% water.

Hot Lime–Soda Ash

This process differs from the cold lime–soda ash mainly in that the reactions are conducted at elevated temperatures, approximating the boiling point of water. This, of course, increases the rate of the precipitation reactions considerably. Also, the solids are larger and denser, and sedimentation (where appropriate) occurs faster. Finally, this process eliminates the use of lime for neutralization of the $CO_{2(g)}$. The reactors used in the hot lime–soda ash process are the same as those seen in Figures 8.8 through 8.10.[2,7,19]

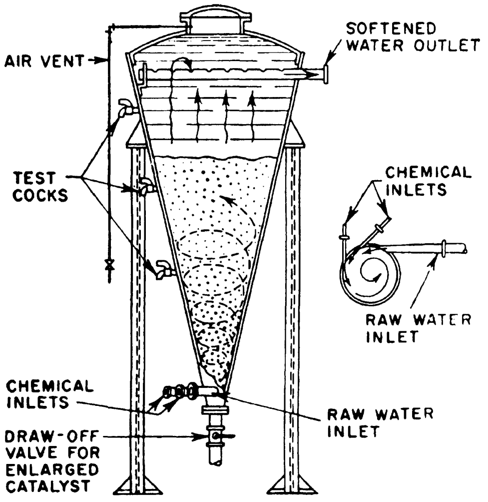


Figure 8.10. Cross-sectional view of the Permutit Spiractor, showing flow. Reproduced from Powell,[2] courtesy of the McGraw-Hill Book Company.

Ion Exchange

Water softening by ion exchange—i.e., the exchange of Ca^{2+} and Mg^{2+} ions for Na^+, H^+, etc.—evolved from the 1756 "discovery" of zeolites by Cronstedt, a Swedish geologist.[7] These naturally occurring minerals are hydrated double silicates consisting of an alkali or alkali-earth oxide, alumina, silica and water. An example is thomsonite: $(Na_2O, CaO) \bullet Al_2O_3 \bullet 2SiO_2 \bullet 2.5\ H_2O$. Almost 100 years later, J. Thomas Way, a chemist for the Royal Agricultural Society of England, published his extensive studies of the ion-exchange properties of zeolites. This work paved the way for today's ion-exchange chromatographic techniques. In 1905, Robert Gans, a German chemist, discovered that zeolites could be used to soften hard waters. He also invented processes for synthesizing zeolites and designed, perhaps, the first zeolite water softener. In 1934 and 1935 new types of cation exchanges became available: the so-called carbonaceous types, made by the sulfonation of coal and the sulfonated synthetic resins. Later work led to the development of sulfonated styrene types of resins. These are made by sulfonation of a resin produced in a bead form by the copolymerization of styrene and divinylbenzene (Figure 8.11).

Principles of Operation

There are four major classes of ion exchange resins: strongly acidic and weakly acidic cation exchangers, and strongly basic and weakly basic anion exchangers. The "strength" of the resin refers to the type of functional group that holds the exchangeable cation or anion. The exchangeable counterion of an acidic cation resin is either H^+ or a monovalent cation such as Na^+. For a basic anion resin, the exchangeable counterion is either OH^- or some other monovalent anion, e.g., Cl^-. These resins are regenerated, therefore, with an acid, a base, or a salt. Typical exchange reactions are:

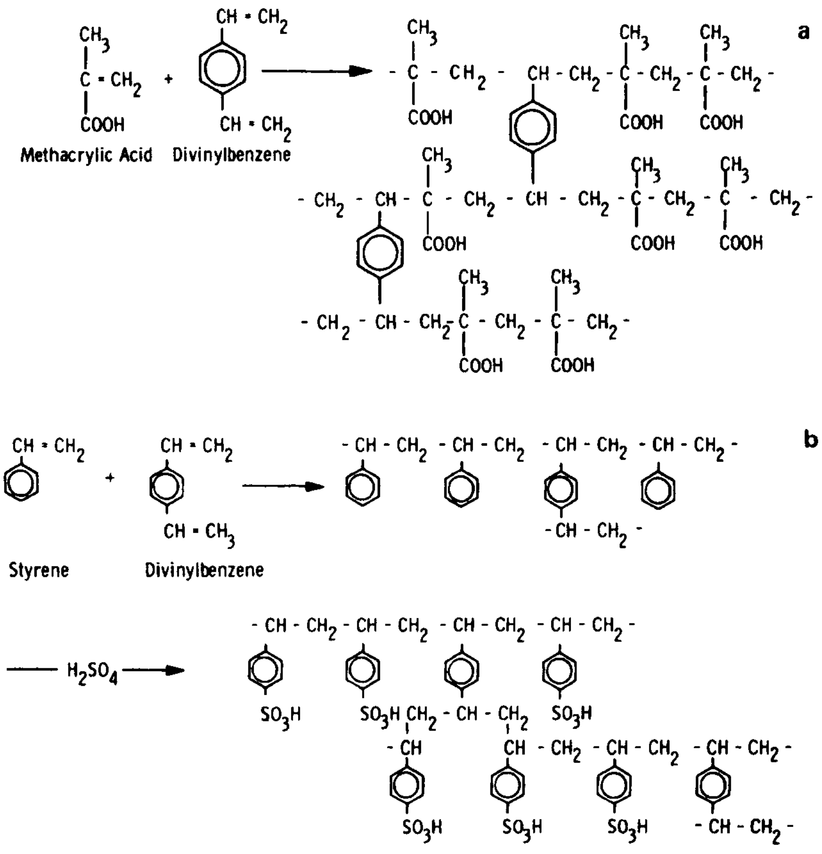


Figure 8.11. Preparation of a cation exchange resin by polymerization of (a) an organic electrolyte (polymerization of methacrylic acid, with divinylbenzene cross-linking); and (b) a neutral organic molecule followed by addition of functional groups (polymerization of styrene, with divinylbenzene crosslinking followed by sulfonation). Reproduced from Weber,[25] courtesy of John Wiley & Sons, Inc.

Strongly acidic cation exchangers:

(1) hydrogen form, regenerate with HCl or H_2SO_4

$$2R - SO_3H + Ca^{2+} = (R-SO_3)_2Ca + 2H^+ \tag{49}$$

(2) sodium form, regenerate with NaCl

$$2R - SO_3Na + Ca^{2+} = (R-SO_3)_2Ca + 2Na^+ \tag{50}$$

Weakly acidic cation exchangers:

(1) hydrogen form, regenerate with HCl or H_2SO_4

$$2R - COOH + Ca^{2+} = (R-COO)_2Ca + 2H^+ \tag{51}$$

(2) sodium form, regenerate with NaOH

$$2R - COONa + Ca^{2+} = (R-COO)_2Ca + 2Na^+ \tag{52}$$

Strongly basic anion exchangers:

(1) hydroxide form, regenerate with NaOH

$$\begin{aligned} 2R - R_3NOH + SO_4^{2-} &= \\ (R-R_3N)_2SO_4 + 2OH^- & \end{aligned} \tag{53}$$

(2) chloride form, regenerate with NaCl or HCl

$$2R - R_3NCl + SO_4^{2-} = (R-R_3N)_2SO_4 + 2Cl^- \tag{54}$$

Weakly basic anion exchangers:

(1) free base or hydroxide form, regenerate with NaOH, NH_4OH, or Na_2CO_3:

$$\begin{aligned} 2R - NH_3OH + SO_4^{2-} &= \\ (R-NH_3)_2SO_4 + 2OH^- & \end{aligned} \tag{55}$$

(2) chloride form, regenerate with HCl

$$2R - NH_3CL + SO_4^{2-} = (R-NH_3)_2SO_4 + 2Cl^- \quad (56)$$

The R refers to one of the polymers in Figure 8.11 that hold the functional groups. Chemical classification and dissociation constants are seen in Figure 8.12 for the various types of ion exchange resins.

The general order of selectivity of ion exchange is given in Table 8.7a for waters less than 1000 mg/L TDS.[19] On the basis of these selectivity coefficients, relative affinities of ions for an ion exchanger can be quantitatively evaluated. This suggests that an order can be established for ions of the same valence on the basis of their selectivity coefficients. The affinity of an ion for a resin can be generalized by the following rules:[20]

1. In general, ions of high valence are preferred over ions of low valence; i.e., the extent of the exchange reaction increases with increasing ion valence (e.g., $Fe^{3+} > Mg^{2+} > Na^+$; $PO_4^{3-} > SO_4^{2-} > NO_3^-$). This preference increases with a decrease in the total ionic concentration of the solution.
2. For ions of the same valence, the extent of the exchange reaction increases with decreasing hydrated radius and increasing atomic number (e.g., $Ca^{2+} > Mg^{2+} > Be^{2+}$; $K^+ > Na^+ > Li^+$). This type of response is a result of swelling pressure within the resin. Ions of larger hydrated radius increase the swelling pressure within the resin and decrease the affinity of the resin for such ions.
3. For a solution with a high total ionic concentration, the extent of the exchange reaction follows no general rule and is often reversed. This type of response is the basis for the reversibility of regeneration.
4. The relationship between the degree of cross-linking and the size of the hydrated ion may affect the extent of the exchange reaction. If the resin has a high degree of cross-linking, the ion may be too large to penetrate into the matrix of the resin.

Equilibria

Equations 49–56 are written as equilibrium reactions; that is, the reactions are reversible for the exchange of ions in solution and ions attached to a resin matrix. There are several approaches for the quantitative description of ion-exchange equilibria. In short, these equilibria are treated either as a chemical reaction, i.e., the law of mass action is applied to describe the distribution of ions between the resin phase and solution phase,[21] or they are treated as membrane exclusion phenomena, i.e., the Donnan equilibrium model of membranes is applied.[22]

A generalized reaction suffices for a cation exchange:

$$\underset{\text{solution}}{C^{x+}} + \underset{\text{resin}}{x(R^-)D^+} = \underset{\text{solution}}{xD^+} + \underset{\text{resin}}{(R^-)_xC^{x+}} \quad (57)$$

The law of mass action accords the relation:

$$K_D^C = \frac{(D^+)^x\,((R^-)_xC^{x+})}{(C^{x+})\,((R^-)D^+)^x} \quad (58)$$

where $(D^+)^x, (C^{x+})$ = the activities of D and C, respectively, in solution

$((R^-)_xC^{x+}), ((R^-)D^+)$ = the corresponding activities of the ions in the resins

The K_D^C in Equation 58 is not strictly an equilibrium constant, but a ratio of ions in solution and in the resin phase. An "apparent equilibrium constant" may be derived from Equation 58 by inserting the appropriate activity coefficients, γ_i. This may be simplified by assuming that the γ_i values for ions in natural freshwaters are close to unity. Thus, the activities of C and D may be replaced by their respective molar concentrations $[C^{x+}]$ and $[D^+]^x$. It is somewhat more difficult to assume unity for the γ values for ions in the resin phase because ion contents may be several molal. This is circumvented by an experimentally determined equivalent ionic fraction, y_i. The equivalent ionic fraction of a counterion species in a given phase (solution of resin) is defined as the ratio of equivalents of that species to all counterion species in the given phase. Consequently, Equation 58 may be written:

$$K_D^C = \frac{[D^+]^x\,(y_{RxC})(\gamma_{RxC})}{[C^{x+}]\,(y_{RD})^x\,(\gamma_{RD})^x} \quad (59)$$

Rearranging,

$$\frac{[D^+]^x\,(y_{RxC})}{[C^{x+}]\,(y_{RD})^x} = K_D^C\,\frac{(\gamma_{RD})^x}{(\gamma_{RxC})} \quad (60)$$

The left side of Equation 60 is obtained experimentally and is the "apparent equilibrium constant," K_{app}. The literature contains values of K_{app} for specific systems which, in turn, may have limited use for water softening. Nevertheless, the equilibrium aspect of ion exchange phenomena is emphasized here.[23,24] The reader is referred to the literature[23–25] for details of the Donnan membrane theory.

Resin Characteristics

Several hundreds of different resins are available from U.S. (Table 8.7b) and European manufacturers.[27] Those

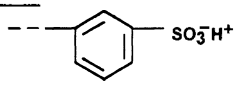
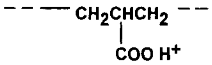
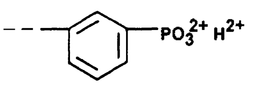
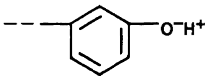
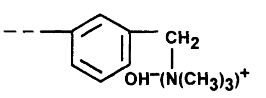
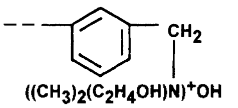
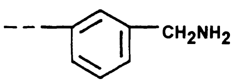
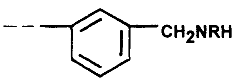
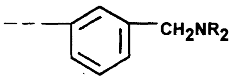
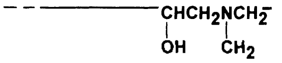
Classification	*Active Groups*	*Dissociation Constant pK_a*	*Typical Configuration*
	Cation Exchange Resins		
Strong acid:	**Sulfonic**	**1**	 $SO_3^-H^+$
	Methylene sulfonic	**1**	$-\,-\,-CH_2SO_3^-H^+$
Weak acid:	**Carboxylic**	**4-6**	 $-\,-\,-CH_2\underset{COO\ H^+}{CH}CH_2-\,-$
	Phosphonic	**2-3 7-8**	 $PO_3^{2+}H^{2+}$
	Phenolic hydroxyl	**9-10**	 O^-H^+
	Anion Exchange Resins		
Strong base:	**Quarternary ammonium (type I)**	**13**	 CH_2, $OH^-(N(CH_3)_3)^+$
	(type II)		 CH_2, $((CH_3)_2(C_2H_4OH)N)^+OH$
Weak base:	**Primary amine**	**6-9**	 CH_2NH_2
	Secondary amine	**7-9**	 CH_2NRH
	Tertiary amine (aromatic matrix)	**9-11**	 CH_2NR_2
	(aliphatic matrix)		 $-\,-\,-\underset{OH}{CH}CH_2\underset{CH_2}{N}CH_2^-$

Figure 8.12. Chemical classification and dissociation constants of ion exchange resins.[19]

resins based on polystyrene divinylbenzene have the widest application. Representative ranges of properties of these resins are seen in Tables 8.7c and d for the two major categories of resins used in drinking water treatment.[20] Ion exchange capacity is expressed in meq/mL (wet-volume capacity) since resins are installed on a volumetric basis (meq/mL × 0.0458 = kgr $CaCO_3/ft^3$). Frequently, capacities are expressed as meq/g (dry), kgr/ft^3, and lb/ft^3.

The "operating" capacity is a measure of the actual performance of a resin under a defined set of conditions that includes such items as feedwater composition, service rate, and degree of regeneration. This operating capacity is always less than the advertised exchange capacity because of incomplete regeneration and contamination leakage. Table 8.9 shows some example operating capacities during softening, where the operating capacity is seen to be a function of the amount of regenerant used.

Design and Operation

For water softening, the columnar flow-through system is utilized throughout municipal, industrial, and domestic situations. A typical unit is seen in Figure 8.13. For most situations, the sodium form of the resins is employed. In accord with Equation 50, Ca^{2+} and Mg^{2+} ions in the raw water are exchanged for the Na^+ ion. Such other multivalent ions as Fe^{2+} are exchanged also for Na^+. Most of the Na^+ ions in the resin are eventually exchanged by the counterions,

Table 8.7a. General Order of Ion Selectivity in Waters With Less Than 1000 mg/L TDS.[19]

Cations		Anions
Fe^{3+}	Exchanged first	CrO_4^{2-} [a]
Al^{3+}		SO_4^{2-} [a]
Pb^{2+}		SO_3^{2-} [a]
Ba^{2+}		HPO_4^{2-} [a]
Sr^{2+}		CNS^-
Cd^{2+}		CNO^-
Zn^{2+}		NO_3^-
Cu^{2+}		NO_2^-
Fe^{2+}		Br^-
Mn^{2+}		Cl^-
Ca^{2+}		CN^-
Mg^{2+}		HCO_3^-
K^+		$HSiO_3^-$
NH_4^+		OH^-
Na^+		F^-
H^+		
Li^+	Exchanged last	

[a] These may be displaced as they are protonated at low pH to $HCrO_4^-$, HSO_3^-, and $H_2PO_4^-$.

Table 8.7b. Ion Exchangers Available in the United States.[27]

Rohm & Haas Amerlite	Dow Chemical Dowex	Sybron Corp. Ionac	Rohm & Haas Duolite
	Cation		
IR–120 plus	HGR–S	C–249	C–20
IR–122	HGR	C–250	C–20 X 10
IR–130C	HGR–W2	C–298	C–225
IR–132C	HGR–W2	C–299	C–225 X 10
IR–200,252	MSC–1	CFP–110	C–26
IRC–50,84	MWC–1	CC,CNN	C–464,433
	Anion		
IRA–400	SBR	ASB–1	A–109
IRA–402	SBR–P	ASB–1P	A–101D
IRA–410	SAR	ASB–2	A–104
IRA–900	MSA–1	A–641	A–161
IRA–401S	Dowex 11	—	A–143
IRA–910	MSA–2	A–651	A–162
IRA–93,94	MWA–1	AFP–328,329	A–368,378
IRA–47	WGR–1,2	A–305	A–340,A–30B

whereupon the capacity for softening becomes "exhausted." The unit then is removed from service, backwashed to remove any particulate matter, and regenerated to the Na cycle by passing a concentrated solution of NaCl through the bed. A rinse with water is needed to remove excess NaCl. Downflow rates of the hard water are in the range of 2–8 gpm/ft^2 of resin.

It is necessary to know the capacity of the resin bed and the process efficiency. The "theoretical" capacity of a resin is the equivalent number of exchangeable sites per unit volume or unit weight of resin. However, the practice is to operate the unit at a level less than theoretical. The exchange reactions, Ca^{2+} and Mg^{2+} for Na^+, and the regeneration reactions, Na^+ for Ca^{2+} and Mg^{2+}, are equilibrium reactions. It would be time-consuming either to operate the bed to complete exhaustion or to regenerate to 100% capacity. The latter would require large quantities of salt for the Na cycle, or acid for the H cycle.

Table 8.7c. Effect of Degree of Cross-Linking on Relative Affinities of Various Cations for Polystyrene Cation Exchange Resins.[20]

	% Divinylbenzene		
Ion	**4**	**8**	**15**
	Monovalent Cations		
H	1.0	1.0	1.0
Li	0.9	0.85	0.81
Na	1.3	1.5	1.7
NH_4	1.6	1.95	2.3
K	1.75	2.5	3.05
Rb	1.9	2.6	3.1
Cs	2.0	2.7	3.2
Cu	3.2	5.3	9.5
Ag	6.0	7.6	12.0
	Divalent Cations		
Mn	2.2	2.35	2.5
Mg	2.4	2.5	2.6
Fe	2.4	2.55	2.7
Zn	2.6	2.7	2.8
Co	2.65	2.8	2.9
Cu	2.7	2.9	3.1
Cd	2.8	2.95	3.3
Ni	2.85	3.0	3.1
Ca	3.4	3.9	4.6
Sr	3.85	4.95	6.25
Hg	5.1	7.2	9.7
Pb	5.4	7.5	10.1
Ba	6.15	8.7	11.6

Note: The constants given in this table are referred to H^+.

The degree of theoretical capacity is called the "degree of column utilization," which is the ratio of the practical operation to the theoretical exchange capacity.[28] "Efficiency" designates the degree of utilization of the regenerant. Column efficiency, therefore, is the ratio of the operating exchange capacity of a unit to the exchange that, theoretically, could be obtained from a given weight of applied regenerant. Consequently, higher efficiencies are realized with lower levels of regeneration, but this is at the loss of bed capacity. In actual practice, some efficiency is sacrificed in order to obtain a reasonable column utilization. According to Nordell,[7] levels of regeneration are usually 3–10 lb of NaCl/ft^3 of resin, which represent efficiencies of 70–45% and column utilizations of 30–65%. Table 8.10 shows some typical relationships among regeneration level, efficiency, and column utilization. They were calculated[28] from some data from Kunin[25] for Amberlite IR-120, a raw water hardness of 500 mg/L as $CaCO_3$, a hydraulic loading of 2 gpm/ft^3 and a regenerant solution of 10% NaCl.

Table 8.7d. Relative Affinities of Various Anions for Polystyrene-Based Strong-Base Anion Exchange Resins.[20]

	Relative Affinity	
Ion	**Type I[a]**	**Type II[b]**
Hydroxide (reference)	1.0	1.0
Benzenesulfonate	500.0	75.0
Salicylate	450.0	65.0
Citrate	220.0	23.0
Iodide	175.0	17.0
Phenoxide	110.0	27.0
Bisulfate	85.0	15.0
Chlorate	74.0	12.0
Nitrate	65.0	8.0
Bromide	50.0	6.0
Bromate	27.0	3.0
Nitrite	24.0	3.0
Chloride	22.0	2.3
Bicarbonate	6.0	1.2
Iodate	5.5	0.5
Formate	4.6	0.5
Acetate	3.2	0.5
Fluoride	1.6	0.3

[a] Reactive group, $-CH_2N{\bullet}(CH_3)_3$.

[b] Reactive group, $-CH_2N{\bullet}(CH_3)_2OH$.

Note: The constants given in this table are referred to OH^-.

A typical calculation for the sizing of a sodium ion exchange system is given in Example Problem 8.7. These calculations take into consideration "leakage" of the hardness cations into the softened water. This may occur either from incomplete regeneration of the resin or from operation of the bed to, or near, complete exhaustion. The average hydraulic flowrate is 833 gpm/196 ft^3=4.25 gpm/ft^3, or 6.12 gpm/ft^3 at peak flow. The reader is directed to References 2, 7, 20, 26, and 27 for complete details on the design of many kinds of available ion exchange systems for domestic, municipal, and industrial applications.

Example Problem 8.7: Sample Calculation of Sodium Exchange System[a]

Water Analysis: Total hardness=200 mg/L, allowable leakage=3 mg/L, TE[b]=300 mg/L.

Plant Requirements: 1,200,000 gpd=average flow of 1,200,000/1440=833 gpm; must accommodate extended peak flow of 1200 gpm.

1. Calculation of required size to handle 1200 gpm. Use three 10 ft diameter units.
2. Calculation of required resin volume.
   (a) Required capacity in kilograins:
   Hardness=200 mg/L; 200/17.1=11.7 gr/gal, 1,200,000×11.7/1000=14,035 kgr/day.
   Schedule all three units to be regenerated each shift.
   ∴ Required capacity=14,035/3=4678 kgr total
   4678/3 units=1560 kgr/unit

Table 8.8. Properties of Styrene Divinylbenzyl, Gel-Type Strong-Acid and Strong-Base Resins.[26]

Note	Strong Acid	Type 1 Strong Base
Screen size, U.S. mesh	−16 + 50	−16 + 50
Shipping weight, lb/ft^3 (kg/m^3)	53 (850)	44 (700)
Moisture content, %	45–48	43–49
pH range	0–14	0–14
Maximum operating temperature, °F (°C)	280 (140)	OH^- form 140 (60) Cl^- form 212 (100)
Turbidity tolerance, ntu	5	5
Iron tolerance, mg/L as Fe	5	0.1
Chlorine tolerance, mg/L as Cl_2	1.0	0.1
Backwash rate, gpm/ft^2 (m/h)	5–8 (12–20)	2–3 (4.9–7.4)
Backwash period, min	5–15	5–20
Expansion volume, %	50	50–75
Regenerant and concentration[a]	NaCl, 3–12%	NaCl, 1.5–12%
Regenerant dose, lb/ft^3 (kg/m^3)	5–20 (80–320)	5–20 (80–320)
Regenerant rate, gpm/ft^3 (min/BV)	0.5 (15)	0.5 (15)
Rinse volume, gal/ft^3 (BV)	15–35 (2–5)	15–75 (2–10)
Exchange capacity,[b] kgr $CaCO_3$/ft^3 (meq/mL)	39–41 (1.8–2.0)	22–28 (1–1.3)
Operating capacity,[c] kgr $CaCO_3$ft^3/ft^3 (meq/mL)	20–30 (0.9–1.4)	12–16 (0.4–0.8)
Service rate, gpm/ft^3 (BV/h)	1–5 (8–40)	1–5 (8–40)

[a] Other regenerants such as H_2SO_4, HCl, and $CaCl_2$, can be used for SAC resins, while NaOH, KOH, and $CaCl_2$ can be used for SBA regeneration.

[b] Kilograins of $CaCO_3$ per cubic foot are the units commonly reported in resin manufacturer literature. To convert kgr $CaCO_3$/ft^3 to meq/mL, multiply by 21.8.

[c] Operating capacity depends on method of regeneration, particularly on the amount of regenerant applied. See Table 8.9.

Table 8.9. Softening Capacity as a Function of Regeneration Level[a].[26]

Regeneration Level		Hardness Capacity		Regeneration Efficiency	
lb NaCl ft^3 Resin	kg NaCl m^3 Resin	kg $CaCO_3$ ft^3 Resin	Equiv $CaCO_3$ L Resin	lb NaCl kgr $CaCO_3$	Equiv NaCL Equiv $CaCO_3$
4	64	17	0.78	0.24	1.40
6	96	20	0.92	0.30	1.78
8	128	22	1.00	0.36	2.19
10	160	25	1.14	0.40	2.38
15	240	27	1.24	0.56	3.30
20	320	29	1.33	0.69	4.11
∞	∞	45	2.06	∞	∞

[a] These operating capacity data are based on the performance of Amberlite IR–120 SAC resin. Other manufacturers' resins are comparable. Values given are independent of EBCT and bed depth, providing the minimum criteria are met. kgr is kilograins.

(b) Allowable leakage=3 mg/L

This leakage can be achieved @ 6 lb NaCl/ft^3. (Actual leakage @ 6 lb/ft^3 will be only 1.5 mg/L H)[c]

Capacity at 6 lb/ft^3=20 kgr/ft^3

∴ Required resin=1560/20=78 ft^3 minimum

(c) Bed depth: Area of 10 ft diameter unit=78.5 ft^2; therefore, bed would be approximately 1 ft deep. To achieve the desired leakage, minimum bed depth is 30 in.; therefore, each unit requires:

2.5 ft deep × 78.5 ft^2 area=196 ft^3

(d) The actual regeneration period will be:

$$\frac{196\ \text{ft}^3 \times 3\ \text{units} \times 20\ \text{kgr}/\text{ft}^3}{14{,}035\ \text{kgr}/\text{day}} = 0.84\ \text{day}$$

$$0.84 \times 24\ \text{hr} = 20\ \text{hr}$$

or one unit will be regenerated every 6.66 hr

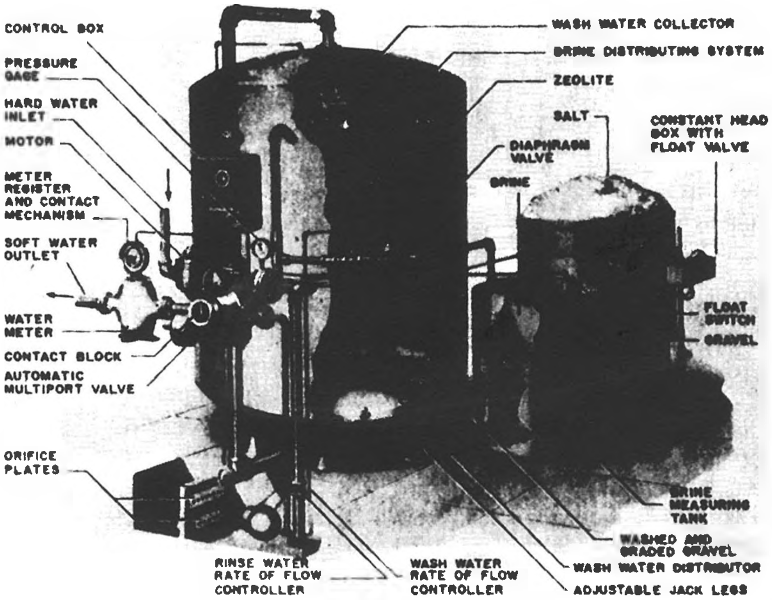


Figure 8.13. Automatic-pressure zeolite softener, showing brine distributor, mineral bed, and underdraining system. Reproduced from Powell,[2] courtesy of the McGraw-Hill Book Company.

Table 8.10. Efficiency and Column Utilization as a Function of Regeneration Level.[a]

Regeneration Level (lb NaCl/ft^3 Resin)	Hardness Removed (lb CaCO$_3$/ft^3 resin) Theoretical[b]	Actual	Regeneration Efficiency (%)	Column Utilization[c] (%)
1	0.85	0.83	98	14
2	1.70	1.32	78	22
3	2.55	1.83	72	30
5	4.25	2.85	67	47
10	8.50	3.90	46	64
15	12.75	4.65	36	76
20	17.00	5.00	29	82

[a] Reproduced from Weber,[28] courtesy of John Wiley & Sons, Inc.
[b] Based on quantity of NaCl used.
[c] Based on total exchange capacity of resin of 6.1 lb/ft^3.

3. Salt consumption @ 6 lb salt-20 kgr/ft^3
   6/20=0.3 lb/kgr (2.1 mg/L salt/mg/L hardness), 14,035 kgr/day × 0.3 lb NaCl/kgr = 4200 lb NaCl; this requires bulk deliveries for practical handling by plant labor.

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[a] Reproduced from Kemmer,[27] courtesy of the McGraw-Hill Book Company.
[b] TE = total electrolyte.
[c] H = hardness.

Typical water softening data are seen in Table 8.11 for the Mississippi River.[2] This is an example of a combined treatment, i.e., the raw water is softened first by the cold lime–soda ash process, which is followed by ion exchange. It should be noted that the sodium content of the softened water has been increased and 2.2 mg/L of silica has been removed. Here again, operation results will vary in accord with the choice of the ion exchange system.

Selection of the softening process(es) is dictated largely by economic considerations. Many combinations of chemical precipitation and ion exchange systems can be devised. The cold lime–soda ash method can reduce concentrations of Ca^{2+} and Mg^{2} to approximately 50±20 mg/L as CaCO$_3$. Ion exchange can reduce this to near the zero level. In general, 50 mg/L is acceptable for municipal drinking waters, whereas many industrial applications require zero hardness.

Table 8.11. Cold-Process Lime Softening, Silica Removal, and Zeolite Softening of Mississippi River Water.[a]

Constituents	Raw (mg/L)	Lime Softened (mg/L)	Zeolite Softened (mg/L)
As $CaCo_3$:			
Calcium	118.0	91.0	1.0
Magnesium	40.0	18.0	1.0
Total hardness	158.0	109.0	2.0
Sodium	84.0	84.0	191.0
Total cations	242.0	193.0	193.0
Sulfate	44.0	73.0	73.0
Chloride	96.0	96.0	96.0
Mineral-acid ions	140.0	169.0	169.0
Bicarbonate	102.0	0	0
Carbonate		24.0	24.0
Total anions	242.0	193.0	193.0
Silica	5.7	3.5	3.5
pH 8.0	10.0	10.0	

[a] Reproduced from Powell,[2] courtesy of the McGraw-Hill Book Company.

Almost all domestic waters are softened by ion exchange where it is unnecessary to achieve a zero hardness level. If the latter prevails, the water frequently becomes corrosive to copper pipes due to $CO_{2(g)}$ acidity (see Chapter 10). Domestic softeners should be designated to reduce hardness levels to 50 to 75 mg/L as $CaCO_{3(s)}$.

According to Weber:[28]

> Raw water conditions and operating factors favoring the use of ion exchange include: (a) low color and turbidity levels, (b) hardness largely not associated with carbonate alkalinity, (c) raw water hardness variable, (d) equipment relatively simple to operate, and (e) no sludge disposal problems. Factors favoring use of chemical precipitation include: (a) raw water requires clarification in any event, and (b) hardness largely balanced by carbonate alkalinity.

Ion exchange processes do have the brine disposal problem, which may be solved by dilution with surface waters, discharge into a sanitary sewer, discharge into evaporation ponds, or injection into brine disposal wells.

Variations of Exchanger Systems

Figure 8.14 shows six cycles or modes of ion exchange systems for municipal and industrial operations. Cycle 1 is used for boiler feed waters, whereas cycle 2 is applied for the same purpose when a "high" quality water is required. Cycles 3 and 4 are used for $CO_{2(g)}$ and silica removal. Here the water passes through a H-cation exchanger that converts all carbonates to H_2CO_3 which, in turn, is removed by neutralization on the strongly basic anion exchanger or by degasification. Silica is reduced to the range of 0.05 to 0.2 mg/L by the strongly basic anion exchanger. Cycle 5 is a highly unique and speciality system. Cycle 6 is a mixed bed of cation and anion exchangers. The resins frequently are in the H and OH cycles, respectively. This yields demineralized water. Many of these cycles carry trade names from the various manufacturers of ion exchange resins and the concomitant equipment.

Operation Modes

The fixed ion exchange beds can be operated on a downflow or an upflow mode for service, and the same for regeneration. When service is in one direction and regeneration is in the opposite direction, the operation is called *countercurrent ion exchange.* When both service and regeneration are in the same direction, this is called cocurrent ion exchange. These operations are seen in Figure 8.15. Countercurrent ion exchange is preferred for strong-acid cation or strong-base anion exchangers, according to some operations.[29] Apparently, there is a relatively unfavorable equilibrium in the regeneration of these resins. In this case, the resin has a very high affinity for the exchanged ions and requires a considerable excess of regenerant to restore the resin. Even an excess of regenerant will not restore the resin at the effluent end of the column. This will result in a significant column leakage at the beginning of the next service run (see Figure 8.15).

The following advantages of countercurrent ion exchange over cocurrent ion exchange for strong ionic resins are:[29] (a) lower leakage of ions during service, (b) lower consumption of regenerants, (c) decrease in quan-

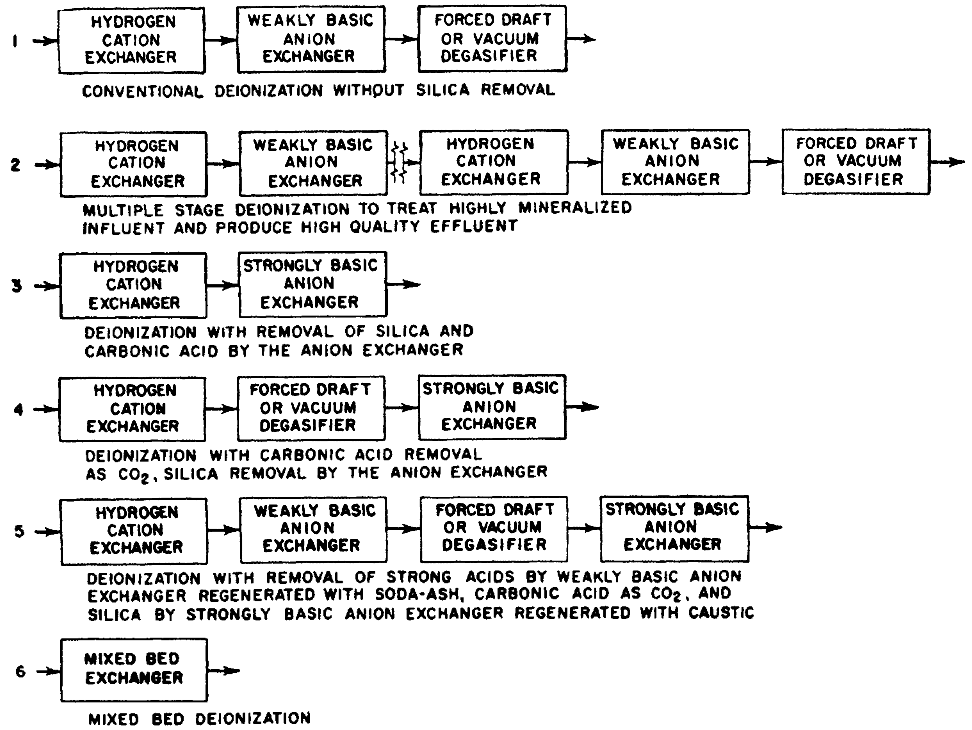

Figure 8.14. Flowsheet showing arrangements of deionization cycles used for water purification. Reproduced from Powell,[2] courtesy of the McGraw-Hill Book Company.

tity of regenerant wastes, and (d) lower consumption of water for rinse and backwash.

Countercurrent operation is less advantageous with weak ionic resins.[29]

Case Studies—Split Treatment

One of the treatment options for water softening by lime–soda ash (and ion exchange, for that matter) is split treatment. Only a portion of the water is softened and then is combined with unsoftened water before being discharged into the distribution system. The case study below points to the several advantages of this method over the conventional lime–soda ash treatment.

Owosso, Michigan[30] draws its water supply from several deep wells wherein the Ca^{2+} hardness is approximately 290 mg/L as $CaCO_3$, and the Mg^{2+} hardness is about 130 mg/L as $CaCO_3$. Most is carbonate hardness. In 1972 their facilities were upgraded for conventional and split (75%) treatments with lime–soda ash (Figure 8.16). Prior to this, there were operating problems caused by sludge deposits in the recarbonation basins and filter-influent piping, which were cleaned every six months or so. Filter runs were as short as 12 hr. In-plant rests were conducted to account for these operational problems. First, it was discovered that the Langelier Index (LI) was in the +0.2 to 0.8 range, which was consistent with the sludge deposits (mainly $CaCO_3$) (see Chapter 10). Second, an attempt was made to redissolve this sludge through a negative LI by recarbonation. A poor $CO_{2(g)}$ transfer efficiency caused the failure of this test, whereupon it was decided to soften about 75% of the water.

Split treatment requires a $[OH^-]$ of sufficient magnitude to precipitate all of the magnesium to prevent additional formation of $Mg(OH)_2$ after the waters are recombined. Appropriate calculations were made for the split-treatment dosages of lime, soda ash, and $CO_{2(g)}$. After several months of experimentation, these conclusions were drawn:

1. Optimum $[OH^-]$ should yield a pH value of 12.1 or 12.2 in the first-stage effluent. $Mg(OH)_2$ apparently was precipitated first.
2. HCO_3^- alkalinity of 50–70 mg/L as $CaCO_3$ is optimum for the secondary effluent. Any content of HCO_3^- above this quantity will result in a greater effluent hardness, caused by dissolution of $CaCO_{3(s)}$.
3. The optimum pH value of the secondary effluent should be 9.2 to 9.5.

Table 8.12 shows the raw and treated water hardness before and after institution of split treatment. In addition to

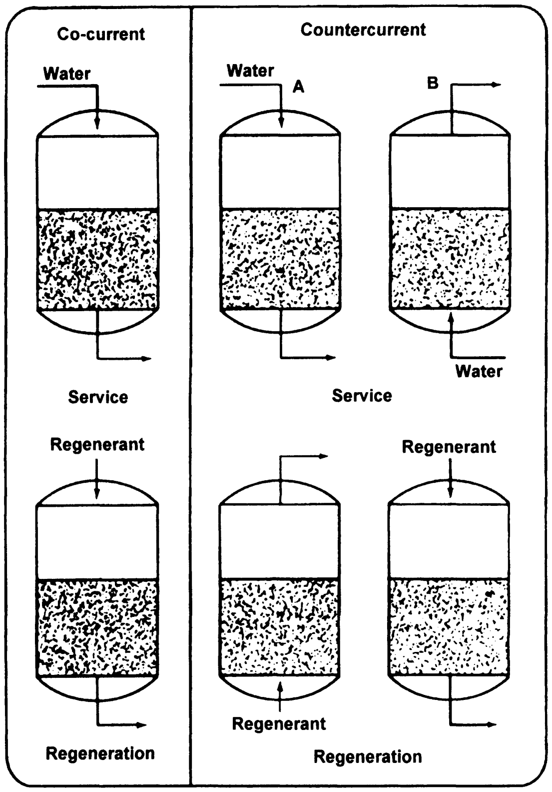

Figure 8.15. Cocurrent and countercurrent ion exchange. By definition, countercurrent operation implies service in one direction and regeneration in the opposite direction. Service can be downflow, as in (A), or upflow, as in (B).[29]

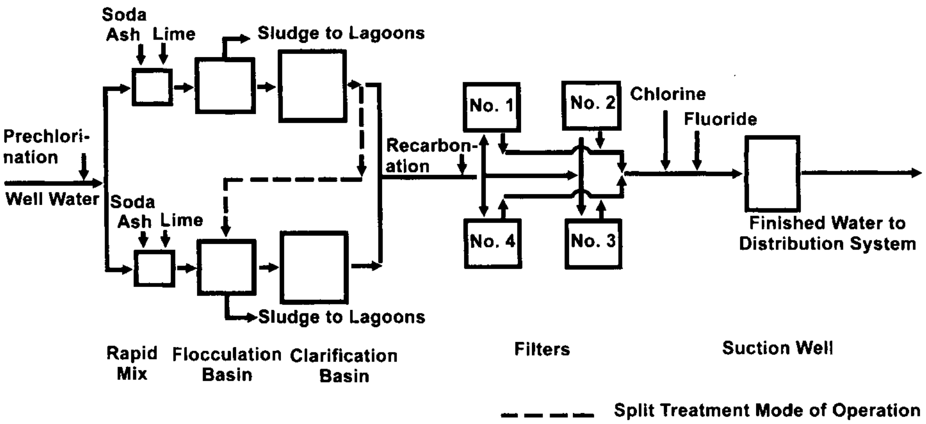

Figure 8.16. Schematic process flow diagram, Owosso, Michigan, water treatment plant. Reproduced from Singhal,[30] courtesy of the American Water Works Association.

the improved water quality, there was a greater efficiency of filter performance.

Split treatment resulted in considerable savings in chemical costs: 25% less lime was used, 13.7% more soda ash was used, and $CO_{2(g)}$ was completely eliminated. All of this yielded a net reduction in chemical costs.

A split-treatment softening has been reported for waters with a "high" magnesium content that removes only

Table 8.12. Summary of Raw and Treated Water Quality at Owosso, Michigan, Water Treatment Plant (April 1973–July 1974).[a]

Year and Month	Raw Water Quality (mg/L $CaCO_3$)			Treated Water Quality (mg/L $CaCO_3$)			Remarks
	Ca^{2+}	Mg^{2+}	Alk.	Ca^{2+}	Mg^{2+}	Alk.	
1973							
April	339	164	368	137	18		Conventional treatment from April 1973 to November 1973
May	302	147	370	135	20		
June	289	152	356	121	44	102	Average soda ash 1006 lb/mil gal 1722 x 10^3 kg/m^3
July	278	143	340	111	56	109	Average lime 4146 lb/mil gal, 7100 x 10^3 kg/m^3
August	288	161	361	112	24	83	Average final hardness 148 mg/L
September	284	137	339	108	20		
October	289	139	341	121	19		
November	289	141	337	105	49	84	
December	290	123	340	85	34	93	Split treatment from December 1973 to July 1974
1974							
January	292	121	343	98	37	105	Average soda ash 1144 lb/mil gal 1900 x 10^3 kg/m^3
February	286	126	341	89	44	113	Average lime 3093 lb/mil gal 5280 x 10^3 kg/m^3
March	284	132	343	63	52	98	Average final hardness 128 mg/L
April	279	115	331	71	55	118	
May	280	134	340	64	52	101	
June	299	133	350	72	58		
July	291	124	345	77	78	81	

[a] Reproduced from Singhail,[30] courtesy of the American Water Works Association.

a portion of the hardness.[31,32] Groundwaters are appropriate because these waters generally do not require a separate stage of treatment for taste, odor, etc. As depicted in Figure 8.17, the water is divided into two streams: one is treated with an excess dose of $Ca(OH)_2$ for "complete" precipitation of the magnesium and some calcium, and one is untreated. These two streams are recombined, whereupon Na_2CO_3 is added to remove additional CaNCH, if desired.

In order to effect split-treatment softening, Zipf and Luthy[31] derived nine basic equations to calculate the lime dosage for Mg removal (ten basic equations are needed if Na_2CO_3 is included). Figure 8.18 shows the acidity mass balance for this treatment as well as the symbolism for the three waters. All concentrations and equilibrium constants (H^+ excepted) are expressed in equivalents of $CaCO_3$ at 25°C and 0.01 *M* ionic strength. The equilibrium equations are:

$$\begin{aligned} HCO_3^- &= H^+ + CO_3^{2-} \\ K_{61} &= 10^{-9.85}(\text{mg/L as } CaCO_3),\ 25^\circ C \end{aligned} \tag{61}$$

$$\begin{aligned} CaCO_3 &= Ca^{2+} + CO_3^{2-} \\ K_{62} &= 10^{2}(\text{mg/L as } CaCO_3) \end{aligned} \tag{62}$$

Combining Equations 61 and 62 gives:

$$\frac{K_{62}}{K_{61}} = \frac{(Ca^{2+})(HCO_3^-)}{(H^+)} \tag{63}$$

From this, a parameter F_1 is obtained:

$$F_1 = (Ca^{2+})(HCO_3^-) \tag{64}$$

and

$$F_1 = \frac{K^{62}}{K_{61}}(H^+) \tag{65}$$

Neglecting (H^+) and (OH^-), alkalinity is expressed:

$$ALK = (HCO_3^-) + (CO_3^{2-}) \tag{66}$$

and

$$ALK = (HCO_3^-)\left(1 + \frac{K_2}{(H^+)}\right) \tag{67}$$

From this, a second parameter, F_2, is obtained:

$$(HCO_3^-) = ALKF_2 \tag{68}$$

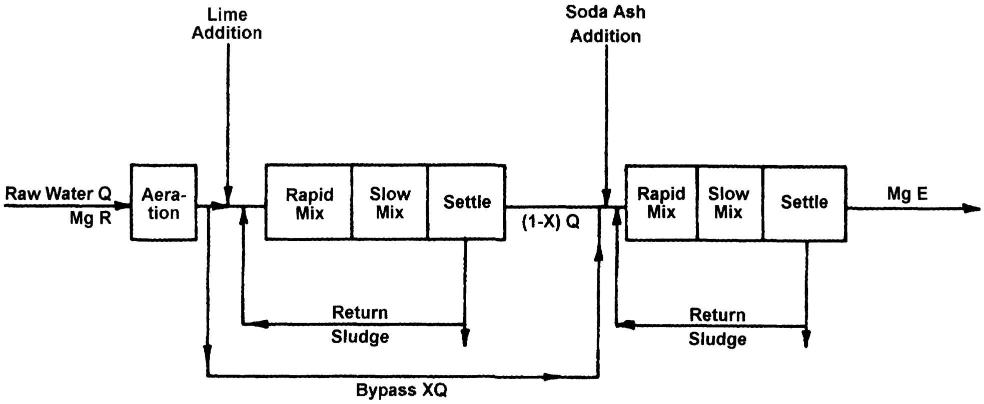

Figure 8.17. Flow diagram for typical split-treatment lime–soda ash softening process. Reproduced from Zipf and Luthy,[31] courtesy of the American Water Works Association.

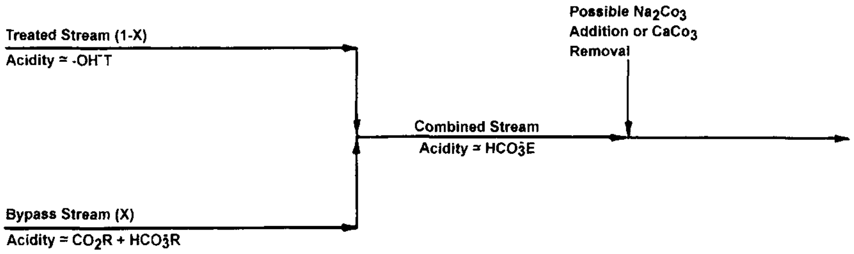

Figure 8.18. Acidity mass balance relationships during split treatment. Reproduced from Zipf and Luthy,[31] courtesy of the American Water Works Association.

where

$$F_2 = \frac{1}{1 + K_2/(H^+)} \qquad (69)$$

Equations 64, 65, 68, and 69 are four of the basic equations. A fifth basic equation is derived from the assumption that all Mg^{2+} in the treated stream is precipitated as $Mg(OH)_{2(s)}$. For purposes of calculation, it can be neglected. Consequently, the effluent $[Mg^{2+}]$ becomes equal to the fraction of Mg in the bypass stream:

$$Mg^{2+}E = X(Mg^{2+}R) \qquad (70)$$

where X is the bypass fraction. The sixth basic equation is:

$$\text{Hardness E} = Ca^{2+}E + Mg^{2+}E \qquad (71)$$

The seventh basic equation is derived from a mass balance for total acidity (ACY) at the point where the treated and untreated streams are combined:

$$ACY = (CO_2) + (HCO_3^-) + (H^+) - (OH^-) \qquad (72)$$

As seen in Figure 8.18, ACY in the treated stream is $-OH^-T$, whereas the ACY in the untreated stream is $CO_2R + HCO_3^-R$. When the pH values are ≥8.2, CO_2R is small compared to HCO_3^-R, whereupon:

$$HCO_3^-E = X(CO_2R + HCO_3^-R) - (1-X)(OH^-T) \qquad (73)$$

This equation is valued for lime or lime–soda ash treatment because the addition or removal of CO_3^{2-} does not affect the effluent's total acidity statement.

The eighth and ninth basic equations are modified conventional lime and soda ash expressions. The lime dosage is modified to account for some Mg^{2+} in the treated water and for HCO_3^- in the effluent. Neglecting CO_2E:

$$Ca(OH)_2 = CO_2R + HCO_3^-R - HCO_3^-E + (1-X)Mg^{2+}R \qquad (74)$$

Soda ash dosage is:

$$\begin{gathered}\mathrm{Na_2CO_3} = \\ \text{Hardness R} - \text{Hardness E} - \text{ALKR} + \text{ALKE}\end{gathered} \tag{75}$$

Equations 74 and 75 apply either to lime or lime–soda ash treatment. A tenth basic equation is needed for lime–soda ash treatment to provide a relation between the effluent hardness and alkalinity. Combining Equations 64, 69, and 70 yields:

$$\text{Hardness E} = \frac{F_1}{\mathrm{HCO_3^-E}} + X(\mathrm{Mg^{2+}R}) \tag{76}$$

From Equation 73:

$$X = \frac{\mathrm{HCO_3^-E} + \mathrm{OH^-T}}{\mathrm{HCO_3^-R} + \mathrm{CO_2R} + \mathrm{OH^-T}} \tag{77}$$

Combining Equation 76 and 77 through the X term:

$$\begin{gathered}\text{Hardness E} = \frac{F_1}{\mathrm{HCO_3^-E}} + \\ (\mathrm{Mg^{2+}R})\left[\frac{\mathrm{HCO_3^-E} + \mathrm{OH^-T}}{\mathrm{HCO_3^-R} + \mathrm{CO_2R} + \mathrm{OH^-T}}\right]\end{gathered} \tag{78}$$

Minimum hardness is obtained by taking the derivative of Equation 78 and equating it to zero:

$$\begin{gathered}\frac{\text{dHardness E}}{\mathrm{dHCO_3^-E}} = \frac{-F_1}{(\mathrm{HCO_3^-E})^2} + \\ \frac{\mathrm{Mg^{2+}R}}{\mathrm{HCO_3^-R} + \mathrm{CO_2R} + \mathrm{OH^-T}} = 0\end{gathered} \tag{79}$$

Rearranging gives the tenth basic equation:

$$\begin{gathered}\frac{F_1}{\mathrm{Mg^{2+}R}}[\mathrm{HCO_3^-R} + \mathrm{CO_2R} + \mathrm{OH^-T}] - \\ (\mathrm{HCO_3^-E})^2 = 0\end{gathered} \tag{80}$$

All this leads to the 10 basic equations and 12 operational variables. Since there are 2 variables more than the 10 equations, they must be selected from the 12, and their values must be set arbitrarily. For example, these "decision variables" may be: hardness E and pH, ALKE and pH, and lime dosage and bypass fraction X.

A solution set for the lime–soda ash treatment is shown by selection of hardness E and pHE as "decision variables." This results in a matrix of variables in the basic equations as seen in Table 8.13. It also gives the partitioning of each variable and the appropriate equation as well as the precedence order of solving these equations. This precedence is achieved by inspection where functions that have only one unknown are computed and eliminated from the matrix. This process continues until all variables and equations are accounted for. The order in which the variables and equations are eliminated becomes the order of the solution set. The matrix is rearranged to reflect this consideration, which gives the correct partitioning and precedence order for the solution set (Table 8.14).

A sample calculation is seen in Table 8.15 for a lime–soda ash treatment with hardness E and pHE as "decision variables." Other examples, in the form of exponential curves, are given in Reference 31. A computer program is available to solve a wide variety of "decision variables." In addition, some general observations about split-treatment were: (1) the bypass fraction may be as high as 0.9;(2) effluent pH values range from 8.0 to 9.4, with 7.8 to 8.0 as minimum values; and (3) $[\mathrm{OH^-}]$ in the treated water is usually a limiting factor, with 50 mg/L as $\mathrm{CaCO_3}$ as a practical lower limit. F_1 and F_2 values are given in Table 8.16.[33]

Sludge Handling and Disposal

The problem posed by sludge disposal from water treatment plants was discussed in two committee reports for the American Water Works Association.[34,35] PL 92-500—the Water Pollution Control Act Amendments of 1972—included these sludges as an industrial waste requiring a discharge permit under the National Pollutant Discharge Elimination System (NPDES). Thus, the previous practice of disposal by direct discharge into a waterway was forbidden.

Sludge Characteristics

Sludges from the lime–soda ash process have a volume ranging from 0.3 to 5% of the raw water treated. The solids content of settled sludge varies widely—from 2 to 30%.[34] Table 8.17 shows the calculated composition of lime–soda ash sludge, which is more or less typical.[36] For this example, $\mathrm{CaCO_{3(s)}}$ was 84.4% of the sludge's total weight. The composition, sludge volumes, and sludge solids, of course, will vary from plant to plant according to raw water hardness, degree of treatment, use of split treatment, etc. Any means of treatment and disposal becomes a problem of handling a by-product, which in most cases is an added cost to treatment of the water.

Table 8.13. Partioned Matrix for Solution of Lime-Soda Split Treatment with Effluent Hardness and pH as Decision Variables.[31]

	Process Variable										
Equation	F_1	F_2	OH^-T	$Ca^{2+}E$	Mg^{2+}	E	HCO_2^-E	X	Alkalinity E	Lime	Soda
7	[x][a]										
11		[x]									
6	x			x		x					
22	x		x			x					
12					x		x				
13				x	x						
15			x			x	x				
10		x				x		[x]			
16						x	x		[x]		
17								x		[x]	

[a] Brackets indicate the precedence order of equations for the solution set.

Table 8.14. Solution Set for Lime and Soda Ash Treatment with Effluent Hardness and pH as Decision Variables.[31]

	Process Variable									
Equation	F_1	F_2	HCO^-_2E	$Ca^{2+}E$	$Mg^{2+}E$	X	OH^-T	Alkalinity E	Lime	Soda
7	[x][a]									
11		[x]								
29	x		[x]							
6	x		x	[x]						
13				x	[x]					
12					x	[x]				
15			x			x	[x]			
10		x	x					[x]		
16			x			x			[x]	
17								x		[x]

[a] Brackets indicate the precedence order of equations for the solution set.

Table 8.15. Sample Calculation for Lime and Soda Treatment with Effluent Hardness and pH as Decision Variables.[a]

Raw Water Characteristics (mg/L as $CaCO_3$ except pH)		Equation	Variable	Result
Hardness	350.0			
Ca^{2+}	250.0	65	F_1	1774.2
Mg^{2+}	100.0	69	F_2	0.9466
Alkalinity	220.6	[b]	HCO_3^-E	96.2
HCO_3^-	220.0	64	$Ca^{2+}E$	20.6
CO_2	78.5	71	$Mg^{2+}E$	49.4
pH	7.28	70	X	0.494
Equilibrium Constants				
log K_2	−9.849	73	O^-HT	121.5
log K_5	2.00 (LSI = 0.0)	68	ALKE	91.0
Select Decision Variables				
Effluent Hardness	70.0	74	$Ca(OH)_2$	263.0
Effluent pH, pH E	8.60	75	Na_2CO_3	150.4

[a] Reproduced from Zipf and Luthy,[31] courtesy of the American Water Works Association.
[b] Equation not given.

Table 8.16. Values of Constants F_1 and F_2 for Various Values of pH.[a]

pH	$F_1=K_{57}(H^+)/K_{56}$	$F_2=1/[1+K_2/(H^+)]$	F_1/F_2
8.0	7080	0.9861	7180
8.2	4467	0.9781	4567
8.4	2818	0.9657	2918
8.6	1778	0.9468	1878
8.8	1122	0.9106	1232
9.0	708	0.8762	808
9.2	447	0.8171	547

[a] Reproduced from Rossum,[33] courtesy of the American Chemical Society.

Table 8.17. Calculated Composition of Primary Sludge.[a]

Sludge Components[b]	ppm	lb/mil gal	% by weight
$CaCO_3$			
From Free CO_2	32	266	
From CH	530	4,420	
From NCH	20	167	
Subtotal	**582**	**4,853**	**84.4**
$Mg(OH)_2$	81	675	11.7
SiO_2	4	33	0.6
Insolubles from Lime		190	3.3
Total lb/mil gal		**5,750**	**100.0**
Total primary and secondary sludge per mil gal=6,900 lb			

[a] Reproduced from Black et al.,[36] courtesy of the American Water Works Association.

[b] Calculations based on free CO_2 in raw water—14 ppm; carbonate hardness in raw water—265 ppm; noncarbonate hardness removed—20 ppm; insolubles in lime, SiO_2, R_2O_3, and MgO—8%.

Treatment Methods

Several methods are available to concentrate, dewater, and dispose of lime softening sludges:

- Gravity thickening
- Nonmechanical dewatering (dewatering lagoons and sand drying beds)
- Mechanical dewatering (centrifugation, vacuum filtration, pressure filtration, and belt filtration)
- Sludge pelletization
- Recalcination
- Codisposal
- Land application

Many of these methods are used in combination to accomplish an overall sludge management plan. Figure 8.19 shows separate or combinations of arrangements. Details of these treatment/disposal methods are given in Reference 37. Examples are given below.

Sludge Dewatering

Reduction of the moisture content of lime–soda ash sludges is a prerequisite for ultimate disposal; that is, the lesser the sludge volume, the lower the cost. Lime sludges can be dewatered to about 50% within a reasonable time period on drying beds.[35] This practice, like lagooning, has the disadvantage of requiring substantial surface area, a climate conducive to drying, and a location for ultimate disposal. An advantage may be the relatively low cost. The Louisville Water Company[38] has had experience with sludge disposal lagoons. An extensive field study revealed the life expectancy of three existing lagoons to be about 21.2 yr instead of the 30–40 yr projected prior to construction. Difficulty with dewatering of the sludge was the apparent reason. This study also provided operational data for the lagoons at temperatures less than 0°C.

Dewatering lime–soda ash sludges by vacuum filtration is reasonably successful, and yields a crumbly cake with a solids content up to 65%.[35] Vacuum filtration of softening

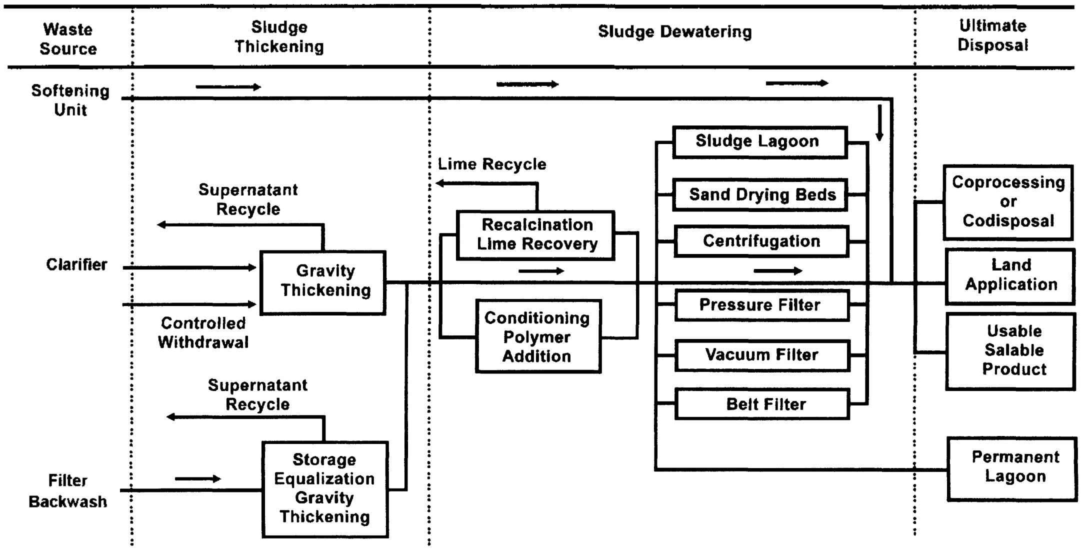

Figure 8.19. Alternative waste treatment and disposal methods.[37]

sludges was evaluated by the specific resistance method.[39] There are two general considerations: (1) sludges high in magnesium content are more difficult to dewater than sludges low in magnesium, and (2) calcium hardness has no significant effect on the filterability of lime-softening sludges.

In other processes, Schwayer and Luttinger[40] describe a dual-cell gravity (DCG) concentrator for mechanical gravity dewatering of softening sludges, especially metal hydroxides. Reh[41] reported the state-of-the-art of water treatment sludge disposal and handling.

Recalcination

A process for recovery of lime and magnesium carbonate from softening sludges was developed at Dayton, Ohio.[36] Briefly described, a mixed sludge of $CaCO_{3(s)}$ and $Mg(OH)_{2(s)}$ is treated with stack gas [20% $CO_{2(g)}$] from a lime kiln. This selectively dissolves the gelatinous $Mg(OH)_{2(s)}$ from the crystalline $CaCO_{3(s)}$, which, in turn, is calcined to $CaO_{(s)}$ (92–93%). The flow diagram of the $MgCO_3$ recovery portion of the process is seen in Figure 8.20.[36] Several benefits were noted from the recovery treatment: (1) cost of softening the water was reduced substantially (by 1970 dollar values and energy costs); (2) for each ton of lime used for softening, 1.2 to 1.3 tons of lime were recovered; the excess was sold; (3) it eliminated disposal of the $CaCO_{3(s)}$ sludge; the recovered $MgCO_{3(s)}$ was discharged into a sanitary sewer; (4) it eliminated also the need for extra-plant supplies of $CO_{2(g)}$ for recarbonation. There was a sufficient supply of this gas from the lime kiln. Thus, recalcination is largely an economic decision.

Coagulation of Sludges

The electrophoretic characteristics of $CaCO_{3(s)}$ and $Mg(OH)_{2(s)}$ have been researched,[42] and the electrophoretic mobility values are given in Figure 8.21. These values are related to the alkaline pH values at which they are formed. For $CaCO_{3(s)}$, electromobility values are in the range of -0.9 to -1.0 µm/sec/V/cm, whereas $Mg(OH)_{2(s)}$ has a slightly positive charge. This positive value is attributed to the formation of $Mg(OH)_{2(s)}$ in the presence of Ca^{2+} ions. Subsequent experiments confirmed this point.

Coagulation of $CaCO_{3(s)}$ with alum and four coagulant aids has been studied.[42] Typical results are seen in Figure 8.22, where aid B is an anionic acrylamide (Separan NP10), aid C is a nonionic potato starch, and aid D is a high-molecular-weight cationic polymer (Nalco 600). Coagulation occurs in all systems, and is accompanied with and without charge reversal. Researchers have drawn the following conclusions from 8.22a and b: "the mobility value in itself is not a reliable indication of the degree of coagulation to be expected with the use of a coagulant aid and softening sludges... The best coagulation was usually obtained at substantially negative mobility values."[42]

Membrane Processes

Membrane processes (see Chapter 7) are in operation for the primary purpose of removing the hardness cations, Ca^{2+} and Mg^{2+}. Advantages of these processes have been cited as:[43] (a) all contaminant ions and most dissolved non-ions are removed, (b) relatively insensitive to flow and total dissolved solids level, (c) low effluent concentration of ions possible, and (d) bacteria and particles are removed in re-

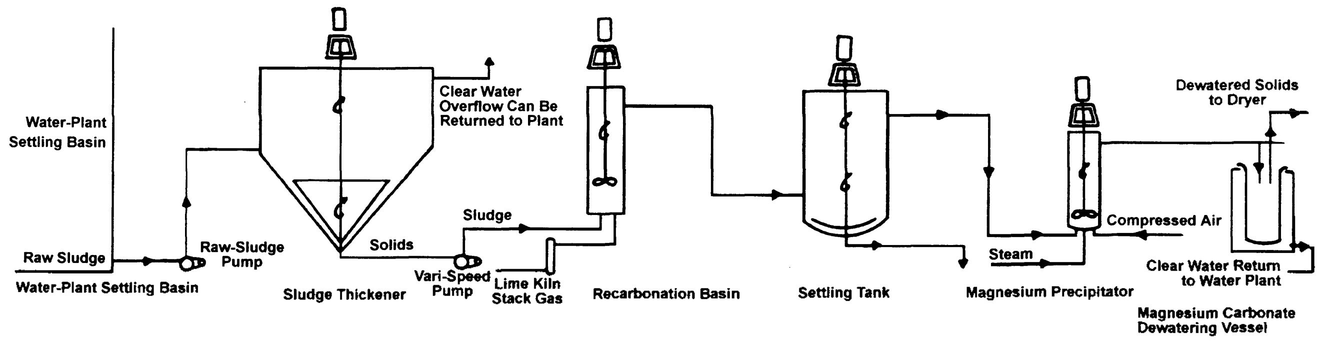

Figure 8.20. Total recovery of lime softening sludge; magnesium recovery pilot plant. Reproduced from Black et al.,[36] courtesy of the American Water Works Association.

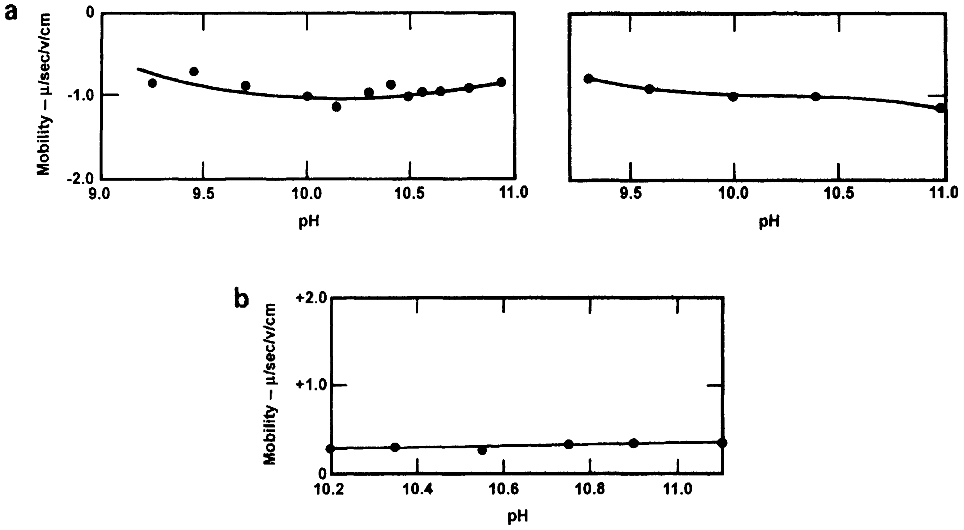

Figure 8.21. (a) Effect of pH on mobility of $CaCO_3$. The curve at the left pertains to $CaCO_3$ sludge produced by softening water A with varying dosages of lime in the pH range 9.0 to 11.0. The curve at the right shows the effect of pH on the same sludge suspended in deionized water. (b) Effect of pH on mobility of $Mg(OH)_2$. The relatively constant mobility throughout the pH range shown is probably the result of the protective action of the water molecules surrounding the strongly hydrophilic $Mg(OH)_2$ particles. Reproduced from Black and Christman,[42] courtesy of the American Water Works Association.

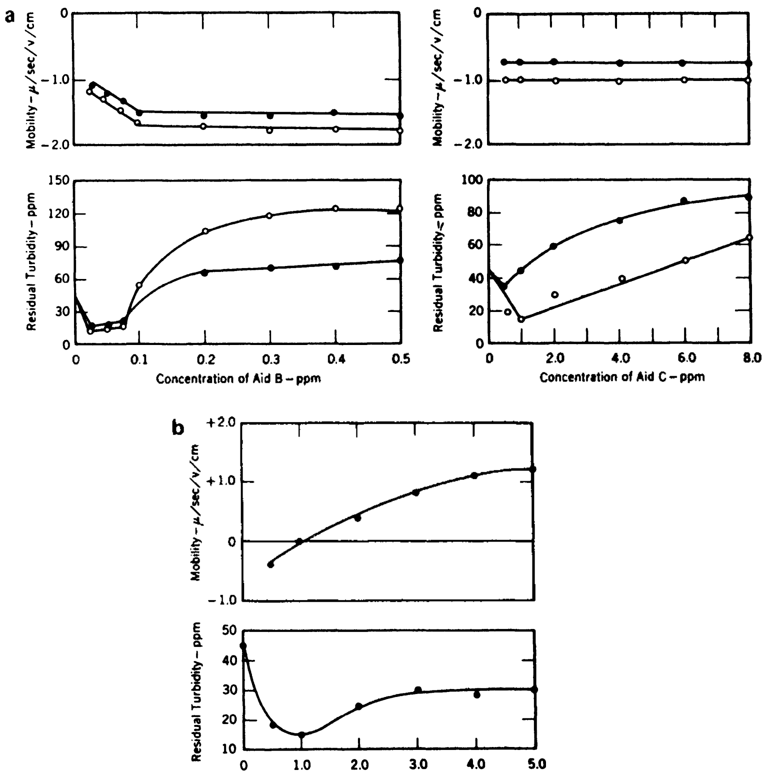

Figure 8.22. Effects of (a) aids B and C, and (b) aid D on mobility and coagulation of $CaCO_3$ at pH 9.8. Aid D was added after the lime. Coagulation was accompanied by charge reversal. Reproduced from Black and Christman,[42] courtesy of the American Water Works Association.

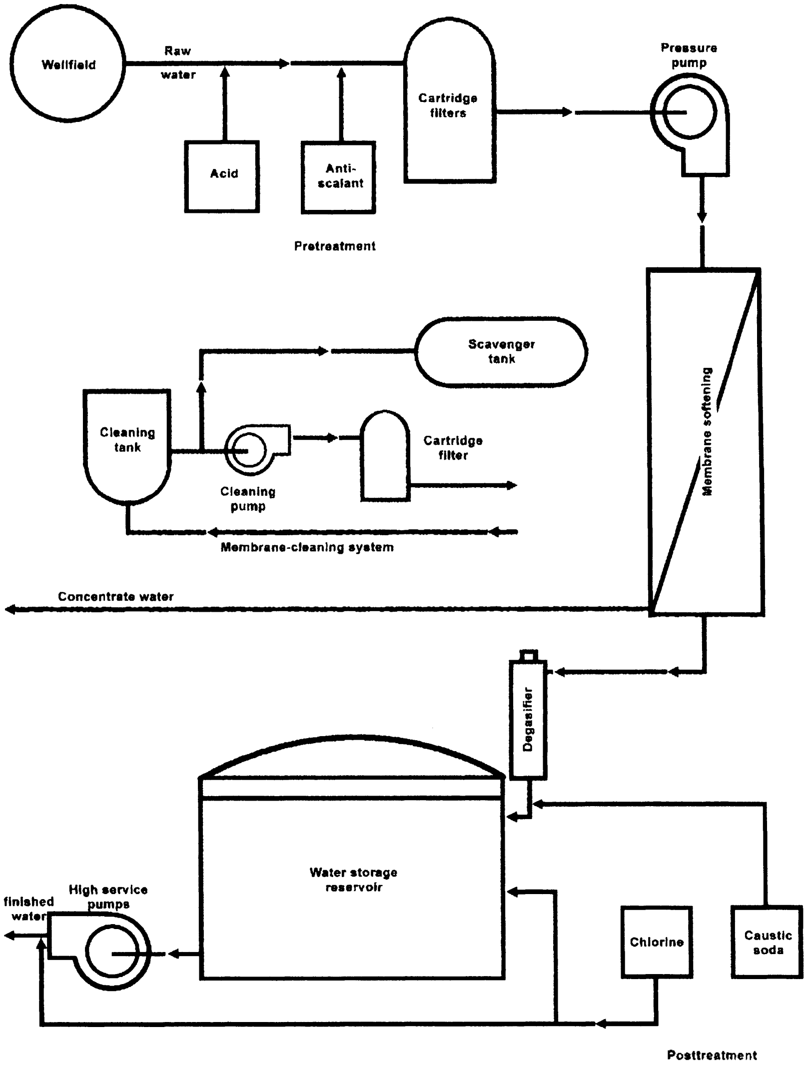

Figure 8.23. Schematic of process flow.[44]

verse osmosis as well. Disadvantages are: (a) high capital and operating costs, (b) high level of pretreatment required, (c) membranes are subject to fouling, and (d) reject stream is 20–90% of the feed flow.

Considerable field experience has been obtained in Florida, where 10 years of operational data have been tabulated from 20 or more installations.[44] Reverse osmosis membranes were employed instead of the traditional lime–soda ash process for softening. A typical schematic of the RO process flow is seen in Figure 8.23, where the pretreatments of acidification, antiscalant, and cartridge filtration are employed. Posttreatment by degasification is necessary to eliminate the CO_2 gas that results from the acidification of the bicarbonate alkalinity. Table 8.18 gives the commercially available spiral-wound softening membranes in 1989 for the various plants in Florida. Subsequently, the NF-20 nanofiltration membrane was selected for, at least, two pilot plant studies on the basis, perhaps, of its high $MgSO_4$ rejection (98% at 70 psi). Table 8.19 shows the performance data for two membrane softening plants after one year of continuous operation. The permeate concentrations of the inorganics indicate satisfactory removal of the hardness constituents. Removal of the organics should be noted also (see Chapters 6 and 7 for organics removal by softening processes).

Two important considerations of the RO removal softening process are disposal of the concentrate and, of course, the capital, operating, and maintenance costs. The concentrate stream from a membrane softening plant is not as difficult to dispose of as a concentrate from a brackish water RO plant. The reason is simply that the concentration of salts in the waste stream is considerably lower, usually

Table 8.18. Currently Available Spiral-Wound Softening Membranes[a].[44]

Membrane Manufacturer	Membrane Designation	MWC[b]	Design $MgSO_4$ Rejection (%)	Design Permeate Productivity at Cited Pressure (gpd)	Membrane Material
Fluid Systems	8231 LP	50–200	95 at 200 psi	13,000	Cellulose acetate blend
Fluid Systems	8231 UP	50–200	95 (minimum TH[c] reduction) at 80 psi net	4,800	TFCS polyamide
Film Tec	NF–70	200	98 at 70 psi	7,000	Polyamide thin-film composite on polysulfone base
Flim Tec	NF–40	300	93 at 225 psi	7,000	Polyamide thin-film composite on polysulfone base
Toray	SCL–100	[d]	[d] at 215 psi	6,560	Modified cellulose acetate
Toray[e]	SU–600	190–250	99 at 107 psi	10,570	Cross-linked polyamide composite
Nitto Denko	NTR–729 HF	100–300	98 at 286 psi	15,800	PVA polymer composite on polysulfone base
DSI	Desal 5	180	98 at 100 psi	6,500	Thin file on polysulfone base
DuPont	SM15	75–350	95 at 100 psi	8,000	Polyamide

[a] 8 X 40 in. elements.

[b] Molecular weight cutoff; depends on steric size and polarity of benchmark organic species.

[c] Total hardness.

[d] Data not available.

[e] Chlorine-tolerant membrane.

Table 8.19. Performance Data for Two Membrane Softening Plants After One Year of Continuous Operation[a].[44]

Parameter	Plant A Feed	Plant A Permeate	Plant B Feed	Plant B Permeate
Organics				
Total organic halogen FP[b]—µg/L	2,000.0	51.0	1,050.0	4.3
Total trihalomethane FP[b]—µg/L	630.0	56.0	429.0	4.3
Total organic carbon—mg/L	15.4	1.5		
Nonpurgeable organic carbon—mg C/L			13.4	0.24
Chloroform—µg/L			222.0	4.3
Dichlorobromomethane—µg/L			142.0	BDL
Chlorodibromomethane—µg/L			60.3	BDL
Bromoform—µg/L			5.1	BDL
Inorganics				
Alkalinity—mg $CaCO_3$/L	238.0	85.0	126.0	55.0
Total hardness—mg $CaCO_3$/L	316.0	24.0	382.0	64.0
Chloride—mg/L	64.0	22.0	213.0	113.0
Sulfate—mg/L	20.0	8.0	248.0	7.0
Metals				
Sodium—mg/L	54.0	38.0	126.0	68.0
Calcium—mg/L	114.0	9.0	126.0	21.0
Iron—mg/L	14.0	5.0	444.0	64.0
Miscellaneous				
Color—cpu	38.0	2.0	85.0	3.0
Total dissolved solids—mg/L	396.0	134.0	917.0	277.0

[a] The NF-70 nanofiltration membrane was used. The information is based on analytical work completed in the Priority Pollutants Lab at the University of Central Florida, Orlando. Plant A is a 42,000 gpd unit installed at Palm Beach County's Elementary School No. 17 in Loxahatchee Groves, Florida; it was commissioned in fall 1987 to treat a surficial aquifer; it operates at a feed pressure of 100 psig and 75% recovery. Plant B is a 180,000 gpd unit in a plant expandable to 1.4 mgd, installed at the Palm Beach Park of Commerce in West Jupiter, Florida; it was commissioned in spring 1988 to treat a surficial aquifer; it operates at feed pressure of 90 psig and 75% recovery.

[b] Seven-day formation potential.

[c] Below detection limit.

Table 8.20. Operations and Maintenance Costs Based on Recent Studies.[44]

Study	Proposed Capacity (MGD)	Cost $/1,000 gal
Brevard County[a]	28.5	0.852
Gulf Utilities[b]	0.5	0.660
Boynton Beach[c]	16.0	0.423
Acme Improvement District[c]	4.5	0.441
USEPA[d]	1.0	0.680
USEPA[d]	2.5	0.545
City of Hollywood[b]	16.0	0.403

[a] Cost includes capital and O&M for water supply conveyance and treatment, but excludes distribution.

[b] Costs for finished water high-service pumping are not included in these figures. Estimated inflation, escalation, or amortization factors are not included. A utility service factor of 1.0 was used.[18]

[c] Cost includes supply wells and high-service pump energy. Estimated inflation, escalation, or amortization factors are not included. A utility service factor of 1.0 was used.

[d] Costs for finished water high-service pumping are included in these figures ($0.07/1,000 gal.). Estimated inflation, escalation, or amortization factors are not included. A utility service factor of 1.0 was used.

<2000 mg TDS/L. In the Florida study, disposal of the concentrate was by spray irrigation on a golf course—"without any negative effects."[44]

The economics of RO softening processes were difficult to assess in the Florida study because a history of capital costs was not available at that time (1987–1989). Estimates were given for capital costs, in dollars of installed capacity: \$0.95 for <1 MGD, \$0.75 for 1–5 MGD, and \$0.65 for >5 MGD. Table 8.20 gives the O&M costs that were predicted on several studies.[44] In general, these costs for labor, chemicals, power, membrane replacement, and routine maintenance were between \$0.40 and \$0.65/1000 gal.

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Chapter 9

Removal of Inorganic Contaminants

9

Removal of Inorganic Contaminants

WATER QUALITY WITH INORGANICS

The nearly ubiquitous distribution in natural waters of such inorganic chemicals (IOCs) as: Ag, Al, As, asbestos, B, Ba, Be, Cd, Cr, Cu, F, Fe, Hg, H_2S, Mn, Mo, Na, Ni, Pb, radionuclides, Sb, Se, SO_4^{2-}, Sr, Tl, V, and Zn has caused concern about their physiological and other effects on humans[1] (see Chapter 1). Three of these constituents—Cu, Fe, and Mn—clearly are nuisance types of constituents. Cu affects the taste quality of drinking water and the oxidative products of Fe and Mn impart turbidity to the water, stain clothing in laundry processes, and interfere with the brewing of tea and coffee and the flavor of other beverages.[2] Ferrous (II), copper (II), and plumbous (II) ions are corrosion products of distribution pipes (see Chapter 10). Because of their various effects on drinking water quality, it is necessary to lower the contents of these constituents to the current MCL standards set by the U.S. Environmental Protection Agency (EPA) (see Chapter 1). For a description of the geologic sources and typical contents of these metals, semimetals, and other IOCs in water, see Reference 2.

IRON

Aqueous Chemistry

The aqueous chemistry of iron is rather complex, since this metal enters into several protolysis and oxidation-reduction reactions.[2-4] Some of the more pertinent reactions are given in Table 9.l, from which the pE-pH stability diagram was drawn for Figure 9.1. Construction details for this figure are given in Faust and Aly.[2]

Briefly explained, the pE-pH diagram gives the boundaries in which a given ion species is stable or predominant. The diagram also is useful for determining the pE-pH conditions under which Fe(II) is oxidized to Fe(III)—with $O_{2(g)}$ as the electron acceptor—and subsequently precipitated as $Fe(OH)_{3(s)}$. Most natural waters have pH values ranging from 5.0 to 8.5, and pE values ranging from +2 to +12. Thus, Fe(II) would be the predominant iron species in the absence of an electron acceptor such as $O_{2(g)}$. In order to oxidize Fe(II) to Fe(III), it is necessary to raise both the pE and pH values. The former may be raised by adding such an electron acceptor as $O_{2(g)}$, Cl_2, or $KMnO_4$, whereas the pH value is increased through addition of OH^- from $Ca(OH)_2$ or NaOH. This diagram also shows that the pE value required for oxidation is lowered as the pH value is increased. This interpretation has very pragmatic operational applications in iron removal from natural waters. This is also a factor in the oxygenation kinetics of Fe(II) discussed below. The thermodynamic instability of iron pipes is seen in Equation 1 (see also Chapter 10).

Removal

Current water treatment practice employs three general methods for reducing iron contents to less than the MCL. The primary method uses oxidation of the Fe(II) and subsequent precipitation to $Fe(OH)_{3(s)}$, followed by sedimentation and filtration. Ion exchange is frequently employed where iron contents are less than 10 mg/L and where "low" volumes exist at municipal plants or for domestic purposes. A third method utilizes the stabilization of iron in a suspended state by a dispersing agent, usually a polyphosphate or a silicate, to prevent deposition. This is not a removal method per se, and is limited to iron contents of 1.0 mg/L or less. All of this may be summarized as follows:

1. Oxidation and precipitation methods: aeration ($O_{2(g)}$), sedimentation and filtration; oxidation by $KMnO_4$, Cl_2, O_3, or ClO_2, followed by sedimentation and filtration; and calcined magnesite-diatomaceous earth filtration
2. Ion-exchange methods: "zeolite" softening (also see Chapter 8), and "manganese-zeolite" processes
3. Stabilization with polyphosphates and silicates

Table 9.1. Some Aqueous Reactions for Iron at 25°C.

Reaction No.	Reaction	log K[a]	E^0
1	$Fe^{2+} + 2e = Fe^0_{(s)}$	–14.9	–0.440
2	$Fe^{3+} + e = Fe^{2+}$	+13.17	+0.771
3	$FeOH^{2+} + H^+ + e = Fe^{2+} + H_2O$	+15.5	+0.914
4	$Fe(OH)_{3(s)} + 3H^+ + e = Fe^{2+} + H_2O$	+17.8	+1.052
5	$Fe^{3+} + H_2O = FeOH^{2+} + H^+$	–2.2	
6	$FeOH^{2+} + H_2O = Fe(OH)_{2(s)} + H^+$	–4.6	
7	$FeOH^{2+} + 2H_2O = Fe(OH)_{3(s)} + 2\ H^+$	–2.41	
8	$O_{2(g)} + 4H^+ + 4e = 2H_2O$	+83.3	+1.229
9	$2H_2O + 2e = H_{2(g)} + OH^-$	–28.1	–0.828
10	$Fe_{(s)} + 0.5O_{2(g)} + 2H^+ = Fe^{2+} + H_2O$	+56.4	+1.67
11	$O_{2(g)} + 4Fe^{2+} + 10H_2O = 4Fe(OH)_{3(s)} + 8H^+$	+11.6	+0.177

[a] $K = K_{RED}$ for reduction reaction and = K_{eq} for protolysis reaction.

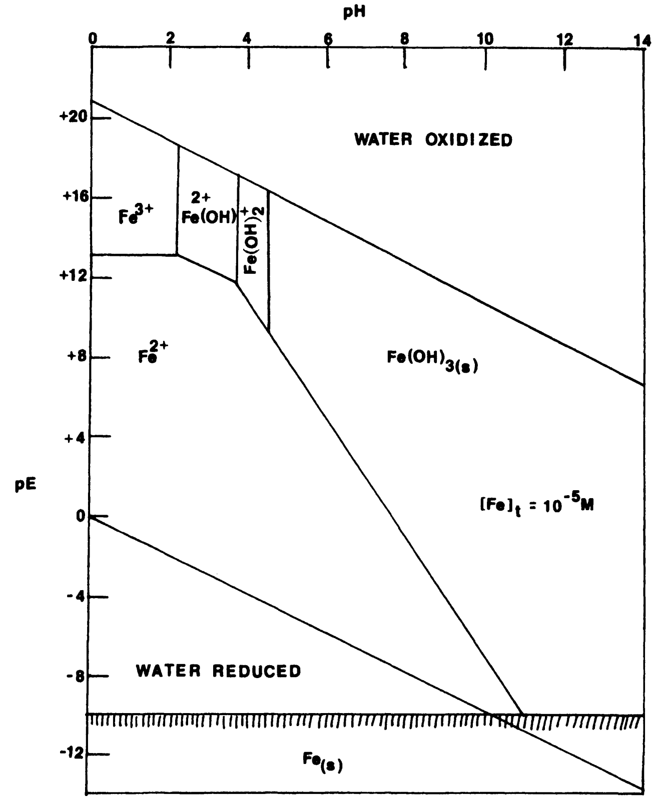

Figure 9.1. pE-pH diagram for the iron system. Reproduced from Faust and Aly.[2]

Kinetics of Oxygenation

Reactions 10 and 11 from Table 9.1 indicate that the oxidations of Fe(0) to Fe(II) and Fe(III) are thermodynamically feasible with oxygen as an electron acceptor. In addition to the use of oxygenation of iron for its removal at water treatment plants, these reactions are also encountered in waters polluted by acid mine drainage or iron pickling wastes, and, of course, in the corrosion of iron water distribution pipes (see Chapter 10). Consequently, the oxygenation of the lower valence states of iron has been studied extensively. For example, Weiss[5] suggested that the oxygenation of Fe(II) follows this sequence:

$$Fe(II) + O_{2(g)} = Fe(III) + HO_2^{\cdot} \qquad (12)$$

$$Fe(II) + HO_2^{\cdot} = Fe(III) + H_2O_2 \qquad (13)$$

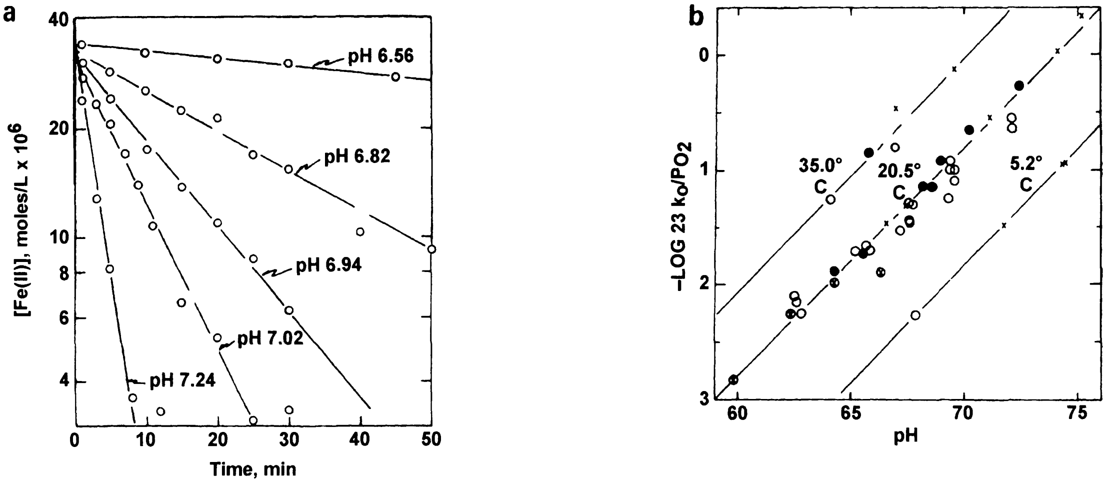

Figure 9.2. (a) Oxygenation rate of ferrous iron is proportional to Fe(II) and is strongly influenced by pH (20.5°C, P_{O_2} = constant). (b) An increase by one pH unit must increase oxygenation rate 100-fold. Reproduced from Stumm and Lee,[6] courtesy of the American Chemical Society.

$$\mathrm{Fe(II)} + \mathrm{H_2O_2} = \mathrm{Fe(III)} + \mathrm{HO}^{\cdot} + \mathrm{H_2O} \qquad (14)$$

$$\mathrm{Fe(II)} + \mathrm{HO}^{\cdot} = \mathrm{Fe(III)} + \mathrm{H_2O} \qquad (15)$$

These reactions are not balanced with respect to H^+, and do not specify any dependence of the reaction rate on this variable. It is believed that the rate-limiting step is Equation 12, which indicates that the rate of oxidation is first-order with respect both to [Fe(II)] and $[O_{2(g)}]$:

$$-\frac{d[\mathrm{Fe(II)}]}{dt} = k[\mathrm{Fe(II)}]\,[O_{2(g)}] \qquad (16)$$

This reaction is considerably more complex than Equations 12–15 indicate. Among other things, the rate of oxidation is dependent on the nature of the anion present in water and increases as the complexing affinity of the anion to ferric iron increases.[6]

Manometric techniques were employed to investigate the kinetics of oxygenation of Fe(II).[6] The stoichiometric reaction is:

$$\mathrm{Fe^{2+}} + 0.25\,\mathrm{O_{2(g)}} + 2\mathrm{OH^-} + 0.5\,\mathrm{H_2O} = \mathrm{Fe(OH)_{3(s)}} \qquad (17)$$

In bicarbonate solutions (alkalinities, 2.9–3.9×10^{-2} eq/L), the general rate law is:

$$-\frac{d[\mathrm{Fe(II)}]}{dt} = k[\mathrm{OH^-}]^2 P_{O_2}[\mathrm{Fe(II)}] \qquad (18)$$

where
k = rate constant (M^{-2}-atm^{-1}-min^{-1})
$[OH^-]$ = hydroxyl ion concentration
[Fe(II)] = concentration of total ferrous iron

Equation 18 can be reduced to first-order:

$$-\frac{d[\mathrm{Fe(II)}]}{dt} = k_1\,[\mathrm{Fe(II)}] \qquad (19)$$

where $k_1 = K[OH^-]^2 P_{O_2}$ (holding OH^- and O_2 constant) and has units of $time^{-1}$. Integration of Equation 19 yields

$$[\mathrm{Fe(II)}] = [\mathrm{Fe(II)}]_0 e^{-k_1 t} \qquad (20)$$

Figure 9.2 shows typical rate data from Stumm and Lee,[6] which suggested a first-order reaction with respect to Fe(II) and independent of [Fe(II)]. However, Figure 9.2a shows the effect of pH value or, more precisely, $[OH^-]$. Here, the log of the rate constant k_1 divided by the P_{O_2} is plotted as a function of the solution's pH. Slopes of the straight lines indicate a 100-fold increase in oxygenation rate with an increase of one pH unit. This relationship is seen in another manner by calculating the $t_{1/2}$ value from:

$$t_{1/2} = \frac{0.693}{k_1} \qquad (21)$$

where
$t_{1/2}$ = the time required for 1/2 of the remaining reaction to occur
0.693 = a constant (2.303 log 2)
k_1 = a first-order rate constant that must be based on natural logarithms

Using data from Stumm and Lee:[6]

when $P_{O_2} = 0.107$ atm, $[OH^-] = 1.86 \times 10^{-8}$ (pH 6.27)

$$t_{1/2} = \frac{0.693}{3.33 \times 10^{-3}\ \text{min}^{-1}} = 208.1 \text{ min}$$

when $P_{O_2} = 0.195$ atm, $[OH^-] = 2.24 \times 10^{-7}$ (pH 7.35)

$$t_{1/2} = \frac{0.693}{0.942\ \text{min}^{-1}} = 0.73 \text{ min}$$

These calculations, of course, demonstrate the effect of $[OH^-]$ on the oxidation of Fe(II) in accord with the data of Stumm and Lee.[6] There are some water treatment plant design implications in these chemical kinetic data. Catalytic effects of Cu^{2+}, $MnO_{2(s)}$, and $H_2PO_4^-$ were observed also. The presence of these constituents increased the rate of oxygenation of Fe(II).

This research was extended to include the effects of ionic media, alkalinity, and temperature on the kinetics of ferrous iron oxygenation, and to identify oxidative product(s).[7] In this study, the general rate law, Equation 18, was confirmed. Table 9.2 summarizes these kinetics, and Table 9.3 shows that an increase of ionic strength decreases the rate constant and increases the $t_{1/2}$ value. This effect may be due to complexation of Fe^{2+} by ClO_4^-. The effect of temperature on the rate of oxygenation was expected to follow the normal course, as can be seen in Figure 9.3. However, when the data were normalized with respect to changes in Kw and O_2 solubility, the rate constant varied slightly with increasing temperature (data not given here). Sung and Morgan[7] were uncertain about the role of bicarbonate alkalinity in the oxygenation of kinetics. Their data showed that effects of alkalinity variation from 9 to 50 m*M* were explained reasonably well by ionic strength.

When the dependency of the oxygenation rate on $[H^+]$ was reinvestigated, the researchers noted that "one of the major uncertainties in the numerical value for the rate constant arises from the variation of pH within an experiment."[7] Figure 9.4 shows typical variation by which pH drops initially 0.1 unit following the addition of the stock Fe(II) solution which introduces 1 m*M* protons. This pH decrease effect was not mentioned in the work of Stumm and Lee.[6]

A semikinetic study of the aeration of iron-bearing groundwaters in Illinois was reported.[8] Table 9.4 shows $t_{1/2}$ values, in minutes, obtained for eight natural waters. It is rare for researchers to use natural waters. Most prefer to utilize synthetic waters. In any event, a comparison of the $t_{1/2}$ values of 4.3–54 min with a theoretical detention time of 60 min for aerators shows the inadequate design of most iron removal units.

The study of Ghosh et al.[8] provoked an interesting discussion by Stumm and Singer,[9] Winklehaus et al.,[10] and Morgan and Birkner.[11] The major objections of Stumm and Singer[9] were: (1) the uncertainty of the analytical method for determining Fe^{2+} in the presence of solid iron-bearing phases and organic matter, and (2) the incorrectness of interpreting the effect of bicarbonate alkalinity on the kinetics of Fe(II) removal as the result of the precipitation of $FeCO_{3(s)}$. Winklehaus et al.[10] were also concerned about the assertion that the formation of $FeCO_{3(s)}$ affected the oxygenation kinetics, since the reported values for pH and alkalinity (Table 9.4) do not show any correlation of $t_{1/2}$ to $[CO_3^-]$. Difficulties arise from attempts to compare directly Ghosh's[8] rate data to those of Stumm and Lee.[6] First, the two experimental systems were different, and no rate constants were presented by Ghosh et al.[8] Also, there was a mathematical error in the rate constants presented by Stumm and Lee.[6] Another objection to the $FeCO_{3(s)}$ explanation[11] concerned the inadequacy of the thermodynamic data as a basis for computing the supersaturation of the eight groundwaters. In addition, Morgan and Birkner[11] presented and compared their own kinetic data with those of Stumm and Lee[6] and Ghosh et al.[8] These data are given in Table 9.5, where there are 4- to 18-fold differences in the observed and computed $t_{1/2}$ values. No rational explanation was given for these differences.[11]

The oxidation of iron pyrite (FeS_2) with subsequent release of acidity into waters draining through coal mines has been investigated.[12,13] Figure 9.5 shows that the rate of oxidation of Fe^{2+} by oxygen in abiotic systems is a function of $[H^+]$ when the pH value is greater than 4.5. Equation 18 is valid for these conditions. At pH values less than 3.5, the reaction proceeds at a rate independent of $[H^+]$:

$$-\frac{d[Fe^{2+}]}{dt} = k'[Fe^{2+}][O_{2(g)}] \qquad (22)$$

where $k' = 1.0 \times 10^{-7}$ atm^{-1}-min^{-1} at 25°C

Another study was conducted on the oxygenation kinetics of Fe^{2+} and the effect of dissolved silica upon this oxidation.[14] The overall rate constant $k = 2.1 \pm 0.5 \times 10^{13} M^{-1}$.

Alternative Oxidants

Ozone, chlorine dioxide, chlorine, and potassium permanganate are feasible alternative oxidants for iron removal. The half-cell reduction reactions for these four oxidants are given in Table 9.6. Each of these four reactions are combined with Equation 4 to indicate the thermodynamic feasibility of Fe(II) oxidation to $Fe(OH)_{3(s)}$. Kinetic data for these reactions are rather sparse. Nordell[15] reported that "with chlorine it is possible to oxidize iron rapidly at a lower pH

Table 9.2. Summary of the Oxygenation Kinetics of Ferrous Irons.[a]

Investigators	Solution Composition	Reported Rate Information	Remarks
Stumm and Lee	29–39 meq/L of alk as $NaHCO_3$, P_{O_2} varies, T=20.5°C	k=8.0 ± 2.5 x 10^{13} M^{-2}-atm^{-1}-min^{-1}	Assume ionic strength ≈ 34 x 10^{-3} *M*, γ_{OH} ≈ 0.84, K_H oxygen at 20.5°C= 0.00138 *M*-atm^{-1}
Morgan and Birkner	P_{O_2}=0.6 atm, T=25°C, alk=32 meq/L	$T_{1/2}$ ≈ 16 min at pH 6.70 — k=2.0 × 10^{13} M^{-2}-atm^{-1}-min^{-1} $T_{1/2}$ 47 min at pH 6.52 — k=1.7 × 10^{13} M^{-2}-atm^{-1}-min^{-1}	
Schenk and Weber	P_{O_2}=0.21atm, T=25°C, alk=30–50 meq/L	k=2.1 ± 0.5 × 10^{13} M^{-2}-atm^{-1}-min^{-1}	Assume ionic strenth=40 × 10^{-3} *M*
Theis	P_{O_2}=0.5 atm, T=25°C, alk=0.0158 *M* as NaOH initially	$T_{1/2}$=25.4 min at pH 6.3 — k=1.36 × 10^{14} M^{-2}-atm^{-1}-min^{-1}	
Kester et al.	T=?, P_{O_2}=0.21 atm, Narrangansett seawater Sargasso seawater	$T_{1/2}$=5.5 min at pH 8.0 — k=6 × 10^{11} M^{-2}–atm^{-1}–min^{-1} $T_{1/2}$=3.3 min at pH 8.0 — k=1 × 10^{12} M^{-2}–atm^{-1}–min^{-1}	Kinetics were followed by ferric iron absorbance in the UV region
Tamura et al.	T=25°C, P_{O_2} varies, alk=10^{-2} *M* $NaHCO_3$, total ionic strength=0.11 *M*	0.1 *M* ClO_4^-: k=2.38 × 10^{14} M^{-3}-sec^{-1} =1.8 × 10^{13} M^{-2}-atm^{-1}-min^{-1} 0.1 *M* NO_3^-: k=2.04 × 10^{14} M^{-3}-sec^{-1} =1.6 × 10^{13} M^{-2}-atm^{-1}-min^{-1} 0.1 *M* Cl^-: k=1.63 × 10^{14} M^{-3}-sec^{-1} =2 × 10^{13} M^{-2}-atm^{-1}-min^{-1} 0.1 *M* Br^-, 0.1 *M* 1^-, 0.033 *M* SO_4^{2-}: k=1.36 × 10^{14} M^{-3}-sec^{-1} =1.0 × 10^{13} M^{-2}-atm^{-1}-min^{-1}	
Murray and Gill	T=?, Puget Sound seawater	$T_{½}$=3.9 min at pH 8.0 — k=8.9 × 10^{11} M^{-2}-atm^{-1}-min^{-1}	First 5 min linear on first-order plot

[a] Reproduced from Sung and Morgan,[7] courtesy of the American Chemical Society.

Table 9.3. Variation of k with Ionic Strength (Adjusted by $NaClO_4$).[a,b]

Ionic Strength (*M*)	$\tau_{1/2}$(min), Least Squares	k(M^{-2}-atm^{-1}-min^{-1})
0.009	18.0	$4.0 \pm 0.6 \times 10^{13}$
0.012	18.2	$3.1 \pm 0.7 \times 10^{13}$
0.020	18.5	$2.9 \pm 0.6 \times 10^{13}$
0.040	21.5	$2.2 \pm 0.5 \times 10^{13}$
0.060	26.8	$1.8 \pm 0.3 \times 10^{13}$
0.110	37.9	$1.2 \pm 0.2 \times 10^{13}$

[a] Reproduced from Sung and Morgan,[7] courtesy of the American Chemical Society.
[b] T=25°C; alkalinity = 9×10^{-3} *M* $NaHCO_3^-$; $[Fe(II)]_0$ = 34.7 µ*M*; P_{O_2}=0.20 atm; pH ≈ 6.84.

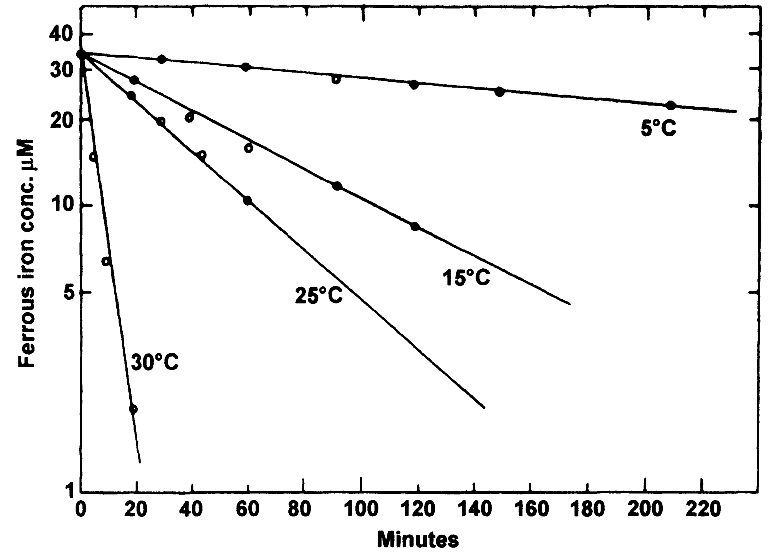

Figure 9.3. Effect of temperature on the oxygenation kinetics of ferrous iron. All experiments were conducted in 0.11 *M* ionic strength adjusted with $NaClO_4$; alkalinity = 9 m*M* as HCO_3; P_{O_2} = 0.2 atm; pH = 6.82; $[Fe(II)]_o$ = 34.7 m*M*. Reproduced from Sung and Morgan,[7] courtesy of the American Chemical Society.

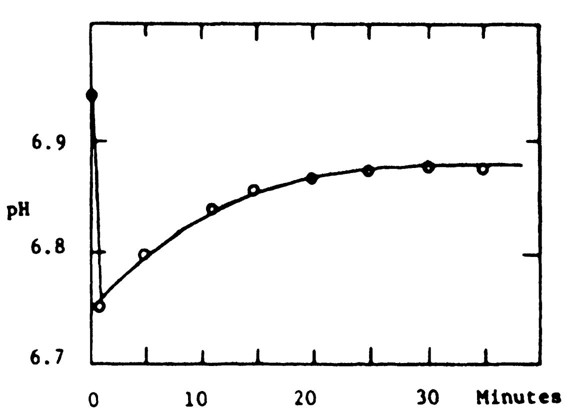

Figure 9.4. Variation of pH during an oxygenation experiment. Initial alkalinity = 10^{-2} *M*; P_{O_2} = 0.2 atm; P_{CO_2} = 0.071 atm; T = 25°C. The initial drop in pH coincides with the addition of stock ferrous solution, which introduces 1 m*M* protons. Reproduced from Sung and Morgan,[7] courtesy of the American Chemical Society.

Table 9.4. Characteristics of Illinois Groundwaters.[a]

	Raw Water				Aerated Water				
Plant	pH	Fe(II), (10^4 mol/L)	CO_3^{2-} (10^6 mol/L)	Molar Conc.[b] Product $[Fe(II)][CO_3^{2-}]$	Half-Life,[c] $t_{1/2}$ (min)	Equil. pH[d]	Alk. (mg/L as $CaCO_3$)	Dissolved Oxygen (mg/L)[e]	Temp. (°C)
Clinton	7.58	0.33	15.3	5.06×10^{-10}	4.3	7.78	610	7.35	13.0
Danvers	7.47	0.36	16.3	5.88×10^{-10}	6.5	7.68	512	6.40	13.5
Windsor	7.10	0.90	6.91	6.22×10^{-10}	13.2	7.48	520	7.20	14.5
Forrest	7.40	0.46	11.2	5.15×10^{-10}	16.0	7.72	475	7.72	10.5
Deland	7.10	0.72	5.3	3.82×10^{-10}	22.5	7.67	456	7.67	13.0
Cisco	7.45	0.63	12.5	7.90×10^{-10}	25.6	7.71	458	6.70	13.5
Wapella	7.32	0.85	9.0	7.65×10^{-10}	36.0	7.67	410	6.40	12.0
Arcola	7.30	0.75	6.7	5.01×10^{-10}	54.0	7.49	355	6.90	12.5

[a] Reproduced from Ghosh et al.,[8] courtesy of the American Society of Civil Engineers.

[b] Theoretical K_{sp} for $FeCO_3=2.11 \times 10^{-11}$ at 25°C.

[c] The half-life, $t_{1/2}$, is the time required to reduce the Fe(II) to one-half its original value.

[d] Equilibrium pH refers to the pH obtained following aeration of the raw water.

[e] Dissolved oxygen following aeration of the raw water.

Table 9.5. Data Related to Rate of Fe(II) Removal from Aerated Illinois Groundwater.[a]

Plant Number	Temperature (°C)	$[O_2]$ (10^4 mol/L)	$[OH^-]$ (10^4 mol/L)	k_m[b] (10^{-16} sec)	k_o[c] (10 min^{-1})	$t_{1/2}$ (min) Computed	$t_{1/2}$ (min) Observed[d]	Apparent Supersaturation
1	13.0	2.30	2.14	5.4	5.7	1.2	4.3	9.2
2	13.5	2.00	1.90	5.5	4.0	1.7	6.5	6.4
3	14.5	2.25	1.26	5.6	2.5	2.7	13.2	11.5
4	10.5	2.41	1.66	5.0	3.3	2.1	16.0	7.8
5	13.0	2.40	1.66	5.4	3.6	1.9	22.5	10.4
6	13.5	2.09	2.04	5.5	4.8	1.4	25.6	10.5
7	12.0	2.00	1.55	5.2	2.5	2.8	36.0	11.9
8	12.5	2.16	1.07	5.4	1.3	5.2	54.0	5.9

[a] Reproduced from Morgan and Birkner,[11] courtesy of the American Society of Civil Engineers.

[b] Estimated from rate data of Stumm and Lee.[6]

[c] Computed first-order rate constant for oxidation: $k_o=k_m[O_2](OH^-)^2$.

[d] From Table 3 of Ghosh et al.[8]

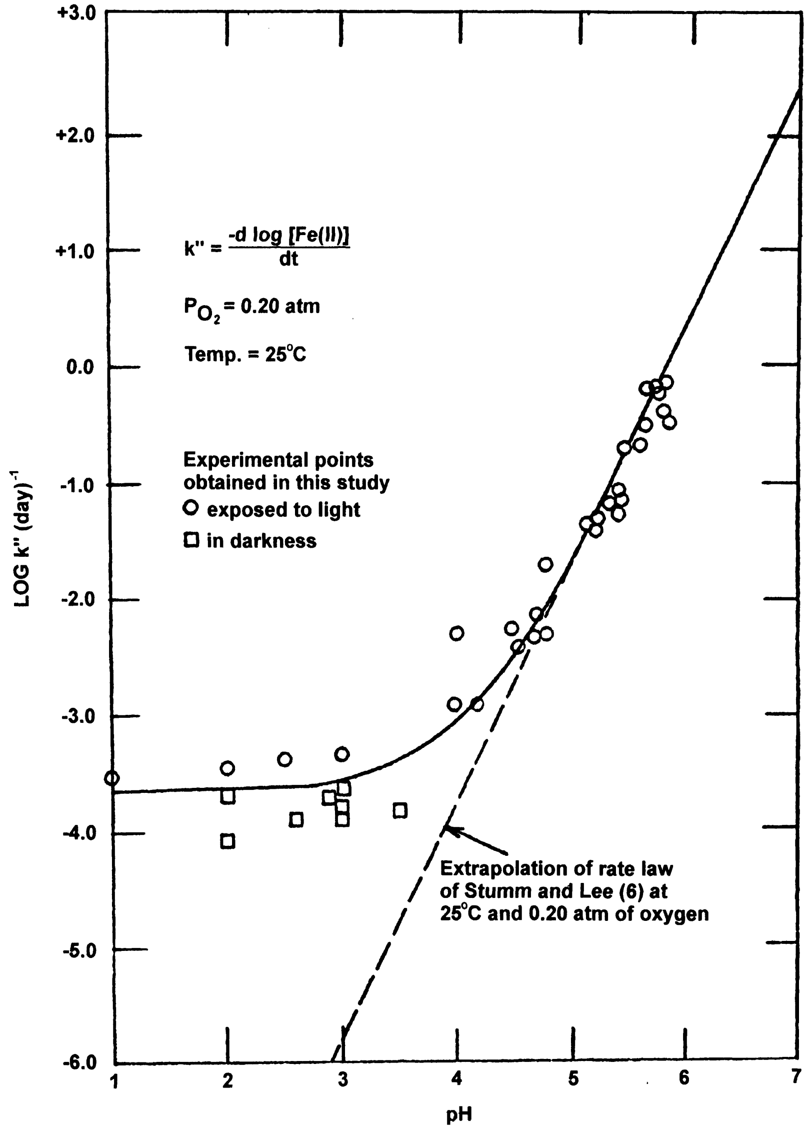

Figure 9.5. Oxygenation rate of ferrous iron as a function of pH.[13]

Table 9.6. Reactions of Fe(II) with Alternative Oxidants at 25°C.

Reaction Number	Reaction	E°
4	$Fe^{2+} + 3\ H_2O = Fe(OH)_{3(s)} + 3\ H^+ + e$	+1.052[a]
24	$O_{3(g)} + 2\ H^+ + 2e = O_{2(g)} + H_2O$	+2.07
4 and 24	$2Fe^{2+} + 5\ H_2O + O_{3(g)} + 4\ H^+ + O_2$	+1.06
25	$ClO_{2(g)} + 4\ H^+ + 5\ e = Cl^- + 2\ H_2O$	+1.511
4 and 25	$ClO_{2(g)} + 5\ Fe^{2+} + 13\ H_2O = 5\ Fe(OH)_{3(s)} + 11\ H^+ + Cl$	+0.501
26	$Cl_{2(g)} + 2\ e = 2\ Cl^-$	+1.3595
4 and 26	$2\ Fe^{2+} + 6\ H_2O + Cl_{2(g)} = 2\ Fe(OH)_{3(s)} + 2\ Cl^- + 6\ H^+$	+0.385
27	$MnO_4^- + 4\ H^+ + 3\ e = MnO_{2(s)} + 2\ H_2O$	+1.695
4 and 27	$3\ Fe^{2+} + 7\ H_2O + MnO_4^- = 3\ Fe(OH)_{3(s)} + MnO_{2(s)} + 5\ H^+$	+0.685

[a] As a reduction reaction.

than with dissolved oxygen." A rather qualitative laboratory study indicated that with chlorine, 10 ppm of Fe^{2+} "was completely oxidized in less than 15 minutes at a pH of 5.0, whereas with air a pH of 7.0 was required." In a pilot plant test, Matthews[16] reported that a 9.5 ppm dosage of chlorine "completely removed" 4.5 ppm iron and 1.8 ppm manganese as measured after the reaction time, sedimentation, and filtration. Willey and Jennings[17] concluded that "dissolved iron and manganese can be effectively removed from water by the continuous feeding of $KMnO_4$ to a water before it is passed through a manganese greensand filter." A permanganate "demand curve" (not shown here) was drawn in which the implied stoichiometry of the reaction was 6 ppm $KMnO_4$ for 10 ppm of ferrous iron. Cromley and O'Connor[18] investigated the use of $O_{3(g)}$ as an alternative to aeration for iron removal where organic compounds (see below) interfered. Some relevant kinetic information is seen in Figure 9.6, where there is a comparison of ferrous iron removal by continuous aeration and ozone.

Experimental data for Fe(II) oxidation in the absence of organic matter indicated that either $KMnO_4$ or ClO_2 provided extremely rapid oxidation rates.[19] For example, a reaction time of 0.1 second was observed with $KMnO_4$ under the coldest water temperature studied (2°C) to oxidize all of the reduced iron. Oxidation rates with ClO_2 were somewhat slower. At pH 5.5, and with a 125% stoichiometric dose of ClO_2, more than 90% of the initial [Fe(II)] was oxidized within 5 seconds (Table 9.7). These results are consistent with the earlier studies cited above. The influence of organic matter (DOC) on the oxidation of Fe(II) by $KMnO_4$ and ClO_2 is cited below.

Ion Exchange

Fe(II) is removed by ion exchange processes, provided the water is reasonably free from particulate matter. The cation exchangers are usually the high-capacity resin types in the sodium cycle:

$$Fe^{2+} + 2NaR = FeR_2 + 2Na^+ \qquad (24)$$

Regeneration is accomplished with NaCl. It is necessary to consider the hardness content when sizing and designing the capacity of the ion exchanger for Fe^{2+} removal. A "rule of thumb" is 0.5 ppm Fe/ppm of hardness up to a maximum of 50 ppm.[15] The raw water should not be aerated before the ion exchange unit, because $Fe(OH)_{3(s)}$ would precipitate and "foul" the bed. All of this limits the ion exchange to groundwaters.

Ferrous iron may also be removed by the so-called manganese zeolite process. This is not an ion exchange process per se, but the filtering medium is a mixture of anthracite and zeolite or greensand material. According to Nordell,[15] the manganese zeolite is prepared by alternate treatments of a greensand zeolite with manganous sulfate and potassium permanganate. This results in the precipitation of $MnO_{2(s)}$ in the zeolite bed, where it presumably catalyzes the oxidation of Fe(II) by continuous addition of $KMnO_4$ with subsequent filtration of the $Fe(OH)_{3(s)}$. The zeolite is regenerated first by backwashing and then by treating with $KMnO_4$ with subsequent filtration of the $Fe(OH)_{3(s)}$. The zeolite is regenerated first by backwashing and then by treating with $KMnO_4$. This process is limited to groundwaters with iron contents of 5 mg/L or less. This process may be utilized to remove manganese and hydrogen sulfide from water. Figure 9.7 shows a typical municipal unit operated at a flow rate of 3 gpm/ft^2. Water treatment plants range from 30 to 2800 gpm.

Effect of Organic Matter

That iron is complexed by naturally occurring organic acids has been reported in the limnological[20] and water treatment[15] literature for decades. This is the so-called filterable iron associated with waters "high" in organic color. This type of iron is difficult to remove by the conventional treatment methods cited above. Considerable research[21,22] has been conducted to explain the chemical nature of this complexed iron. For example, Shapiro[21] reported the Fe^{3+} holding capacity of "yellow" organic acids (Figure 9.8). The $[H^+]$ apparently is a factor, since the acids showed a maximum capacity of yellow organic acids to hold iron; rather, it was the maximum response to $[H^+]$ in the experimental system. From 5 to 50 ppm of tannic (digallic) acid reduces dissolved Fe(III) to Fe(II) when pH values are less than 4.[22] Above this pH value, a "black material" containing Fe(III) and tannic acid was precipitated. In a 500 ppm solution of tannic acid, a fairly stable complex with Fe(II) is formed—stable, that is, toward air oxidation. Tannic acid is present in many types of plant material.

The reductive and complexation properties of humic acids (HA) for Fe^{3+} and Fe^{2+} have been investigated.[23] These so-called humic acids[2] were prepared from well decomposed leaves. A typical result was that 50 mg/L HA, pH 5.0, did not complex any Fe^{2+}, but with an increase to pH 8.0, 2.1 mg/L iron was complexed. This increase in complexing ability was attributed to greater dissociation of carboxyl groups of the HA. Also, it was proposed that humic acids could chemically reduce Fe^{3+} to Fe^{2+} with subsequent complexation.[23]

It is difficult to oxygenate Fe(II) in the presence of humic and tannic acids.[24] In Figure 9.9, tannic acid appears to retard the oxidation of Fe(II) more than the humic acids. The mechanism is probably:

$$\begin{aligned} &Fe(II) + 0.25\,O_2 + \text{organics} = \\ &Fe(III) - \text{organic complex} \end{aligned} \qquad (25)$$

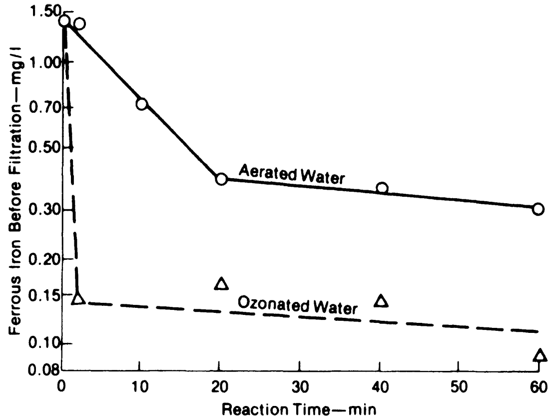

Figure 9.6. Comparison of the ferrous iron concentrations in an aerated and ozonated groundwater. Reproduced from Cromley and O'Connor,[8] courtesy of the American Water Works Association.

Table 9.7. Oxidation of Ferrous Iron by Chlorine Dioxide[a].[19]

	Reaction Time (s)	Residual Iron (mg/L)
Test 1:		
ClO_2 dose = 125% stoichiometric	0	1.98
	2–3	0.27
	5	0.13
	10	0.12
Test 2:		
ClO_2 dose = 250% stoichiometric	0	1.63
	2–3	0.16
	10	0.11

[a] Test conditions: pH = 5.5; temperature = 2°C; no added humic or fulvic acids (DOC = <1.0 mg/L).

$$\text{Fe(III)} - \text{organic complex} = \text{Fe(II)} + \text{oxidized organic} \qquad (26)$$

$$\text{Fe(II)} + 0.25\ O_2 + \text{organics} = \text{Fe(III)} - \text{organic complex} \qquad (27)$$

Such organic compounds as humic acid and tannic acid with –OH and –COOH groups apparently can reduce Fe(III) reasonably fast in synthetic solutions.[9,13] Reactions 25 and 26 suggest catalytic effect of the Fe(II)–Fe(III) couple in the aerobic oxidation of organic matter with subsequent oxidation of Fe(II) in Reaction 27. The relative rates of Reactions 25 and 26 dictate the eventual oxidation of Fe(II) in the presence of organics. This explanation is offered for the apparent two rates of Fe(II) oxygenation in the presence of humic acid, as seen in Figure 9.10. Manometric studies showed that the rate of oxygen consumption by the Fe(II)–tannic acid system at a pH value of 7.0 was appreciably slower than the rate in the absence of organic material. By the same token, the presence of Fe(II) retarded the oxidation of tannic acid at pH values of 7.0, 9.5, and 10.8.

What does all this mean for the removal of iron in highly colored waters? Obviously, oxygenation is not effective since the kinetics are too slow for normal treatment plant design. The obvious solution to this is to remove the organic color by carbon adsorption and/or chemical coagulation (see Chapters 4 and 6); hence the iron is removed also.

The capability of either $KMnO_4$ or ClO_2 to oxidize Fe(II) complexed with DOC is greatly reduced.[19] Tables 9.8 and 9.9 show results that involved natural (Provencial Brook) humic acid. These systems indicate that complexed iron is highly resistant to oxidation by $KMnO_4$ and ClO_2. On the other hand, Fe(II) that has been complexed by fulvic acids can be oxidized by $KMnO_4$, given sufficient contact time (>1 hr) and an oxidant dosage above the stoichiometric requirement.[19] Obviously, additional oxidant must be applied to satisfy the competitive demand exerted by the organic matter. Other experiments with free chlorine, hydrogen per-

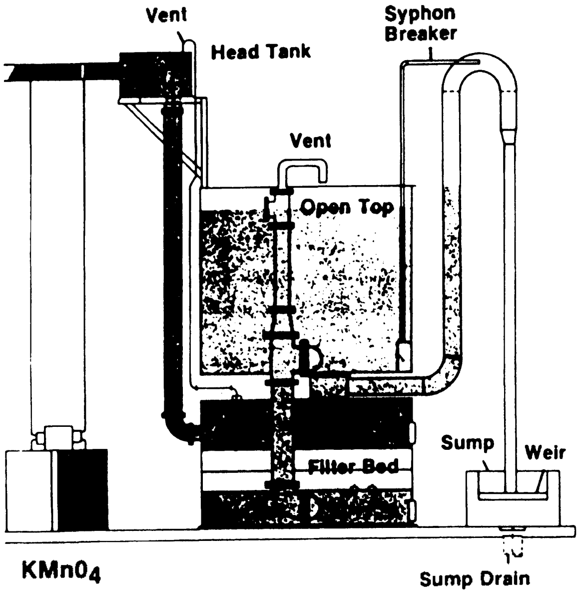

Figure 9.7. Schematic drawing of Zeo-Rex iron removal system showing chemical feed system. Reproduced courtesy of the Permutit Co., Inc.

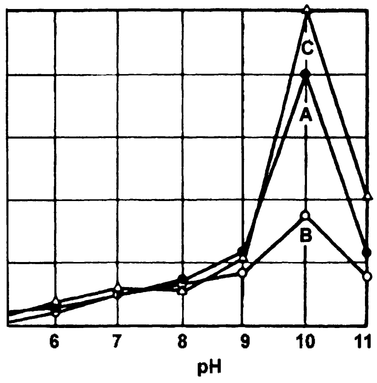

Figure 9.8. Iron-holding capacity of yellow acids as a function of pH. The pH during filtration and the pH at which the iron was added were the same. The three curves are for the following experimental conditions: A = iron added as $FeCl_3$ to 1 mg acids in 50 mL water; B = iron added as $FeCl_3$ to mg acids in 50 mL water; C = iron added as $Fe(NO_3)_3$ to 1 mg acids in 50 mL water. Reproduced from Shapiro,[21] courtesy of the American Water Works Association.

oxide, and even ozone indicated that these oxidants were ineffective for Fe(II) oxidation when the iron was complexed by certain samples of humic and fulvic acids.[27]

Effects of Dissolved Silica

Dissolved silica [H_4SiO_4 or $Si(OH)_4$] affects the aqueous treatment chemistry of iron by catalyzing the rate of oxygenation of Fe(II)[14] and by preventing iron deposition in distribution systems.[28] The solubility of amorphous silica in water at 0°C is approximately 1 to 1.3 m*M* (60–80 mg/L as SiO_2), and at 25°C it is 1.7 to 2.3 m*M* (100–140 mg/L).[29]

The following reaction demonstrates that dissolved silica reacts with iron:[30]

$$\begin{aligned} &Fe^{3+} + Si(OH)_4 + H_2O = \\ &FeSiO(OH)_3^{2+} + H_3^+O \end{aligned} \tag{28}$$

Using a stability constant of 1.8×10^9 for Reaction 28, it may be calculated that an acid mine water with a $[Si]_t$ of 60 mg/L and a $[Fe]_t$ of 5.6 mg/L, at a pH value of 3 would have approximately one-third of the iron complexed with silica.

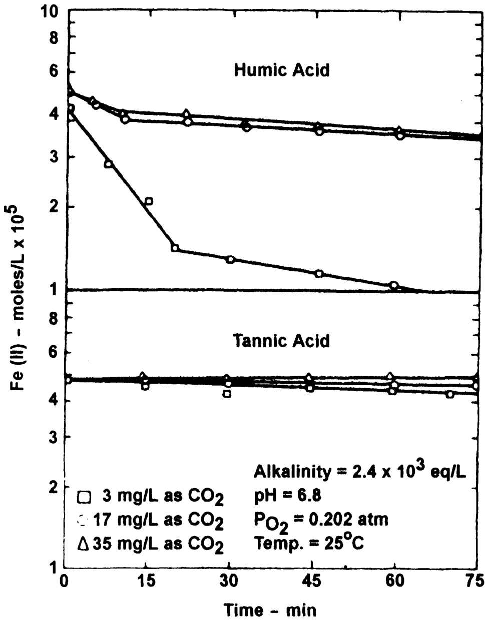

Figure 9.9. Oxygenation of Fe(II) in the presence of organic acids. Reproduced from Jobin and Ghosh,[24] courtesy of the American Water Works Association.

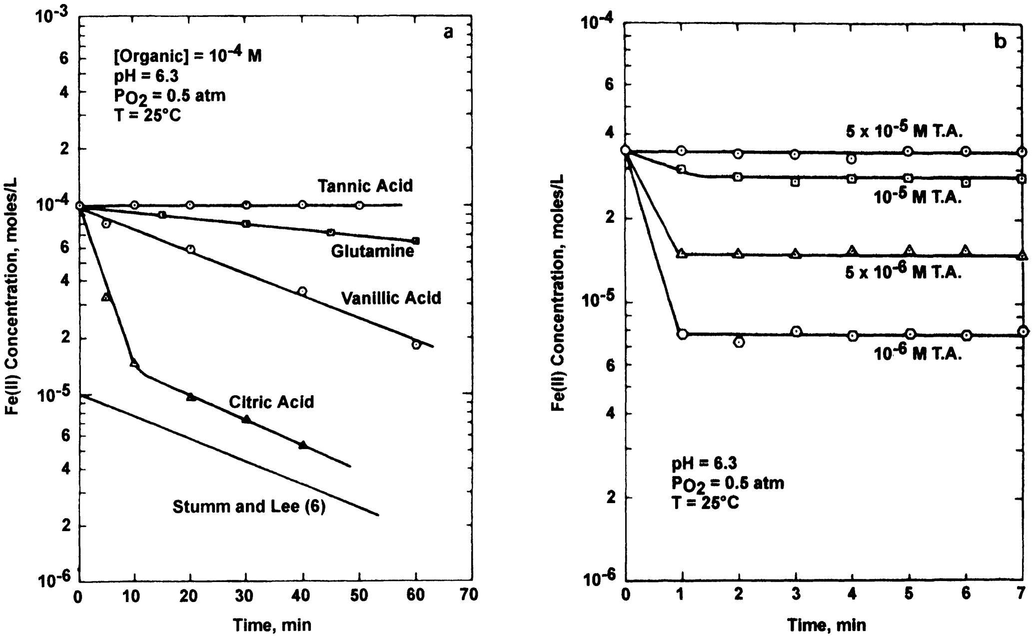

Figure 9.10. (a) Effects of representative organic compounds on rate of oxidation of ferrous iron at pH 6.3, P_{O_2} = 0.5 atm and T = 25°C as compared with the rate in simple aqueous media. (b) Inhibition of ferrous iron oxidation in the presence of various concentrations of tannic acid at pH 6.3, P_{O_2} = 0.5 atm and T = 25°C. Reproduced from Theis and Singer,[25,26] courtesy of the American Chemical Society.

Table 9.8. Effect of Provencial Brook Humic Acids on the Oxidation of Ferrous Iron by $KMnO_4$[a].[19]

	$KMnO_4$ Dosage (% Stoichiometric)	Residual Iron (mg/L)
Test 1:		
Solution pH = 6.5;	0	1.04
Solution temperature = 25°C	220	0.96
	440	0.89
	660	0.85
	880	0.82
Test 2:		
Solution pH = 7.5;	0	2.05
Solution temperature = 25°C	110	1.87
	220	1.69
	330	1.63
	440	1.55

[a] Different initial iron concentrations were used in tests 1 and 2. Stoichiometric dosage = 0.94 mg $KMnO_4$/mg Fe^{2+}; reaction time = 30 min; humic acid concentration = 5.0 mg/L DOC.

Table 9.9. Effect of the Addition of Provencial Brook Humic Acids on the Oxidation of Ferrous Iron by Chlorine Dioxide[a].[19]

Reaction Time (min)	Residual ClO_2 Concentration (mg/L)	Residual Fe Concentration (mg/L)
Test 1: Solution pH = 6.5		
0	7.2	1.98
25	2.9	1.93
50	1.9	1.94
80	1.2	1.71
0	3.6	1.97
20		1.95
30	0.7	1.95
50	<0.2	1.95
Test 2: Solution pH = 8.0		
0	7.2	1.89
12	3.0	1.84
30	2.2	1.84
50		1.82
70	0.8	
160	<0.2	1.81

[a] All solutions contained a humic acid concentration of 5 mg/L DOC. Solution temperature equaled 25°C for all studies.

Figures 9.11a and 9.11b show typical rates of Fe(II) oxidation in the presence of silica at pH values of 6.7 and 6.9, respectively. Equation 23, cited above, describes the linear relationship noted in the rate curves. Figure 9.11c gives the effect of dissolved silica concentration on the Fe(II) oxidation. Figure 9.11d shows that the catalytic effect is a function of $[H^+]$. No explanation was offered for the greater rates of oxidation of Fe(II) in the presence of silica. A complex cation undoubtedly is formed, but its precise role is uncertain.

Dart and Foley[28] present some actual operational experiences that appear to be opposite to the conclusions drawn by Schenk and Weber.[14] Reports had noted that "iron removal problems were experienced in "waters with 30 or 40 mg/L SiO_2 [that] often released very little of their iron content on either aeration or chlorination, followed by filtration." The silica apparently reacts with the $Fe(OH)_{3(s)}$ and holds it in suspension. This suspension was tested at four water treatment plants in the province of Ontario, Canada. Well waters served four communities whose iron

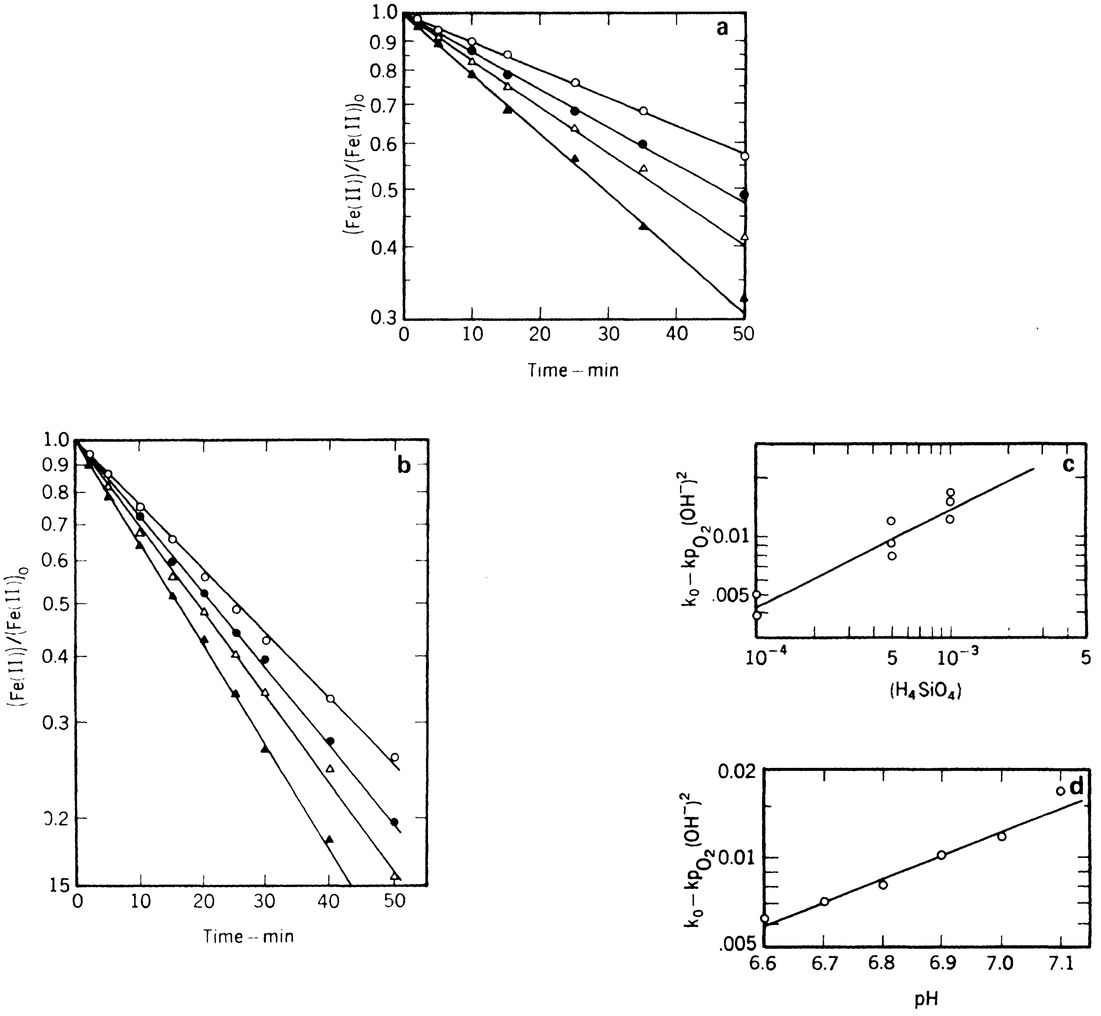

Figure 9.11. (a) Rates of iron(II) oxidation at pH 6.7, as a function of silica concentration, and (b) rates of iron(II) oxidation at pH 6.9 as a function of silica concentration. T = 25°C, P_{O_2} = 0.2095 atm. H_4SiO_4 concentrations are: ○ = zero; ● = 0.1; △ = 0.5; ▲ = 1 mmol/L. (c) Catalytic effect of silicic acid on iron(II) oxidation. A plot of the logarithm of the apparent increase in oxidation rate vs. the logarithm of H_4SiO_4 for various pH values results in a family of lines with a common slope of 0.5, indicating a 0.5-order dependence of oxidation rate on the silicic acid concentration. One such line, for pH 6.9, is plotted here to illustrate the observed dependence. (d) Catalytic effect of silicic acid as a function of pH. A plot of the logarithm of the increase in oxidation rate vs. pH results in a family of parallel lines for various H_4SiO_4 concentrations with a slope of 0.5. The line obtained for $[H_4SiO_4]$ = 5×10^{-5} *M* is plotted in this figure as an example to illustrate the observed relationship. Reproduced from Schenk and Weber,[14] courtesy of the American Water Works Association.

contents ranged from 0.2 to 1.45 mg/L. Natural silica contents were 15–20 mg/L. These iron contents are insufficient to install removal equipment, yet they are high enough to precipitate in the presence of chlorine added for disinfection. A trial-and-error procedure was employed in one of the communities to establish the optimum silica concentration for prevention of iron deposition in the distribution system. This content was 2.7 mg/L of sodium silicate to 0.5 mg/L of iron, and was fed continuously into the system. No staining of water fixtures nor complaints of "red water" were received. For another community, the optimum $[H_4SiO_4]$ was 4.6 mg/L for iron contents varying between 0.2 and 0.7 mg/L. It was noted also that the pH value should be above 7.5 for "effective and efficient" treatment. Application of sodium silicate should be simultaneous with chlorination or other oxidative treatments. Manganese was stabilized with greater effectiveness than iron. The mechanism for prevention of iron deposition apparently is a complex formation with Fe^{3+} similar to the one proposed by Weber and Stumm.[30] Attempts to complex Fe^{2+} were unsuccessful.[28]

A treatment method that stabilizes iron by the addition of sodium silicate and chlorine was examined under laboratory conditions.[31] Iron was stabilized for more than 10 days at 12 mg/L silicate dosage as SiO_2 without Ca, but precipitated after 3 days in the presence of 10 mg/L Ca as $CaCO_3$. Iron was precipitated within 24 hours with 100 mg/L Ca. The treatment of iron with sodium silicate and chlorine has been employed extensively in Ontario, Canada.[31] This research also attempted to explain the mechanism of the iron-silica reaction. It was the authors' opinion that their results refuted an iron-silica complex[30] as the treatment mechanism. Instead, a colloidal sol was more consistent with the evidence.[31]

Polyphosphate Treatment

There are occasions where the addition of sodium hexametaphosphate stabilizes or disperses iron in water distribution systems. The pragmatic dosage is 5 mg/L of phosphate per 1 mg/L of iron. Also, the treatment is limited to iron concentrations less than 1 mg/L. When the water is heated, polyphosphate reverts to orthophosphate and the dispersive property is lost. Application of the polyphosphate must be ahead of any oxidative step because $Fe(OH)_{3(s)}$ cannot be stabilized. Also, see Chapter 10 for the use of polyphosphates for corrosion control in cast iron distribution systems.

Filtration

Rapid sand filtration usually follows the oxidation of Fe(II) for removal of $Fe(OH)_{3(s)}$. This filtration, of course, removes such particulate matter as flocculents from chemical coagulation, softening sludges, etc. (see Chapter 6). There are occasions, however, when filtration is unique for iron removal, especially groundwaters. A diatomite filtration process has been developed for iron and manganese removal from the groundwaters of Massachusetts.[32] The flow diagram of a pilot plant is seen in Figure 9.12, where aeration and $KMnO_4$ are used to oxidize the Fe(II) before diatomite filtration. In view of the kinetic data cited above, the detention times may be inadequate. Iron and manganese contents of the raw water typically were 6–11 ppm and 0.25 to 0.45 ppm, respectively. The pressure filter was precoated with 0.15 lb/ft^2 of diatomaceous earth (body feed in Figure 9.12), and was operated at a flow of 1 gpm/ft^2. Typical results are given in Table 9.10, where the 0.02 ppm of iron in the filtrate was obtained at least 50% of the time. One of the operational difficulties arose from the use of lime for alkalinity control. Filter runs, as measured by head loss, were short with lime, but were lengthened considerably when soda ash was employed.

A pilot plant composed of (1) a constant-flow regulator, (2) aerator, (3) reaction-sedimentation basin, and (4) a bank of four rapid sand filters with different depths of filtering medium (downflow rate = 2 gpm/ft^2) was employed for iron removal.[33] This study demonstrated a difficulty frequently associated with the operation of sand filters for iron removal; that is, the growth and accumulation of bacterial slimes in the filters. Typical operational results are seen in Figure 9.13 for unripened (i.e., no bacterial slime) sand filters.[33] Only the 30-in. filter reduced total iron to acceptable contents. In Figure 9.14, iron removal after 16–18 hr of filtration was extremely erratic.[33] For the 18- and 30-in. filters, the iron content in the effluent was higher than in the influent. These "ripened" filters contain heavy bacterial slimes that create anaerobic or reducing conditions, leading to the reduction of previously removed Fe(III) to Fe(II). Only an excessively high dosage of chlorine, 50 mg/L, removed the bacterial slime and maintained oxidizing conditions in the sand filters.

Bituminous coal, 1.0 mm geometric size, has been proposed for removing iron from groundwater without preaeration.[34] Figure 9.15 shows a comparison of coal and sand filters for iron removal over a 48-hr period. Better removal by coal is apparent. Furthermore, the coal filter can be operated at four times (8 gpm/ft^2) the rate of a sand filter (2 gpm/ft^2) for comparable head loss and acceptable effluent quality up to about 12 hr. Also, the coal filter was more effective than the sand filter in removing soluble Fe(II), apparently by adsorption. No data were given on backwashing or cleaning of the coal filters.

MANGANESE

Aqueous Chemistry

Manganese has eight oxidation states: (0):Mn, (II):Mn^{2+}, +2.67-$Mn_3O_{4(s)}$, (III):$Mn_2O_{3(s)}$, (IV):MnO_2, (V):MnO_4^{3-}, (VI):MnO_4^{2-}, and (VII):MnO_4^-. Not all of these are relevant to the aqueous chemistry of manganese. Some of the more pertinent reactions are given in Table 9.11, from which the pE-pH diagram in Figure 9.16 was drawn.[35] It is apparent that $Mn^{2+}_{(aq)}$ occupies a large portion of the normal pE-pH values in natural waters. It is also obvious that oxidation of Mn^{2+} to one or more of the three oxides of manganese is thermodynamically feasible under the appropriate pE-pH conditions.

Removal

Kinetics of Oxygenation

That the oxygenation kinetics of Mn^{2+} to $MnO_{2(s)}$ or to $MnO_{x(s)}$ does not follow the same rate law as Fe(II) is seen by comparing Figure 9.17a to 9.17b.[4,36,37] Rather, the decrease of $[Mn^{2+}]$ with time suggests an autocatalytic reaction. The rate equation is:

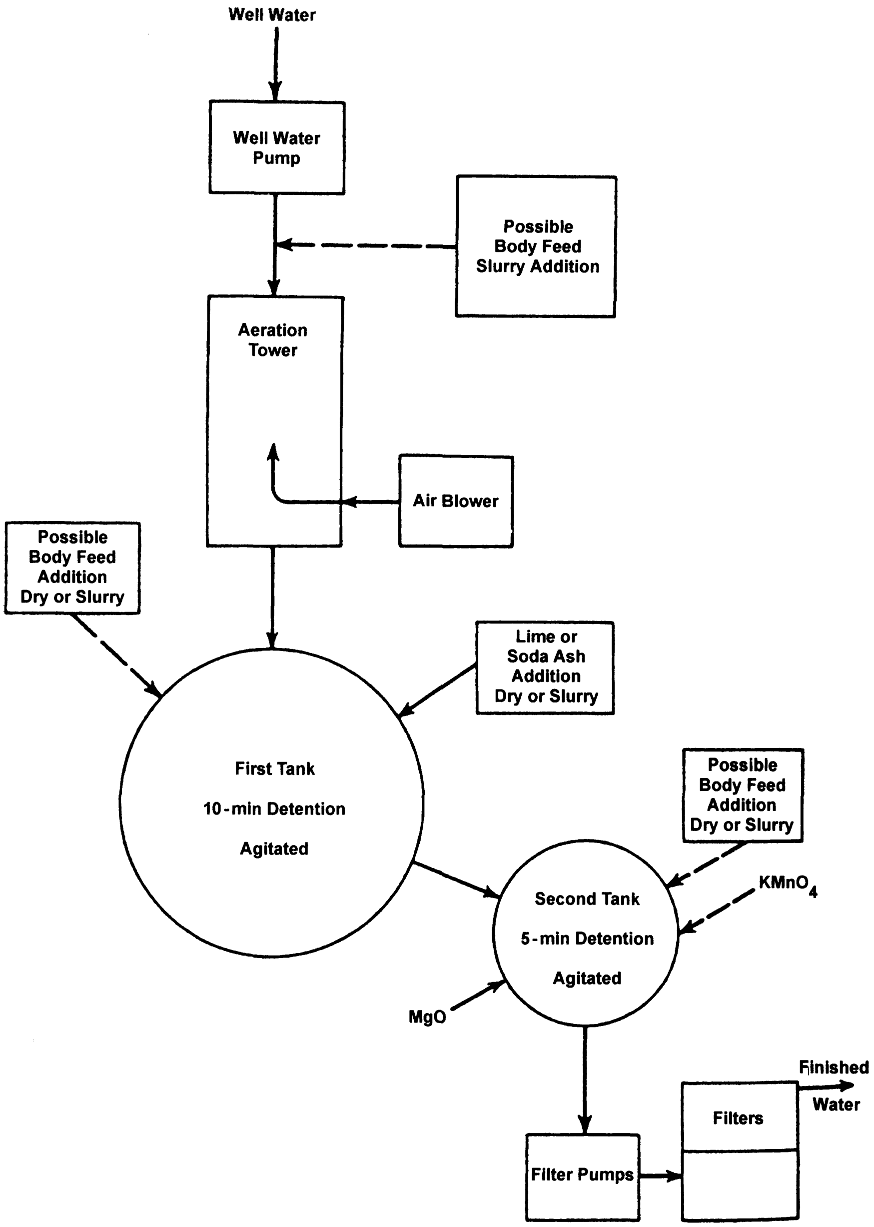

Figure 9.12. Flow diagram of diatomite pilot plant. Reproduced from Coogan,[32] courtesy of the American Water Works Association.

$$-\frac{d[Mn(II)]}{dt} = k_1\,[Mn(II)] + K_2\,[Mn(II)]\,[MnO_{2(s)}] \qquad (38)$$

The integrated form of Equation 38 was fitted to the experimental data extremely well (Figure 9.17c). According to Morgan,[36] the reaction sequence is:

$$Mn(II) + 0.5\,O_2 \xrightarrow{slow} MnO_{2(s)} \qquad (39)$$

$$Mn(II) + MnO_{2(s)} \xrightarrow{fast} Mn(II)\cdot MnO_{2(s)} \qquad (40)$$

$$Mn(II)\cdot MnO_{2(s)} + 0.5\,O_2 \xrightarrow{slow} 2MnO_{2(s)} \qquad (41)$$

Table 9.10. Iron Removal at Amesbury.[a]

Dosage[b] (ppm)	Body Feed: Grade	Body Feed: Feed	pH	Rate of Increase in Head Loss (lb/hr)	Results: Iron in Raw Water (ppm)	Results: Iron in Filtrate (ppm)
60	1[c]	As slurry in pump line	7.7–8.1	1.3	6–10	0.02
60	1[c]	As slurry in pump line	8.0–8.4	0.65	8.0	0.02
60	1[c]	Dry in first tank	8.0–8.4	1.7	6.5	0.02
60	2[d]	Dry in second tank	8.0–8.3	1.4	6.0	0.02

[a] Reproduced fro Coogan,[32] courtesy of the American Water Works Association.
[b] On pressure filters.
[c] Celite 503.
[d] Celite 545.

When these three equations are summed, a stoichiometry similar to Reaction 37 is observed. However, Stumm and Morgan[4] indicate that the experimental data are consistent with an autocatalytic model, because the extent of Mn(II) removal is not in accord with the stoichiometry. Some Mn(II) is adsorbed onto high oxides of Mn in slightly alkaline solutions. Also, oxidation to MnO_2 is not complete, since the solid phase from the oxygenation has been found to range from $MnO_{1.3}$ to $MnO_{1.9}$. In any event, the rate dependence on the $P_{O_{2(g)}}$ and $[OH^-]$ is the same as for iron. Therefore, k_2 in Equation 38 is:

$$k_2 = k_3[OH^-]^2 P_{O_2} \tag{42}$$

This is seen in Figure 9.17d. It should be noted that the maximum rates of oxygenation of Fe(II) and Mn(II) are separated by 3 pH units. This may cause some operational difficulties at treatment plants where both of these constituents occur. According to Stumm and Morgan,[4] such metal ions as Cu^{2+} and such metal complexes as SO_4^{2-} do not have an appreciable effect on the oxygenation rate of Mn(II). This is somewhat at variance with the experimental data from Hem,[38] who observed a considerable decrease in the rate of oxygenation at a pH value of 9.0 in the presence of 2000 mg/L SO_4^{2-}.

Alternative Oxidants

Chlorine, chlorine dioxide, and potassium permanganate are also employed for oxidation of Mn(II). Table 9.12 shows the thermodynamic feasibility for each oxidative reaction. Kinetic data are sparse and many are empirical and pragmatic in nature. For example, Griffin[39] published a review paper on the removal of Mn(II) from water which stated:

> Chlorine oxidizes Mn(II) to Mn(IV) over a wide range of pH values. At pH values of 8.0 or more and at alkalinities of 50 ppm or more, the oxidation is relatively rapid. At pH 8.0, the time requirements may be approximately 2–3 hours. As the pH increases, the time requirements diminish to the pH values in the softening zone, where the oxidation appears to be complete within minutes. At pH values lower than 8.0, the rate of oxidation appears to be progressively slower as the pH is depressed, until at pH 6.0 the time requirement can be 12 hours or longer.

These statements undoubtedly were made from operational experiences. Some qualitative kinetic data are seen in Table 9.13.[15] Also, it is necessary to have a minimum of 0.5 ppm free available chlorine residual throughout the treatment plant for effective removal.[37] This point had been observed years earlier by Mathews[40] in an experimental water treatment plant. Combined chlorine, i.e., chloramines (see Chapter 11), has very little oxidative effect on Mn(II).

"Chlorine dioxide, generally speaking, oxidizes Mn(II) much more rapidly than chlorine." Griffin's pragmatic statement[39] has no data to support it. "Best results are obtained when the pH is more than 7.0."

"Potassium permanganate oxidizes Mn(II) to Mn(IV) very rapidly."[39] The optimum pH range apparently is 7.2 to 8.3 based on some operational experiences.[41] Here again, some qualitative experimental kinetic data suggest a "rapid" reaction: less than 5 min occurs when 1.0 ppm of Mn^{2+} is treated with 0.5 ppm total residual chlorine and 1.0 to 1.8 ppm $KMnO_4$ over the pH range of 5.0 to 9.0. An interesting observation was reported in 1960[41] that is related to the autocatalytical model cited above.[36,37] Samples of manganese deposits were taken from a distribution system and, when added to solutions of soluble manganese, completely removed this constituent from water.

Such alternative oxidants to oxygen as Cl_2, $KMnO_4$, ClO_2, and H_2O_2 were investigated for the removal of manganese from three natural water sources containing considerable

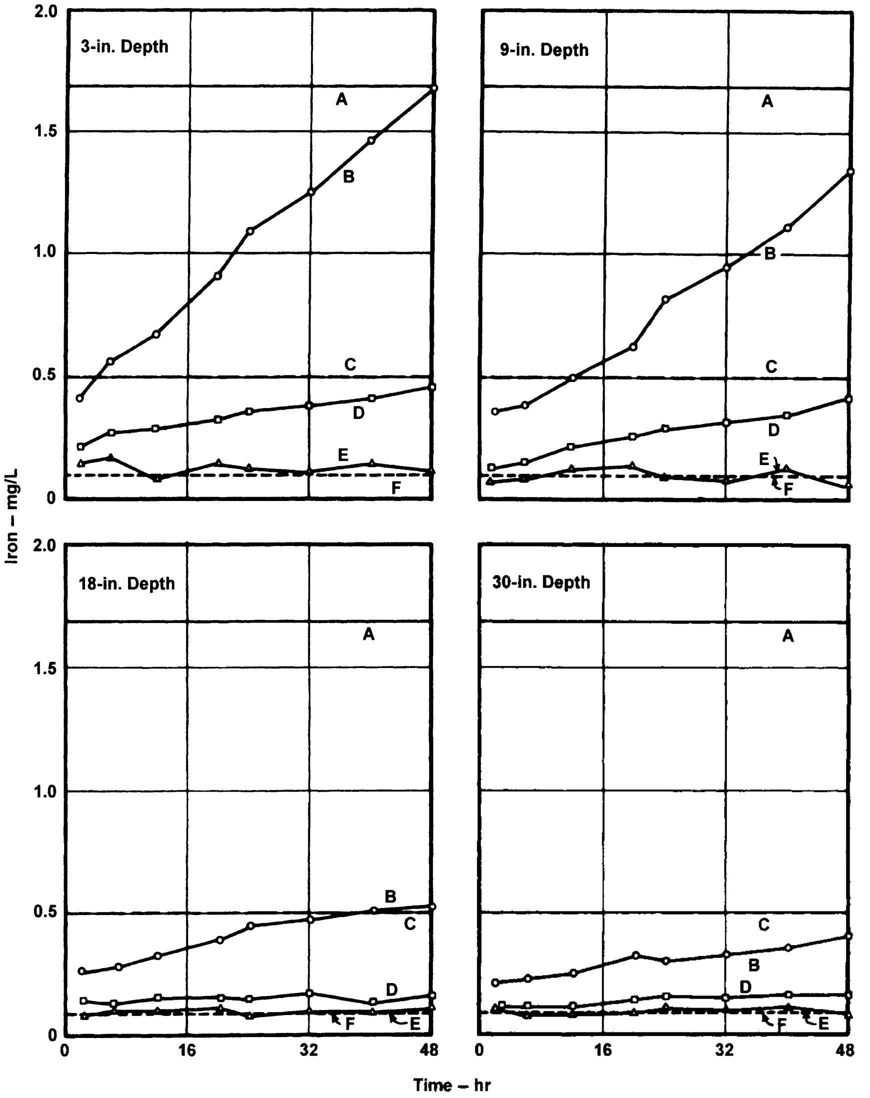

Figure 9.13. Iron concentration in filtered water from "unripe" filters. A = average influent total iron; B = total iron; C = average influent ferrous iron; D = total ferrous iron; E = filterable ferrous iron; F = average influent filterable ferrous iron. Only the 30-in. filter reduced the total iron to an acceptable level. Reproduced from Ghosh et al.,[33] courtesy of the American Water Works Association.

quantities of TOC.[42] Two Virginia rivers and one artificial impoundment were the sources of water for this study. That the [H^+] is an important factor in the Cl_2 oxidation of Mn(II) is seen in Figure 9.18. It was necessary to have the pH value >7.0 in order achieve any significant oxidation within one hour. This is an important water treatment plant operational variable wherein the removal of organics by metal coagulants at pH values <7.0 precludes the oxidation of Mn(II) by Cl_2. On the other hand, $KMn0_4$ achieved a rapid rate of oxidation (5 minutes of contact) at a pH value of 5.5. Chlorine dioxide was, however, one of the more effective oxidants examined in this study. Figure 9.19 shows that dosages of $Cl0_2$ of 1 to 1.5 mg/L effectively oxidized 0.25 mg/L Mn(II) over a wide pH range (5.0 to 8.0). Hydrogen peroxide, up to 3.0 mg/L, was an ineffective oxidant for Mn(II).

An attempt to determine, quantitatively, the kinetics of oxidation of Mn(II) by $KMn0_4$ and $Cl0_2$[19,27] followed the pragmatic study cited above.[19] These oxidations were extremely rapid under most solution conditions. For example, the half-life reaction times ($t_{1/2}$) were 1 to 2 seconds at a pH value of 7.0, and was increased to 6 to 10 seconds at pH 5.5. The rapidity of these reactions may have been affected

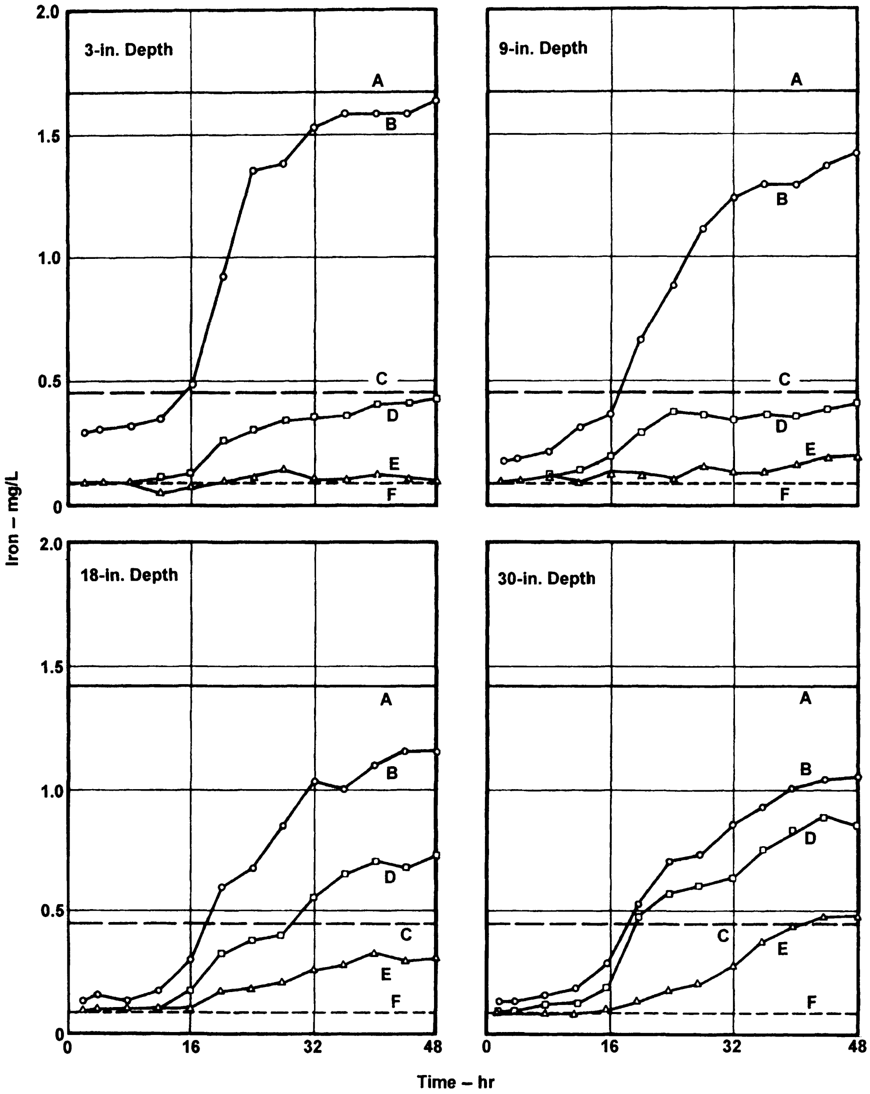

Figure 9.14. Iron concentration in filtered water from "ripe" filters. Lines A to F as in Figure 9.8. After 16–18 hours of filtration, the filterable ferrous iron in the effluent from the 18- and 30-in. filters was higher than that present in the influent. Reproduced from Ghosh et al.,[33] courtesy of the American Water Works Association.

by adsorption of Mn(II) on MnO_x solids formed in the early stages of contact. Inasmuch as Mn(II) is not strongly complexed by dissolved humic or fulvic acids, acceptable rates of oxidation may be obtained in the presence of DOC (Figure 9.20a and b). Of course, the DOC's oxidant demand must be considered in the removal of Mn(II) by $KMnO_4$ and ClO_2.

Filtration

Laboratory-scale studies were conducted to assess the potential for soluble Mn(II) removal with oxide-coated (MnO_x), mixed-media (anthracite coal and sand) filtration systems.[43] Soluble and total Mn removals were evaluated as a function of such parameters as $[H^+]$, presence or absence of an oxidant, quantity and oxidation state of the filter media surface oxide coating, and temperature. Mn(II) removal was rapid and efficient under a variety of solution conditions (pH 6.1 to 9.0, temperature 14 to 17°C). Alkaline pH values promoted efficient removal of Mn(II) on the oxide surface. Such oxidants as $KMnO_4$, ClO_2, and O_3 resulted in Mn(II) oxidation immediately upon addition to the filter that was accomplished, apparently, by retention of colloidal $MnO_{x(s)}$. These results are similar to removal of Fe(II) by bituminous coal filters cited above.[34] However, Mn(II) removal appears to be more efficient and with greater rapidity.

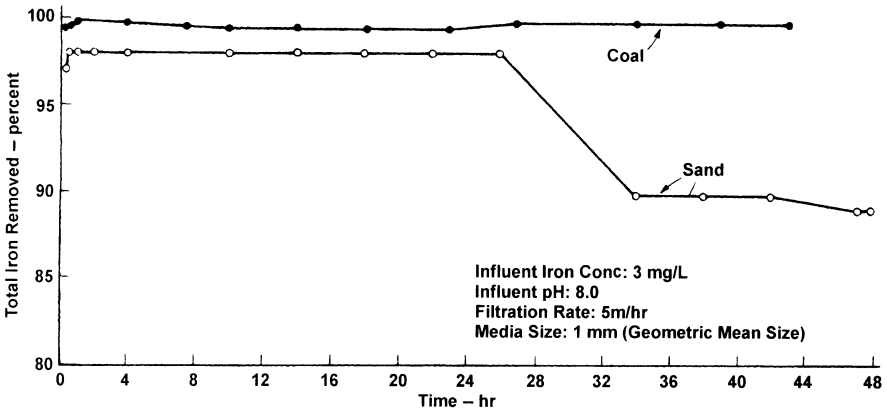

Figure 9.15. Performance of coal and sand filters of equal media size during a 48-hr filtration run. Reproduced from George and Chanduri,[34] courtesy of the American Water Works Association.

Table 9.11. Some Aqueous Reactions for Manganese at 25°C.

Reaction Number	Reaction	log K[a]	E°[c]
29	$Mn^{2+} + 2e = Mn_{(s)}$	–40.0	–1.179
30	$Mn^{2+} + 2OH^{-} = Mn(OH)_{2(s)}$	+12.96[b]	
31	$MnO_{2(s)} + 4H^{+} + 2e = Mn^{2+} + 2H_2O$	+41.6	+1.228
32	$MnO_4^{-} + 4H^{+} + 3e = MnO_{2(s)} + 2H_2O$	+86.0	+1.692
33	$MnO_4^{2-} + 4H^{+} + 2e = MnO_{2(s)} + 2H_2O$	+76.5	+2.257
34	$Mn_2O_{3(s)} + 6H^{+} + 2e = 2Mn^{2+} + 3H_2O$	+48.9	+1.443
35	$Mn_3O_{4(s)} + 8H^{+} + 2e = 3Mn^{2+} + 4H_2O$	+61.8	+1.824
36	$2MnO_{2(s)} + 2H^{+} + 2e = Mn_2O_{3(s)} + H_2O$	+34.4[c]	+1.014
37	$O_2 + 2Mn^{2+} + 2H_2O = 2MnO_{2(s)} + 4H^{+}$		0.0

[a] $K = K_{RED}$ for a reduction reaction and $= K_{eq}$ for a protolysis reaction.
[b] From Morgan.[35]
[c] From Pourbaix.[35]

Kinetic and mechanistic studies were conducted subsequently on the removal of Mn(II) by oxide-coated filter media.[44] Such factors as $[H^+]$, surface concentration of $MnO_{x(s)}$, and free $[Cl_2]$ were examined under laboratory conditions. That the kinetics of adsorption of Mn(II) on the oxide-coated surface is rapid may be seen in Figure 9.21a, where pseudo first-order rate constants are given. The MCL value for Mn, 0.05 mg/L, appears to be attainable within one minute. Figure 9.21b shows the influence of $[H^+]$ on the sorption of Mn by the filter media. Here, greater removal occurred under alkaline conditions than under acidic conditions, where Mn(II) and H^+ ions compete for surface sites. Also, Mn(II) removal rates were enhanced by the presence of free chlorine in the filter-applied water (Figure 9.21c). Apparently, the chlorine was promoting the oxidation of the sorbed Mn(II) on the media surface since "the presence of free chlorine at pH 7.1 did not result in any measurable oxidation of Mn(II) in the filter-applied water."[44] (This statement is inconsistent with earlier studies by the same investigator; see Figure 9.17.) In any event, the chlorine was promoting the oxidation of sorbed Mn(II) on the media surface, which minimized the Mn(II) adsorption density and regenerated the available adsorption sites. All of this research does, indeed, have practical application for full-scale treatment where Mn(II) removal is effected by free chlorine followed by filtration on sand and/or mixed media. This, apparently, has been observed at Durham, North Carolina, for more than a decade.[44]

Ion Exchange

In a manner similar to iron, manganese is removed from water by the manganese-zeolite process.[15,29] The capacity of this zeolite is 0.09 lb/ft^3, and 0.18 lb/ft^3 of $KMnO_4$ is required to regenerate the bed.[39] The usual rate of flow is 3 gpm/ft^2. Here again, the zeolite acts as an oxidizing contact medium, an adsorber of soluble manganese, and a filter medium. For small industrial household uses, manganese-

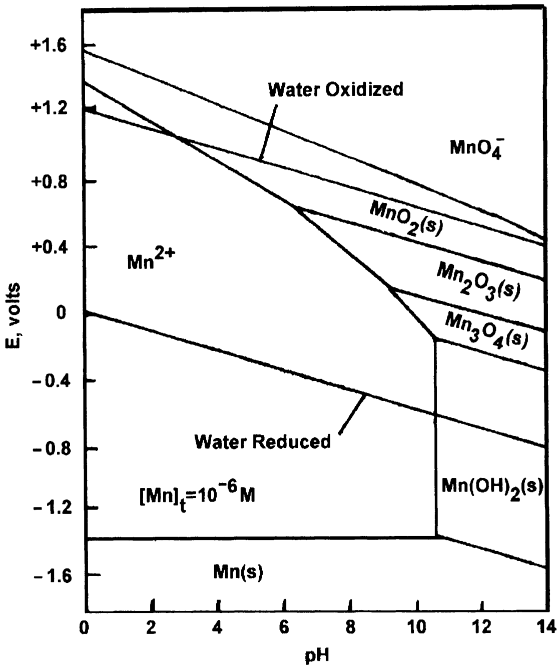

Figure 9.16. pE-pH stability diagram for the system manganese-water at 25°C. Reproduced from Pourbaix,[35] courtesy of Pergamon Press, Inc.

zeolite filters remove Mn or Fe up to 10 mg/L. For large municipal and industrial uses, this process is limited to 1.0 mg/L of these two constituents.[39] The pH value of the water should be 7.5 or greater for the most effective removal.

Settleability and Filterability Difficulties of $MnO_{x(s)}$

Under the proper conditions of pH, the oxidation of Mn(II) by $0_{2(g)}$, Cl_2, and $KMn0_4$ is fairly rapid kinetically. However, the formation and precipitation of $Mn0_{2(s)}$ and/or $Mn0_{x(s)}$ are frequently slow under treatment plant conditions. Furthermore, these oxides have colloidal properties. Some of the operational problems with manganese at a water treatment plant employing chemical coagulation, sedimentation, sand filtration, and postchlorination are indicated here: "Filter runs averaged 24 hours. The fine sand grains were coated with $Mn0_{2(s)}$ deposits; the coarse sand grains were stained dark brown with $Mn0_{2(s)}$, and the gravel beds were heavily coated and cemented with it. The distribution mains, service line, and meters carried heavy deposits of $Mn0_{2(s)}$. Consumer complaints about the water, with regard to the laundering of clothes and staining of porcelain fixtures, were numerous."[39]

$Mn0_{2(s)}$ suspensions can be colloidally dispersed for "several months" in neutral and alkaline pH ranges and in the absence of multivalent cations.[45] Some flocculation occurs slowly when the pH value is lowered to 3.0 and below. Mn(II) ions and other multivalent cations destabilize $Mn0_{2(s)}$ dispersions. Mn^{2+} concentrations of 10^{-4}–10^{-5} *M* cause rapid flocculation of $Mn0_{2(s)}$ colloids within the pH range of normal stability.

Chemical coagulation, sedimentation and sand filtration are imperative treatments following the oxidative step for Mn^{2+}. Briefly stated, alum $[Al_2(SO_4)_3]$ and a coagulant aid (activated silica, for example) are used for flocculation of colloidal $Mn0_{2(s)}$. This $Mn0_{2(s)}$ occurs as a negatively charged colloid over a broad range of pH values (5 to 11). A rather comprehensive study of the electrophoretic characteristics and the coagulation of $Mn0_{2(s)}$ was reported by Posselt et al.[46] For the former, an electromobility value of −2.5 μm/sec/V/cm at a pH value of 5 was measured. This negative value was reduced to −1.0 with 10 mg/L and higher of Ca^{2+} with concurrent destabilization of colloidal $Mn0_{2(s)}$. This clearly demonstrates the role of surface charge in the coagulation of this colloid. Subsequent experiments were conducted at pH values of 5, 7, and 9 with the polycation PDADMA, ferric sulfate, alum, and various combinations of these coagulants and aids. Figure 9.22 shows typical results with PDADMA and alum. The V-shaped curves in Figure 9.22a show that destabilization of the colloid occurs from sorption of the PDADMA, and restabilization occurs from an excessive quantity of the polycation. This was confirmed by separate electromobility measurements where complete restabilization corresponded to a more or less con-

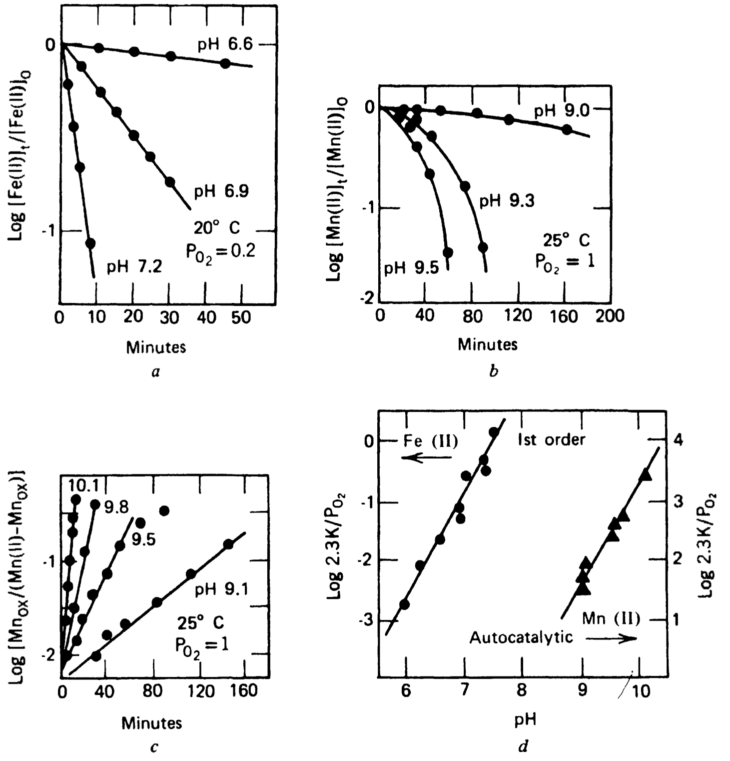

Figure 9.17. Oxidation of Fe(II) and Mn(II) by oxygen. All experiments were conducted with dissolved Fe(II) or Mn(II) concentrations of less than 5 x 10^{-4} *M*. In each series of experiments, the pH was controlled by continuously bubbling CO_2- and O_2-containing gas mixtures through HCO_3^- solutions of known alkalinity. (a) Oxygenation of Fe(II) in bicarbonate solutions. (b) Removal of Mn(II) by oxygenation in bicarbonate solutions. (c) Oxidation of Mn(II) in HCO_3^- solutions (autocatalytic plot). (d) Effect of pH on oxygenation rates. Reproduced from Stumm and Morgan,[4] courtesy of John Wiley & Sons, Inc.

Table 9.12. Reactions of Mn(II) with Alternative Oxidants at 25°C.

Reaction Number	Reaction	E°
31	$Mn^{2+} + 2H_2O = MnO_{2(s)} + 4H^+ + 2e$	+1.228
25 and 31	$5Mn^{2+} + 6H_2O + 2ClO_{2(g)} = 5MnO_{2(s)} + 12H^+ + 2Cl^-$	+0.283
26 and 31	$Mn^{2+} + 2H_2O + Cl_{2(g)} = MnO_{2(s)} + 4H^+ + 2Cl^-$	+0.131
27 and 31	$3Mn^{2+} + 2H_2O + 2MnO_4^- = 5MnO_{2(s)} + 4H^+$	+0.467

Table 9.13. Manganese: Effect of pH on the Oxidation of Manganous Manganese by Chlorine, Without Stirring.[a]

Raw Water		Manganese in Treated and Filtered Water (ppm)		
pH	Manganese (ppm)	15 min	30 min	60 min
8.05	10.0			9.0
9.0	10.0	8.0	6.5	5.0
9.45	10.0	4.5	2.5	1.3
10.0	10.0	0.3	0.1	<0.02

[a] Reproduced from Nordell,[15] courtesy of Van Nostrand Reinhold Company.

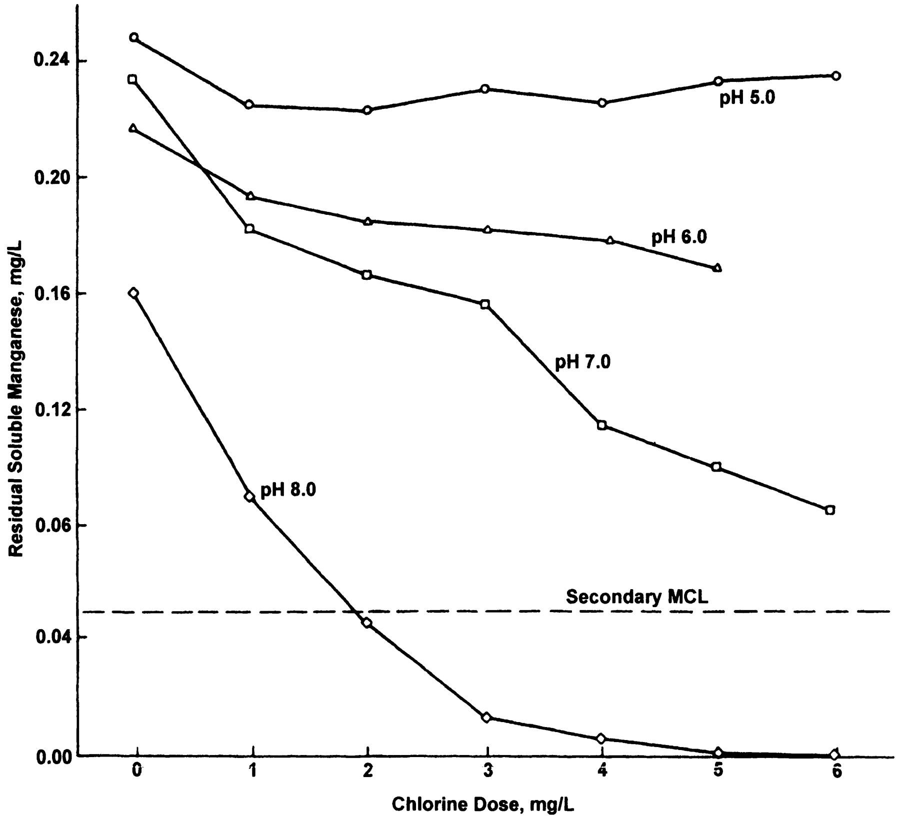

Figure 9.18. Effect of solution pH and oxidant dosage on the oxidation of soluble manganese by free chlorine (raw water—New River; temperature—68°F [20°C]).[42]

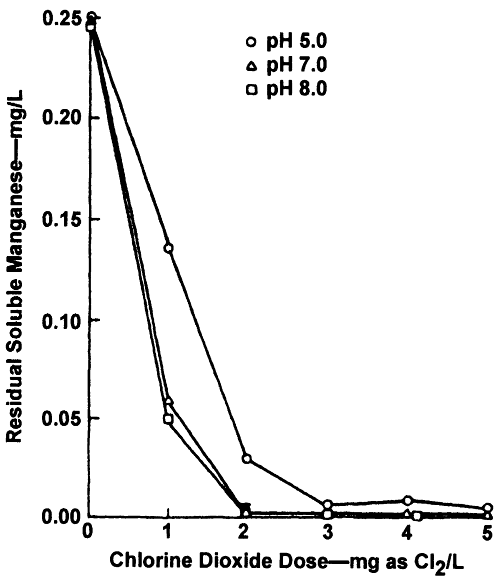

Figure 9.19. Effect of solution pH and oxidant dosage on the oxidation of soluble manganese by chlorine dioxide (raw water—New River; temperature—68°F [20°C]).[42]

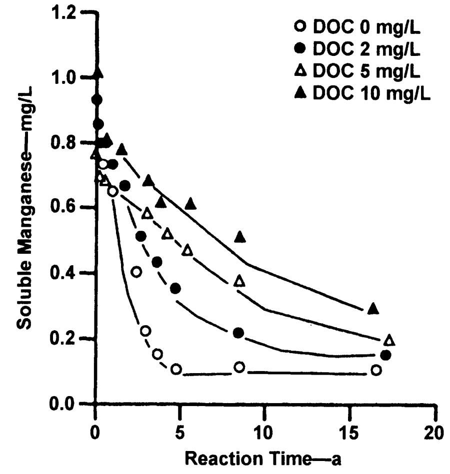

Figure 9.20a. Mn(II) oxidation by potassium permanganate in the presence of different concentrations of Thousand Acre fulvic acids (temperature = 25°C; target pH = 7.0).[19]

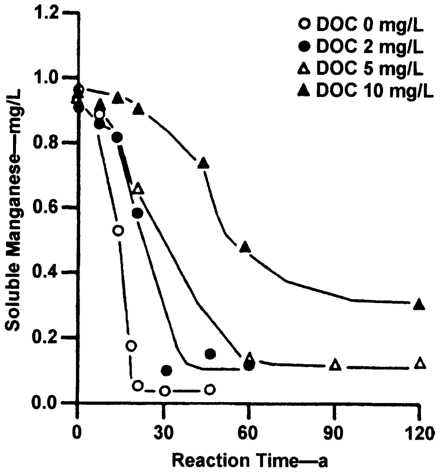

Figure 9.20b. Mn(II) oxidation by chlorine dioxide in the presence of different concentrations of Thousand Acre fulvic acids (temperature = 25°C; target pH = 5.5).[19]

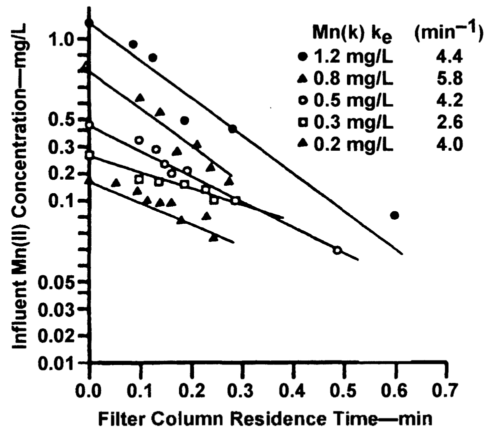

Figure 9.21a. Effect of initial Mn(II) concentration on observed Mn(II) sorption rate at pH 7.1 (media surface oxide concentration = 3.3 mg Mn/g media; no free chlorine present in filter-applied water).[44]

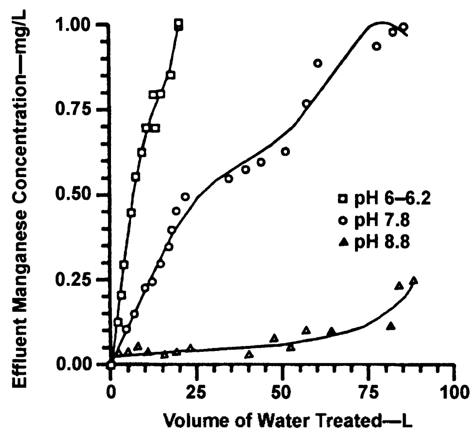

Figure 9.21b. Effect of solution pH on Mn(II) removal by media A [3 mg/g Mn(II) on surface] in the absence of free chlorine [influent Mn(II) = 1.0 mg/L].[44]

stant value of +1.5 to 2 μm/sec/V/cm. Figure 9.22b shows the coagulation of $MnO_{2(s)}$ by alum, for which the optimum dosage was somewhat dependent on the pH value. Similar results were obtained for ferric sulfate. Parallel experiments were conducted for each of the coagulants in the presence of Ca^{2+} ions. In each case, the coagulant dose was lowered considerably due to neutralization of negative surface charges by the Ca^{2+}, especially at pH values of 7 and 9.

Sodium hexametaphosphate has been used to stabilize Mn^{2+} where concentrations are 2.0 mg/L and below.[47] A 2:1 ratio of phosphate usually is effective for stabilization, and pH values are in the 7 to 8 range. This treatment is confined mostly to groundwaters.

CASE STUDIES OF IRON AND MANGANESE REMOVAL

The Allegheny River at Wilkinsburg, Pennsylvania was treated for removal of 0.5 to 4.0 mg/L Mn with an average annual concentration of 1.2 mg/L.[41] Experimentation on a pilot-plant scale led to this order of chemical addition: chlorine, lime, $KMnO_4$, alum, and polyelectrolyte (coagulation aid). pH values were maintained in the 7.2 to 8.3 range. Considerable experimentation with the quantities and order of the addition of these chemicals produced a 10-yr average of 0.05 mg/L Mn in the treated water.

A split-flow treatment was used for Fe and Mn removal from groundwater supplies (12 wells) of Eau Claire, Wis-

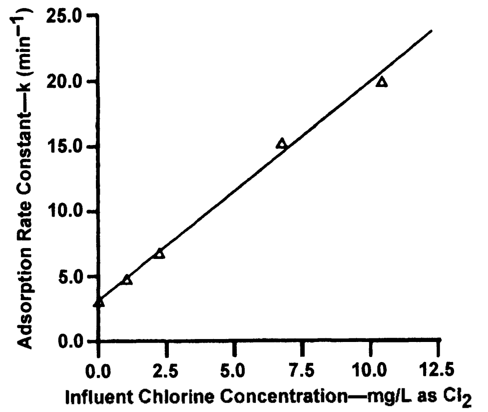

Figure 9.21c. Effect of free chlorine concentration on observed rate of Mn(II) sorption onto $MnO_{x(s)}$-coated media [pH = 7.1; $MnO_{x(s)}$ concentration = 3.3 mg Mn/g media].[44]

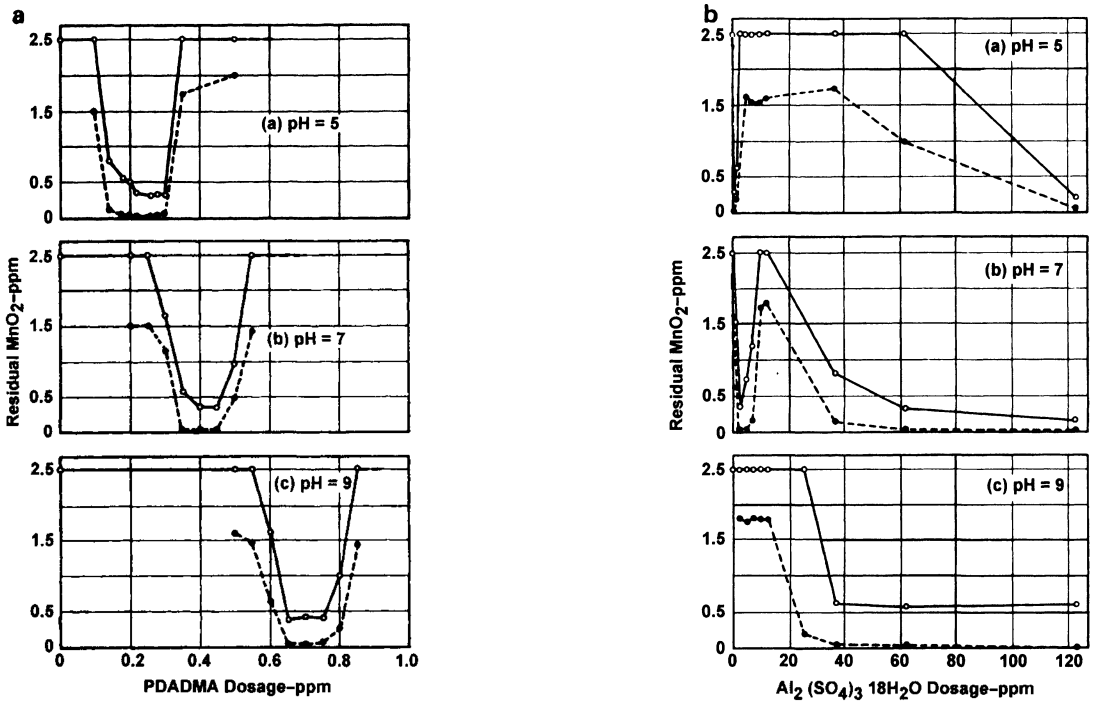

Figure 9.22. (a) Effect of a polycation on the stability of colloidal hydrous $MnO_{2(s)}$. The polyelectrolyte used in these experiments was PDADMA polycation. The solid lines represent unfiltered samples, and filtered samples are represented by dashed lines. HCl was used for adjustment and maintenance of pH 5; Na_2CO_3 was used for pH 7 and 9. (b) Coagulation of hydrous $MnO_{2(s)}$ with aluminum sulfate. Solid lines represent unfiltered samples; dashed lines represent filtered samples. Reproduced from Posselt et al.,[46] courtesy of the American Water Works Association.

consin.[48] Iron contents ranged from 0 to 2.4 mg/L, and manganese contents ranged from 0 to 5.66 mg/L. The treatment process consisted of pre- and postchlorination, coagulation, and precipitation with $Ca(OH)_2$, and activated silica for coagulant aid. The plant was equipped with two solids contact units (see Chapter 6 for a descriptive illustration) and four rapid sand filters, each rated at 6 MGD. The $Ca(OH)_2$ was the essence of the treatment, where Fe and Mn were removed by coagulation and precipitation in the suspended sludge blanket in the solids contact unit. It was necessary to raise the pH value to 9.5 or so for 100% removal of Mn. Split-flow treatment was achieved by treating the well waters containing the Fe, Mn, and "high" alkalinity. With the aid of activated silica, a controlled sludge blanket was maintained for these waters. The effluent from the solids contact unit was mixed with other well waters with low alkalinities and no Fe and Mn. The combined waters had a pH value of 8.5, and required very little or no recarbonation. The combined waters were 45% treated and 55% raw water.

A survey of 29 iron and manganese removal plants in eastern Nebraska was conducted for conformance to the drinking water standards of 0.3 and 0.05 mg/L, respectively.[49] This study also provided an excellent opportunity for a concurrent evaluation of various treatment schemes. A compilation and summary of the data are given in Table 9.14. From this study, it was concluded that the percentage of plants meeting the standards were: 45% where only aeration, contact time, and filtration were used (data not shown), 58% where aeration, chemical addition, contact time, and filtration were used (Table 9.14a), and 100% where aeration and partial softening were used (Table 9.14b).

The municipality of Fredericton, New Brunswick, Canada maintains 23 active wells as its water source, where Mn content is "far in excess of the 0.05 mg/L level recommended by the Canadian drinking water guidelines."[50] Two systems were chosen for pilot studies: (a) a conventional manganese greensand filter that used Cl_2 and MnO_4 as oxidants, and (b) a "new" type filter media (electro-media) that uses Cl_2. After a few months of operation, the flow diagram and treatment scheme (Figure 9.23) was installed for Mn(II) removal and pH control. Water is chlorinated first (1 minute contact time, 2.0 mg/L), after which lime, soda ash, and SO_2 were added. Manganese is "precipitated" and filtered from solution. Subsequently, the SO_2 reduces the excessive quantity of Cl_2. Lime and soda ash, of course, raises the pH value for rapid oxidation of the Mn(II) and subsequent precipitation. However, it is not clear from the report why both lime and soda ash were applied unless the water supply required softening. Figure 9.24 shows the results for seven months of operation that produced Mn levels consistently below 0.05 mg/L except for four days.

PROCESSES FOR IRON AND MANGANESE REMOVAL PLANTS

Several designs and flow schematics are available for the removal of iron and manganese from raw water supplies. The following represent systems that are in current use by various water utilities in the United States:[51]

- aeration and filtration using pressure aeration
- aeration, detention, and filtration using forced draft aeration
- aeration, detention, and filtration using multiple-tray aerators
- manganese-zeolite filter system
- zeolite softener with manganese-zeolite on bypass portion
- aeration, settling, and filtration
- chlorination and filtration

The reader is directed to Reference 51 for the details of design and operation of the systems seen in Figures 9.25 to 9.30. It should be noted that these schematics reflect only the engineering aspects of iron and manganese removal. Any adjustment of the chemical water quality is not evident in these schematics. The reader should review the above information about iron and manganese removal.

PRIMARY DRINKING WATER INORGANICS

Table 9.15 gives the current drinking water standards for the primary (health-related) inorganics. BATs are given also for their removal from raw water supplies. This section of Chapter 9 briefly reviews the chemistry of each contaminant and their method of removal. An excellent overview article for removal of dissolved inorganics from water is to be found in Reference 52.

ANTIMONY

Aqueous Chemistry

Small quantities of antimony are found in such diverse locations as Borneo; Sweden; Germany; Portugal; Italy; Sardinia, New Brunswick, Canada; and Kern County, California.[53] It is found usually in hydrothermal lodes containing sulfo-arsenides and sulfo-antimonides. Its occurrence in natural waters would be rare, indeed.

The aqueous acid-base chemistry is given in Table 9.16 for two oxidation states, (III) and (V). Two weak acids may occur in the water phase: $HSbO_2$ [antimonious acid, (III)] and $HSbO_3$ [antimonic acid, (V)]. Since the latter is an extremely strong acid in water, its amphoteric nature yields the SbO_3^- (antimonate) ion directly from the reaction of the SbO_2^+ (antimonic) ion with H_2O. The aqueous chemistry of Sb is similar to that of As seen below. The MCL for Sb in drinking water is 0.006 mg/L.[1]

Removal

Reverse osmosis is the recommended BAT (Table 9.15) for removal of Sb from water. Very little information is available for the efficacy of this process for Sb elimination from drinking water. Since the chemistry of Sb is similar to that of As, treatment processes for the latter may be effective also for Sb (see below).

Table 9.14a. Iron and Manganese Data on Nebraska Water Supplies (Treatment Provided: Aeration, Chemical Addition, Contact Time, and Filtration).[a]

Municipality No.	Population[b]	Treatment Provided[c]	Iron (mg/L) Inf.	Iron (mg/L) Eff.	Manganese (mg/L as $CaCO_3$) Inf.	Manganese (mg/L as $CaCO_3$) Eff.	Chlorine Residual (mg/L) Eff.	pH Eff.
13	3,650	ApCclDfgs	0.50	0.03	0.15	<0.02	0.35	7.4
14	642	ApCcsDFps	2.40	0.85	0.50	0.45	0.30	7.8
15	323	ApCcDFps	1.15	0.10	0.55	0.20	0.30	7.6
16	149,518	CcAcCcDFgsCn	0.10	0.05	0.10	<0.02	1.00	7.8
17	2,669	ApCcDFgs	0.70	0.65	0.20	0.08	0.10	8.0
18	7,441	CclApDFgsCcf	(3.80)[d]	0.05	(1.50)	<0.02	0.40	8.4
19	1,355	ApCcDfp	(0.90)	0.20	(0.20)	<0.02	0.20	6.9
20	6,371	AccDFgs	(6.50)	0.20	(2.00)	0.02	0.25	7.9
21	291	ApCcFp	10.00	0.10	2.50	0.02		7.5
9[e]	7,920	AtCcDFgs	(3.00)	0.10	(0.60)	<0.02	0.20	
22	1,215	ACcDFgs	0.06	0.06	0.25	0.12		
23	285	ApCcDFps	3.55	0.60	0.95	<0.02	1.00	7.0

[a] Reproduced from Andersen et al.,[49] courtesy of the American Water Works Association.

[b] Preliminary U.S. census figures for 1970.

[c] Explanation of treatment symbols:

A—Aeration or oxidation; c—contact beds or trap filled with coke or other material; p—patented aerator; t—overflow trays, cascade, or other splash aerator

C—Chemicals added; c—chlorine; f—fluoride; l—lime; n—ammonia

D—Detention

F—Filter; g—gravity; p—pressure; s—sand

[d] Concentrations in parentheses are average values obtained for wells pumping at the time of plant visitation.

[e] Municipality has two iron- and manganese-removal plants.

Table 9.14b. Iron and Manganese Data on Nebraska Water Supplies (Treatment Provided: Aeration and Partial Lime Softening).[a]

Municipality		Treatment	Iron (mg/L)		Manganese (mg/L)		Hardness (mg/L as $CaCO_3$)		Chlorine Residual (mg/L)	pH
No.	Population[b]	Provided[c]	Inf.	Eff.	Inf.	Eff.	Inf.	Eff.	Eff.	Eff.
24	19,449	AtSlFgsCcFp	7.50	0.05	0.40	<0.02	472	160	0.60	9.4
25	6,106	ACcSlFgs	(4.40)[d]	0.03	(0.75)	<0.02			0.20	8.5
26	5,444	ApCcDSalFgs	4.00	0.03	1.10	<0.02	330	196		8.4
27	1,177	ADSalFgs	0.60	0.03	1.05	<0.02	300	152	0.00	8.5
28	2,779	ApCcSalFgs	(0.75)	0.05	(0.75)	<0.02	310	106	0.70	8.5

[a] Reproduced from Anderson et al.,[49] courtesy of the American Water Works Association.

[b] Preliminary U.S. census figures for 1970.

[c] Explanation of treatment symbols:
A—Aeration or oxidation; p—patented aerator; t—overflow trays, cascade, or other splash aerator
C—Chemicals added; c—chlorine
D—Detention
F—Filter; g—gravity; p—pressure; s—sand
S—Softening unit; a—alum; l—lime

[d] Concentrations in parentheses are average values obtained for wells pumping at the time of plant visitation.

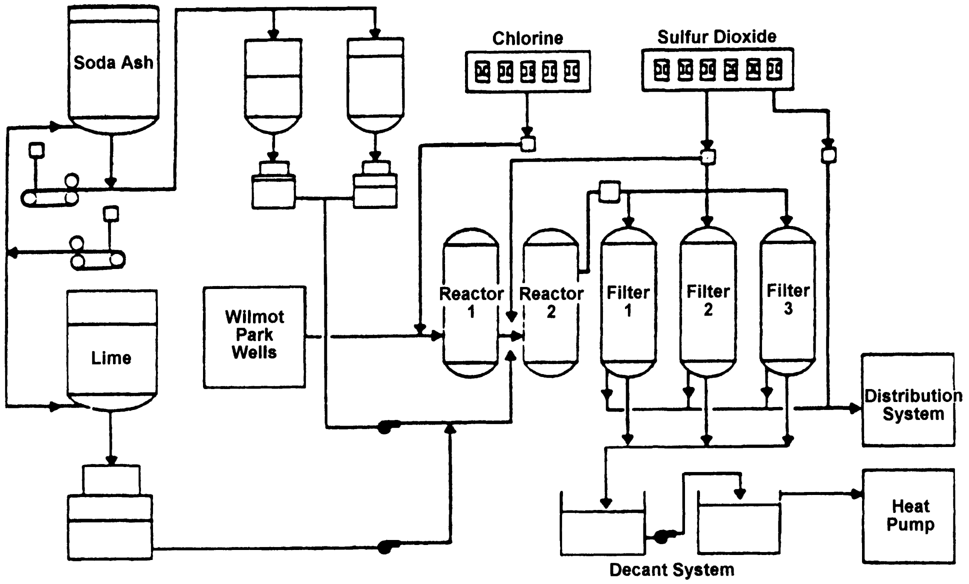

Figure 9.23. Manganese removal plant.[50]

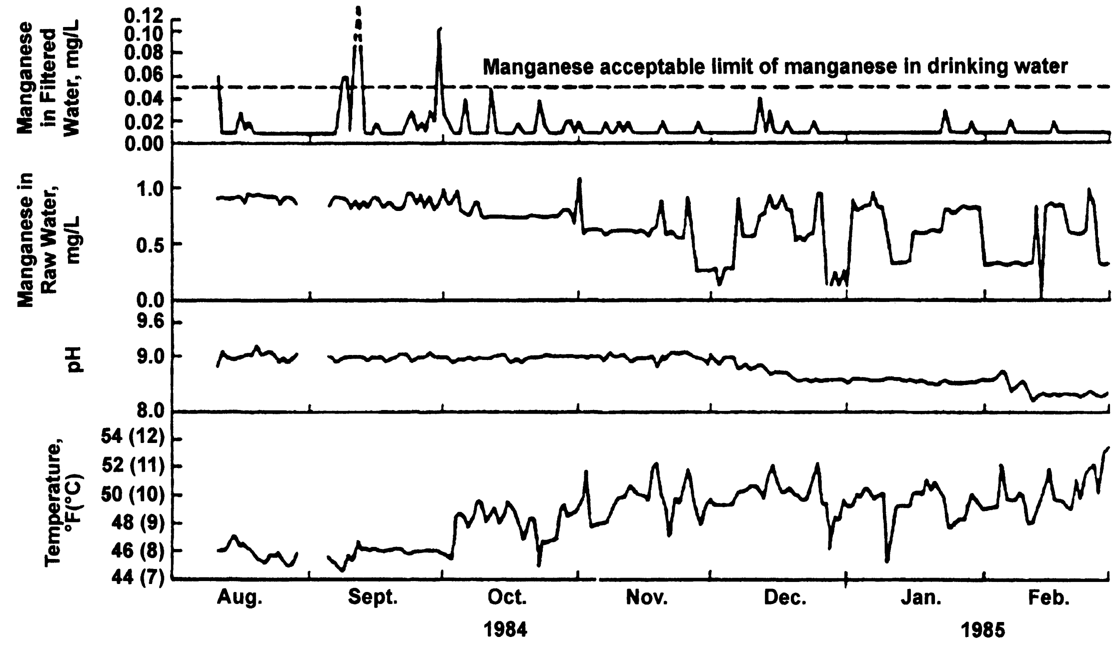

Figure 9.24. Manganese in raw water and manganese, pH, and temperature in filtered water.[50]

ARSENIC

Aqueous Chemistry

Arsenical compounds are among the most widely distributed elements in the earth's crust and in the biosphere. The concern about arsenic in the environment is given in Chapter 1 and in Faust and Aly.[2] For the most part, arsenic occurs in an inorganic form in aquatic environments resulting from the dissolution of such solid phases as $As_20_{3(s)}$ (arsenolite), $As_20_{5(s)}$ (arsenic anhydride), and $AsS_{2(s)}$ (realgar). Two weak acids may occur in the water phase: $HAs0_2$ [arsenious acid (III oxidation state)] and H_3As0_4 [arsenic acid (V oxidation state)]. The acid-base equilibria are given in Table 9.17. Since the solubilities of the oxides are "high,"

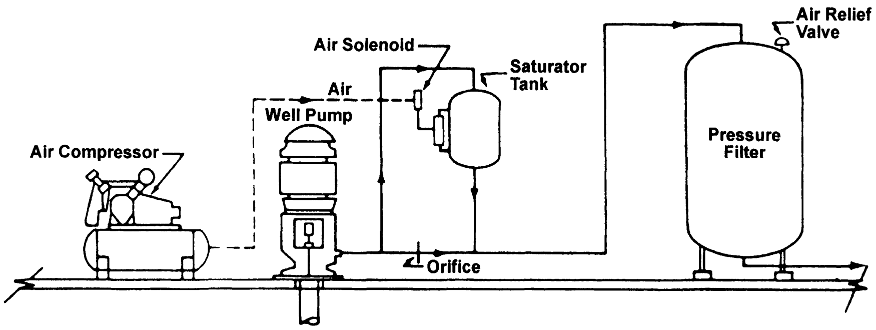

Figure 9.25. Aeration and filtration (using pressure aeration for iron removal).[51]

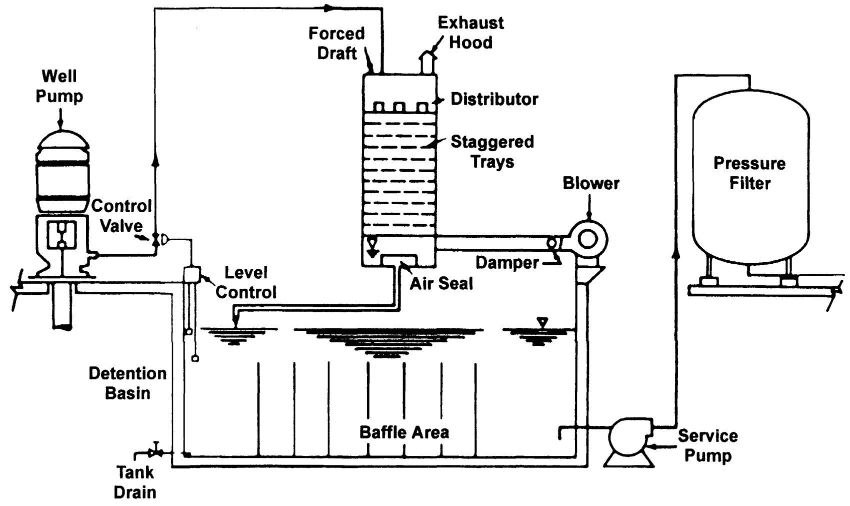

Figure 9.26. Aeration, detention, and filtration (iron removal).[51]

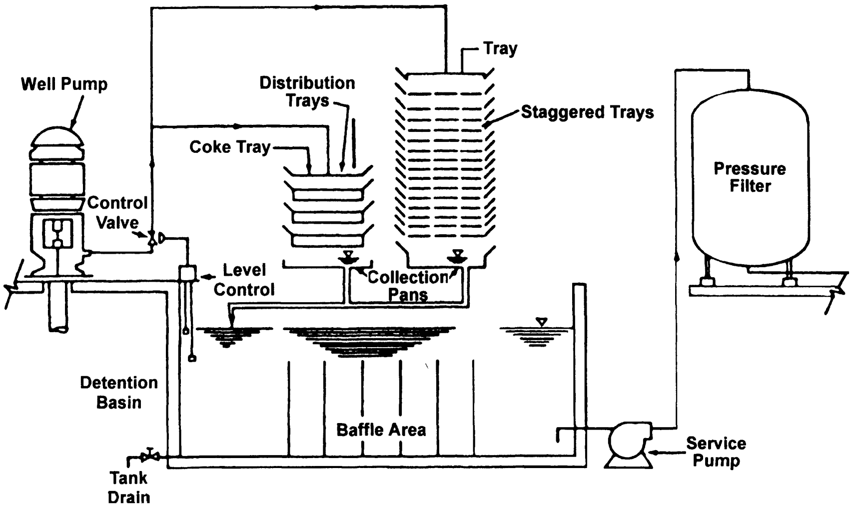

Figure 9.27. Aeration, detention, and filtration (iron and manganese removal).[51]

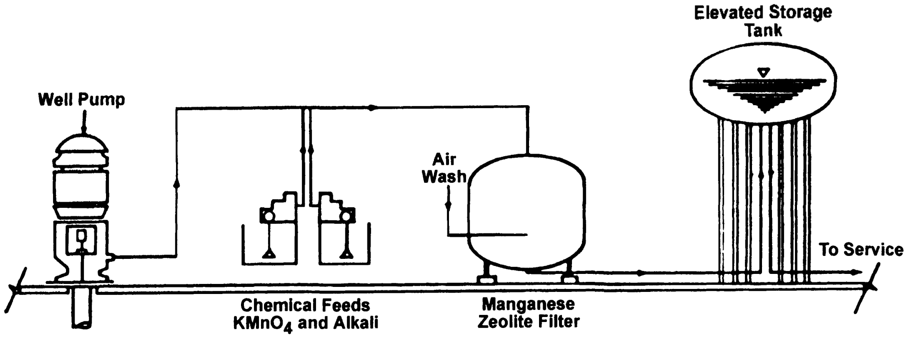

Figure 9.28. Manganese zeolite filter (iron and manganese removal).[51]

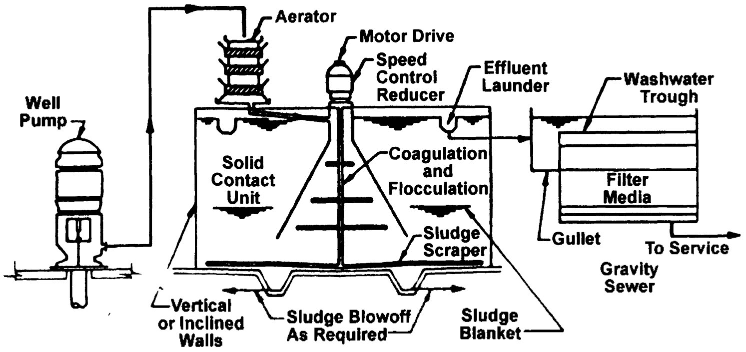

Figure 9.29. Aeration, settling, and filtration (iron and manganese removal).[51]

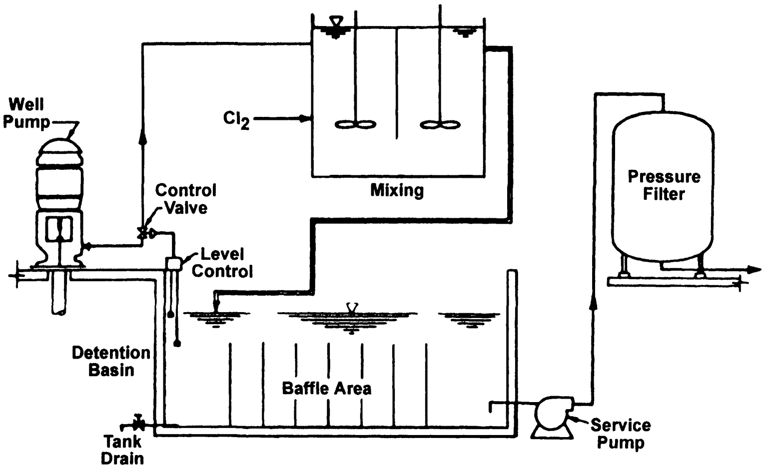

Figure 9.30. Chlorination, detention, and filtration (iron and manganese removal).[51]

arsenic occurs in the anionic form, which is dependent on the pH value of the water. There are environments of pH values and redox values where reduced oxidation states and methylated forms of arsenic occur: $CH_3H_2AsO_3$ (monomethylarsenic acid), $(CH_3)_3As$ (trimethylarsine), and AsH_3 (arsine). These arsenical compounds, however, are not stable in the oxidizing conditions of water treatment plants. Faust and Aly[2] give more information about the environmental chemistry of arsenic. The MCL value for arsenic in drinking water is 0.05 mg/L.[1]

Table 9.15. USEPA Drinking Water Standards and BAT for Regulated Inorganic Contaminants[a].[1]

	Standards				Best Available Technology	
Contaminant	**Regulation**	**Status**	**MCGL (mg/L)**	**MCL (mg/L)**	**Conventional Processes**	**Specialized Processes**
Antimony	Phase V	Final	0.006	0.006	C–F[b]	RO
Arsenic	Interim			0.05		
Asbestos (fibers/L>10 µm)	Phase II	Final	7 MFL	7 MFL	C–F;[b] DF; DEF; CC	
Barium	Phase II	Final	2	2	LS[b]	IX; RO
Beryllium	Phase V	Final	zero	0.001	C–F;[b] LS[b]	AA; IX; RO
Cadmium	Phase II	Final	0.005	0.005	C–F;[b] LS[b]	IX; RO
Chromium (total)	Phase II	Final	0.1	0.1	C–F;[b] LS (Cr III)	IX; RO
Copper	Lead and copper	Final	1.3	TT	CC; SWT	
Cyanide	Phase V	Final	0.2	0.2	Cl_2	IX; RO
Fluoride	Fluoride	Final	4.0	4.0		AA; RO
Lead	Lead and copper	Final	zero	TT	CC; PE; SWT; LSLR	
Mercury	Phase II	Final	0.002	0.002	C–F (influent <10 µg/L);[b] LS[b]	GAC; RO (influent ≤10 µg/L)
Nickel	Phase V	Final	0.1	0.1	LS[b]	IX; RO
Nitrate (as N)	Phase II	Final	10.0	10.0		IX; RO
Nitrate (as N)	Phase II	Final	1.0	1.0		IX; RO
Nitrate + nitrite (both as N)	Phase II	Final	10	10		IX; RO
Selenium	Phase II	Final	0.05	0.05	C–F (Se IV);[b] LS[b]	AA; RO
Sulfate	Sulfate	Proposed	400/500	400/500	C–F	IX; RO
Thallium	Phase V	Final	0.0005	0.002		AA; IX
Radionuclides						
Beta-particle and	Interim			4 mrem	C–F	
photon emitters	Rad	Proposed	zero	4 mrem	C–F	IX; RO
Alpha emitters	Interim			15 pCi/L	C–F	
		Rad	Proposed	zero	15 pCi/L	C–F RO
Radium 226 + 228	Interim			5 pCi/L	C–F	
Radium 226	Rad	Proposed	zero	20 pCi/L	LS[b]	IX; RO
Radium 228	Rad	Proposed	zero	20 pCi/L	LS[b]	IX; RO
Radon	Rad	Proposed	zero	300 pCi/L		Aeration
Uranium	Rad	Proposed	zero	20 µg/L	C–F;[b] LS[b]	AX; LS

[a] Abbreviations used in this table: AA—activated alumina; AX—anion exchange; CC—corrosion control; C–F—coagulation–filtration; Cl_2—chlorination; DEF—diatomaceous earth filtration; DF—direct filtration; GAC—granular activated carbon; IX—ion exchange; LS—lime softening; LSLR—lead service line removal; MFL—million fiber/liter; PE—public education; RO—reverse osmosis; SWT—source water treatment; TT—treatment technique.

[b] Coagulation–filtration and lime softening are not BAT for small systems for variances unless treatment is already installed.

Table 9.16. Acid-Base Equilibria of Antimonious and Antimonic Acids at 25°C.[53]

Reaction Number		Reaction	log Ka
43	+3	$SbO^- + H_2O = HSbO_2 + H^-$	–00.87
44	+3	$HSbO_2 = SbO_2^- + 2H+$	–11.00
45	+5	$SbO_2^- + H_2O = SbO_3^- + 2H^-$	0.54

Table 9.17. Acid-Base Equilibria of Arsenious and Arsenic Acids at 25°C.[52]

Reaction Number	Reaction	log Ka
	+3	
46	$AsO^+ + H_2O = HAsO_2 + H^+$	0.34
47	$HAsO_2 = AsO_2^- + H^-$ +5	–9.21
	+5	
48	$H_3AsO_4 = H_2AsO_4^- + H^+$	–3.60
49	$H_2AsO_4^- = HAsO_4^{2-} + H^+$	–7.26
50	$HAsO_4^{2-} = AsO_4^{3-} + H^+$	–12.47

Removal

A laboratory evaluation of conventional water treatment processes for removal of As contents ranging from 0.6 to 2.0 mg/L in Taiwanian groundwaters has been reported.[55] Coagulation by alum and lime (separately) effected removals of 32 and 20%, respectively, of 1.0 mg/L As_t at a pH of 6.8. A 50 mg/L dosage of $FeCl_3$ reduced 1.0 mg/L As_t by 90% at a pH of 6.8. The addition of an oxidant, $KMn0_4$ or Cl_2, to coagulation by $FeCl_3$ produced As removal on the order of 95% to 98%. A combined process of chlorine and ferric chloride can effect As removal up to 100%. Slow and rapid filtration through anthracite or sand were ineffective for As removal. Based on these results from laboratory studies, a pilot plant was constructed in which a combination of conventional schemes was tried. The most effective treatment (100% removal) was 20 mg/L Cl_2 followed by 50 mg/L $FeCl_3$, sedimentation, and sand filtration. The sand filter eventually had to be washed with NaOH to remove the As. A permanent water treatment plant eventually was constructed consisting of: aeration, mixer, sedimentation tank, two slow sand filters, storage tank, elevation tank and a sand-washing basin.

Removal of arsenic (III and V) by hydrous oxides of Al and Fe is seen in Figure 9.31.[56] More than 90% of As(V) can be removed by alum at pH values <7, by ferric chloride at pH values <8.5, or by lime softening at pH values <10.5, (*Author's Note:* the MCL of 0.3 for As cited in Figure 9.31 was in effect in the 1970s). Presumably, the removal of As in the last case was due to adsorption on $Mg(OH)_{2(s)}$. Best removals of As(III) occurred by oxidation first to As(V) before coagulation or softening.

Adsorption "fronts" for As(V) on $Fe(OH)_{3(am)}$, $Al(OH)_{3(am)}$, activated alumina, and activated carbon are seen in Figure 9.32.[56] Adsorption on each of these solids is greatest in the pH range of 4 to 7 when the adsorbate is negatively charged and the adsorbents are positively charged. This is a generic statement since the four adsorbents have a variety of sorption sites and surface densities. Nonetheless, amorphous $Al(OH)_3$ appears to be the most efficient adsorbent of the four seen in Figure 9.32.[56] That As(II) is less strongly adsorbed than As(V) is seen in Figure 9.33. Presumably this is due to the nonionic nature of arsenous acid (pKa=9.21) in the neutral pH range. Some relevant references for Figures 9.32 and 9.33 are References 57–59.

Recent reports have claimed that chemical coagulation is an effective treatment technique for arsenic removal.[59a,b] Alum and ferric coagulants are almost equally effective (on a molar basis) for the removal of As(V) at pH values <7.5.[59a] However, iron is more efficient than alum in removing As(III) and As(V) at pH values >7.5. For As(III), an 80% removal of a 300 µg/L was effected by Fe(III), 90 µ*M* (5 mg/L) over a pH range of 5.5 to 9.0. On the other hand, the same concentration of Al(III) removed, on the average, only 40% of the As(III).

The use of enhanced coagulation for arsenic removal was examined at the facilities of a California utility in the early 1990s.[59b] Alum and ferric chloride with a cationic polymer were investigated for their removal of arsenic from spiked

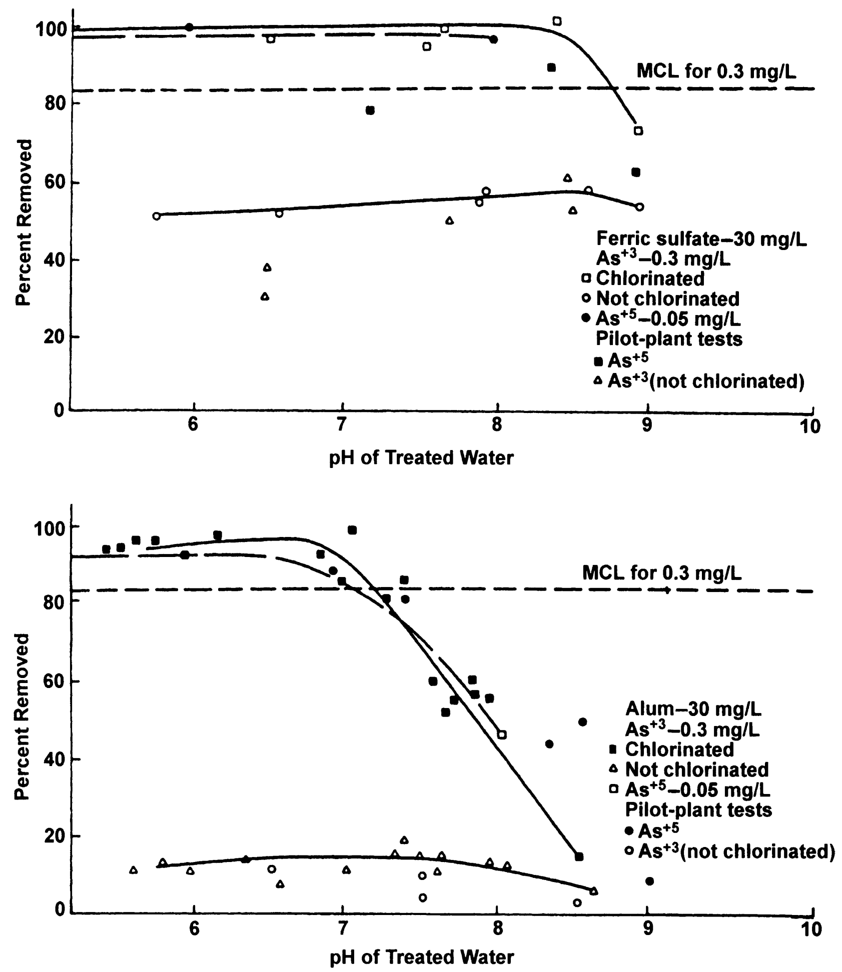

Figure 9.31. Removal of arsenic during water treatment [As(III) cannot be removed as readily as As(V); ferric chloride is a more effective adsorbent than alum for removal of most trace inorganic materials].[56]

(circa 20 μg/L) source waters via bench, pilot, and demonstration experiments. The bench- and pilot-scale data suggest that: (a) $FeCl_3$ is more effective than alum with dosages ranging from 10 to 30 mg/L, (b) the effectiveness of alum is pH-dependent where the greatest As(V) removals are achieved at pH <7 with dosages in the 10–30 mg/L range, and (c) the effectiveness of $FeCl_3$ coagulation is not pH-dependent between 5.5 and 7.0. These coagulation studies were oriented toward the achievement of an effluent As(V) content of <0.5 μg/L, a proposed MCL for arsenical species.

In anticipation of the establishment of an MCL for arsenic (see Chapter 1), the Metropolitan Water District of Southern California (MWDSC) analyzed the feasibility of meeting this standard in its conventional treatment plants through treatment with ferric chloride or alum.[59c] MWDSC typically has 2–5 μg/L arsenic (V) in its surface water supplies. However, future water sources could potentially include water with arsenic levels exceeding 20 μg/L. Consequently, a goal of 90% arsenic removal (from 20 to 2 μg/L) was chosen for this study. When the source water was treated with 3–10 mg/L of ferric chloride or 6, 10, or 20 mg/L of alum, arsenic removal was 81–96% (ferric chloride) and 23–71% (alum). On a metal-equivalent basis, Fe(III) removed more arsenic than Al (III)in the pH range from 7.18 to 7.8. Removal studies conducted at bench, pilot, and demonstration scales produced trends similar to those found in this full-scale study.

Arsenic "profiles" were obtained from 15 full-scale conventional treatment plants (5 coagulation, 5 Fe-Mn oxidation, or 5 softening plants that facilitated testing of theories relative to arsenic removal).[59d] The speciation of arsenic [particulate As, As(V), and As(III)] through the plants, raw-water qualities, and treatment strategies that influenced removal were explored as part of this evaluation. At full-scale treatment plants, oxidation of >1.5 mg/L Fe^{2+} resulted in an 80–95% removal of arsenic. Oxidation of Mn^{2+} did

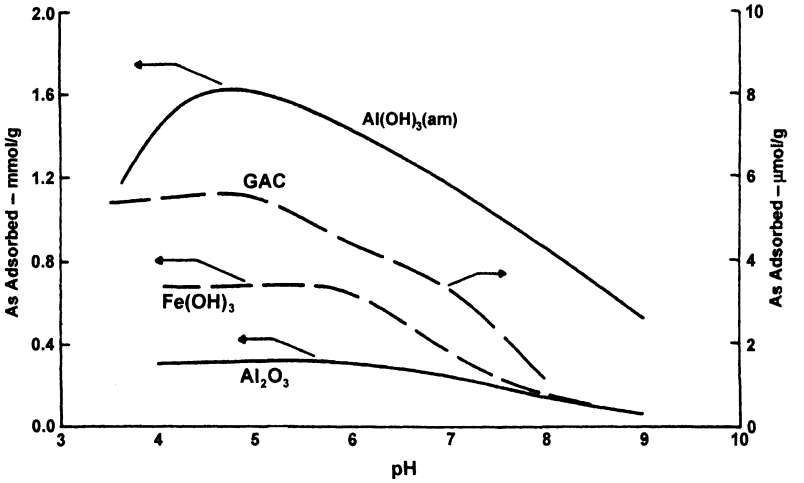

Figure 9.32. Adsorption fronts for arsenic(V) on four adsorbents (the decreasing extent of adsorption with increasing pH is typical for the removal of anions).[56]

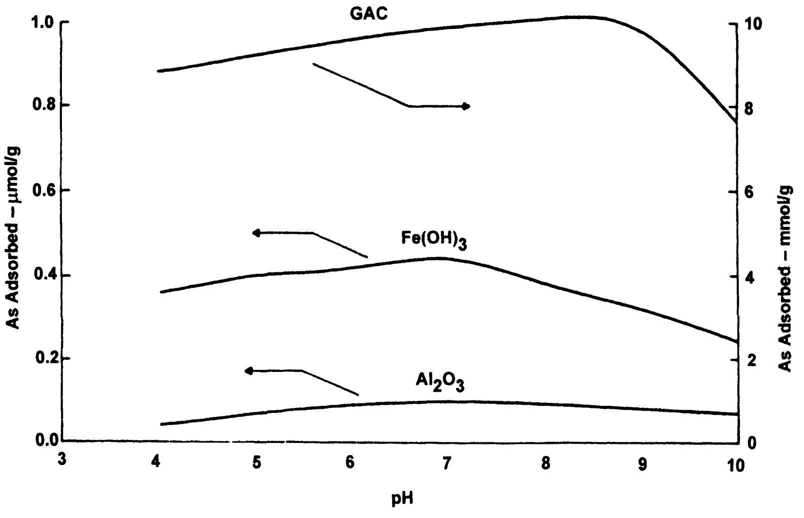

Figure 9.33. Adsorption fronts for arsenic(III) on four adsorbents (arsenous acid is nonionic and is predominant until a pH of 9.2; at higher pH values, the typical anionic adsorption behavior is exhibited).[56]

not remove significant concentrations of arsenic. The formation of particulate Al during alum coagulation affected arsenic removal. When a greater mass of Al flocs was captured by filters, greater percentages of soluble arsenic were obtained. At one utility, a reduction of the coagulation pH from 7.4 to 6.8 (at constant alum dose) improved removal of particulate Al that enhanced soluble As(V) removal. At softening facilities where only calcite ($CaCO_3$) was precipitated, soluble As(V) removal was between 0 and 10%. At softening plants where $Mg(OH)_2$ and ($CaCO_3$) were precipitated, soluble As(V) ranged between 60 and 95%, which was sorbed, apparently, by the solids of Mg.

In this chapter, activated alumina (AA) is the recommended BAT for removal of several inorganic constituents from water. The typical activated aluminas used in water treatment are 28×48 mesh (0.3 to 0.6 mm diameter) mixtures of amorphous and gamma aluminum oxide (γ-Al_2O_3) prepared by low-temperature (300–600°C) dehydration of $Al(OH)_3$. They have surface areas of 50–300 m^2/g. The hydroxylated alumina surface is subject to protonation and deprotonation, which removes the inorganic by a ligand-exchange reaction. AA is prepared and/or regenerated by a series of HCl and NaOH solutions.

As(III) and As(V) have been removed from fresh water and seawater by adsorption on alumina (28×48 mesh), bauxite (30×60 mesh), and GAC (8×30 mesh).[60] Batch systems, 25°C, were shaken continuously for 36 hr for alumina and bauxite and 48 hr for activated carbon. Table 9.18 shows the efficiencies of As(III) and As(V) removal by the three adsorbents. Activated alumina removed the highest quantity of As(V), whereas As(III) was adsorbed equally by the bauxite and alumina. As(III) removal on activated carbon apparently was negligible. Table 9.18 also shows the arsenic removal necessary to attain the 0.05 mg/L drinking water standard. All of this led to the conclusion that these adsorbents were technically feasible. Additional data of As removal are given below in the Se section, since their chemistries are similar.

Pilot plant tests of two treatment methods—activated alumina and ion exchange—for removing arsenic (presumably V) were evaluated at the Naval Air Station, Fallon, Nevada.[57] The arsenic concentration ranged from 0.080 to 0.116 mg/L in the groundwater supply, which was chlorinated. The activated alumina and ion exchange systems were operated through three different loadings and regeneration cycles of each column. Figure 9.34 summarizes the results from the three experimental columns, of which two were activated alumina (Al and Bl) and one was a strong-base anion exchange resin (Cl). Apparently it was necessary to adjust the pH value of the raw water supply to 5.5 in order to achieve any significant removal of the arsenic. Activated alumina and the ion exchange resin were ineffective at the raw water's pH value of 9.1. Effluent water from column Al was treated with caustic soda and/or aerated for $CO_{2(g)}$ removal in order to raise the pH value to 7.5. It should be noted that regeneration of the activated alumina produced a waste product high in dissolved solids, aluminum, and soluble arsenic. This waste stream was treated by adjusting its pH value to 5 to 6.5 wherein $Al(OH)_3$ was precipitated that, in turn, adsorbed the arsenic. This produced a sludge high in arsenic (1627 mg/kg dry solid) that was acceptable for disposal.

Three point-of-use treatment systems—ion exchange, activated alumina, and reverse osmosis—were evaluated for arsenic removal.[58] These units were tested under field conditions in Oregon and Alaska. The ion exchange (presumably a strong based anion resin) and the activated alumina units successfully removed arsenic to below the MCL value of 0.05 mg/L up to 1500 days of running time. On the other hand, the RO unit was inconsistent in arsenic removal to the MCL value. In one instance, the RO unit was unable to reduce an initial [As] of 1.08 mg/L to 0.05 mg/L.

Reverse osmosis (RO) is recommended as a BAT for removal of many of the inorganic contaminants cited in this chapter (Table 9.15). Chapter 7 gives the principles of this ultrafiltration process. Specific information on the efficacy of RO to remove inorganics from the aqueous phase is rather sparse. Table 9.19 compares the values from an EPA pilot plant program for the rejection of several inorganics by several commonly used RO membranes.[52] These data show no major variations in the various membranes' ability to remove the contaminants. As(V) was rejected at a 98–99% level, whereas As(III) rejection varied with type of membrane within a 46% to 75% range.

ASBESTOS

Mineralogy

The chrysotile fiber is a phyliosilicate member of the serpentine group. It is a hydrous magnesium silicate with the formula $Mg_3Si_2O_5(OH)_4$. The fibrous variety of serpentine (asbestos) has a characteristic structure with individual layers recurved that give it an elongated tube-like or fibrous appearance. It is produced by metamorphic alteration of ultramafic rocks in a low-grade environment rich in water.[53] Large masses are found in Quebec, Canada; Eden Mills, Vermont; Brewster, New York; and the Urals, Russia. Generic forms of asbestos may be found also in the amphibole group of silicates. The MCL for asbestos in drinking water is 7×10^6 fibers/L.[1]

Removal

Some field monitoring of the occurrence of chrysotile asbestos fibers in drinking water supplies comes from California.[61,62] There are substantial deposits of serpentine and peridotite in northern California that are conveyed south via the aqueduct. Extensive surveys were conducted in the late 1970s and early 1980s by the Metropolitan Water District of Southern California[61] and the California Department of Health Services.[62] Typical results from the latter survey are seen in Table 9.20, where the ubiquitous distribution of asbestos fibers exceeds the MCL.

Removal of asbestos from surface waters occurs mainly by the conventional techniques of chemical coagulation and/or filtration (sand, mixed media, and diatomite). Large-scale water treatment plant studies were conducted by the MWDSC for an evaluation of asbestos removal.[63] The conventional treatments of coagulation, sedimentation, filtration, and polymer addition were evaluated at five large-scale plants. An "optimized" treatment was devised for these plants that consisted, essentially, of using "fine" sand in some of the filters. A goal of 0.1 ntu was established for each plant during the optimized treatment runs. Table 9.21 is a summary of the filtration plant performances for the "optimized" asbestos removal.[63] The ability of each plant to remove asbestos fibers was dependent on its initial concentration in the influent water and, of course, on the efficiencies of the individual treatment processes. The 0.10 ntu goal for filter effluent turbidity was not achieved on a consistent basis by all five treatment plants. This may be

Table 9.18. Efficiency of As(III) and As(V) Removal by Different Adsorbents Under Different Solution Conditions.[a,b]

	q_{100}[c]	q[d]	%	pH	Arsenic Removed[e] (mg/g of Solids)
Activated Bauxite, 2 g/L					
As(III)					0.12
6.54 μ*M*	3.27	2.6	79.6	7.99	
13.4 μ*M*	6.65	4.86	73.0	7.69	
26.7 μ*M*	13.3	9.31	70.0	7.80	
As(V)					2.0
24.7 μ*M*	12.3	12.3	100.0	6.5	
60.1 μ*M*	30.0	29.76	99.0	6.7	
104.0 μ*M*	52.0	50.2	97.0	6.8	
Activated Alumina, 2 g/L					
As(III)					0.2
6.65 μ*M*	3.26	2.9	88.8	8.47	
13.4 μ*M*	6.66	5.53	83.0	8.04	
26.7 μ*M*	13.3	10.5	79.3	8.20	
As(V)					4.1
32.0 μ*M*	16.0	16.0	100.0	6.9	
66.7 μ*M*	33.4	33.3	99.7	6.8	
133.0 μ*M*	66.5	65.9	99.0	6.9	
Activated Carbon, 3 mg/L					
As(V)					0.34
12.8 μ*M*	4.26	4.11	96.5	3.1	
25.4 μ*M*	8.46	7.82	92.4	3.1	
34.7 μ*M*	11.6	9.69	85.5	3.2	

[a] Reproduced from Gupta and Chen,[62] courtesy of the Water Pollution Control Federation.
[b] Solvent matrix: water.
[c] q_{100}=adsorption density at 100% removal.
[d] q=adsorption density (μ*M*/g of solids).
[e] At optimum pH, 50 μg/L arsenic concentration.

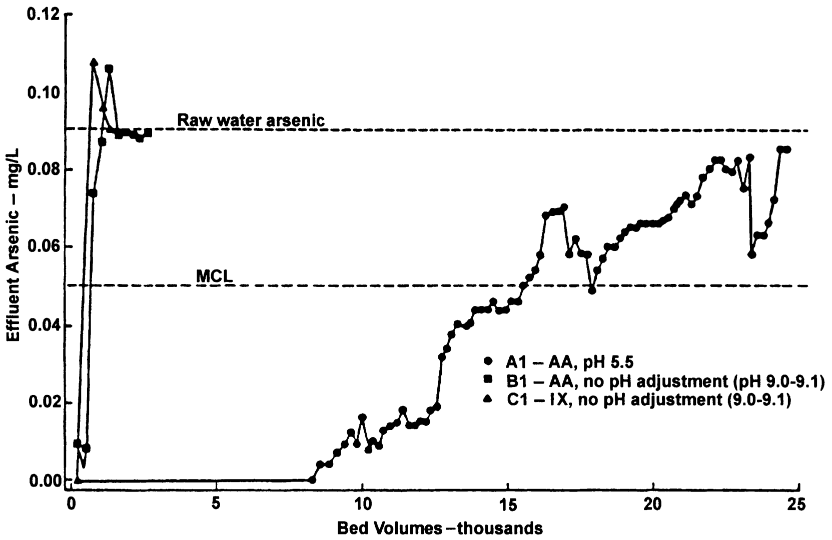

Figure 9.34. Arsenic removal by activated alumina and anion exchange treatment.[59]

Table 9.19. Inorganic-Contaminant Removal by Membranes[a].[52]

Contaminant	Feed Concentration Range (mg/L)	Dow CTA HF	DuPont ARAMID HF	Filmtec TFC SW	Hydranautics MCA SW	Toray CA SW
As(III)	0.04–1.3	75	71	69	48	65
As(V)	0.11–1.9	98	99	99	98	99
Cd	0.18–3.7	98	99	96	99	98
Cl	80.0–730.0	93	94	92	95	93
Cr(III)	0.05–1.5	97	99	99	99	
Cr(V)	0.1–3.6	96	98	97	98	98
F^-	5.5–16.0	91	92	83	98	90
Hardness	100.0–720.0	98	99	98	99	99
Pb	0.09–1.3	96	98	97	97	98
Hg	0.002–0.185	64	80	78	64	
Mo	1.6–4.3				97	
NO_3^-–N	2.0–25.0	85	94	75	99	67
Ra, pCi/L	2.2–9.8	97	96		97	
Se(IV)	0.2–2.4	98	98		95	97
Se(VI)	0.25–3.2	99	99	98	99	99
U(IV)	0.103–1.65	99	98	99	99	
Test Conditions						
Average % recovery		59.0	50.0	10.4	10.7	9.8
Average feed pressure (psi)	277.0	384.0	191.0	283.0	282.0	

[a] CA = cellulose acetate; CTA = cellulose triacetate; MCA = modified cellulose acetate; HF = hollow fiber; SW = spiral-wound; TFC = thin-film composite.

related to particle size of the asbestos fibers that remain after treatment (see below).

Large numbers of very small particles can exist in filtered water with turbidity less than 1 ntu, the MCL value. For example, a poor correlation was found between numbers of asbestos fibers and turbidity in both source and filtered water from Lake Superior at Duluth, Minnesota.[64] The amphibole fibers had diameters of 0.1 to 0.4 μm. These small fibers cannot be detected by turbidity measurements. Frequently, the amphibole fiber count was less than the detection limit of the analytical method used when the filtered water turbidity was less than 0.1 ntu. It was concluded from this study that the pretreatment should consist of alum at 12 to 20 mg/L with a nonionic polymer at 0.05 mg/L. Also, triple-media filters should be used to achieve a finished water turbidity of not greater than 0.1 ntu.

BARIUM

Aqueous Chemistry

This element is one of the inorganics whose content in drinking waters is limited to 2.0 mg/L (see Chapter 1). Trace concentrations, 9 to 152 μg/L, were found in several surface waters in North America.[2] Barium contents in the groundwaters of northern Illinois have been as high as 19 mg/l, with 2–7 mg/L being a more common range.[65] Since barium is one of the alkaline earth elements, its chemical properties are similar to Ca and Mg. Consequently, the treatments of lime-soda softening and ion exchange are appropriate also for Ba. The softening reactions at 25°C are:

$$Ba^{2+} + CO_3^{2} = BaCO_{3(s)}\ \text{(witherite)} \qquad (51)$$

$$\Delta G^\circ_{REX} = 10.41\ \text{kcal/mol}$$

$$\log K_s = 7.63$$

$$Ba^{2+} + SO_4^{2-} = BaSO_{4(s)}\ \text{(barite)} \qquad (52)$$

$$\Delta G^\circ_{REX} = 13.58\ \text{kcal/mol}$$

$$\log K_s = 9.96$$

$$Ba^{2+} + 2OH^- = Ba(OH)_{2(s)} \qquad (53)$$

$$\Delta G^\circ_{REX} = -3.14\ \text{kcal/mol}$$

$$\log K_s = 2.3$$

Equation 51 represents the formation of $BaCO_{3(s)}$, whose solubility is about 1 mg/L. Barium hydroxide is too soluble

Table 9.20. Results of Raw Surface Water Sampling in Sacramento and San Joaquin River Basins.[64]

Location	Date	Asbestos (MFL)	Turbidity (ntu)
Feather River basin			
North fork Feather River at northeast fork	5/83	55	1.0
North fork Feather River at Pulga	5/83	170	7.4
North fork Feather River at Milsap Bar	5/83	48	1.3
Feather River at Oroville	5/83	250	4.2
Feather River at Yuba River	9/82	380	3.9
Yuba River at Marysville	9/82	120	2.0
Bear River at Highway 174	4/82	520	62.4
Bear River at Highway 70	4/82	1000	46.0
Feather River at Nicholas	1/82	1800	18.5
	4/82	1400	42.0
American River basin			
North fork American River	9/81	14	
Middle fork American River	9/81	30	
Bowman Canal at water treatment plant	1/82	3000	35.0
South Canal at water treatment plant	1/82	2100	41.0
Roadman Canal	9/82	20	1.95
Whitney Reservoir	9/82	160	4.3
South fork at Salmon Falls	12/80	2100	
	1/81	260	
City of Roseville	8/81	43	
Cordova Water Service	8/81	190	
Folsom Reservoir	5/81	130	
City of Folsom	4/81	195	
American River at Sacramento	12/80	250	
	4/81	53	
	1/82	5600	14.8
Sacramento River			
At Freeport bridge	10/81	560	
surface	10/81	360	
mid-depth	10/81	760	
	2/82	6000	47.1
	6/82	1300	13.9
	9/82	680	6.2
	12/82	1700	18.5
	3/83	2400	27.0

for precipitation at Ba contents of natural waters. It appears that lime-soda softening is the preferred treatment by precipitation.

Removal

Laboratory jar tests were conducted for an evaluation of the softening treatment.[65] It was found that maximum Ba removal was effected in the pH range of 9.5 to 11.5. The equilibrium content of 30 µg/L apparently was not obtained because of the coprecipitation of Ca and Mg in the synthetic water. However, attainment of the MCL of 2.0 mg/L is feasible in the softening process (Table 9.22). There is, of course, a sludge disposal problem (see Chapter 8).

Ion exchange is also a feasible treatment for Ba removal. Several field laboratory studies have been conducted for Ba exchange on strong and weak acid resins.[65–68] In these studies, a strong acid polystyrene divinylbenzene cross-linked resin with sulfonate functional groups (total exchange capacity of 4.9 meq/dry g) was used in the Ca^{2+} form[66] or H^+ form.[67,68] For the weak-acid resin tests, a H^+ form polyacrylic divinylbenzene cross-linked resin with carboxyl functional groups (capacity of 11.5 meq/dry g) was used. A typical process schematic for these ion exchange systems is seen in Figure 9.35.[66] That Ba^{2+} can be removed from water with an initial concentration of 15–30 mg/L by a strong acid resin in the Ca^{2+} form is seen in Figure 9.36.[66] The resin was easily regenerated with $CaCl_2$ brine.

Weak-acid resin in the H^+ form was found to remove Ba^{2+}, Ra^{2+}, and hardness without increasing the sodium content of the product water.[67] The maximum capacity of the weak-acid resin was about 2.3 times that of a strong-acid resin

Table 9.21. Summary of Filtration Plant Performances for Optimized Asbestos Removal.[65]

Parameter	Weymouth	Diemer	Jensen	Skinner	Mills
Asbestos in influent (MFL)					
Mean	690.0	650.0	5.7	1.9	770.0
Median	730.0	600.0	2.6	1.1	690.0
Maximum	1300.0	1300.0	45.0	6.4	1900.0
Minimum	230.0	280.0	0.19	BDL[a]	230.0
Asbestos in effluent (MFL)					
Mean	8.3	35.0	0.41	0.34	6.7
Median	5.2	2.5	BDL	0.13	0.86
Maximum	31.0	200.0	5.6	2.3	58.0
Minimum	0.37	0.25	BDL	BDL	0.11
Effluent samples with an asbestos level ≤ MFL (%)	7.0	33.0	93.0	93.0	53.0
Mean removal of asbestos (%)	98.89	94.74			99.33
Time the turbidity was ≤ 0.10 ntu (%)	75.0	86.0	43.0	4.0	33.0
Median effluent turbidity for optimized treatment (ntu)	0.07	0.09	0.12	0.18	0.12

[a] Below detection level.

that required less regenerant per unit volume of treated water than a strong-acid column. However, there are some major disadvantages to weak-acid ion exchange: the resin swells during exhaustion, there is a need to use acid-resistant materials, noncarbonate hardness is not removed, it is necessary to strip $CO_{2(g)}$ from the treated water, and the pH value must be adjusted.

Subsequent research with a strong-acid ion exchange resin in the Na^+ form demonstrated the feasibility of this process to remove Ba^{2+} in the presence of hardness and Ra^{226}.[70] Barium accumulates on the strong-acid resin with successive cycles because the resin has a greater affinity for Ba^{2+} than for Ca^{2+} and Mg^{2+}. There is a disadvantage to this process because of the increase in Na content of the product water. This may affect persons who must limit their dietary intake of Na (see Chapter 1).

Other studies have shown that powdered (PAC) and granular activated carbon (GAC) are ineffective methods for Ba removal.[65] Less than 7% was removed by PAC, and none was removed by GAC in laboratory studies. Reverse osmosis (RO) and electrodialysis (ED) were effective methods, giving 95–98% removal of 9.15 mg/L Ba in tap water.[65]

BERYLLIUM

Aqueous Chemistry

The MCL for Be in drinking water is 0.001 mg/L. On a mass basis, Be is only 0.0006% of the Earth's crust. It is very widespread, but only in trace amounts. The only important Be mineral found in any quantity is a silicate, beryl ($Be_3Al_2Si_6O_{18}$). This element is not commonly found in raw water sources. Some groundwaters were surveyed between 1962 and 1967 that had a 5.4% detection frequency with a maximum concentration of 1.22 μg/L. In the same survey, surface waters yielded a 1.1% detection frequency with a maximum concentration of 0.17 μg/L.[2] Some appropriate aqueous reactions are:

$$Be^{2+} + 2OH^- = \underset{\text{amorphous}}{Be(OH)_{2(s)}} \qquad (54)$$

$$\Delta G^\circ_{REX} = -29.73 \text{ kcal/mol}$$

$$\log K_s = 21.8$$

$$Be^{2+} + CO_3^{2-} + 4H_2O = BeCO_3 \cdot 4H_2O \qquad (55)$$

$$\Delta G^\circ_{REX} = -4.09 \text{ kcal/mol}$$

$$\log K_s = 3$$

At a pH value of 10, Be contents would be 1.43×10^{-6} μg/L from Reaction 54. At a $[CO_3^{2-}]$ of 10^{-3} *M* for Reaction 55, the equilibrium solubility of Be would be 9.02 g/L (1*M*). Obviously, the solubility of Be in natural waters would be controlled by the amorphous $Be(OH)_{2(s)}$.

Removal

The BATs for Be removal from water are coagulation-filtration, lime-soda softening, activated alumina, IX, and RO (Table 9.15). Here again, very little information is available from the literature concerning the removal of Be from water. Certainly, Reaction 54 suggests that lime-soda soft-

Table 9.22. Barium Removal from Well Water by Full-Scale Lime Softening Water Treatment Plants.[a]

			Barium Concentration (mg/L)				Hardness Concentration (as $CaCO_3$) (mg/L)	
Treatment Plant	Treatment pH	Water Sample	Raw Water	Settled Water	Recarbonated Water	Filtered Water	Raw Water	Filtered Water
A	10.5	1	7.5	0.91	1.08	0.63	276	72
		2	7.5	0.95	1.18	1.00	268	68
		3	7.5	0.95	1.00	0.73		
Average Concentration			7.5	0.94	1.09	0.88	272	70
(Average percent removed)				88.0	86.0	88.0		
B	10.3	1	17.3	1.60		0.90	240	72
		2	18.0	1.90		0.84	252	80
		3	17.0	2.05		0.69		
Average Concentration			17.4	1.85		0.81	246	76
(Average percent removed)				89.4		95.3		69

[a] Reproduced from Sorg and Logsdon,[67] courtesy of the American Water Works Association.

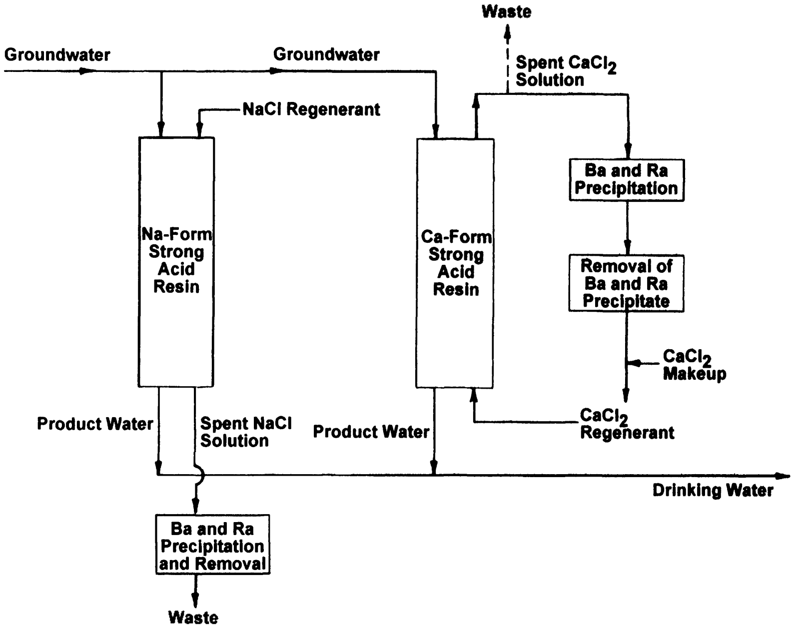

Figure 9.35. Process schematic.[68]

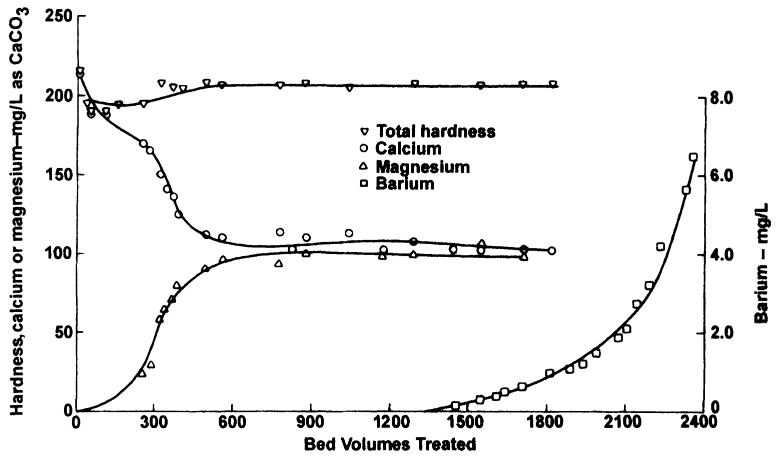

Figure 9.36. Divalent cations in the effluent from a virgin strong-acid calcium-form resin column.[68]

ening would be effective in meeting the MCL for Be. The efficacies of the other BATs are uncertain at this writing.

CADMIUM

Aqueous Chemistry

The MCL for cadmium in drinking water is 0.005 mg/L (see Chapter 1). Surface water contents of Cd in North America[2] ranged from 21 to 130 μg/L. It is not especially widespread from natural geologic sources, but may occur in substantial concentrations due to the discharge of wastewaters, especially plating wastes. The aqueous chemistry of cadmium is, for the most part, dominated by Cd^{2+}, $CdCO_{3(s)}$ (otavite), and $Cd(OH)_{2(s)}$.[2,71] The appropriate reactions are:

$$Cd^{2+} + CO_3^{2-} = CdCO_{3(s)} \text{ (otavite)} \qquad (56)$$

$$\Delta G^\circ_{REX} = -15.25 \text{ kcal/mol}$$

$$\log K_s = 11.18$$

$$Cd^{2+} + 2OH^- = Cd(OH)_{2(s)} \qquad (57)$$

$$\Delta G^\circ_{REX} = -19.62 \text{ kcal/mol}$$

$$\log K_s = 14.4 \text{ (aged)}$$

$$\log K_s = 13.7 \text{ (fresh)} \qquad (48)$$

Reaction 55 represents the formation of $CdCO_{3(s)}$, whose solubility is about 300 µg/L for pH values greater than 10. Reaction 57 is the formation of cadmium hydroxide, whose solubility at pH 10 is 44 µg/L for the "aged" form and 225 µg/L for the "fresh" precipitate. In the Cd-S-CO_2-H_2O system, Cd solubility is below 10 µg/L in the pH value range 8.9 to 10.7, according to Hem's thermodynamic calculations.[72]

Removal

Few studies have reported the specific removal of Cd from water because it is an infrequent problem. Consequently, it is necessary to evaluate the effectiveness of conventional water treatments before seeking processes specifically for Cd. Chemical coagulation (jar tests) was investigated for Cd-spiked (0.03 mg/L) Ohio River water and a well water in Ohio.[69] Alum and ferric sulfate removals with "high alkalinity" [200 mg/L as $CaCO_{3(s)}$] well water were about 10% at pH 7; this was increased to about 100% at pH 9. The dosages were 20 mg/L for ferric sulfate and 30 mg/L for alum. Removals from spiked Ohio River water for ferric sulfate (30 mg/L) were 20–30% at pH 7. That was increased to nearly 100% at pH 8.5 to 9.0. Removals by alum were not reproducible for pH values greater than 8.0. Low turbidities (1–20 tu) and the alkalinity (50–60 mg/L) of the river water were the apparent reasons for poor removals of Cd by alum. Pilot plant studies, in general, confirmed the coagulation results from the jar tests. Also, jar tests conducted for the effect of coagulant dosage showed that an increase in the quantity of alum effected greater removal. However, a slight increase in Cd removal was observed with ferric sulfate (Figure 9.37a). (Note that the MCL for Cd was 0.01 mg/L at the time of this study.[66]) When the coagulant doses were held constant and [Cd^{2+}] was increased (Figure 9.37b), the percentage removal decreased, even at the optimum pH. All of this limits chemical coagulation as a viable treatment for soluble Cd contents to 0.1 mg/L and below, according to Sorg et al.[71] Furthermore, it is not feasible to treat clear groundwaters for specific removal of soluble constituents by coagulation. On the other hand, some Cd removal is, perhaps, incidental to the coagulation of turbid surface waters. Here again, specific coagulation of surface waters for Cd is not warranted.

Reaction 55 suggests that the lime-soda softening treatment of hard waters should also reduce [Cd^{2+}]. Here again, laboratory jar tests demonstrated that the spiked Ohio well water was treated for complete Cd removal by the softening process (Figure 9.37c).[71] No chemical dosages were given, so it is presumed that they were added in excess of stoichiometric quantities. Pilot plant tests confirmed the results seen in Figure 9.37c. Furthermore, complete removal was observed for Cd contents up to 10 mg/L. Thus, lime-soda softening is a feasible process for Cd removal, provided, of course, it is applied to hard waters (see Chapter 8).

Ferric sulfate coagulation at pH values greater than 8.0, lime softening, and excess lime softening are the most effective treatment methods for cadmium removal according to a committee report that surveyed the literature.[73]

Some Cd removal is experienced with PAC. For example, two types of PAC gave 29 and 26% removal of 0.05 mg/L Cd at pH 7 at 100 mg/L doses. When the pH value was increased to 9, removals were increased to 53 and 56%.[71] This is a very unlikely pH value for PAC treatment of drinking water.

Two PAC (Nuchar S-N and Nuchar S-A) and two GAC (Darco HD 3000 and Filtrasorb 400) were examined in the laboratory for Cd removal from plating wastes.[74] Figure 9.38 shows the adsorptive capacity of the four carbons, 1 g/L, over the pH range of 3 to 10. These data were obtained from batch experiments with a reaction time of 2 hr. It is obvious that PAC is more effective than GAC. That the [H^+] affects the adsorption of Cd is seen also. The convergence of the four curves to the maximum adsorption at pH 10 is explained by "substantial precipitation of $Cd(OH)_{2(s)}$ and/or $CdCO_{3(s)}$." Typical adsorption isotherms are seen in Figure 9.39 for two carbons and for Cd-BF_4 and $Cd(CN)_2$—components of plating solutions. Here again, the PAC was more effective. In this study, Langmuir adsorption isotherms and pH effects were also presented.[74] This study tends to confirm the data presented by Sorg et al.[71] Cadmium adsorption by 10 g/L of three GAC (Nuchar C-190N, Nuchar 722, and Filtrasorb 400) were reported.[74,76] These studies were oriented toward treatment of plating wastes. This strongly suggests that GAC is not a practical drinking water treatment for Cd removal.

Cadmium sorption by the oxides of Mn(IV), Fe(III), and Al(III) was reported.[77] It was indicated that sorption on hydrous oxides of Mn and Fe is feasible for removal of Cd from water and wastewater. Manganese dioxide was the most effective of the three, and sorption was influenced by [H^+], with greater removal of Cd at pH 8.3 than at 5.

That RO is a feasible process for Cd removal from water is seen in Table 9.19, where the rejection was greater than 96% for five membranes.[52]

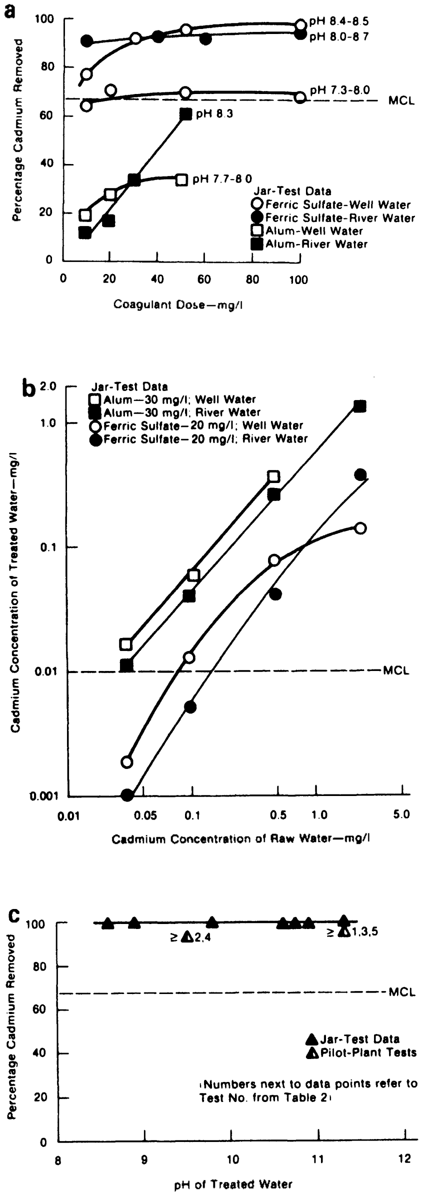

Figure 9.37. (a) Effect of coagulant dose on cadmium removal by coagulation treatment. Cadmium concentration = 0.03 mg/L. (b) Effect of initial concentration on cadmium removal by coagulation treatment. (c) Effect of pH on cadmium removal by lime softening. Cadmium concentration = 0.03 mg/L. Reproduced from Sorg et al.,[71] courtesy of the American Water Works Association.

CHROMIUM

Aqueous Chemistry

The MCL for total chromium in drinking water is 0.1 mg/L.[1] Chromium concentrations in natural waters are limited by the low solubility of Cr(III) oxides. Chromium contents in 15 rivers of North America ranged from 0.7 μg/L (Sacramento River) to 84 μg/L (Mississippi River).[2] There is the possibility of contamination from discharge of industrial wastewaters. The essential aqueous chemistry of Cr is its occurrence in either the +3 or +6 oxidation state. Cr(III) occurs as a cation, with $Cr(OH)_3$ being very insoluble in water:

$$\mathrm{Cr^{3+} + 3OH^- = Cr(OH)_{3(s)}} \tag{58}$$

$$\Delta G^\circ_{\mathrm{REX}} = -51.018\ \mathrm{kcal/mol}$$

$$\log K_s = 37.4$$

At pH 7, the solubility of chromic hydroxide has been reported to be $10^{-14.3}$ M as Cr.[54] Cr(VI) occurs as anions in water:

$$\mathrm{H_2CrO_4} = \underset{\text{acid chromate ion}}{\mathrm{HCrO_4^- + H^+}} \tag{59}$$

$$\log K_{eq} = -0.75$$

$$\mathrm{H_2CrO_4} = \underset{\text{chromate ion}}{\mathrm{CrO_4^{2-} + 2H^+}} \tag{60}$$

$$\log K_{eq} = -7.20$$

$$\mathrm{2H_2CrO_4} = \underset{\text{dichromate ion}}{\mathrm{Cr_2O_7^{2-} + H_2O + H^+}} \tag{61}$$

$$\log K_{eq} = -0.18$$

Removal

The effects of conventional water treatments have been evaluated for Cr removal, although it is not expected to be a serious drinking water quality problem.[78] It is not commonly found in ground or surface waters. Any removal of Cr in a conventional water treatment plant, therefore, would be incidental. Figures 9.40a and 9.40b give the results of jar and pilot plant tests for chemical coagulation of Cr-spiked (0.15 mg/L) well and river waters. Cr(III) undoubtedly was precipitated as its hydroxide rather than removed by coagulation per se. Coagulation by ferric sulfate and alum was ineffective for Cr(VI), as seen in Figure 9.40b. However, when ferrous sulfate was employed, nearly 100% Cr removal was achieved. Cr(VI) was reduced to Cr(III) by the Fe(II) ion, with subsequent precipitation as $Cr(OH)_{3(s)}$. However, $FeSO_4$ is not a commonly used coagulant or reductant for drinking water treatment. There is a disparity between

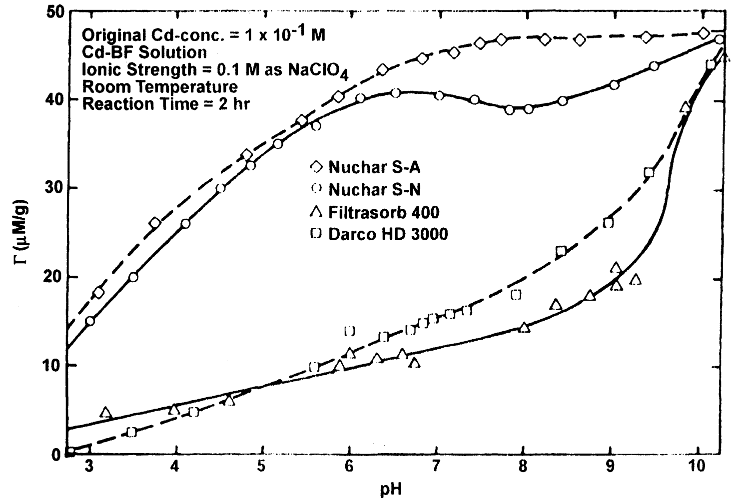

Figure 9.38. Comparison of Cd(II) adsorption capacity by GAC and PAC, as affected by pH. Reproduced from Huang and Smith.[74]

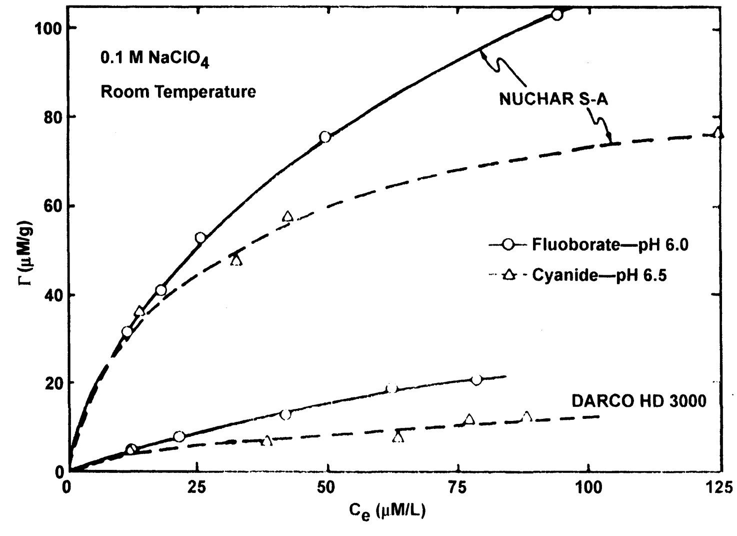

Figure 9.39. Typical adsorption isotherm—comparison of various systems. Removal efficiency is generally better with Cd-BF, than Cd-CN solution. Reproduced from Huang and Smith.[74]

the pH of optimum coagulation by $FeSO_4$ (8–10) and the pH for Cr(VI) reduction by Fe(II) (acid medium). It would not be very pragmatic to require two pH adjustments in a water treatment plant specifically for Cr removal. That the lime-soda softening process is effective for Cr(III) removal, but ineffective for Cr(VI), is seen in Figure 9.40c.

Of the several studies of the removal of Cr by PAC and GAC,[78–81] some are oriented to the treatment of industrial wastewaters. For example, a 10 g/L batchwise quantity of a GAC (a calcined coke) was used for Cr(VI) removal over the pH range of 2 to 10.[79] Greatest removals occurred at pH 2, whereupon there was an exponential decrease of effectiveness to a pH value of about 6, where there was virtually no reduction in [Cr]. In another batch study, a 10,000 mg/L quantity of Filtrasorb 400 was utilized for Cr(VI) and Cr(III) removal.[80] This GAC responded somewhat differently to pH effects. Virtually no adsorption of Cr (either valence) occurred below pH 2 or above pH 8, with the maximum occurring at pH values 5 to 6. Loosely packed columns of various quantities of Filtrasorb 400 were operated continuously at 2 gpm/ft^2 at pH 2.5 and 10^{-3} *M* Cr(VI).[81] No Cr was removed within the first 50 or so bed volumes because of the number of H^+ ions required to hydrolyze the carbon surface. All of this work was directed to treating industrial wastewaters and has lim-

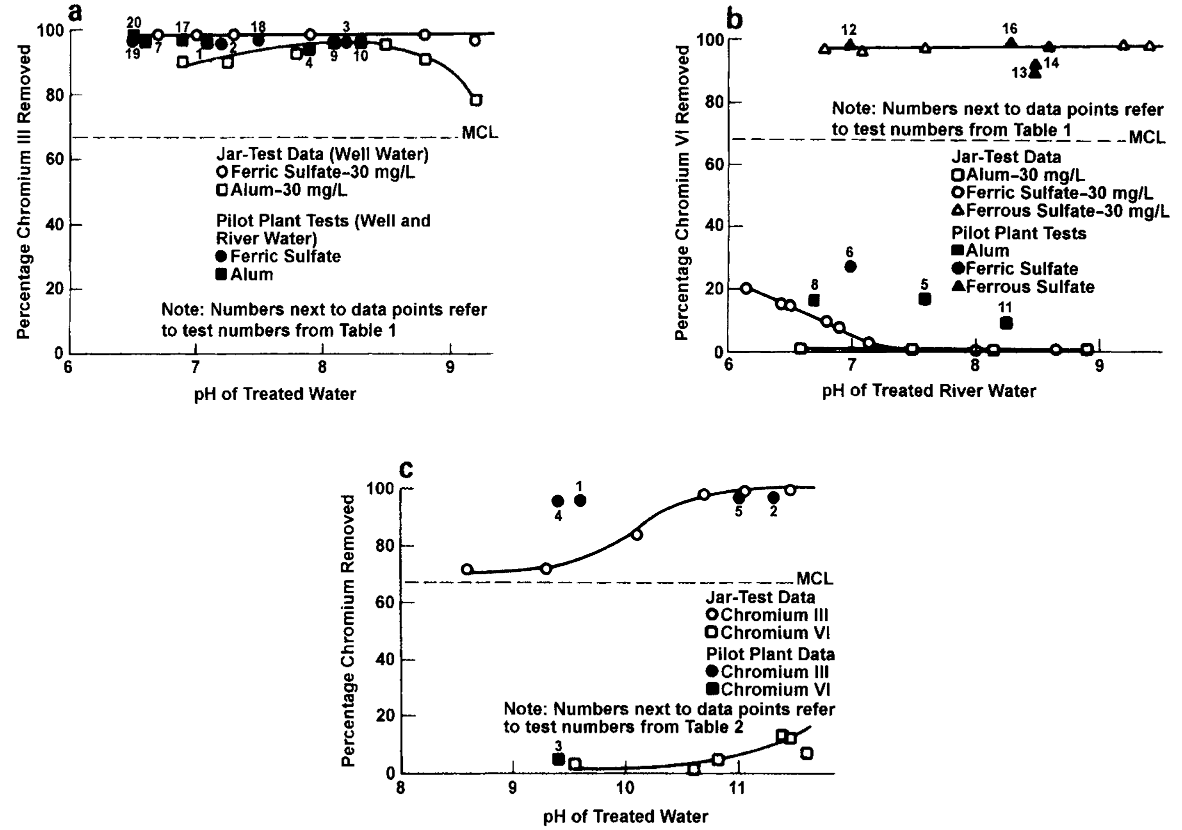

Figure 9.40. Effect of pH on (a) 0.15 mg/L Cr(III) removal by coagulation treatment; (b) 0.15 mg/L Cr(VI) removal by coagulation treatment; and (c) 0.15 mg/L Cr removal from well water by lime softening. Reproduced from Sorg,[78] courtesy of the American Water Works Association.

ited application to drinking waters. Sorg[78] reported that several jar test studies with PAC (Filtrasorb 400) dosages of 10–200 mg/L showed very low removals, about 10% of 0.15 mg/L Cr(VI), from pH 6.8 to 8.3. It was concluded "that GAC treatment probably is not a very effective method for Cr(VI) [removal] from drinking water with low organic concentrations." The same conclusion may be drawn for PAC. Sorg[78] cited some laboratory data that suggested that reverse osmosis was reasonably effective for removing both oxidation states of Cr (Table 9.19).

The USEPA lists coagulation-filtration and lime-soda softening as the BATs for conventional processes in the removal of total Cr from water (see Chapter 1). Ion exchange and reverse osmosis (Table 9.19) are given as specialized processes for BAT of Cr removal.

COPPER

Aqueous Chemistry

The MCLG for copper is 1.3 mg/L in drinking water (see Chapters 1 and 10). Copper is not distributed widely in natural waters. In the famous study of 15 North American rivers,[2] copper contents ranged from 0.83 to 105 μg/L. Discharge of industrial wastewaters may increase copper contents to greater than 1.0 mg/L. As cited in Chapter 10, copper ions may originate from the acidic corrosion of copper pipes. As high as 3.0 mg/L has been measured in a household wellwater.[82] In these cases, neutralization of the water with calcite beds will eliminate the corrosive condition and the copper ions. The aqueous chemistry of copper is covered in Chapter 10. Here, only the treatments of waters with copper contents arising from sources other than corrosion are considered.

Removal

Since the concern about copper in drinking water was secondary, there are few reports on its specific removal. There are studies of Cu(II) removal by six activated carbons from synthetic seawater, 1.65 *M* NaCl.[75] This is not applicable to treatment of fresh waters. Some research has been conducted on adsorption of Cu(II) on hydrous oxides of Mn and Fe. Copper(II) adsorption on $MnO_{2(s)}$ was ob-

Table 9.23. Heavy Metal Extraction by Exchange Materials.[a]

	Metals Remaining after Contact (all at 20 ppm to start) (ppm)									
Material[b]	**Cd**	**Cu**	**Hg**	**Zn**	**Na**	**Fe**	**Mg**	**Ca**	**Si**	**Ba**
Activated Carbon (Darco–G 60)	19.7	7.4	0.4	19.9						
Cation Exchange Resin (Dowex HCR–W)	0.4	0.4	19.3	0.5	pH = 2.0					
Anion Exchange Resin (R–H IRA–93)	19.4	14.5	0.8	18.5	7.1					
Mg_2Si	0.3	0.3	0.1	0.4			38.0		1.6	
CaSiBa	<0.1	<0.1	0.1	<0.05				10.0	45.0	129.0
MgFeSi	3.1	0.5	1.3	0.6		0.1	27.0		0.3	
SiFe	16.8	2.3	0.4	6.9		36.2			0.5	

[a] Reproduced from McKaveney et al.,[85] courtesy of the American Chemical Society.

[b] 0.50 g of material in contact with 100 mL solution for 30 min.

served over the pH range of 0.5 to 3.0, which is not very practical for water treatment.[83] The hydrous oxide of Fe(III) sorbed Cu(II) over the pH range 4.3 to 6.5.[84] The removal of Cu(II) and other metals from water by silicon alloys Mg_2Si, CaSiBa, MgFeSi, and SiF was reported.[85] These alloys and metal exchangers were placed on a shaker for 30 min, presumably at room temperature. Table 9.23 shows Cu removal by ion exchange with the alloys at a pH value of 4.5. Parallel studies were conducted with GAC and a cation and an anion exchanger. It should be noted that the heavy metals were contained in a single solution; hence, competitive effects should be noted. The alum coagulation of Cu^{2+}-, Cd^{2+}-, and Zn^{2+}-fulvic acid complexes was investigated.[86] The conditions were 0.5 to 1.0 mg/L Me^{2+}, 30–50 mg/L alum and a pH value of 7. A 96% removal of the Cu^{2+} complex, 59% for Cd^{2+} and 82% for Zn^{2+} were effected with 30-mg/L alum.

CYANIDE

Aqueous Chemistry

The MCL for CN in drinking water is 0.2 mg/L.[1] It may occur as an industrial pollutant and/or from an accidental spill in water supplies. However, it is not found commonly in drinking water at any significant concentration. A national survey in 1970 of 969 community water supplied found an average [CN] of 0.09 μg/L and a maximum of 8 μg/L (see Chapter 1). CN is easily degraded biologically and chemically. Hence, it should not be a major threat to potable water.

Removal

Any of the chemical oxidants that are used in treatment and production of potable water are capable of removing CN. These oxidants include: Cl_2, $Cl0_2$, 0_3, and $KMn0_4$. Also, it should be easily adsorbed by PAC and GAC.

LEAD

Aqueous Chemistry

The MCLG for lead in drinking water is zero, with an action level of 0.015 mg/L (see Chapters 1 and 10). Natural sources of lead include: $PbCO_{3(s)}$(cerussite), $PbS_{(s)}$(galena), and $PbS0_{4(s)}$(anlesite). Lead contents in natural waters may range from <1.0 to 890 μg/L.[2] The principal problem with lead in drinking water comes from corrosion in water distribution systems (see Chapter 10). Other sources of lead would come from weathering of lead paints, metallic products, industrial wastewaters, etc.[2] The appropriate chemistry is (25°C):

$$Pb^{2+} + 2OH^- = \begin{array}{l} Pb(OH)_{2(s)} \\ \text{plumbous hydroxide} \\ \text{(fresh)} \end{array} \qquad (62)$$

$$\Delta G^\circ_{REX} = -20.36\ \text{kcal/mol}$$

$$\log K_s = 14.93$$

$$Pb^{2+} + CO_3^{2-} = \begin{array}{l} PbCO_{3(s)} \\ \text{(cerussite)} \end{array} \qquad (63)$$

$$\Delta G^\circ_{REX} = -18.83\ \text{kcal/mol}$$

$$\log K_s = 13.8$$

At a pH value of 10, Pb contents would be 33 μg/L from Reaction 62 and 26 μg/L from Reaction 63. These values are above the action level of 15 μg/L. Additional aqueous chemistry of lead may be found in Chapter 10.

Removal

Since lead was not recognized as a widespread problem in drinking water prior to the advent of the lead and copper rule (Chapters 1 and 10), very few papers had been published for the specific treatment of Pb removal. Conventional water treatments were tested for Pb removal through laboratory jar tests and by a pilot plant.[71] That alum and ferric sulfate coagulation were effective over the pH range 6–10 is seen in Figure 9.41a. Turbidity affects the removal wherein Pb is adsorbed by particulate matter that is eventually coagulated. An 80% removal of Pb, 0.15 mg/L, was observed with a 48 tu water, whereas a 20–60% reduction was observed with a 9.5 tu water. Since no coagulant was added in these two experiments, Pb removals were obtained by adsorption on the suspended particles with subsequent precipitation. The lime-softening process was extremely effective for Pb removal via Reaction 59 (Figure 9.41b). Sorg[71] speculated on the use of a strong acid cation exchange process for Pb removal from groundwaters. The selectivity series for cations indicates that this process should be effective:[87] $Ba^{2+} > Pb^{2+} > Sr^{2+} > Ca^{2+} > Ni^{2+} > Cd^{2+} > Cu^{2+} > Co^{2+} > Zn^{2+} > Mg^{2+}$ and $Ag^+ > Cs^+ > Rb^+ > K^+ > NH_4^+ > Na^+ > H^+ > Li^+$. Few studies have been conducted with the removal of Pb by PAC or GAC. In laboratory jar tests, it was reported that 10 mg/L PAC effected a 98% reduction at pH 7.3 to 7.4.[71] In a parallel study using GAC (Filtrasorb 200) in a pilot plant, Pb removals were 95% greater, from 0.11 to 0.20 mg/L Pb in the raw water. The use of powdered $CaCO_{3(s)}$ was added to the filtrate from which the data for Figure 9.41c was obtained. Swallow et al.[84] reported that the hydrous oxide of Fe(III) sorbed Pb(II) over the pH range of 4.3 to 7.0.

MERCURY

Aqueous Chemistry

The MCL for mercury in drinking water is 0.002 mg/L.[1] There are very few historical data on the occurrence of Hg in ground, surface, and finished waters in the United States. This is due mainly to the cumbersome analytical techniques for Hg in water. Mercury contents of <0.5 to 6.8 μg/L were reported for several surface waters in the United States.[2] Of the several mercury-bearing minerals in nature, only a few exist abundantly. The most common are the sulfides [cinnabar and metacinnabar (HgS)] and native mercury. In aqueous systems, mercury can exist in one of three oxidation states: as the free metal, Hg^0, as the mercurous ion, $Hg_2{}^{2+}$ or as the mercuric ion, Hg^{2+}. Mercury readily forms complexes with many inorganic anions and organic constituents, for which the methylation reactions have been documented.[2] An important characteristic of Hg is its tendency to adsorb and adhere to various types of surfaces. This, of course, has immediate application to water treatment.

Removal

Conventional water treatment processes have been evaluated for Hg removal.[78,89,90] The coagulation work[78] is seen in Figure 9.42. The $[H^+]$ apparently exerts little, if any, influence on Hg removal over the pH range of 6.5 to 9. (Figure 9.42a); that is, either there was not very much adsorption of Hg on the oxides of Al and Fe, or there was no coprecipitation of mercury. Only when turbidity was present at the 90 ntu (nephelometric turbidity units) level was there an 80% removal of Hg. This observation was at variance with the 100% removal at pH 8 reported in another study.[90] It can also be seen that for a given level of turbidity ferric sulfate was more effective than alum. This is also at variance with the results of Logsdon and Symons,[89] who observed a 60% Hg reduction in a coagulation system of turbidity, 100 ntu and alum. To summarize, the MCL for Hg is reached only if the initial concentration does not exceed 0.003 mg/L for alum and about 0.006 mg/L for iron (Figure 9.42).[78] That organic mercury is not removed at all by coagulation is seen in Figure 9.42b. Lime softening is more effective than coagulation for a spiked well water treated to a pH of 11, as seen in Figure 9.42b. However, the $[Hg]_t$ should not exceed 0.006 to 0.007 mg/L in order to achieve the MCL for Hg by lime softening. No organic Hg is removed in this treatment.

Several investigations have been conducted on the utilization of PAC and GAC for Hg removal. Figure 9.42d shows the log-log plot of the adsorption data for inorganic Hg and CH_3Hg^+.[89] These data indicate that each mg/L of PAC (Nuchar Aqua A) removes 0.0001 mg of inorganic Hg and CH_3Hg^+. Pilot plant studies with PAC (Darco-B and Darco-M) and GAC (Hydrodarco 1030 and Filtrasorb 100) were conducted.[78] When PAC was used in conjunction with ferric sulfate, Hg removals were greater than by either treatment alone. Cumulative removals for inorganic mercury by GAC filtration ranged from 49 to 97%, whereas organic Hg removals ranged from 80 to nearly 100%.[78] Exhausted GAC was as effective as fresh GAC. Figure 9.43a shows the effect of pH on the removal of inorganic mercury by PAC (Darco HDB).[91] Figure 9.43b shows the adsorption of CH_3Hg^+ by three different types of PAC: PAC-1 lignite base (Darco HDB), PAC-2, petroleum base (Amoco PX-21), and PAC-3, bituminous base (Nuchar Aqua).[91] With the exception of PAC-3, methyl mercury removals were decreased as the pH value was increased from 7 to 9. PAC-1 apparently was the most effective of the three powdered carbons. At pH 7, the MCL for Hg was reached by 80 and 100 mg/L PAC-1.[91] Batch and column tests were conducted for Hg removal by PAC (Filtrasorb 300, 270 mesh) and GAC (Filtrasorb 300, 8×30 mesh).[92] Typical log-log plots of the adsorption data from batch tests for pH values of 4 and 10 are seen in Figure 9.44. Experimental conditions were: 2.0 g carbon, 100 mL of 10.0-mg/L Hg(II), and 6 hr of agitation

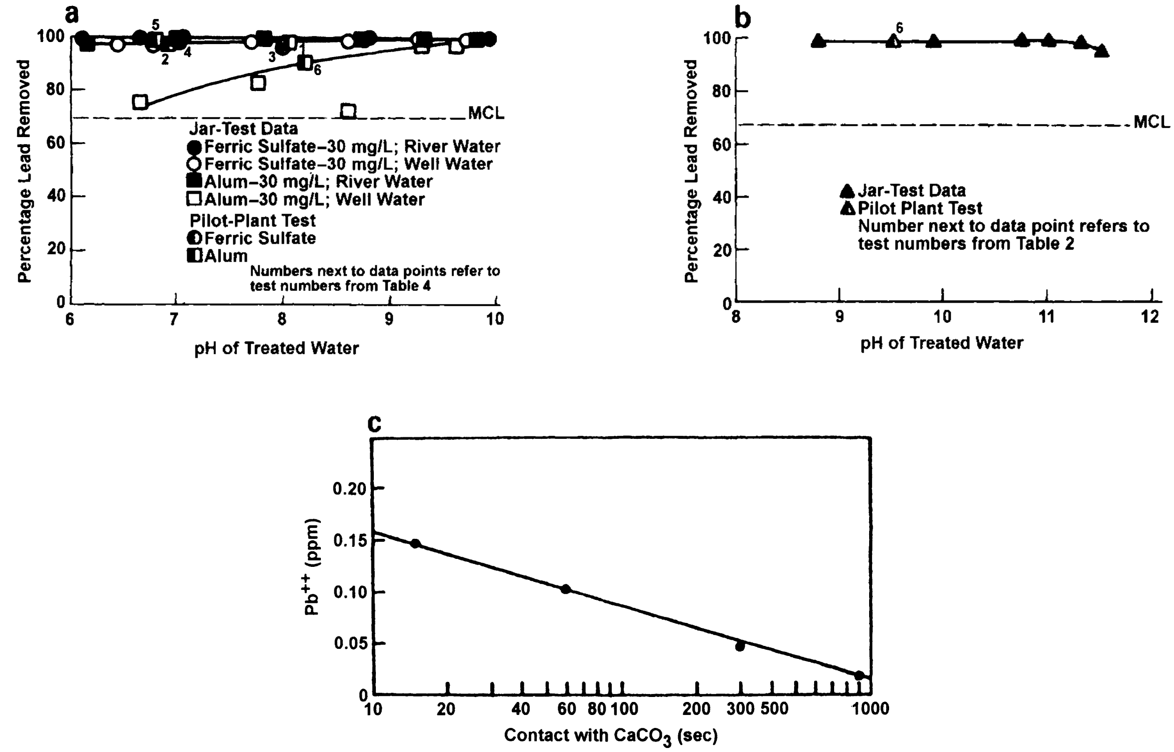

Figure 9.41. (a) Effect of pH on lead removal by coagulation treatment. Lead concentration = 0.15 mg/L. (b) Effect of pH on lead removal by lime softening. Lead concentration = 0.15 mg/L. Reproduced from Sorg and Logsdon,[67] courtesy of the American Water Works Association. (c) Residual lead in solution after treatment with $CaCO_3$ as a function of $CaCO_3$ contact time before filtration. Reproduced from Hautala et al.,[88] courtesy of the International Association on Water Pollution Research.

at 20°C. Greater adsorption occurred at the lower pH value of 4. For example, at 1 mg/L Hg, the quantity at pH 4 was 1 mg Hg/g. Breakthrough curves for the carbon columns are seen in Figure 9.45 for pH values 4 and 10. For the latter system, Hg broke through within the first day, whereas no breakthrough occurred within 5 days as at pH 4.

The coprecipitation of Hg(II) with iron(III) hydroxide over the pH range of 4 to 12 was observed.[93] At pH 8, a 95% removal of 100 mg/L Hg was effected by 388 mg/L Fe. Formation and coprecipitation of $Hg(OH)_{2(s)}$ was the apparent mechanism for the removal.

Coagulation-filtration, lime-soda softening, GAC, and RO are listed by the USEPA as the BATs for removal of Hg from water. However, RO is not particularly effective for Hg removal, as seen in Table 9.19.

NICKEL

Aqueous Chemistry

The MCL for nickel in drinking water is 0.1 mg/L.[1] That Ni may occur in natural waters is seen by the 0 to 71 μg/L concentrations reported for several rivers in North America and the 11 μg/L found in a spring water in California.[2] However, the most probable source of Ni in ground- and surface waters would be from electrochemical plating wastewaters. Some reactions that may occur in aqueous systems are (25°C):

$$Ni^{2+} + 2OH^- = \begin{array}{c} Ni(OH)_{2(s)} \\ \text{nickel hydroxide, fresh} \end{array} \qquad (64)$$

$$\Delta G^\circ_{REX} = -20.05 \text{ kcal/mol}$$

$$\log K_s = 14.7$$

$$Ni^{2+} + CO_3^{2-} = \begin{array}{c} NiCO_{3(s)} \\ \text{nickel carbonate} \end{array} \qquad (65)$$

$$\Delta G^\circ_{REX} = -11.16 \text{ kcal/mol}$$

$$\log K_s = 8.18$$

At a pH value of 10, the equilibrium Ni solubility for Reaction 64 would be 11.7 μg/L. At a $[CO_3^{2-}]$ of 10^{-3} *M*

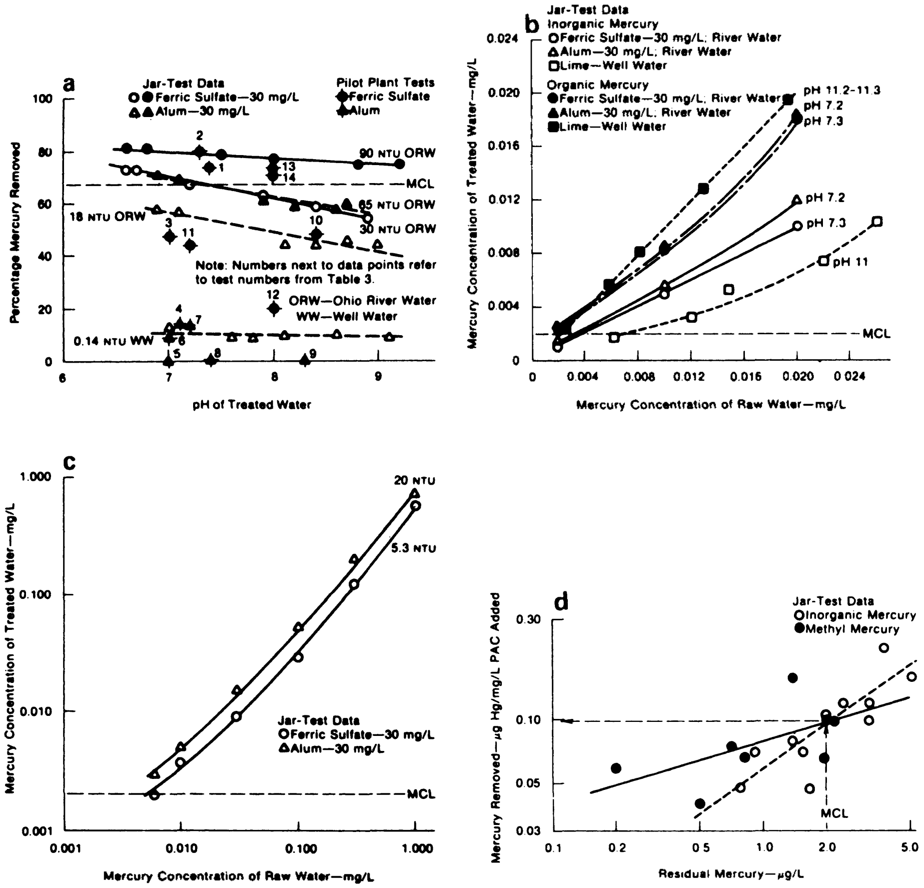

Figure 9.42. (a) Effect of pH and turbidity on inorganic mercury (0.006 mg/L) removal by coagulation treatment. (b) Effect of initial concentration on mercury removal by coagulation and lime softening treatment. (c) Effect of initial concentration on inorganic mercury removal from river water by conventional coagulation. (d) Freundlich isotherms for mercury adsorption with PC. Reproduced from Sorg[78] and Logsdon and Symons,[89] courtesy of the American Water Works Association.

for Reaction 65, the equilibrium solubility of Ni would be 388 µg/L.

Removal

The BATs for nickel removal from drinking water are lime-soda softening, IX, and RO. Very little information is in the literature about these processes for the removal of Ni^{2+} from raw sources. Certainly, Reactions 64 and 65 suggest that the lime-soda softening process would be a feasible process to meet the MCL for Ni in potable water.

NITRATE

Concern

The MCL for nitrate (NO_3^-) remains at 10 mg/L as NO_3-N (see Chapter 1). This standard was established several years ago to prevent methemoglobinemia in infants. However, concern has been expressed about the epidemiological link between nitrate and cancer.[94] Nitrate that is consumed in drinking water is reduced to nitrite (NO_2^-) in the body. In turn, NO_2^- can react with secondary amines, amides, and carbamates to form N-nitroso compounds, of which several are potential human carcinogens. For example, a statistically significant correlation was found between death from gastric cancer and the amount of nitrate fertilizer used in 25 provinces of Chile.[94] In this study, a positive correlation was found for both the general population and for farm workers. Similar studies are reported in Reference 92. Groundwaters with excessive quantities of NO_3^- are, in general, targeted for treatment.

Removal

Ion exchange of chloride for nitrate currently is the simplest and least expensive method for removing nitrate from contaminated groundwaters. To date, only a few applications of the process are in existence and these are restricted

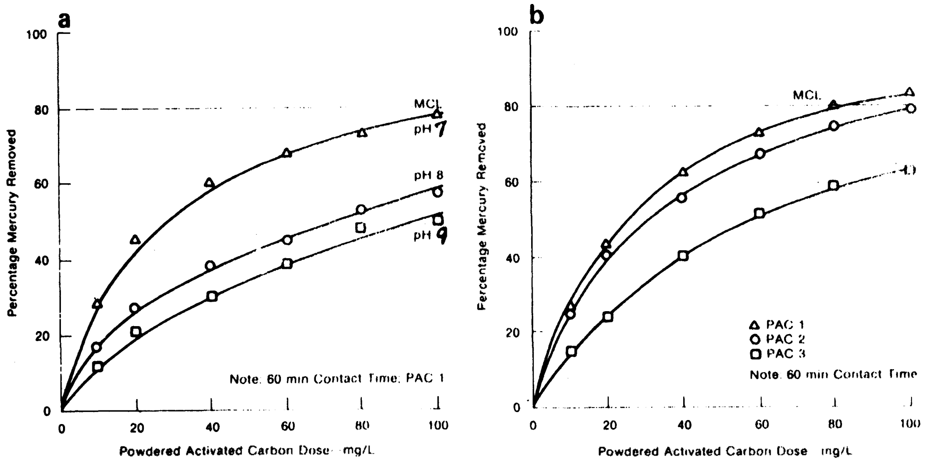

Figure 9.43. (a) Effect of pH on removal of inorganic mercury (0.010 mg/L) with PAC treatment. (b) Removal of methyl mercury (0.10 mg/L as Hg) by PAC at pH 7. Reproduced from Thiem et al.[91] and Sorg,[78] courtesy of the American Water Works Association.

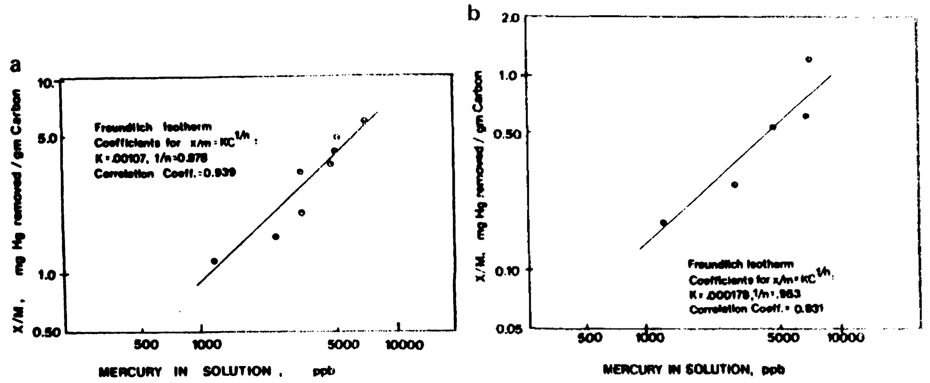

Figure 9.44. Adsorption isotherm for Hg(III) and PAC at 20°C and (a) pH 4 and (b) pH 10. Reproduced from Humenick and Schnoor,[92] courtesy of the American Society of Civil Engineers.

mainly to small community and noncommunity water supplies. However, more of these types of water supplies will be forced into compliance with the MCL for NO_3.

Anion exchange is similar to cation exchange processes, except, of course, that anions are exchanged rather than cations. Also, nitrate is not the most preferred common ion involved in the multicomponent ion exchange process with contaminated groundwaters. The ion selectivity series for anions is: $SO_4^{2-} > I^- > NO_3^- > CrO_4^{2-} > Br^-$. Consequently, SO_4^{2-} is a major interference in the removal of NO_3 by the Cl^- form of strong base anion (SBA) exchange resins.

A 1 MGD ion exchange plant was built in McFarland, California to remove excess amounts of NO_3 from one of the city's supply wells.[95] Briefly, the plant consists of three reaction vessels containing the anion exchange resin (A-101-D, Duolite). Each vessel was designed to contain either 3 or 5 ft bed depth of the resin; the normal operation is to treat part of the water and blend it in order that the total well production is 1 MGD, with its NO_3 content less than the MCL. Design details are given in Reference 95. Typically, each vessel was regenerated after 160 bed volumes of water with a 6% brine solution. The influent NO_3-N content averaged 16 mg/L, and the effluent contents ranged from 1.1 to 9.5 mg/L over the 260 BVs. The waste brine was disposed of at the municipal wastewater treatment plant.

A nitrate removal process that drastically reduces salt consumption and water discharge has been developed on a bench scale.[96] It consists of chloride IX and 0.5 N (3%) NaCl regeneration, followed by batch denitrification and reuse of the spent brine. This process is referred to as the American or IX-SBR (sequencing batch reactor), as opposed to the Dutch IX-USBR (upflow sludge blanket reactor). Fig-

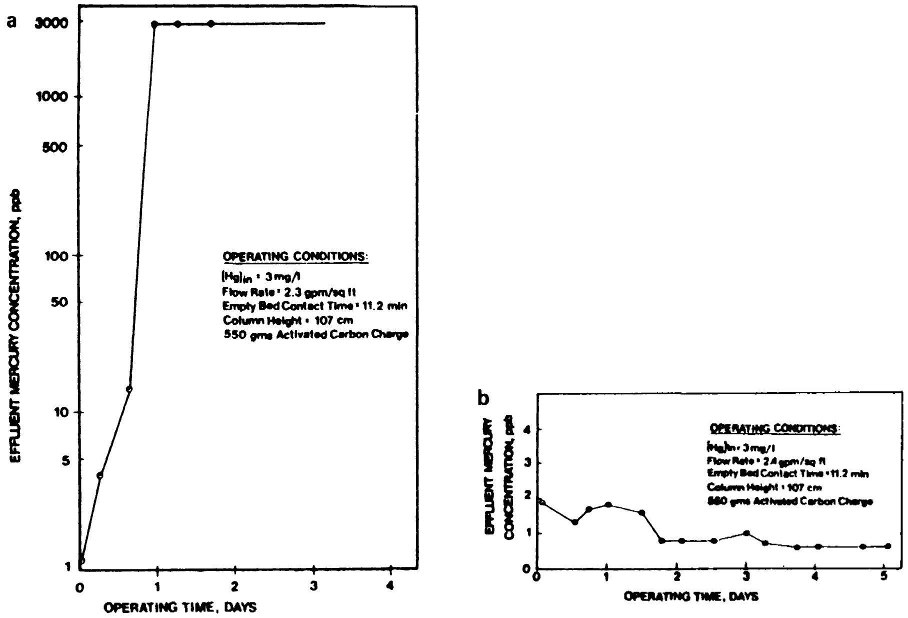

Figure 9.45. Carbon-only system: column run at 25°C and (a) pH 10 and (b) pH 4. Reproduced from Humenick and Schnoor,[92] courtesy of the American Society of Civil Engineers.

ure 9.46 shows a schematic flow diagram for the American system. During the recycle-reuse experiments, essentially complete (>99%) denitrification of the spent 0.5 N NaCl brine was achieved in 20 hours using a nonoptimum methanol-to-nitrate-nitrogen ratio (R) of 2.2. Figure 9.47 gives the effluent history for cycle 12 of a nitrate-selective resin with regenerant recycling. This breakthrough curve is virtually identical to one that was generated from a cycle where regenerant reuse was not employed. That the SO_4^{2-} broke through before the NO_3^- ion should be noted in Figure 9.47 (see below).

An innovative process that utilizes a biological fluidized-bed plant has been in operation for several years at the De Blankaart (Belgium) drinking water production center for removal of NO_3^- from surface water.[97] Methanol is used as the reductant. The nitrate removal efficiency was 9.0 kg NO_3^-/M^3 (264.2 gal) at 3.5°C. With an influent concentration of 75 mg/L NO_3^-, complete removal was achieved at an EBCT of 15 min. Nitrate was not detected in the effluent, provided there was a slight excess of methanol (1–2 mg/L). This residual of methanol was removed easily by downstream drinking water processes (biological oxidation and GAC).

That the sulfate content of natural waters affects the removal of NO_3^- by IX is seen in Figure 9.48. This curve was constructed from data obtained by spiking Glendale, Arizona water with Na_2SO_4.[98] As the $[SO_4^{2-}]$ was increased from the natural value of 43 mg/L (0.9 meq/L) to 310 mg/L (6.5 meq/L), length of the experimental run to NO_3^- breakthrough was decreased 55% from 400 to 180 BV. Another problem with IX removal of NO_3^- removal is the SBA resins prefer SO_4^{2-} to NO_3^- at the total dissolved solids (TDS) levels and ionic strengths of typical groundwater. This results in chromatographic peaking of nitrate after its breakthrough. The SO_4^{2-} elutes NO_3^- ions from the column, which results in an effluent concentration greater than the original source water. The obvious solution to this problem is to terminate the cycle just before the breakthrough, and to regenerate the column.

The BATs for NO_3^- removal from water are IX and RO[1]. That the latter process ranges from ineffective to excellent efficiencies is seen in Table 9.19, where the percentage recoveries range from 67 to 99%.

RADIONUCLIDES

Aqueous Chemistry

The radionuclides of greatest concern are radium 226, radium 228, uranium, and radon 222. These are all naturally occurring isotopes. Radium 228 is a beta emitter whose decay genes rise to a series of alpha-emitting daughters, while the others are all alpha emitters. Natural uranium actually is a combination of U^{234}, U^{235} plus U^{238}. However, U^{238} comprises 99.27% of the composition. At this writing, the proposed MCLs for radionuclides in drinking water are: Rn^{222}, 300 pCi/L, Ra^{226}, 20 pCi/L, Ra^{228}, 20 pCi/L, and U^{238}, 30 pCi/L.[1]

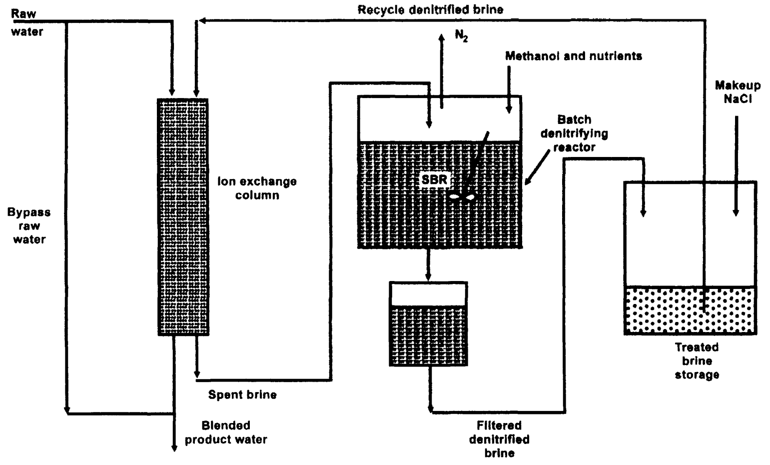

Figure 9.46. American ion exchange–biological denitrification process with sequencing batch reactor (IX-SBR process).[96]

The chemistry of Ra in aqueous systems is that it occurs mostly as a divalent cation. Since Ra^{2+} is a member of the alkaline earth metals, its chemistry would be similar to that of Be^{2+}, Ca^{2+}, Mg^{2+}, etc. Geologically it is very rare, with an average abundance in the earth's crust less than 1 part per 10^{12} parts. Its principal source is uranium ore (U_3O_8).

In aqueous systems, uranium would exist in the (VI) oxidation state as the soluble UO_2^{+2} uranyl ion below a pH value of 6.0. Above this pH, $UO_2(OH)_2$ would form a solid substance with a K_{sp} of 10^{-21}.[95] Other uranium solids that have significance in aqueous systems would be UO_2 (uranous oxide), U_3O_8 (the "green" oxide), and UO_3 (uranic oxide).

Removal

The BATs for radionuclides are: coagulation-filtration for Ra^{226} and Ra^{228}, lime-soda softening, IX, and RO for Ra^{226} and Ra^{228} separately and coagulation-filtration, lime-soda softening, and anion exchange (AX) for uranium. The removal technology for gaseous radon is aeration (see Chapter 5).

Table 9.24 summarizes the conventional technologies that can be effective for removal of radionuclides.[99] The highest efficiencies for some technologies are associated with point-of-entry (POE) and point-of-use (POU) devices. Emerging technologies for radionuclide removal include addition of hydrous Mn oxides (HMOs) with filtration for Ra removal, GAC adsorption–decay for Rn removal, and compact multistaged defused bubble aeration for Rn removal (see Chapter 5).

Ion Exchange

IX appears to be the current choice of technology for removal of radium and uranium from water.[100] A considerable amount of bench-, pilot-, and full-scale ion exchange research has been conducted within the last 10 years on radium and uranium removal. For example, USEPA-funded studies suggested that the cost-effective method for treating small groundwater systems for uranium removal would be SBA resins, which have an enormous capacity for the uranyl carbonate complexes: $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$ (Reference 101). The exchange reaction with the chloride-form anion resin (RCl) is:

$$4RCl + UO_2(CO_3)_3^{4-} = R_4UO_2(CO_3)_3 + 4Cl^- \qquad (66)$$

Radium can be removed by SAC resins, which are employed for hardness removal. Normally, the exchange reaction is:

$$2RNa + Ra^{2+} = R_2Ra + 2Na^+ \qquad (67)$$

An example of this recent research comes from an IX system where a small amount (~10%) of a SBA resin is added to a SAC resin in a conventional water softener.[102] This mixture provides a reasonably good removal of uranium and radium from water. In tests on a groundwater containing 25 pCi/L radium and 120 µg/L uranium, a mixed bed of 10% SBA and 90% SAC resins, the product water had less than 1 pCi/L Ra and 20 µg/L U. NaCl was used as the regenerant. These removals were accomplished in the presence of a total hardness of 150 mg/L as $CaCO_3$. This research also revealed that too much anion resin or stratified resin beds caused excessive Ra and U leakage. Various empty bed contact times were investigated also. Evidence was presented that KCl was superior to NaCl as a regenerant. This research was conducted on a well water in Chimney Hill, Texas.

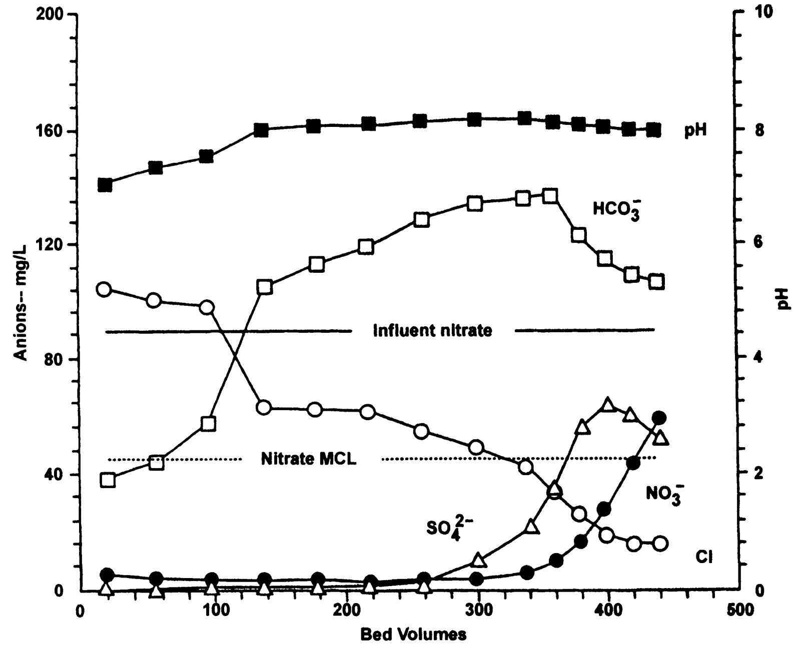

Figure 9.47. Effluent history for cycle 12 of nitrate-selective resin with regenerant recycling (flow rate—20 BV/h).[94]

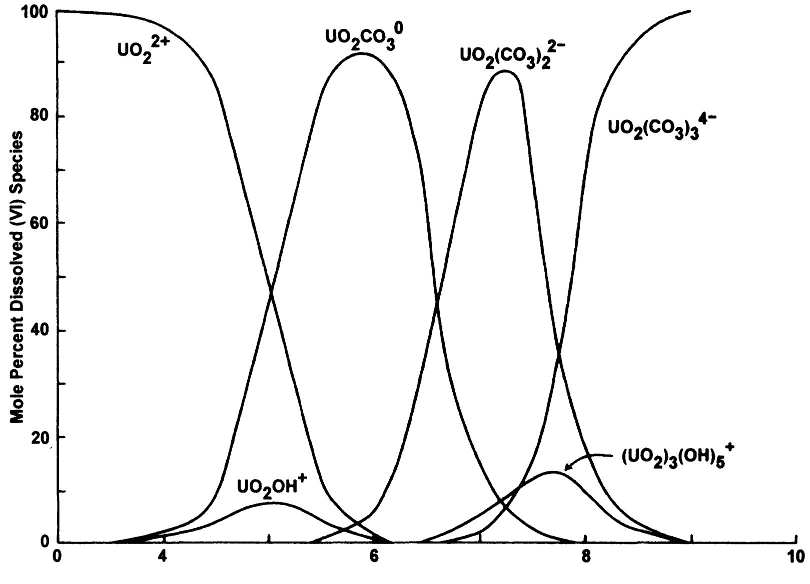

Figure 9.48. Distribution of uranyl hydroxy and carbonate complexes vs. pH.[104]

The above research was followed by a study on U removal with a Cl-form of an anion exchange resin on the same groundwater.[103] The macroporous SBA resin (Ionac A-642) exhibited an enormous capacity for removing the uranium-carbonate complex anions. For example, a bed was operated continuously for 478 days at pH 7.6 to 8.2 for a total throughput of 302,000 BVs, at which time its effluent [U] was still <6 µg/L for a 95% and greater removal. It should be noted that the SO_4^{2-} content was <1 mg/L and the only competing anion was HCO_3^- (150 mg/L as $CaCO_3$). The [H^+] was investigated as a factor influencing the removal of U by the SBA. Figure 9.48 shows a pH distribution diagram of various cationic and anionic U species. An increase in the [H^+] decreases the formation of the uranyl

Table 9.24. Summary of Technology and Performance[a] of Processes for Removing Radionuclides from Drinking Water.[99]

Radon		Radium		Uranium	
Method	**Efficiency**	**Method**	**Efficiency**	**Method**	**Efficiency**
Aeration		Ion exchange	81–99	Ion exchange	90–100
Packed tower	to 99+	Reverse osmosis	90–95+	Lime softening	85–99
Diffused bubble	to 99+	Lime softening	80–92	Reverse osmosis	90–99
Spray	70–95+	Electrodialysis	90	Coagulation-filtration	80–98
GAC		Ra complexer	90–99	Activated alumina	90
Adsorption-decay	62–99+	Greensand	25–50		
		HMO–filter	90		

[a] The highest efficiencies for some technologies are associated with POE and POU devices.

carbonate complexes and promotes the formation of neutral and cationic species. At a feed pH value of 4.3, a U leakage of 55% was observed and a virgin column was completely exhausted at only 6000 BVs. At a feed pH value of 5.8 where the predominant species is the neutral $UO_2CO_3^0$, there was no significant effect on U removal on a column that was partially exhausted for 41,000 BUs at a pH of 8. NaCl was used as the regenerant, the concentration of which was researched. Efficiency of regeneration was increased as the concentration of NaCl was increased from 0.5 to 4.0 N.

A weak-acid resin in the H^- form was found to effectively remove (96–98%) Ra^{226} from water in the presence of 200 mg/L hardness as $CaCO_3$.[69] The feed water content of Ra^{226} was 20 pCi/L. At that time (1987–1988), the MCL for Ra^{226} was 5 pCi/L. As noted above under the Ba section, there are several disadvantages to the use of a weak-acid resin as a cation exchanger in drinking water treatment. Consequently, removal of radionuclides by IX will, undoubtedly, pursue the mixed resin bed cited above. Additional information may be found in Reference 101 on the removal of U by anion IX.

Reverse Osmosis

There have been several RO pilot-plant studies for the removal of radionuclides from drinking water.[52,105–107] One of these studies showed that the removal of natural U from Florida groundwater (300 μg/L) by four different membranes was excellent (99%, Table 9.19).[105] Eight RO treatment systems were used in Sarasota County, Florida, for the removal of Ra^{226} and other dissolved solids from water.[106] Although the age, type, and performance of the eight systems varied, all systems lowered the Ra^{226} contents (highest was 20.5 pCi/L) to below the EPA MCL of 5 pCi/L in 1980.

Three RO membranes were evaluated for the removal of Ra^{226} from groundwater at Lemont, Illinois.[107] For standard pressure (125 and 350 psi) modules, Ra^{226} rejection exceeded 99%, whereas for the low pressure (70 psi), it was 91%. In all three systems, Ra rejection slightly exceeded hardness rejection. This suggested that hardness monitoring might be used as a surrogate for Ra.

Lime-Soda Softening

Softening of hard waters has been reported to reduce the Ra^{226} content by 80–92% and the U content by 85–99% (Table 9.24).[99] Laboratory jar tests were employed for an evaluation of lime softening for U removal from a surface water.[108] Lime dosages ranged from 50 to 250 mg/L, which raised the pH values to 10.6 to 11.5 where 85–90% of the U was removed. Experiments were also conducted with $MgCO_3$ and lime at pH values 9.8 to 10.6 where the effectiveness of U removal was reduced. A pH value of 10.6 appears to be critical in these systems. Above this value, lime and $MgCO_3$ combinations increased U removals to 93–99%. In all probability, $Mg(OH)_2$ is precipitated, which removes a uranyl hydroxide complex, $(UO_2)_3(OH)_5^+$, perhaps by adsorption. Additional information is found in Reference 99 on the lime softening removal of several artificially manufactured radionuclides.

Coagulation-Filtration

The traditional jar test was employed for an early investigation into the removal of U (83 μg/L) from a pond water (low-level radioactive waste settling basin) using iron and aluminum coagulants.[101,107] In these experiments, coagulant dosages ranged from 0.5 to 30 mg/L and the pH values were varied at 4, 6, 8, and 10. It was expected that removal efficiency would be dependent on coagulant dosage and the final pH value of the test solutions. Figure 9.49 shows typical results of the U removal by alum. Similar results were obtained with ferrous and ferric coagulants. The greatest removals were achieved with coagulant dosages greater than 10 mg/L and at a pH value of 10. Apparently this removal is effected by adsorption of a positively charged uranium hydroxide complex $(UO_2)_3(OH)_5^+$. At a pH value of 6, the removal may have occurred with the neutral $UO_2CO_3^0$ complex. In any event, the coagulant of choice would be alum, de-

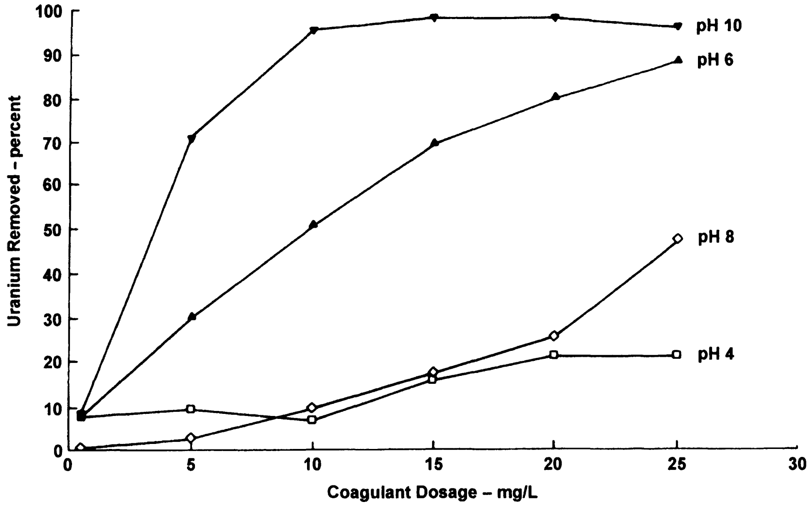

Figure 9.49. Uranium removal by alum coagulation.[101]

spite its amphoteric solubility at high pH values. Other studies for U removal used a chemical clarification system, air flotation, and a rotary vacuum filter with ferric chloride (30 mg/L) as the coagulant.[109] A 100% removal was reported at a pH of 10.0.

Adsorbents

Several different types of solid phase adsorbents have been researched for their effectiveness for removal of Ra and U from raw water supplies. For example, a novel filtration process utilizes the natural capacity of filter sand to sorb radium, which requires a periodic acid rinse to maintain its sorptive capacity.[107] Laboratory pilot studies employed a partially softened groundwater, whereupon the process was capable of reducing Ra^{226} content by 80 to 90% in the presence of iron floc. It was necessary, however, to use a daily rinse of a weak HCl solution (0.04%), which may render the process impractical.

Field studies were conducted in Lemont, Illinois, to evaluate specific adsorbents for removal of Ra from groundwater.[107] These studies focused upon the use of packed beds that contained granular-or bead-form radium-specific adsorbents. For example, a radium-selective complexer (RSC) was investigated that had been employed for the decontamination of U tailing pond effluents:[111] in addition to RSC, manganese-impregnated beads and $BaS0_4$-impregnated activated alumina. These adsorbents were employed in a downflow column operation. The RSC complexer was the best adsorbent of those that were evaluated. This was based on the BV (38,000) to the MCL or maximum capacity (1.18 nCi/cm^3). A major disadvantage of these systems is that it is either impractical or impossible to regenerate the adsorbent. Consequently, the spent media is a low-level radioactive waste that may be disposed of at only one U.S. location, in the state of Washington.

Batch- and pilot-scale studies have demonstrated that the addition of preformed hydrous manganese oxides (HMOs) appears to be a feasible approach to removing Ra^{226} from drinking water.[112] Significant Ra^{226} removals were obtained in batch studies using HMOs in the range of 0.5 to 1.0 mg as Mn/L produced by the $KMn0_4$ oxidation of $MnS0_4$. For example, a dose of 0.5 mg/L Mn resulted in removals of approximately 80 ± 5% from a water (pH 7.4) containing an initial Ra^{226} content of approximately 2.5 pCi/L. Removals did not depend significantly on the pH value of the raw water within a range of 6.5 to 8.5. In batch systems, sorption of Ra^{226} to HMOs appears to be described by a linear isotherm: $q = K_d[Ra]$ where q = amount of radium sorbed per unit mass of HMOs, [Ra] = remaining concentration in solution, and K_d is the distribution coefficient. In these pilot-scale studies, a removal of 80% was achieved with the HMOs, which in turn were removed by a sand filter. Here again, a periodic acid rinse is needed to reactivate the sand filter.

SELENIUM

Aqueous Chemistry

The MCL for selenium in drinking water is 0.05 mg/L. Sulfides or native sulfur deposits often contain Se in significant amounts because of the chemical similarity between S and Se. Since Se is not evenly distributed in geologic materials, its occurrence in natural waters is usually less than 1 μg/L. Sorg and Logsdon[113] noted a survey of 139 groundwaters in Nebraska where 40.3% exceeded the MCL of 0.01 in 1978, and the two highest contents were 0.48 and

0.103 mg/L. Se exists in four oxidation states in aqueous systems: (–II, 0, IV, VI). The reduced state, (–II), is represented by the selenide species, and the elemental state, Se(0), exists in several allotropic forms, whereas the two higher oxidation states are the selenites, (IV), and selenates, (VI).

When selenium is found in groundwater, it is a result of natural, not artificial, contamination. At typical groundwater pH values (7.0 to 9.5), only the anionic forms of selenious [Se(IV)] and selenic [Se(VI)] acid are found. The dissociation equations and constants for the two acids are presented below. Selenious acid dissociation equilibria:

$$H_2SeO_3 = H^+ + HSeO_3^- \qquad pK_1 = 2.55 \qquad (68)$$

$$HSeO_3 = H^+ + SeO_3^{2-} \qquad pK_2 = 8.15 \qquad (69)$$

Selenic acid dissociation equilibria:

$$H_2SeO_4 = H^+ + HSeO_4^- \qquad pK_1 = -3.0 \qquad (70)$$

$$HSeO_4^- = H^+ + SeO_4^{2-} \qquad pK_2 = 1.66 \qquad (71)$$

Under oxidizing conditions, Se(VI) will predominate, and divalent selenate (SeO_4^{2-}), an anion with chemical behavior similar to that of sulfate, will be found. Under reducing conditions Se(IV) will predominate, and at pH values below 8.15 the monovalent biselenite anion ($HSeO_3^-$) will be the dominant form; above pH 8.15, the divalent selenite anion (SeO_3^{2-}), will dominate.

Removal

The BATs for Se removal from water are coagulation-filtration, lime-soda softening, activated alumina (AA), and RO.[1] Some water treatment personnel prefer either IX or AA for Se removal.[98] Selenite (IV) is removed effectively by AA, whereas SBA exchange is the process of choice for selenate (VI). This recommendation is based on the relative affinity values for anions on AA and SBA resins.[98]

Chemical coagulation has been attempted for the removal of Se from potable water supplies. Figure 9.50a shows the attempts to remove Se(IV), 0.03 mg/L, from well water and the Ohio River by chemical coagulation.[113] Ferric sulfate appears to be the better coagulant, with greatest removals occurring in the 6 to 7 range of pH values. However, opposite results were obtained when the effect of coagulant dose on Se(IV), 0.1 mg/L, was studied (Figure 9.50b).[113] Insignificant removals of Se(VI) were effected by the two coagulants in jar and pilot plant tests. Lime softening was not a very effective treatment for either Se(IV) or Se(VI).[113] The maximum removal (50% at pH 11.5) was obtained with a hard well water spiked with 0.1 mg/L Se(IV).

Laboratory tests with alumina columns as an adsorber or ion exchanger have been reasonably efficient, with a removal of 95% of 0.3 mg/L of Se(IV) and Se(VI).[113,114] There are, however, interferences by other anions in water. For example, the order of preference of alumina for anions is: $OH^- > H_2PO_4^- > F^- > H_2AsO_4^- > HSeO_3^-$.

Selenate is so strongly preferred by anion resins that oxidizing selenite to selenate prior to treatment is the best approach. Although Se(IV) is considerably more difficult to oxidize than As(III), laboratory research has demonstrated that this oxidation can be readily accomplished with free chlorine. In synthetic groundwater containing sulfate, chloride, and bicarbonate at pH 8.3, the reaction is first-order in both Se(IV) and free chlorine concentrations.[98]

Some laboratory studies have been conducted with the chloride-form SBA exchange for selenate removal.[98] A source water with 0.1 mg/L Se(VI) yielded an acceptable run length (275 BV) to an effluent concentration of 0.03 mg/L in the presence of 700 mg/L TDS and 192 mg/L SO_4^{2-}. Selenate was eluted after SO_4^{2-} with no chromatographic peaking. In this study, no attempts were made to regenerate the resin. However, this should not be a problem because SeO_4^{2-} is a divalent ion subject to selectivity reversal similar to sulfate, arsenate, and chromate. These strongly adsorbed divalent anions are eluted readily during regeneration with NaCl.[98]

Alumina adsorption has been found to be very effective for removal of Se(IV) from water in the optimum pH range of 5 to 6.[114] In this study, Se(VI) was removed ineffectively by alumina because of strong competition from SO_4^{2-}. Another study reported that alumina was good for $HSeO_3$ removal with a range of pH values from 3 to 8.[115] Since Se(+4) adsorption onto alumina is reasonably strong, complete regeneration of the spent alumina must use an acid-base sequence similar to that for fluoride removal.[98] These laboratory studies demonstrate that the feasibility and cost of an activated alumina process for selenium removal depend on the oxidation state of the selenium. It could be an excellent process for water in which Se(IV) is the only selenium species, but it becomes less attractive as the fraction of Se(VI) increases.

Several experiments have been conducted with PAC removal of Se(IV) and Se(VI).[113] The ineffectiveness of this treatment is observed with removals less than 4% with PAC dosages up to 100 mg/L. Nor did GAC work. Some limited experiments with reverse osmosis (RO) indicated 97% removals of Se(IV) and Se(VI) in tap water spiked with 0.1 mg/L. It would appear, therefore, that only a strong anion exchanger and RO are effective for the specific removal of the two Se species from water.[113] See Table 9.18 for percentage removals of Se(IV, VI).

The arsenic can be removed from hard water by lime softening, as seen in Figure 9.51.[113] The $[H^+]$ obviously is a

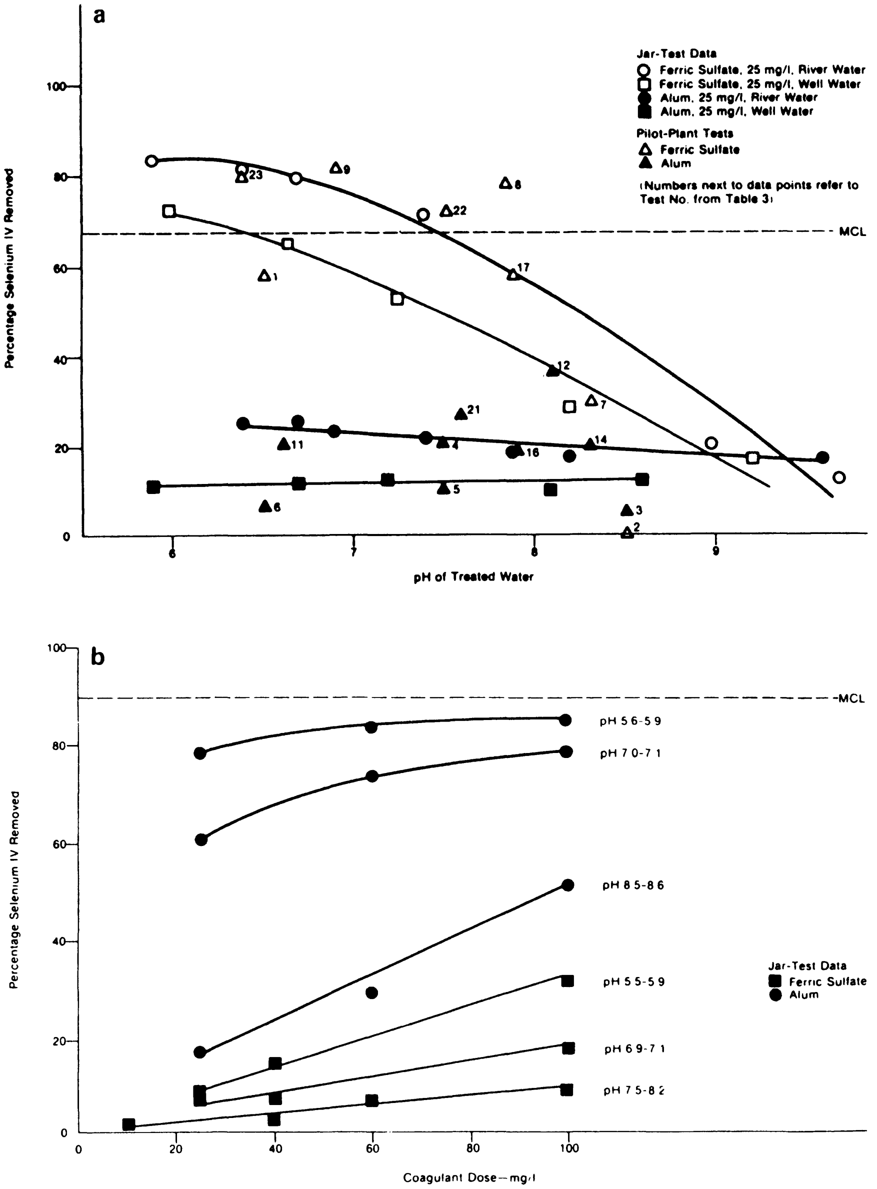

Figure 9.50. (a) Effect of pH on Se(IV) (0.03 mg/L) removal by coagulation treatment. (b) Effect of coagulation dose on Se(IV) (0.1 mg/L) removal from well water. Reproduced from Sorg and Logsdon,[113] courtesy of the American Water Works Association.

factor, with 100% removal of As(V) occurring at pH values greater than 10.5. The formation of calcium arsenate may be responsible for this removal:

$$3Ca^{2+} + 2AsO_4^{3-} = Ca_3(AsO_4)_{2(s)} \qquad (72)$$

$$\Delta G^\circ_{REX} = -24.78\ \text{kcal/mol}$$

$$\log K_s = 18.17$$

As(III) removal was not as effective as As(V) with the lime treatment. Figure 9.51 also shows that As(III) and As(V) removals are nearly the same in pilot plant tests as with the laboratory jar tests.

Table 9.25 summarizes pilot plant tests designed to evaluate the effectiveness of coagulation and filtration through dual media (anthracite and sand) and two types of GAC (Filtrasorb 200 and Hydrodarco). Very little As(III) and As(V) were removed. Removals in excess of 90% were obtained with ferric sulfate coagulation and subsequent filtra-

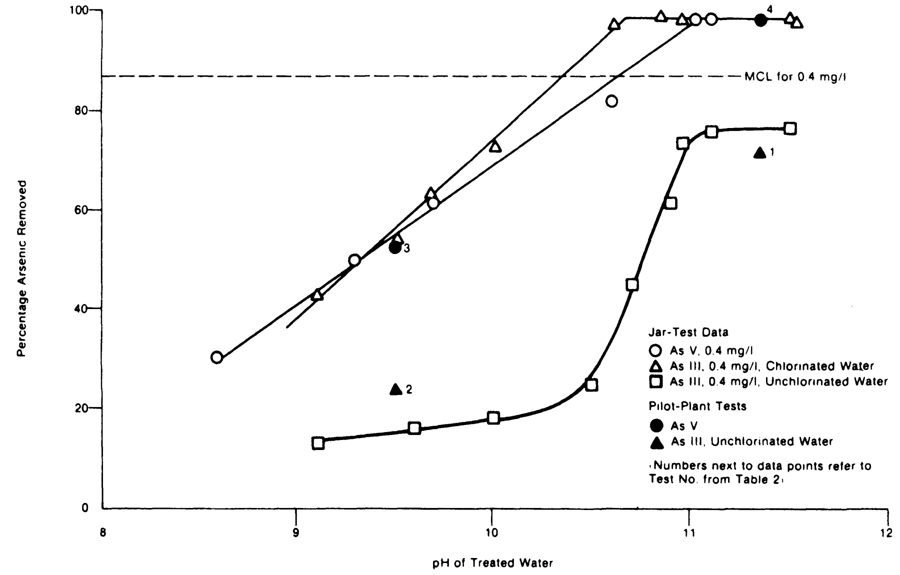

Figure 9.51. Effect on pH on arsenic removal by lime softening. Reproduced from Sorg and Logsdon,[113] courtesy of the American Water Works Association.

tion. There was little difference between the dual-filter media and the GAC for As removal. These tests also indicate that GAC—virgin and exhausted—has an adsorptive capability for As which has been confirmed.[62]

SODIUM

Concern

Sodium is, of course, a constituent in all natural fresh waters. Its content varies with geology and possible contamination by wastewaters.[2] Sodium compounds and exchange resins are utilized extensively in drinking water treatment (Table 9.26). Concern has been expressed frequently about the health effects of sodium.[1] There is some indirect evidence linking excessive sodium intake to hypertension. For most people, the contribution of drinking water to sodium intake is small, relative to total dietary intake. According to the report from the National Academy of Sciences,[116] "it appears that at least 40% of the total population would benefit if total sodium ion intake were maintained [at] not greater than 2,000 mg/day... [W]ith sodium ion concentration in the water supply of not more than 100 mg/L, the contribution of water to the desired total intake sodium would be 10% or less for a daily consumption of two liters."

Removal

The sodium content of drinking water can be controlled through reducing or eliminating its use in the various types of municipal and domestic water treatments. A study of this problem led to these conclusions:[117]

Utilities that use ion exchange softening could switch from sodium exchange to hydrogen exchange followed by pH adjustment, if necessary, with a nonsodium compound.

Private home owners who have ion exchange softeners could change the plumbing in their homes so drinking water is not softened. Changing home softeners to an acid cycle is not advisable.

Utilities that use lime-soda ash softening could reduce or eliminate the addition of soda ash (Na_2CO_3) used to remove NCH. A residual hardness of 125 mg/L is usually not objectionable to water customers, and most of this could be left as NCH.

The use of sodium-containing compounds for pH adjustment, coagulation, and disinfection can easily be minimized. Many compounds that do not contain sodium are readily available to perform these functions.

The addition of sodium to drinking water from compounds added for fluoridation and corrosion control is usually insignificant (<2 mg/L) because only a small quantity of the compound is required to perform these functions.

Specific treatment methods for the removal of sodium from drinking water do not exist. Existing methods for desalination of seawater and treatment of brackish waters are used for the reduction of total dissolved solids (TDS), including sodium; for example, distillation is being used for the desalination of seawater, and reverse osmosis is being used to treat brackish and seawaters with TDS concentrations ranging from 500 to 36,000 mg/L. Ion exchange is being used to deionize water for laboratory and industrial use. A

Table 9.25. Results of Conventional Coagulation Pilot-Plant Tests for Arsenic Removal: Ohio River Water.[a]

Coagulant		pH of Treated Water	Arsenic Contaminant		Percentage Arsenic Removal				
						Filtered Water			
							Granular Activated Carbon Filters		
Type	Dose (mg/L)		Form	Raw Water Concentration (mg/L)	Settled Water	Dual-Media Filter	Virgin GAC	Exhausted GAC	Virgin GAC
Alum	24	8.9	As(V)	0.37	14	14	11	—	—
Ferric sulfate	25	6.7	As(V)	0.39	81	96	98	—	—
Ferric sulfate	26	8.8	As(V)	0.33	46	62	61	—	—
Ferric sulfate	29	7.0	AS(III)	0.12	36	64	90	91	—
Ferric sulfate	28	8.3	As(III)	0.12	61	82	80	84	—
Ferric sulfate	30	8.0	As(V)	0.26	80	95	97	95	—
Alum	29	7.0	As(III)	0.16	14	21	—	35	44

[a] Reproduced from Sorg and Logsdon,[113] courtesy of the American Water Works Association.

Table 9.26. Sodium Addition During Water Treament.[116]

Constituent Name	Constituent Formula	Common Usage	Typical Range of Resulting Sodium Concentration Addition (mg/L)
Sodium exchange resins	NaR	Softening	70.0–340.0
Sodium carbonate	Na_2CO_3	Softening	30.0–200.0
Sodium hypochlorite	NaClO	Disinfection	2.0–10.0
Sodium carbonate	Na_2CO_3	pH adjustment	5.0–18.0
Sodium hydroxide	NaOH	pH adjustment	2.0–9.0
Sodium fluoride	NaF	Fluoridation	0.8–1.5
Sodium fluorosilicate	Na_2SiF_6	Fluoridation	0.3–0.5
Sodium aluminate	$NaAlO_2$	Coagulant aid	1.0–15.0
Sodium silicate	Na_4SiO_4	Coagulant aid/corrosion control	0.54–8.4
Sodium hexametaphosphate	$(NaPO_3)_6$	Sequestering agent	0.2–0.7
Bimetallic glassy phosphates	Na—Zn—PO_4	Corrosion control	0.05–1.4
Sodium glassy phosphates	Na—PO_4	Corrosion control	0.6–4.0

thermally regenerable ion exchange process is producing favorable results on water with a TDS concentration of 500 mg/L. One manufacturer has an ion exchange process for treating brackish water with TDS concentrations from 500 to 5000 mg/L. Another process, electrodialysis, has a TDS removal application range for concentrations from 1000 to 5000 mg/L. Blending is also a feasible approach for the reduction of TDS and sodium in drinking water if an additional source of water lower in sodium is available.

SILVER

Aqueous Chemistry

The secondary drinking water standard for silver is 0.10 mg/L.[1] Silver is an infrequent constituent of natural waters, with a content in 15 major North American rivers ranging from 0 to 1.0 µg/L.[2] It has been reported that less than 7% of 1577 samples from their rivers and lakes survey had detectable amounts of silver, with the maximum value at 0.038 mg/L and a mean value of 0.0026 mg/L.[118] Consequently, silver should not be a problem in either ground- or surface waters, unless there is a wastewater source.

Since silver is a very noble metal, its domain of stability covers a large portion of a pE-pH diagram.[35] The reduction reaction for metallic silver is:

$$Ag^+ + e^- = Ag_{(s)};\ V^0 = +0.799\ \text{V} \qquad (73)$$

Consequently, the redox value in water must exceed +0.799 V before Ag ions form from the corrosion of silver. Under these conditions, argentous oxide (Ag_2O) can form:

$$2Ag^+ + H_2O = Ag_2O + 2H^+,\ \log K_{eq} = -6.33 \qquad (74)$$

The solubility and pH value of a saturated solution of Ag_2O are 16.2 mg/L as Ag_2O and 10.15, respectively, at 25°C.[35]

Removal

Data are scarce for the specific removal of silver from water. Figures 9.52a and b illustrate the removal of silver from water by coagulation, while Figure 9.52b shows the use of PAC and 9.52c shows the results of lime softening.[69] Natural turbidity was a factor in the coagulation removal of silver from Ohio River water. Ferric sulfate was slightly more effective than alum. While pH is a factor with alum, it is not for ferric sulfate. Very little additional silver is removed when either coagulant dosage exceeds 30 mg/L. In order to reach the MCL for silver from 0.15 mg/L, 100 mg/L PAC was required (Figure 9.52b). Lime softening was moderately effective, requiring pH values in excess of 9.0. Since no lime dosages were given, it is presumed that treatment to a specified pH value was the operational mode.

SULFATE

Aqueous Chemistry

Sulfate and other sulfur species are ubiquitous constituents of all natural waters. Sulfate may result from the chemical weathering of geologic formations or from biologically mediated oxidations of reduced sulfur species.

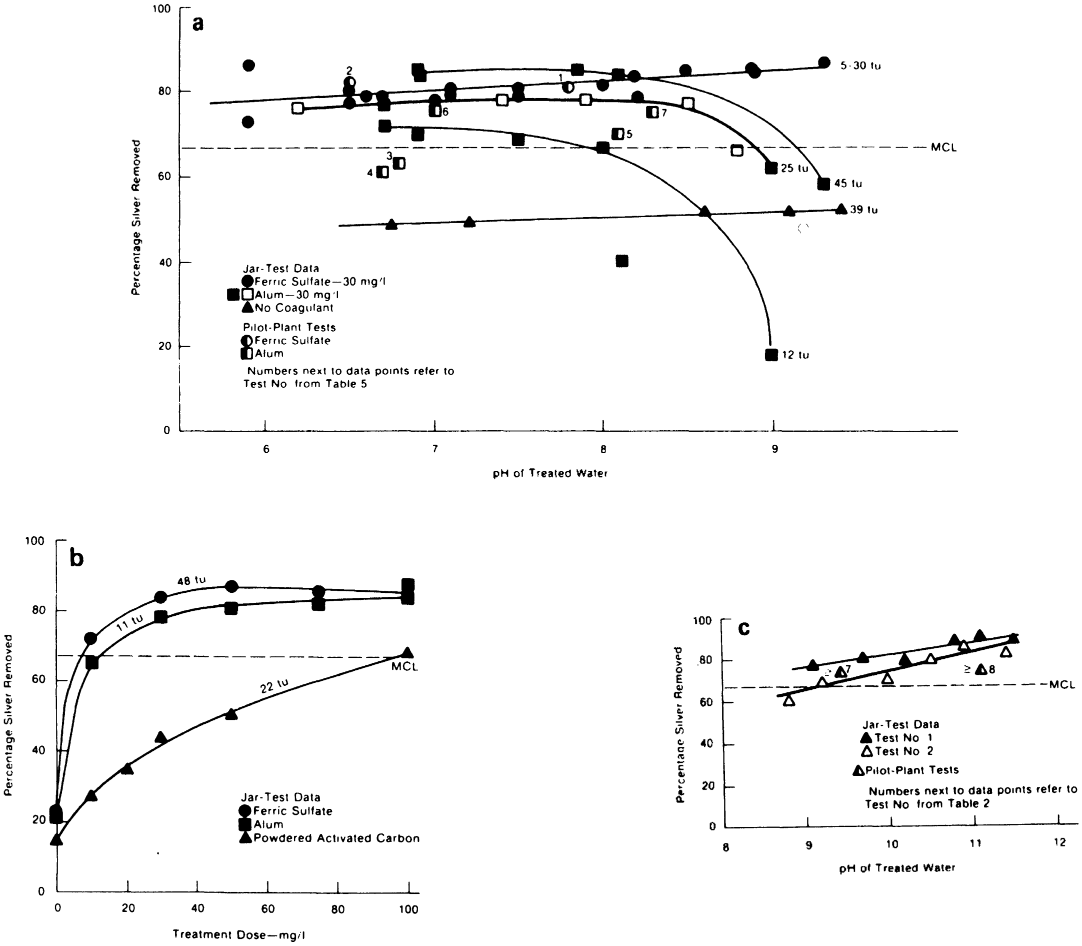

Figure 9.52. (a) Effect of pH and turbidity on silver removal from river water by coagulation treatment. Silver concentration = 0.15 mg/L. (b) Effect of dose on silver removal from river water with ferric sulfate, alum and PAC. Silver concentration = 0.15 mg/L. (c) Effect of pH on silver removal by lime softening. Silver concentration = 0.15 mg/L. Reproduced from Sorg et al.,[71] courtesy of the American Water Works Association.

Sulfate occurs mainly in such evaporite sediments as gypsum ($CaSO_4 \cdot 2H_2O$), anhydrite ($CaSO_4$), epsomite ($MgSO_4 \cdot 7H_2O$), and mirabilite ($Na_2SO_4 \cdot 10H_2O$). An extremely significant source of sulfate is the chemical weathering of pyrite (FeS_2), which yields S_2^{2-} anions to the water phase. In turn, these reduced sulfur anions are oxidized catalytically in microbiological systems to sulfate. Since hydrogen ions are produced in the course of this oxidation, waters with acidic pH values result.

The sulfate content of natural waters is, of course, variable and dependent on the geological source. Gypsum is reasonably soluble in water and can yield sulfate contents in excess of 1000 mg/L. The influence of pyrite dissolution and subsequent oxidation on sulfate content may be seen in acidic waters from coal mine drainage.[2]

Sulfate is usually considered with the hardness constituents calcium and magnesium. Gypsum scales can be formed in hot water systems. Sulfate may be used as a source of oxygen or, more appropriately, as an electron acceptor in microbiological processes. Odorous hydrogen sulfide usually evolves as the result of these transformations. The aluminum and ferric salts of sulfate are employed as chemical coagulants in the treatment of water and wastewaters. Laxative effects are experienced with sulfate concentrations in drinking water are "high, circa 1000 mg/L."[2]

Removal

In order to reach the secondary MCL of 250 mg/L of sulfate for drinking water, IX processes will be utilized.

The reader is referred to the section earlier that describes nitrate removal by SBH-IX. Sulfate is the most preferred anion for exchange on SBA resins. Since it constitutes an interference in the removal of nitrate, the IX technology for sulfate, undoubtedly, would be identical to that for nitrate.

THALLIUM

Aqueous Chemistry

The MCL for Tl in drinking water is 0.002 mg/L. Tl occurs in the natural environment in sulfide or selenides containing various proportions of Cu, Ag, As, and Pb. The major valence states of Tl are (I) and (III), with the former oxidation state predominating in natural waters.[35] Tl^{+3}, the thallic ion, appears only in media that are both very acid and very oxidizing. In acid media, Tl^{3+} ions are readily reduced to Tl^{+1}, thallous ions. The occurrence of Tl in natural waters is, indeed, very rare. Of 989 groundwater supplies reporting Tl results, all but one reported no occurrence, with a minimum reportable content of 8 μg/L. The single positive value was reported to be 10 μg/L in a very small supply. This information was derived from the NIRS survey of groundwater supplies.[119] (See also Chapter 1.) The health effects from drinking water may be kidney, liver, and brain damage from Tl.

Removal

The recommended BATs for Tl removal from water supplies are ion exchange and activated alumina.[119] At this writing, no performance data are available for these processes. However, there are some data available for the adsorption of Tl^1 on hydrous Fe and Mn oxides (see Collective Treatments below).

ZINC

Aqueous Chemistry

The secondary MCL drinking water standard for zinc is 5.0 mg/L. The concern over zinc in potable waters lies with the milky turbidity imparted by the relatively insoluble $Zn(OH)_{2(s)}$. In the citation for the secondary regulations,[120] it is stated: "Zinc, like copper, is an essential and beneficial element in human metabolism. Zinc can also impart an undesirable taste to water. At higher concentrations, zinc salts impart a milky appearance to water." The precipitation reaction is:[121]

$$Zn^{2+} + 2OH^- = Zn(OH)_{2(s)} \qquad (75)$$

$$\Delta G^\circ_{REX} = -23.08 \text{ kcal/mol}$$

$$\log K_{eq} = 16.92$$

At a pH value of 8.0, dissolution of $Zn(OH)_{2(s)}$ would yield 0.78 mg/L Zn^{2+} ions. Additional chemistry of zinc is found in Chapter 10, where the occurrence of this metal results from corrosion of water distribution pipes. In the survey of 1577 surface waters, Zn contents ranged 2–1200 mg/L, and was detected in 77% of these samples.[118] In drinking water samples, the content range was 3–2000 mg/L.

Removal

Since zinc is a secondary drinking water standard and its content in natural waters rarely exceeds the MCL of 5.0 mg/L, there have been few studies of its specific removal from water. Zinc undoubtedly is effectively removed by conventional treatments that employ pH adjustment into the alkaline range where $Zn(OH)_{2(s)}$ would precipitate. In situations where it is necessary to remove more than one metal, a "collective" treatment may be employed. Some of these treatments are cited below. It should be noted also that since the chemistries of Zn and Cd are similar, it would be expected that Zn would react to treatments with carbon, for example, in a similar manner.

Resins with such chelating functional groups as phosphoric acid or ethylenediaminetetraacetic acid (EDTA) have been manufactured. These resins have extremely high affinities for hardness ions and such metal ions as Cu^{2+}, Zn^{2+}, Cr^{3+}, Pb^{2+}, and Ni^{2+}, and have a promising future in trace metal removal and metals recovery operations.[98]

FLUORIDE

Concern

The MCL for F^- in drinking water is 4.0 mg/L and the secondary MCL is 2.0 mg/L. It is considered an essential nutrient in human metabolism.[122] Fluoride is added to many drinking waters in small quantities to prevent dental caries. Above the optimum value for this prevention, the mottling of teeth, i.e., dental fluorosis, occurs. The intake of excessively large amounts of fluoride over prolonged periods of time may produce other health effects: bone changes, crippling fluorosis, and death from a single dose of 2250–4500 mg.[122] In most natural waters, fluoride contents range from a few μg/L to 1–2 mg/L. It was discovered that natural groundwaters with about 1.0 mg/L prevented dental caries. There are occasional natural waters with unusually high $[F^-]$; for example, 32 mg/L; in southeastern Arizona and 67 mg/L in the Union of South Africa.[2]

Removal

The conventional water treatments of coagulation and lime softening require such excessive quantities of chemicals that it is impractical to use them.[122] The latter two were used in the 1930–1950 period, but were abandoned for one reason or another. Activated alumina (Al_2O_3) has been successful as a defluoridation medium in Bartlett, Texas, from 1952 to 1977. There are several advantages of using alumina in downflow columns: (1) it is somewhat specific for F^- and has a relatively high exchange capacity for this ion; (2) this capacity is not affected by the SO_4^{2-} or Cl^- contents of water (the order of decreasing preference for anion exchange on alumina is: OH^-, PO_4^{3-}, $Cr_2O_7^{2-}$, F^-, SO_3^{2-}, CrO_4^{2-}, $\bar{N}O_2$, Cl^-, $\bar{N}O_3$, $M\bar{n}O_4$, and SO_4^{2-});[123] and (3) it has a relatively low cost—about 10% of the cost of a synthetic anion resin (1978 prices). After the alumina bed is exhausted, it is regenerated with 1% NaOH, rinsed with a dilute acid, usually 0.05 N H_2SO_4, and a water rinse. The operational aspects of a 1.5 MGD defluoridation plant at Desert Center, California, were reported[122] where fluoride contents are lowered to less than 1.0 mg/L from 8.0 mg/L.

Strong anion exchange resins are not usually considered for fluoride removal because of their low capacity (88 g/m^3 for Amberlite XE-75) and relatively high cost. There is also an extensive competition by other anions for the exchange sites. Fluoride is usually listed last in the selectivity series of preference of anions.

Current water treatment technology favors the removal of F by AA where two or more adsorption beds are operated alternately or simultaneously.[98] The source water's pH value is adjusted to 5.5 to 6.0, and is passed downward through a 3- to 5-ft deep bed of fine (28×48 mesh) AA. Typical F breakthrough curves are seen in Figure 9.53, where they are not as sharp as the usual ion exchange resin columns.[124] Because there is gradual and increasing leakage of the F, a product water storage tank is provided to equalize the column effluent [F^-] and to maximize the column run length. Some detailed design recommendations are given in Table 9.27.[98]

COLLECTIVE TREATMENTS FOR TRACE METALS

Many of the studies cited above were specific treatments for an individual constituent. On occasion, however, several contaminants may coexist in the raw water supply, in which case a "collective" treatment is needed—a single treatment applied for the collective removal of two or more elements whose chemistries are similar. Several studies cited below have been oriented to wastewater treatment, but can be applied to potable water treatment.

Carbonate and Hydroxide Precipitation

An extensive theoretical and experimental study of the precipitation and solubilities of the carbonates and hydroxides of Zn, Ni, Cd, and Pb has been reported.[125]

The generalized solubility reactions for the metals in Table 9.28 are:

$$K_{S_{OH}} = [Me^{2+}][OH^-]^2 \quad (76)$$

$$K_{S_C} = [Me^{2+}][CO_3^{2-}] \quad (77)$$

The [H^+] affects the solubilities of the metal hydroxides and carbonates, the details of which are not given here. See Faust and Aly[2] and Patterson[125] for solubility diagrams. This study was designed to prepare fresh precipitates (after 4 hr) of the hydroxides and carbonates in individual systems and compare a metal's solubility against the theoretical values calculated from thermodynamic data. There was an experiment in which Zn, Ni, Cd, and Pb were combined into one solution and precipitated. Tables 9.29 and 9.30 summarize the appropriate data for drinking water treatment of these metals. It appears that the optimum treatment of zinc is precipitation as its hydroxide to pH 9.5, where the 0.25 mg/L residual is considerably less than the MCL of 5.0 mg/L. Cadmium and lead can be removed either by the hydroxide or the carbonate at pH values greater than 10.0. The 1978 MCL of 0.01 mg/L for Cd and of 0.05 mg/L for Pb are not reached. On the other hand, Sorg et al.[71] have demonstrated through jar tests and pilot plant studies that lime softening can remove nearly 100% of Cd and Pb, and meet their 1978 MCLs.

Adsorption by Hydrous Iron and Manganese Oxides

The adsorption of lead(II), zinc(II), thallium (I), and Cadmium (II) on hydrous iron (HFO) and manganese (HMO) oxides was investigated.[126] That there was significant adsorption of these three metals on HMO is seen in Figure 9.54a. As usual, [H^+] affects adsorption and, in general, it increases with increasing pH value. There was a 100% removal of 0.1 mM Pb over the pH range of 4.0 to 8.0. Zn and Cd were completely removed by the HMO within the pH values of 6.0 to 8.0. Considerably lesser quantities of these metals were adsorbed by HFO than by HMO (Figure 9.54b). Reaction time in these experiments was 3 hr. Adsorption isotherms are seen in Figure 9.54c for HMO. These results suggest that HMO certainly could be employed as a specific treatment for Pb, Zn, Tl, and Cd, or that these metals would be incidentally removed, if present, during Fe and Mn treatment.

SUMMARY OF WATER TREATMENT EFFECTIVENESS—PRIMARY CONSTITUENTS

A summary of the effectiveness of various water treatments for removing primary drinking water contaminants is seen in Tables 9.31, 9.32, and 9.33.[67,71,78,113,122] Additional

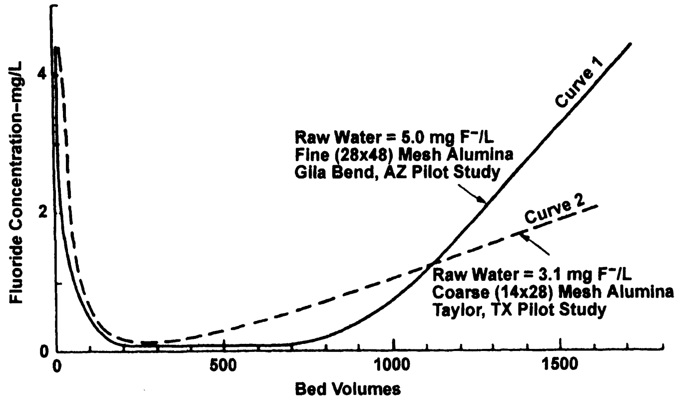

Figure 9.53. Typical fluoride breakthrough curves for activated alumina operated at a feed pH of 5.5 and EBCT of 5 min.[124]

Table 9.27. Process Design Criteria for Fluoride Removal by Activated Alumina.[98]

Parameter	Typical Value or Range
	Exhaustion and Backwash
Fluoride concentration	3–6 mg/L
Medium[a]	Alcoa F–1 activated alumina
Medium size[b]	28 x 48 mesh (0.29 to 0.59 mm)
Medium depth	3–5 ft
Fluoride capacity	1300–2200 gr/ft^3 (3000–5000 g/m^3)
Bed volumes to 1.4 mg F$^-$/L[c]	1000–1500
Exhaustion flow rate	1.5 gpm/ft^3 (EBCT = 5 min)
Exhaustion flow velocity	4–8 gpm/ft^2
Backwash flow velocity	8–9 gpm/ft^2
Backwash time	5–10 min using source water
	NaOH Regeneration
Volume of regenerant	5 BV
Regenerant flow rate[d]	0.5 gpm/ft^3 (EBCT = 15 min)
Regenerant concentration[e]	1% NaOH (0.25 *N*)
Total regenerant contact time	75 min
Displacement rinse volume	2 BV
Displacement rinse rate	0.5 gpm/ft^3
	H_2SO_4 Neutralization
Acid concentration[f]	2.0% (0.4 *N* H_2SO_4)
Acid volume[g]	Sufficient to neutralize bed to pH 5.5, typically 1.5 BV
Displacement rinse volume	2 BV
Displacement rinse rate	0.5 gpm/ft^3

[a] Mention of trade names does not imply endorsement.

[b] Coarse 14 x 28 mesh alumina has also been used successfully.

[c] Capacity and BV to fluoride breakthrough depend to some extent on the fluoride level in the source water, the sulfate level in the pH-adjusted feedwater, and the severity of regeneration.

[d] Cocurrent (downflow) or countercurrent regeneration may be utilized.

[e] Higher regenerant NaOH concentrations, e.g., 4%, have also been used successfully.

[f] Lower and higher H_2SO_4 concentrations have been used successfully. HCl can also be used, and it may be preferred to H_2SO_4 because chloride does not compete with fluoride for adsorption sites.

[g] Alternatively, the neutralization and acidification steps can be combined. In this case the initial feedwater pH is lowered to approximately 2.5, to produce a bed effluent pH slowly dropping from a high initial value (>13) down to a continuous effluent pH in the range of 5.5 to 6.0.

Table 9.28. Metal Carbonate and Hydroxide Solubility Product Constants at 25°C.[125]

Metal	log $K_s(OH)^a$	pH^b	log K_s^c
Zinc (aged)	−17.0	9.8	−10.7
(fresh)	−16.0		
Nickel (aged)	−17.2	10.5	−8.2
(fresh)	−14.7		
Cadmium (aged)	−14.4	10.5	−11.2
(fresh)	−13.7		
Lead (aged)	−15.3	10.0	−13.0
(fresh)	−14.9		

[a] Hydroxide.
[b] Minimum hydroxide solubility.
[c] Carbonate, aged or fresh not specified.

information has been provided from sources other than those given in these references. Some general comments are appropriate here. No single treatment is effective for all contaminants, although osmosis and electrodialysis have some good removals for all contaminants. These two techniques, however, are used mainly for desalting seawater and brackish groundwaters. Any water that is not free from turbidity requires pretreatment. The economics of treatment for these primary and other contaminants must be considered, because the capital and operating costs of an existing facility—or the construction of a single treatment or even a new plant—will influence choice of treatment. The EPA commissioned a study of the costs of water treatments for the primary contaminants that resulted in four publications.[127–130]

SUMMARY OF INORGANIC REMOVAL PROCESSES

Tables 9.34 and 9.35 summarize the more significant processes for removal of cationic and anionic inorganics, respectively. These tables are supplied by Reference 98, which contains important design and operational information. The effectiveness of these processes is given for each individual constituent above.

HYDROGEN SULFIDE

Concern

This constituent is listed in the secondary MCLs as a contributor to odorous water, i.e., it is responsible for a rotten egg smell[120] (see also Chapter 3). Also, H_2S reacts with many of the metals cited above to produce, for example, black stains or black deposits of iron sulfide. H_2S cannot be considered a normal constituent of natural waters, but is associated with waters "high" in sulfate and organic matter.[2] The microbially medicated oxidation of organic matter utilizes SO_4^{2-} as an electron acceptor, which results in reduced sulfur as H_2S. Also, this odorous substance is associated frequently with Fe and Mn from groundwaters in or near former swampy areas. In either case, H_2S can be removed easily from water by aeration, chemical oxidation, or adsorption onto carbon.

Aqueous Chemistry

$$H_2S = H^-;\ \log K_{a1} = 10^{-6.88} \qquad (76)$$

$$HS^- = H^+\ S^{2-};\ \log K_{a2} = 10^{-12.2} \text{ to } 10^{-17.1} \qquad (77)$$

Thus, H_2S is a "weak" acid, and the secondary dissociation is not realized in a practical sense. This gaseous substance can be quite soluble in water: at 760 mm Hg and 25°C, the solubility of H_2S is 3380 ppm.[131] There are 30 or more ionic and molecular sulfur species in existence, of which 5 are thermodynamically stable in water at 25°C and 1 atm: HSO_4^-, SO_4^{2-}, S^0, H_2S, and HS^-.[37] Such other species as thiosulfate, polysulfides, and polythionates are unstable in water. A pE-pH diagram is seen in Figure 9.55 where H_2S and S^0 are stable, generally, under reducing conditions and below pH 7. Sulfate is stable under oxidizing conditions and over the entire pH range. Additional sulfur chemistry is given in the literature.[2,35,131]

Oxygenation and/or Aeration

Aeration has been the traditional treatment for volatile substances causing tastes and odors in water (see Chapter 5). Aerators range from simple mechanical devices to more complex diffusers.[132] However, aeration is not an efficient method for removing tastes and odors because many are not volatile enough. Aeration does, of course, provide dissolved oxygen which can act as an electron acceptor for reduced sulfur species. Chen[131] has summarized several studies of the kinetics and mechanism of the oxygenation of sul-

Table 9.29. Soluble Metal Concentration for a Combined Zinc–Nickel–Cadmium–Lead System.[125]

Test System	Filtered pH	Soluble Zinc Concentration		Soluble Nickel Concentration		Soluble Cadmium Concentration		Soluble Lead Concentration	
		mol/L	mg/L	mol/L	mg/L	mol/L	mg/L	mol/L	mg/L
Hydroxide	7.3	$10^{-2.6}$	150.0	—	—	$10^{-2.2}$	800.0	$10^{-4.3}$	11.4
Hydroxide	8.8	$10^{-5.1}$	0.5	$10^{-4.6}$	1.4	$10^{-3.2}$	65.0	$10^{-4.3}$	10.8
Hydroxide	9.1	$10^{-5.4}$	0.25	$10^{-4.8}$	1.0	$10^{-3.7}$	22.5	$10^{-5.0}$	2.0
Hydroxide	11.0	$10^{-5.1}$	0.55	$10^{-4.8}$	1.0	$10^{-6.1}$	0.1	$10^{-4.7}$	4.0
Carbonate	8.4	$10^{-4.7}$	1.2	$10^{-3.0}$	60.0	$10^{-4.8}$	1.8	$10^{-4.6}$	5.0
Carbonate	8.6	$10^{-4.6}$	1.6	$10^{-4.0}$	5.4	$10^{-5.2}$	0.8	$10^{-4.7}$	3.8
Carbonate	9.1	$10^{-4.9}$	0.8	$10^{-4.5}$	2.0	$10^{-5.7}$	0.25	$10^{-4.8}$	3.2
Carbonate	10.0	$10^{-5.1}$	0.55	$10^{-4.6}$	1.4	$10^{-5.6}$	0.3	$10^{-4.5}$	6.0
Carbonate	10.7	$10^{-5.1}$	0.55	$10^{-4.6}$	1.4	$10^{-5.9}$	0.15	$10^{-4.6}$	5.2

Table 9.30. Summary of Treatment Results.[125]

Metal	Treatment System	Optimum Treatment (pH)	Observed Concentration (mg/L)
Zinc	Hydroxide	9.5	0.25
Nickel	Hydroxide	11.0	0.30
Cadmium	Hydroxide	10.4	0.20
	Carbonate ($10^{-2.7}$)	10.7	0.35
	Carbonate ($10^{-1.2}$)	10.0	0.25
Lead	Hydroxide	10.5	0.60
	Carbonate ($10^{-2.7}$)	10.1	0.60
	Carbonate ($10^{-1.1}$)	7.5	1.00

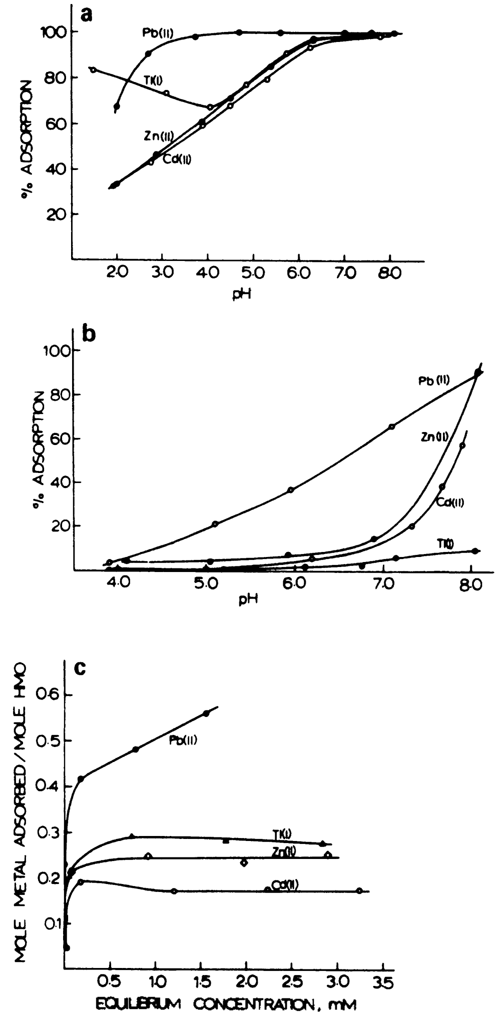

Figure 9.54. (a) Effect of pH on adsorption of heavy metal ions on hydrous manganese oxide (HMO). HMO = 0.436 mmol; heavy metal ion = 0.1 mmol; solution volume = 100 mL. (b) Effect of pH on adsorption of heavy metal ions on hydrous ferric oxide (HFO). HFO = 0.625 mmol; heavy metal ion = 0.1 mmol; solution volume = 100 mL. (c) Effect of heavy metal ion concentration at equilibrium on its adsorption on HMO (0.436 mmol). Reproduced from Gadde and Laitinen,[126] courtesy of the American Chemical Society.

Table 9.31. Summary of Effectiveness of Water Treatment Processes for the Removal of Inorganic Contaminants.[a,b]

Contaminant	Conventional Coagulation		Lime Softening	Ion Exchange		Activated Alumina	Activated Carbon		Reverse Osmosis	Electrodialysis
	Alum	Iron[c]		Cation	Anion		PAC	GAC		
Arsenic[d]										
+III	P	F L–G pH>10.5	P pH<10.5	P	L	F	P	F(bone char)[e]	G–F	G–F[e]
+V	G pH<7.5 F pH>7.5	E E pH>10.8	F pH<10.0 G ph 10.0–10.8	P	E	E	P	E(bone char)	E	E[e]
Barium	P	P	E pH 9.5–10.8	E	P	P[e]	P	P	E	E
Cadmium	G>pH 8.5 F–P<pH 8.5	E pH>8.0 F–L pH<8.0	E	E	P	P[e]	P	P	E	E[e]
Chromium										
+III	E	E G pH<10.5	E pH>10.5	E	P	P[e]	P	P	E	E[e]
+VI	P	P E (ferrous)	P	P	L	E	P	E(bone char)	E	E
Fluoride	P	P	P	P	L	E	P	E(bone char)	E	E[e]
Lead	E	E	E	[f]	P	P[e]	P	P	E	E[e]
Mercury										
Organic	F–P[g]	F–P[g]	P	ID	ID	P[e]	G–P	E	G–F[e]	G–L[e]
Inorganic	F–P[g]	F–G[g]	F	[f]	[f]	P[e]	G–P	E–G	G–F	G–L[e]
Nitrate	P	P	P	P	E	P	P	P	G	G
Selenium										
+IV	P	F pH<7.5 L pH>7.5	L–P	P	E	E–G	P	P	E	E[e]
+VI	P	P	P	P	E	L–G	P	P	E	E[e]
Silver	G pH<8.0	G	G	E	P	P[e]	L	L	E	E[e]
Radium	P	P	E pH 9.5–10.8	E	P	P[e]	P	P	E	E[e]

[a] Reproduced from Sorg and Logsdon,[113] courtesy of the American Water Works Association.

[b] E—excellent, 90–100%; G—good, 70–90%; F—fair, 40–70%; L—low, 20–40%; P—poor, 0–20%; ID—insufficient data.

[c] Results based on ferric iron coagulant except as noted.

[d] Oxidation of As(III) to As(V) will result in As(III) removals similar to As(V).

[e] Estimated.

[f] Possible under controlled conditions, but not practical for water treatment.

[g] Removal dependent on turbidity.

Table 9.32. Most Effective Treatment Methods for Removal of Inorganic Contaminants.[a]

Contaminant	Most Effective Treatment Methods
Arsenic	As(V)—iron coagulation, pH 6–8; alum coagulation, pH 6–7; excess lime softening; activated alumina, pH 5–6 As(III)—oxidation treatment of As(III) to As(V); use same treatment list for As(V)
Barium	Lime softening, pH 11; ion exchange softening
Cadmium	Iron coagulation, above pH 8.0; lime softening; excess lime softening
Chromium	Cr(III)—iron coagulation, pH 6.0–9.0; alum coagulation, pH 7.0–9.0; excess lime softening Cr—ferrous sulfate coagulation, pH 7.0–9.5
Fluoride	Ion exchange with activated alumina or bone char
Lead	Iron coagulation, pH 6.0–9.0; alum coagulation, pH 6.0–9.0; lime or excess lime softening
Mercury	Inorganic—ferric sulfate coagulation, pH 7.0–8.0; granular activated carbon Organic—granular activated carbon
Nitrate	Ion exchange with anion resin
Radium	Lime softening; ion exchange with cation resin
Selenium	Se(VI)—ferric sulfate coagulation, pH 6.0–7.0; ion exchange with anion resin or activated alumina; reverse osmosis Se(VI)—ion exchange with anion resin or activated alumina; reverse osmosis
Silver	Ferric sulfate coagulation, pH 7.0–9.0; alum coagulation, pH 6.0–8.0; lime or excess lime softening

[a] Reproduced from Sorg and Logsdon,[67] courtesy of the American Water Works Association.

fide.[133-136] The reaction of reduced sulfur with oxygen apparently is complex, is slow in the absence of a catalyst, and is dependent on pH. A reaction pathway for slightly acid, alkaline and neutral solutions is proposed:[133]

$$HS^- + O_2 = HS^\bullet + O_2^- \qquad (78)$$

$$HS^\bullet + O_2 = HO_2 + S \qquad (79)$$

$$HS^\bullet + O_2^- = S + HO_2^- \qquad (80)$$

$$HS^- + (x-1)S = H^+ + S_x^{2-},\ x \text{ can be } 2-5 \qquad (81)$$

Equation 81 indicates that the reaction proceeds through polysulfide formation, which, in turn, is pH-dependent.[134] Oxidation of sulfide may produce or consume H^+, depending on the products or other items. The following reactions may represent the stoichiometry of the oxidation:

$$2HS^- + 2O_2 + 2H^+ = 2H_2O + 2SO \qquad (82)$$

$$2HS^- + 2O_2 = H_2O + S_2O_3^{2-} \qquad (83)$$

$$2HS^- + 4O_2 = 2SO_4^{2-} + 2H^+ \qquad (84)$$

Figure 9.56 shows typical rate curves for oxidation of HS^- by O_2.[135] The pH-dependence of this oxidation is seen in Figure 9.57. At pH values less than 6.0, the oxidation reaction is extremely slow where H_2S is the predominant species. As the $[H^+]$ is decreased, the observed specific rate is increased, and reaches a maximum between the pH values of 8 and 8.5. Beyond these pH values, the reaction rate is lowered to a minimum near pH 9, whereupon it is increased again to a second maximum near pH 11, after which it is decreased again.

The rate of sulfide oxidation was described by this expression:

$$-\left[\frac{d(\Sigma S^{2-})}{dt}\right]_{t=0} = R_i = k\left[\Sigma S^{2-}\right]_o^m [O_2]_o^n \qquad (85)$$

where R_i is the initial rate and the brackets represent molar concentrations. The exponents m and n were evaluated, from which the empirical equation evolved:[133]

$$-\left[\frac{d(\Sigma S^{2-})}{dt}\right] = k\left[\Sigma S^{2-}\right]_0^{1.34} [O_2]_0^{0.56} \qquad (86)$$

The catalytic or inhibitive effects of various metallic cations and organic compounds on sulfide oxidation were reported.[136] The decreasing order of reaction rate acceleration by cations is: $Ni^{2+} > Co^{2+} > Mn^{2+} > Cu^{2+} > Mg^{2+} > Ca^{2+}$. A 5×10^{-5} *M* quantity of Ni^{2+} effected a 50-fold increase in the reaction rate at pH 7.29. Such organic compounds as anisole, citrate, EDTA, and nitrilotriacetic acid inhibited the oxygenation of sulfide.

The oxygenation of reduced sulfur species in aqueous solutions at pH values of 4, 7.55, and 10 was researched.[137] The reaction rate was, of course, first-order with respect to reduced sulfur at all pH values, and was nearly first-order

Table 9.33. Most Probable Applications of Water Treatment Processes for Inorganic Contaminant Removal.[a]

Treatment Process	Principal Application for Water Treatment	Inorganic Contaminant Treatment Capability Effectiveness[b]			Most Probable Applications for Inorganic Removal
		High	Moderate	Low	
Conventional coagulation	Clarification of surface waters	Cd Cr(III) Cr(VI) As(V) Ag Pb	As(III) Se(IV) Hg(0) Hg(I)	Ba F NO_3 Ra Se(VI)	Removal of Cd, Cr, As, Ag, or Pb from surface waters
Lime softening	Removal of hardness from ground and surface water	Ba Ra Cd Cr(III) As(V) Pb	Se(V) As(III) Hg(I) F	Cr(VI) NO_3 Se(VI) Hg(O)	Removal of Ba or Ra from groundwaters; removal of Cd, Cr(III), F, As(V), or Pb from hard surface waters requiring softening
Cation exchange	Removal of hardness from groundwaters	Ba Ra Cd Pb Cr(III)		As Se NO_3 F Cr(VI)	Removal of Ba or Ra from groundwaters
Anion exchange	Removal of nitrate from groundwaters	NO_3 Cr(VI) Se Pb Cr(III)	Ba Ra Cd		Removal of NO_3 from groundwaters
Activated alumina	Removal of fluoride from groundwaters	F As Se		Ba Ra Cd	Removal of F, As, or Se from groundwaters
Powdered activated carbon	Removal of taste and odors from surface waters		Hg(I) Hg(O) Cd	Ba Ra Cr(III) F NO_3 Ag	Removal of Hg from surface waters during emergency spills
Granular activated carbon	Removal of taste, odors, and organics	Hg(I) Hg(O)	Cd	Ba Ra Cr(III) F NO_3	Removal of Hg from surface or groundwaters

Table 9.33. Most Probable Applications of Water Treatment Processes for Inorganic Contaminant Removal[a] (Continued).

Treatment Process	Principal Application for Water Treatment	Inorganic Contaminant Treatment Capability Effectiveness[b]			Most Probable Applications for Inorganic Removal
		High	Moderate	Low	
Reverse osmosis and electrodialysis	Desalting of seawater or brackish groundwaters	As(V)	NO_3		Removal of all inorganics from groundwaters
		Ba	As(III)		
		Cr			
		Pb			
		Cd			
		Se			
		Ag			
		F			
		Ra			
		Hg			

[a] Reproduced from Sorg and Logsdon,[113] courtesy of the American Water Works Association.

[b] High—greater than 80%; moderate—20–80%; low—less than 20%.

Table 9.34. Summary of Processes for Removing Inorganic Cations.[98]

Contaminant and its MCL	Usual Form at pH 7–8	Removal Options	Typical BV to MCL[†]	Pretreatment Required	Typical Regenerants and % Recovery of Sorbed Contaminant[‡§]	Effect of TDS on BV	Effect of Hardness of BV	Notes
Hardness (no MCL)	Ca^{2+}, Mg^{2+}	Na IX softening with SAC resin	200–700	Iron removal	6–12% NaCl 90–100% recovery	Very significant reduction		a,b
		H^+ IX softening with WAC resin	200–500	None	1–2 *N* HCl or H_2SO_4	Very significant reduction		c,d,e,f
Barium, 1.0 mg/L	Ba^{2+}	Na IX softening with SAC resin	200–700	Iron removal	1–12% NaCl 70 to 100% recovery	Very significant reduction	Very significant reduction	a–c,g,h
Radium 5 pCi/L	Ra^{2+}	Na IX softening with SAC resin	200–700	Iron removal	6–12% NaCl 0–100% recovery	Very significant reduction	Very significant reduction	a–c,i,j,k,l
		Ca IX with SAC resin	300–1500	Iron removal	10–15% $CaCl_2$ 50–100% recovery	Slight reduction	Slight reduction	l,m,n,o,p
		Dow radium-selective complexer	20,000–50,000	Iron removal	Not regenerable	Slight reduction	Slight reduction	l,o,q,r,s
		$BaSO_4^-$ impregnanted alumina	20,000–50,000	Iron removal	Not regenerable	Slight reduction	Slight reduction	l,o,q,r,s
		Activated alumina	1000–3000	None	2% HCl followed by 1% NaOH 70 to 100% recovery	None	Slight reduction	l,o,q,r

[†] Generally, run length depends on raw water contaminant concentration, allowable effluent concentration, competing ions, leakage, and actual resin or adsorbent used.

[‡] Percent recovery during the first regeneration depends on the amount of regenerant used for steady-state exhaustion-regeneration, 100 percent of the contaminant sorbed during exhaustion is eluted during regeneration.

[§] Spent regenerant disposal may be a problem if sanitary sewer disposal is not allowed.

[a] Hardness capacity depends on regeneration level (NaCl/ft^3 resin).

[b] Typically, spent regenerant is disposed of in sanitary sewer.

[c] Iron removal by oxidation and filtration should be considered if total iron concentration exceeds 0.3 mg/L.

[d] Only carbonate hardness can be removed by using WAC resins.

[e] Carbon dioxide produced in the IX reaction must be removed from product water; and pH adjustment may be necessary.

[f] TDA reduction occurs as a result of removing both the hardness and the alkalinity.

[g] Barium tends to build up on the resin and break through with hardness when insufficient regenerant is used.

[h] If necessary, $BaSO_4$ can be precipitated from the spent regenerant by adding sulfate.

[i] With a virgin resin, radium breaks through long after hardness, but in cyclic operation radium and hardness eventually elute simultaneously.

[j] Even though radium accumulates on the resin, no leakage of radium occurs before hardness breakthrough.

[k] Current disposal practices allow the discharge of radium-contaminated spent regenerant to the sanitary sewer.

[l] Radon 222 is continuously generated from the radium 226 on the resin. Radon peaks can occur after idle periods.

[m] Immediate serious radium leakage occurs if extensive countercurrent regeneration is not used.

[n] $CaCl_2$ is much more expensive than NaCl as a regenerant.

[o] A process advantage is that sodium is not added to the product water.

[p] No softening is achieved in the calcium-exchange process, and magnesium is exchanged for calcium.

[q] Radon generation is more serious with the RSC and $BaSO_4^-$ alumina because of the large amount of radium on the medium.

[r] Disposal of the spent medium is a serious problem because it is considered a low-level radioactive waste.

[s] The RSC and $BaSO_4^-$ alumina may not be commercially available because of disposal problems.

Table 9.35. Summary of Processes for Removing Inorganic Anions.[98]

Contaminant and its MCL	Usual Form at pH 7–8	Removal Options	Typical BV to MCL†	Pretreatment Required	Typical Regenerants and % Recovery of Sorbed Contaminant‡	Effect of TDS on BV	Effect of SO_4^{2-} on Run BV	Notes
Fluoride 4.0 mg/L	F^-	Activated alumina	1000–2500	pH 5.5 to 6.0	1% NaOH followed by 2% H_2SO_4 90–100% recovery	None	Slight reduction	
Nitrate-N, 10 mg/L	NO_3^-	Anion exchange (complete regeneration)	300–600	Usually none	0.25–2.0 *N* NaCl (1.5–12% NaCl), 90–100% recovery	Very significant reduction	Very significant reduction	a,b
		Anion exchange (partial regeneration)	200–500	Usually none	1.0–2.0 *N* NaCl (6.0–12% NaCl), 50% recovery	Very significant reduction	Very significant reduction	a,c,d
Arsenic, 0.05 mg/L	$HAsO_4^{2-}$ As(V)	Activated alumina adsorption	10,000–25,000	pH 5.5 to 6.0, oxidize	4% NaOH followed by 2% H_2SO_4, 70% recovery	None	Slight reduction	e,f
		Anion exchange	1000–5000	Oxidize and prefilter to remove iron	1.0 *N* NaCl, > 95% recovery	Very significant reduction	Very significant reduction	a,g–i
Selenium, 0.01 mg/L	$HSeO_3^-$ Se(IV)	Activated alumina adsorption	1000–2500	pH 5.5 to 6.0	1% NaOH followed by 2% H_2SO_4	None	Slight reduction	j
	SeO_4^{2-} Se(VI)	Anion exchange	300–1500	None	1.0 *N* NaCl, 90–100% recovery	Very significant reduction	Very significant reduction	k
Chromium 0.05 mg/L	CrO_4^{2-}	Anion exchange	10,000–50,000	None	1.0 *N* NaCl, 60–90% recovery	Slight reduction	Slight reduction	l,m

† Generally run length depends on raw water contaminant concentration, allowable effluent concentration, competing ions, leakage, and the actual resin or adsorbent used.

‡ Percent recovery during the first regeneration depends on the amount of regenerant used. For steady-state exhaustion regeneration, 100 percent of the contaminant sorbed during exhaustion is eluted during regeneration.

[a] Chromatographic peaking of contaminant is possible after breakthrough.

[b] No significant leakage of nitrate occurs prior to breakthrough.

[c] Continuous, significant (>5 mg/L) leakage of nitrate occurs following partial regeneration during all runs.

[d] Resin must be mixed mechanically following regeneration to avoid excessive early nitrate leakage.

[e] As(III) in the form of uncharged arsenious acid (H_3AsO_3) must be oxidized to As(V) prior to adsorption or ion exchange.

[f] Arsenic(V) can be coprecipitated from regenerant by lowering pH (to 6 to 8) to precipitate $Al(OH)_{3(g)}$.

[g] Some adsorption capacity may be lost following each exhaustion-regeneration cycle.

[h] Chloride-form anion exchange can be the process of choice for low-sulfate (<50 mg/L) and low-TDS (<500 mg/L) water.

[i] As(V) can be coprecipitated from spent regenerant by using ferric sulfate or alum.

[j] Se(IV) can typically be oxidized to Se(VI) by 1 to 2 mg free chlorine per liter in 30 to 60 min at pH 6.5 to 8.5.

[k] Se(IV) must be absent if ion exchange is used because it peaks before sulfate and selenate [Se(VI)] breakthrough.

[l] Cr(III) can be precipitated from the spent regenerant after reduction of Cr(VI) with ferrous sulfate or acidic sodium sulfite.

[m] Macroporous resins and poystyrene resins have a higher preference for chromate than gel and acrylic resins.

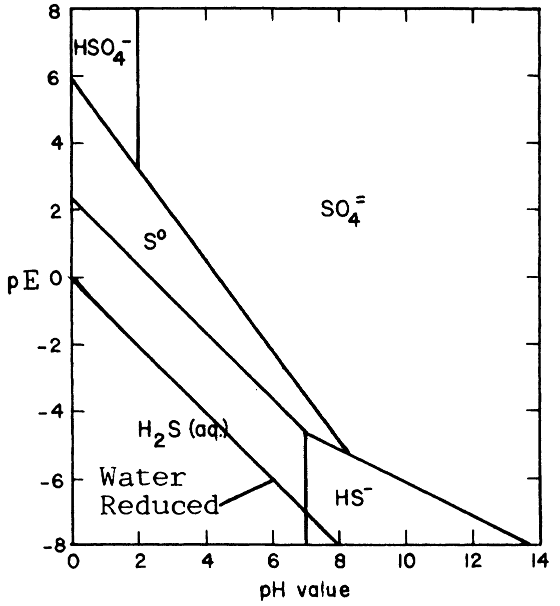

Figure 9.55. pH-pE predominance diagram of sulfur species. Reproduced from Chen.[131]

with respect to O_2 at pH 7.55. The same rate equation as in 85 was used,[139] whereby the empirical values of the exponents, m and n, were 1.02 and 0.80, respectively. The stoichiometric reaction was:

$$4HS^- + 5.5\,O_2 = S_2O_3^{2-} + SO_3^{2-} + SO_4^{2-} + 2H_+ + 2H_2O \tag{87}$$

Data were obtained to confirm the molar ratio of 1.375, $[O_2]/[HS^-]$. Table 9.36 is a summary of the reaction products from several investigations. It is, indeed, a complex reaction.

Chlorination

Reduced species of sulfur are oxidized effectively by Cl_2 in aqueous solutions. The stoichiometry is:[138]

$$Cl_2 + S^{2-} = 2Cl^- + S^0 \tag{88}$$

$$4Cl_2 + S^{2-} + 4H_2O = 8HCl + SO_4^{2-} \tag{89}$$

These reactions occur very rapidly, and 8.5 parts of Cl_2 are required per part of H_2S for complete oxidation. If the predominant reaction is 89, then the acidity produced would have to be neutralized either by natural or added alkalinity. A pH range of 6.5 to 7.3 appears to be optimum.

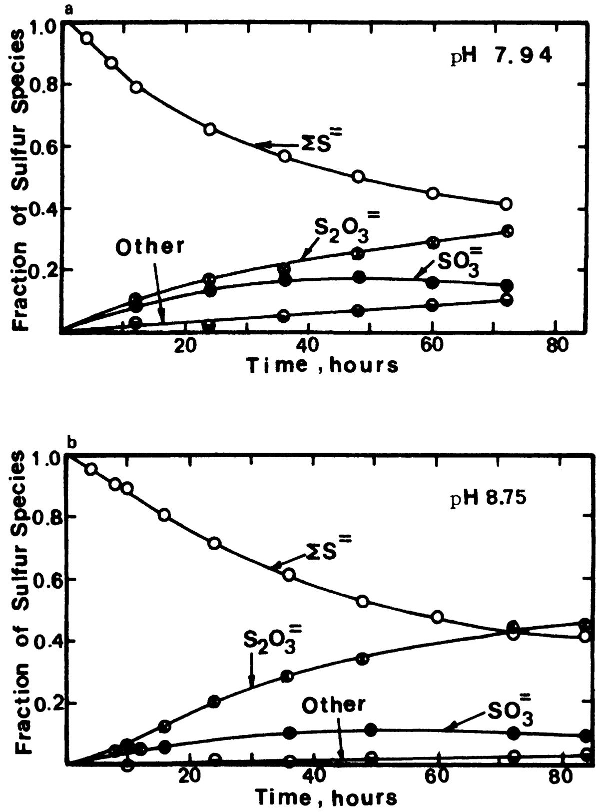

Figure 9.56. Kinetics of sulfide oxidation by O_2 at (a) pH 7.94 and (b) pH 8.75. $[\Sigma S^{2-}] = 1 \times 10^{-4}$ *M*, $[O_2] = 8 \times 10^{-4}$ *M*. Reproduced from Chen and Morris,[133] courtesy of the American Chemical Society.

Ozonation

$O_{3(g)}$ can be used to oxidize reduced sulfur species:

$$S^{2-} + O_{3(g)} + H_2O = S^0 + 2OH^- + O_2 \tag{90}$$

$$S^{2-} + 4O_{3(g)} = SO_4^{2-} + 4O_2 \tag{91}$$

The theoretical molar ratios of $O_{3(g)}/S^{2-}$ of 1:1 for S^0 and 4:1 for SO_4^{2-} have been confirmed.[131] The kinetics of the reaction has been reported to be "instantaneous."[139]

Permanganate

Potassium permanganate has been used successfully to remove H_2S from water:

$$8MnO_4^- + 3S^{2-} + 4H_2O = 8MnO_{2(s)} + 3SO_4^{2-} + 8OH^- \tag{92}$$

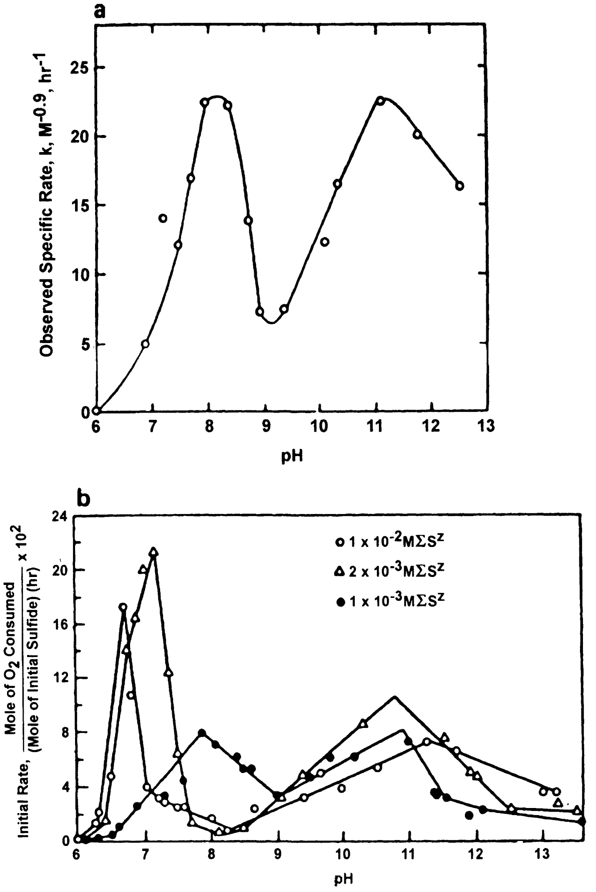

Figure 9.57. pH dependence of (a) observed specific rate of sulfide oxidation and (b) initial oxygen uptake by sulfide (O_2 = 0.21 atm, T = 25°C). Reproduced from Chen and Morris,[133] courtesy of the American Chemical Society.

Table 9.36. Summary of Reaction Products Observed in Investigations of Oxygenation of Reduced Sulfur Species.[a]

Investigator	pH	Reaction Solution	$[S(-H)t]_0/[O_2]_0$	Products Observed
Chen and Morris	6.0–12.0	Controlled	0.06–1.25	S_x^{2-},SO_3^{2-},S^0,$S_2O_3^{2-}$,SO_4^{2-}
Avrahami and Golding	11.0–14.0	Controlled	0.08–0.67	S^0(occasionally), $S_2O_3^{2-}$,SO_4^{2-}
Cline and Richards	7.8	Seawater	0.125–0.5	SO_3^{2-},$S_2O_3^{2-}$,SO_4^{2-}
Skopintsev et al.	8.2	Seawater	0.2–8.0	SO_3^{2-},$S_2O_3^{2-}$
Demirjian	7.0,8.6	Controlled	0.03–5.0	S^0,SO_3^{2-},$S_2O_3^{2-}$,SO_4^{2-}
Alferova and Titova	9.0–13.0	Controlled	20	SO_3^{2-},$S_2O_3^{2-}$,SO_4^{2-}
O'Brien and Birkner	4.0–10.7	Controlled	1.0–1.37	SO_3^{2-},$S_2O_3^{2-}$,SO_4^{2-}

[a] Reproduced from O'Brien and Birkner,[137] courtesy of the American Chemical Society.

Another possible reaction is:[140]

$$4MnO_4^- + 3H_2S = 2SO_4^{2-} + S^0 + 3MnO_{(s)} + MnO_{2(s)} + 3H_2O \qquad (93)$$

The molar ratio of 4:3 was observed in laboratory titrations of several well waters at neutral pH values. Attempts to document the kinetics of $KMnO_4$ reaction with Na_2S were unsuccessful because it is claimed to go to completion within five seconds.

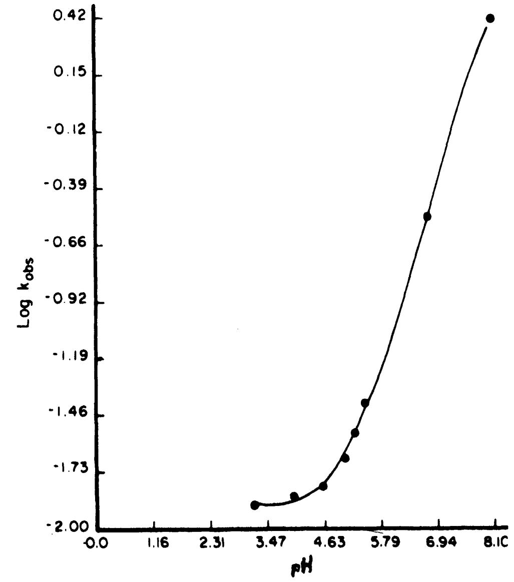

Figure 9.58. Plot of log k_{obs} vs. pH. Reproduced from Hoffmann,[141] courtesy of the American Chemical Society.

Hydrogen Peroxide

A kinetic study[140] reveals that H_2O_2 has found application for treatment of industrial and municipal wastewaters for H_2S removal, and that it has potential for drinking water. The oxidation reaction is:

$$H_2S = H_2O_2 = 1/x\,S_x + H_2O \qquad (94)$$

Frequently, x = 8. Another reaction may be:

$$HS^- + 4H_2O_2 = SO_4^{2-} + 4H_2O + H^+ \qquad (95)$$

A two-term rate law, consistent with the observed kinetic data, is:

$$-\frac{d[H_2S]}{dt} k_1[H_2S][H_2O_2] + k_2K_{a1}\left(\frac{[H_2S][H_2O_2]}{[H^+]}\right) \qquad (96)$$

where K_{a1} is from Equation 76. The values for k_1 and k_2 were determined to be 29.0 M^{-1}-min^{-1} and 0.48 M^{-1}-min^{-1}, respectively, at 25°C. The Reactions, 94 and 95, and the rate law, 96, were manipulated into pseudo first-order kinetics. Figure 9.58 shows the pH-dependence of the reaction and the first-order reaction rate constant. Table 9.37 summarizes the kinetic data. A stoichiometric excess of H_2O_2 operationally should be added to the system in order to effect Reaction 95 within 15 min or so.

Adsorption

Powdered and granular activated carbon are capable of adsorbing H_2S from water. Consequently, any H_2S that occurs in surface and groundwaters will be removed when other constituents are treated by carbon. There are occasions where domestic well waters are contaminated with H_2S. In this situation, a granular activated carbon filter will suffice.

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Table 9.37. Summary of Kinetic Data at 25°C and μ=0.4.[a]

$[S^{2-}]_0 \times 10^3$ *M*	$[H_2O_2]_0 \times 10^2$ *M*	pH	T(°C)	k_{obs} (min^{-1})	σ_x
1.5	1.5	6.81	25.0	0.149	0.012
1.5	3.0	6.81	25.0	0.293	0.034
1.5	4.5	6.78	25.0	0.453	0.013
1.5	6.0	6.76	25.0	0.620	
1.5	8.0	6.75	25.0	0.813	
1.5	10.0	6.80	25.0	0.990	
1.5	3.0	8.10	25.0	2.609	
1.5	3.0	6.81	25.0	0.293	0.034
1.5	3.0	5.47	25.0	0.06	
1.5	3.0	5.05	25.0	0.021	
1.5	3.0	4.58	25.0	0.016	
1.5	3.0	4.01	25.0	0.014	
1.5	3.0	3.20	25.0	0.013	

[a] Reproduced from Hoffmann,[141] courtesy of the American Chemical Society.

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Chapter 10

Removal of Corrosive Substances

10

Removal of Corrosive Substances

CORROSION AS AN ESTHETIC CONCERN

Concern about the corrosive effect of drinking water on distribution and plumbing systems traditionally has been economic and esthetic. It has been estimated that the annual economic loss from water corrosiveness is approximately $700 million.[1] In recent times, however, the corrosion of metallic and asbestos-cement distribution systems has posed a significant threat to health. The presence of contaminants such as lead, cadmium, and asbestos in drinking water has prompted the U.S. Environmental Protection Agency (EPA) to require identification of these corrosion by-products and to report such corrosive characteristics as pH, alkalinity, hardness, temperature, total dissolved solids, and the Langelier saturation index (LI) (see Chapter 1).[2,3]

In addition to chemical characteristics of the water, the following construction materials must be identified and reported if present in a distribution system:[2,3]

- lead from piping, solder, caulking, interior lining of distribution mains, alloys, and home plumbing
- copper from piping and alloys, service lines, and home plumbing
- zinc from galvanized piping, service lines, and home plumbing
- ferrous piping materials such as cast iron and steel
- asbestos-cement pipe

Also, it may be necessary to identify and report vinyl-lined asbestos pipe and coal tar–lined pipes and tanks.

Consequently, it is imperative to establish a monitoring system for the many corrosion by-products. References 2 and 3 give the details of the requirements for the surveillance of corrosive drinking waters.

CHEMISTRY OF CORROSION

In the water treatment industry, corrosion is the chemical decay of the pipe construction materials cited above. For the metallic materials, corrosion is an extremely complex chemical and electrochemical phenomenon. In these oxidative reactions, countless local galvanic couples form on the surface of the corroding metal in which the metal is spontaneously oxidized and its oxidant is reduced. Each couple is actually a microbattery where the corrosion reaction proceeds with a flow of electric current between anodic and cathodic sites on the metal. The basic requirements of metallic corrosion are: (1) differences of electrical potential between adjacent areas on an exposed metallic surface to provide anodes and cathodes; (2) moisture to provide an electrolyte; (3) an oxidizing agent to be reduced at the cathode; and (4) an electrical path in the metal for electron flow from anodes to cathodes.

Corrosion may also be caused by physical action between pipe material and the water. For example, the physical abrasion of a pipe elbow may be caused by excess flow velocity in the pipe. Biological growths in a distribution system may also create a corrosive environment whereupon physical and chemical actions may occur. All of this may be summarized by stating that corrosion in a distribution system is the result of a complex and interrelated combination of physical, chemical, and biological systems. However, most of the corrosion control in distribution systems is accomplished by chemical means, as described below. Table 10.1 summarizes the relationship of the various types of plumbing materials to corrosion resistance and the potential contaminants added to drinking water.

Electrochemical Considerations

In aqueous environments, an electrochemical galvanic cell is required for corrosion of plumbing materials. The components of this cell are an anode $n^{(+)}$, a cathode $n^{(-)}$, a connection between the anode and cathode for electron transport, and an electrolyte solution that will conduct ions between these two electrodes. Also, a potential difference must exist between the cathode and anode. Since metallic plumbing

Table 10.1. Corrosion Properties of Materials Frequently Used in Water Distribution Systems.[4]

Plumbing Material	Corrosion Resistance	Associated Potential Primary Contaminants
Copper	Good overall corrosion resistance; subject to corrosive attack from high velocities, soft water, chlorine, dissolved oxygen, low pH, and high inorganic carbon levels (alkalinities).	Copper and possibly iron, zinc, tin, arsenic, cadmium, and lead from associated pipes and solder.
Lead	Corrodes in soft water with pH <8, and in hard waters with high inorganic carbon levels (alkalinities).	Lead.
Mild steel	Subject to uniform corrosion; affected primarily by high dissolved oxygen levels.	Iron, resulting in turbidity and red water complaints.
Cast or ductile iron (unlined)	Can be subject to surface erosion by aggressive waters.	Iron, resulting in turbidity and red water complaints.
Galvanized iron	Subject to galvanic corrosion of zinc by aggressive waters; corrosion is accelerated at higher temperatures, as in hot-water systems; corrosion is affected by the workmanship of the pipe and galvanized coating.	Zinc and iron; cadmium and lead (impurities in galvanizing process).
Asbestos-cement	Good corrosion resistance; immune to electrolysis; aggressive waters can leach calcium from cement; polyphosphate sequestering agents can deplete the calcium and substantially soften the pipe.	Asbestos fibers; increase in pH, calcium.
Plastic	Resistant to corrosion.	
Brass	Good overall resistance; different types of brass respond differently to water chemistry; subject to dezincification by water of pH >8.3 with high ratio of chloride to carbonate hardness. Conditions causing mechanical failure may not directly correspond to those promoting contaminant leaching.	Lead, copper, zinc.

materials are not completely homogeneous, anodic and cathodic sites do occur on the pipe's surface. Oxidation and dissolution of the metal occurs at the anode. Electrons are generated at the anode that migrate to the cathode, where they are accepted by such molecules as O_2. Consequently, positive ions from the anode will migrate to the cathode, whereas the negative ions will migrate to the anode. These migrations will maintain an electrically neutral solution.

A potential difference exists between the water phase and the solid phase—the metal surface. This potential difference results from metal's tendency to proceed to a state of equilibrium with the electrolytes in solution. This is an oxidation reaction that is written as a loss of electrons (IUPAC convention[5]):

$$\mathrm{Me} = \mathrm{Me}^{n+} + ne \qquad (1)$$

This is the left to right corrosion reaction, which will proceed until the metal reaches an equilibrium state with its ion in solution. An *anodic current* results from this oxidation reaction. In the right to left reaction, metal ions are reduced by acceptance of the electrons, which results in a *cathodic current.* When these two currents are equal, the forward reaction proceeds at the same rate as the reverse reaction. Consequently, no net corrosion occurs in this state of equilibrium. It can be shown that the electric current, which is equal to the velocity of the reaction, depends on the electrode potential.[6] The net current is zero when the rate of reduction is equal to the rate of oxidation, whereupon the system reaches a state of equilibrium.

Anodic and cathodic areas develop on the metal's surface whenever there is a flow of electric current. These areas may be microscopic and when in close proximity, general uniform corrosion occurs. When these areas are large and somewhat remote from each other, pitting occurs, with or without tuberculation. Electrode areas may be induced by various conditions: impurities in the metal, accumulation of sediment, adherent bacterial slimes, and accumulations of corrosion products.

Usually when metallic pipes corrode, metal ions go into solution at the anodic areas (Figure 10.1). Thus, an electric potential is developed. Electrons liberated at the anodes flow through the metal to cathodic areas where another chemical reaction occurs and another electric potential develops. Corrosion control by water treatment methods attempts to retard either or both of the primary electrode reactions.

The Nernst Equation

Metallic corrosion in water occurs when the corrosion products are at a lower free energy level than the parent metal. That is, the free energy, ΔG°, of a corrosion reaction must be negative for it to occur spontaneously. This is the driving force of the reaction. The free energy difference of corrosion reactions depends upon the electrochemical potential, which is expressed as:

$$\Delta G^\circ = -nFE^\circ \tag{2}$$

where n = number of moles of electrons transferred, F = the Faraday constant (23.061 kcal/volt-mole) and E°= the electrode potential in volts (standard state). In turn, the free energy difference depends upon the type of metal and the types of solid and aqueous reaction products.

The equilibrium potential of a single electrode (Reaction 1, for example) is calculated from the Nernst equation:

$$E_{me/me^{n+}} = E^\circ_{me/me^{n+}} - \frac{RT}{nF}\ln[me^{n+}] \tag{3}$$

where $E_{me/me^{n+}}$ = nonstandard state potential (volts)
$E^\circ_{me/me^{n+}}$ = standard state potential (volts)
$[Me^{n+}]$ = molar concentration (activity neglected)
R = ideal gas constant (1.987 cal/mole-deg)
me/me^{N+} = subscript indicates a reduction reaction

Equation 3 is written for a single electrode, which in turn is coupled with the normal hydrogen electrode:

$$2H^+ + 2e = H_{2(g)} \tag{4}$$

The IUPAC convention assigns a value of E°=0.00 to this reaction where the concentrations of the reactants and products are assumed to be 1. Standard "half-cell" potentials are tabulated as reduction reactions in this convention.[5]

A generalized form of the Nernst equation can be written for the balanced net reaction of two half-cells:

$$OX + ne = RED \tag{5}$$

Here the OX and RED are the oxidized and reduced species. Substituting Equation 5 into Equation 3 yields:

$$E_{RED/OX} = E^\circ_{RED/OX} - \frac{RT}{nF}\ln\frac{[RED]}{[OX]} \tag{6}$$

The RED/OX subscript indicates the combined cell potentials for the total balanced reaction. Equation 6 can be rewritten at 25°C with the conversion of ln to log as:

$$E_{RED/OX} = E^\circ_{RED/OX} - \frac{0.591}{n}\log K_{eq} \tag{7}$$

K_{eq} denotes a condition of equilibrium where no electrochemical current is generated and the oxidants and reductants are at their equilibrium concentrations. Frequently, the reaction quotient, Q, is employed with nonequilibrium concentrations in order to determine the feasibility of a left to right corrosion reaction.[7] When $Q = K_{eq}$, the system is at equilibrium.

In distribution systems for drinking water, the oxidation half-cell reaction of the metallic plumbing is combined with the reduction of an oxidizing agent. An example of the latter is:

$$HOCl + H^+ + 2e = Cl^- + H_2OE^\circ = +1.49\ v \tag{8}$$

An example of the former is:

$$Fe^\circ\ (metal) = Fe^{2+} + 2eE^\circ = -0.409\ v \tag{9}$$

A combination of Reactions 8 and 9 yields:

$$\begin{gathered} Fe^\circ\ (metal) + OCl^- + 2H^+ = \\ Fe^{2+} + Cl^- + H_2OE^\circ_{cell} = +1.899 \end{gathered} \tag{10}$$

The positive E° cell value indicates that the left to right reaction is feasible, and that metallic iron will corrode in the presence of chlorine.

Table 10.2 shows the "classical" electromotive force series of pure metals under standard-state conditions (25°C, 1 atm, 1 *M* solution).[8] Metals lying below hydrogen spontaneously corrode in an aqueous environment, whereas those that lie above do not corrode. This generalization applies when the metal's half-cell reaction is combined with the hydrogen half-cell reaction. There are conditions, of course, where the metals lying above hydrogen, especially copper, spontaneously corrode. Table 10.2 also presents a practical galvanic series of metals and alloys[8] based on many laboratory and field tests using several corrosive solutions under a variety of service conditions.

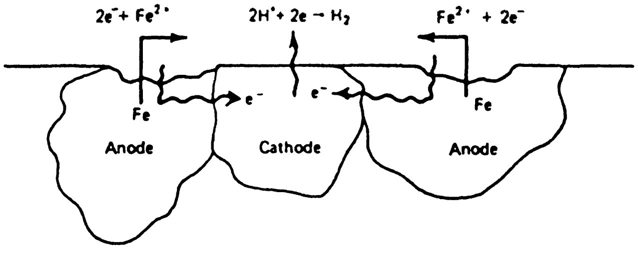

Figure 10.1. Corrosion of iron in acid solution.[7]

Table 10.2. Electromotive Force and Practical Galvanic Series.[a]

Electromotive Force Series	Volts	Practical Galvanic Series of Metals and Alloys
		Protected End (Cathodic or most noble)
1 Au^{3+}	+1.36	1 Platinum
		2 Gold
		3 Graphite
2 Ag^{2+}	+0.8	4 Silver
		5 Hastelloy C (passive)
		6 18–8–3 Chromium–nickel–molybdenum–iron (passive)
3 Cu^{2+}	+0.34	7 18–8 Chromium–nickel–iron (passive)
4 Sb^{3+}	+0.1	8 Chromium–iron (passive)
		9 Inconel (passive)
5 $H_{2(g)}$	0.00	10 Nickel (passive)
		11 Silver Solder
		12 Monel
6 Pb^{2+}	−0.12	13 Copper–nickel alloys
		14 Bronzes
7 Sn^{2+}	−0.14	15 Copper
		16 Brasses
8 Ni^{2+}	−0.23	17 Hastelloy C (active)
		18 Inconel (active)
9 Co^{2+}	−0.29	19 Nickel (active)
		20 Tin
10 Cd^{2+}	−0.40	21 Lead
		22 Lead–tin solders
11 Fe^{2+}	−0.44	23 18–8–3 Chromium–nickel–molybdenum–iron (active)
12 Cr^{2+}	−0.56	24 18–8 Chromium–nickel–iron (active)
13 Zn^{2+}	−0.76	25 Ni–Resist
		26 Chromium–iron (active)
14 Al^{3+}	−1.33	27 Cast iron
		28 Steel or Iron
15 Mg^{2+}	−1.55	29 Aluminum 17ST
		30 Cadmium
		31 Aluminum 25
		32 Zinc
		33 Magnesium alloys
		34 Magnesium

[a] Reproduced from Obrecht and Pourbaix,[8] courtesy of the American Water Works Association.

Iron

The corrosion chemistry of iron is exceedingly complex since Fe(0), Fe(II), and Fe(III) may enter into many oxidation-reduction and precipitation reactions.[7,9] A few of the more relevant reduction reactions are given in Table 10.3 at standard-state conditions. In turn, these reactions can be used to construct a pH-pE diagram, as seen in Figure 10.2.[10] The corrosion Reaction 16 (Table 10.3) Fe(0)-Fe(II) is set at a

Table 10.3. Some Corrosion Reactions for Fe(0)–Fe(II)–Fe(III) at 25°C.

Reaction Number	Reaction	E° (volts)	pE⁰
11	$O_{2(g)} + 4H^+ + 4e = 2H_2O$	+1.229	+83.3
12	$Fe^{3+} + e = Fe^{2+}$	+0.771	+13.07
13	$FeOH^{2+} + H^+ + e = Fe^{2+} + H_2O$	+0.914	+15.51
14	$Fe(OH)_2^+ + 2H^+ + e = Fe^{2+} + H_2O$	+1.191	+20.2
15	$Fe(OH)_{3(s)} + 3H^+ + e = Fe^{2+} + 3H_2O$	+1.052	+17.8
16	$Fe^{2+} + 2e = Fe_{(s)}$	−0.409[a]	−14.9
17	$FeCO_{3(s)} + H^+ + 2e = Fe_{(s)} + HCO_3^-$	−0.413	−14.0
18	$2H_2O + 2e = H_{2(g)} + OH^-$	−0.828	−28.1
19	$2H^+ + 2e = H_{2(g)}$	0.0	0.0
20	$Fe_{(s)} + 2H^+ = Fe^{2+} + H_{2(g)}$	+0.409[a]	+14.9
21	$Fe_{(s)} + 0.5O_{2(g)} + 2H^+ = Fe^{2+} + H_2O$	+1.64[a]	+55.4
22	$O_{2(g)} + 4Fe^{2+} + 10H_2O = 4Fe(OH)_{3(s)} + 8H^+$	+0.177[a]	+11.6

[a] From a compilation by J.F. Hunsberger.[11]

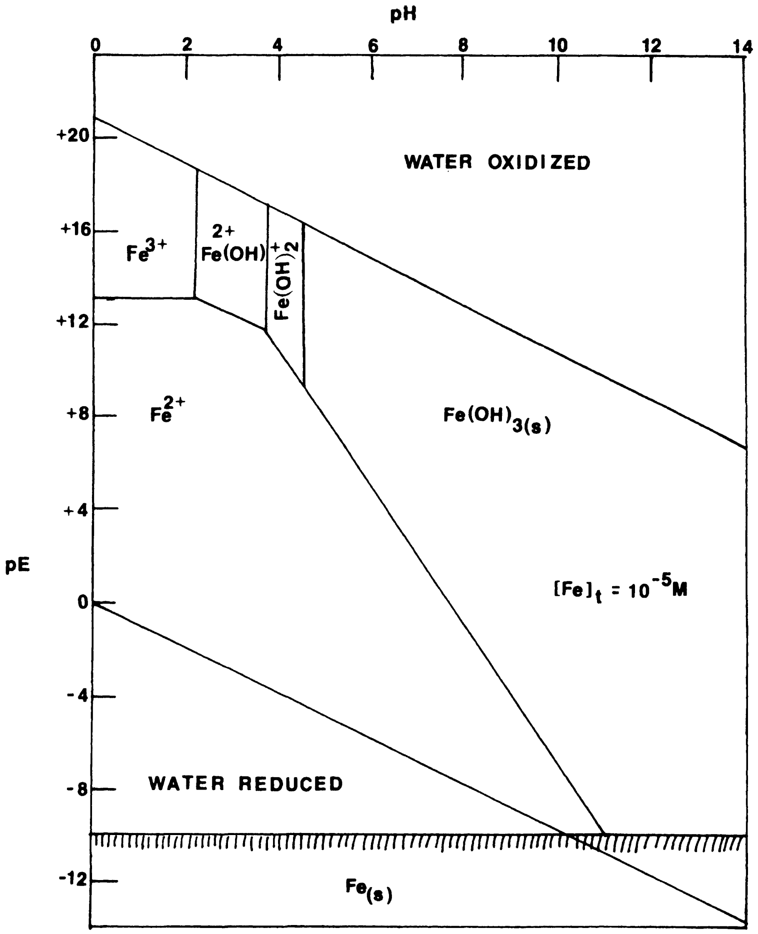

Figure 10.2. pH-pE stability diagram for the iron system. Reproduced from Faust and Aly.[10]

pE value of -9.95 when an assumed concentration of $10^{-5}M$ is used for the soluble Fe(II). Since this reaction is the oxidative portion of the corrosion reaction for metallic iron, it is combined with Equation 19 (Table 10.3) as the reductive reaction, and yields an E° value of +0.409. This shows that metallic iron pipes are thermodynamically unstable in water; i.e., they have an inherent tendency to corrode. The remaining reactions yield the pH-pE conditions at which Fe(II) is oxidized to one or more of the Fe(III) species. The Fe(II)-Fe(III) boundary is computed from Equation 12 (Table 10.3) where the pE° value is +13.07. At pE values >+13.07, Fe(III) is the predominant species, whereas at pE values <+13.07, Fe(II) is the predominant species. This reaction and the $Fe_{(s)}$-Fe^{2+} reaction are independent of $[H^+]$ over the pH range of 0.0 to 2.2. Above the pH value of 2.2, Fe(III) enters into a series of acid-base reactions. For example,

$$Fe^{3+} + H_2O = FeOH^{2+} + H^+;\ \log K_{13} = -2.2 \quad (23)$$

Consequently, $FeOH^{2+}$ is the predominant species over the pH range of 2.2 to 3.7 and above pE values of +12 to 13 $Fe(OH)_2^+$ is the predominant species in the pH range of 3.7 to 4.8. Above the latter pH value, $Fe(OH)_{3(s)}$ is the major ferric species.

That the $[H^+]$ influences the pE value at which $Fe^{2+}{}_{(aq)}$ is oxidized to any one of the three Fe(III) species is seen also in Figure 10.2. For example, the linear form of Equation 15 is:

$$pE = 22.8 - 3pH \quad (24)$$

This equation indicates that there is a three-unit decrease in pE for a one-unit increase in pH. If an appropriate electron acceptor is present, then the pE value of the corrosion reaction to $Fe(OH)_{3(s)}$ is lowered as the pH value is increased. Equation 22 (Table 10.3) is an example of a corrosion reaction at higher pH values. pH-pE diagrams do not give any information on the kinetics, i.e., rate of corrosion of metals. They convey only the pH-pE conditions under which a given oxidation state of iron should be stable, and a given oxidation or reduction reaction should occur.

pE-pH diagrams have been used extensively to relate laboratory data to the various theoretical conditions of corrosion, immunity, and passivation.[8] Immunity is defined as the thermodynamic stability of the metal, whereas passivation is the formation of a stable solid oxide or any other insoluble stable product. Corrosion is the formation of stable soluble metallic products.

Figure 10.3a shows the pH-pE(E) diagram of Obrecht and Pourbaix.[8] It varies slightly from Figure 10.2 because $Fe_2O_{3(s)}$ and $Fe_3O_{4(s)}$ were used for the solid corrosion products rather than $Fe(OH)_{3(s)}$. Figure 10.3b shows the thermodynamically defined areas of corrosion, passivation, and immunity of iron, whereas Figure 10.3c relates these quantities to the experimentally determined rates of iron corrosion. Obrecht and Pourbaix[8] interpret Figure 10.3c as acceptable agreement between the experimental results and theoretical predictions. For example, in the area of immunity, metallic iron is stable theoretically and should not corrode. In the area of passivation, iron is covered by an oxide film, which offers some protection against additional corrosion. This is seen in Figure 10.3c, where the rates of corrosion are extremely slow or nonexistent in the immunity and passivation areas.

The triangular shape of the corrosion area in Figure 10.3b results from the greater solubility of ferrous oxide than ferric oxide. Consequently, it is responsible for the corrosion of iron in water, which in turn leads to the formation of craters covered with tubercles of rust. These tubercles result from localized attack at the discontinuity of the mill scales. This is seen in Figure 10.4, which is the "classic" sketch of pit corrosion. Since an electrode potential difference exists between the inside and outside of the crater, a current is produced that leads to highly localized corrosion. Oxygen is the electron acceptor in this representation of iron corrosion.

Some natural waters may contain a significant amount of bicarbonate ions to form $FeCO_{3(s)}$ (siderite):

$$FeCO_{3(s)} + H^+ = Fe^{2+} + HCO_3^-;\ \log K_{25} = -0.34 \quad (25)$$

This precipitation reaction and the reduction Reaction 17 in Table 10.3 would yield an additional corrosion product. Figure 10.5[11] shows the pH-pE(E) diagram with the presence of 100 ppm (solid lines) and 1000 ppm (dashed lines) of bicarbonate. Formation of $FeCO_{3(s)}$ occurs under alkaline conditions (pH >8.3) and negative pE values. According to Hem,[12] ferrous carbonate is readily oxidized to ferric hydroxide at pE values of an aerated water. This reaction may be:[13]

$$Fe(OH)_{3(s)} + CO_{2(g)} + H^+ + e = FeCO_{3(s)} + 2H_2O;\ \log K_{26} = 10.4 \quad (26)$$

Copper

Since copper is a noble metal, it shows excellent resistance to corrosion; that is, the corrosion of metallic copper to cupric ions via the hydrogen ion reaction (Equation 33, Table 10.4) is not thermodynamically spontaneous. On the other hand, Equation 34, Table 10.4, shows that copper should be corrosive in an oxygenated environment. The theoretical corrosion diagram is seen in Figure 10.6 for a "pure"

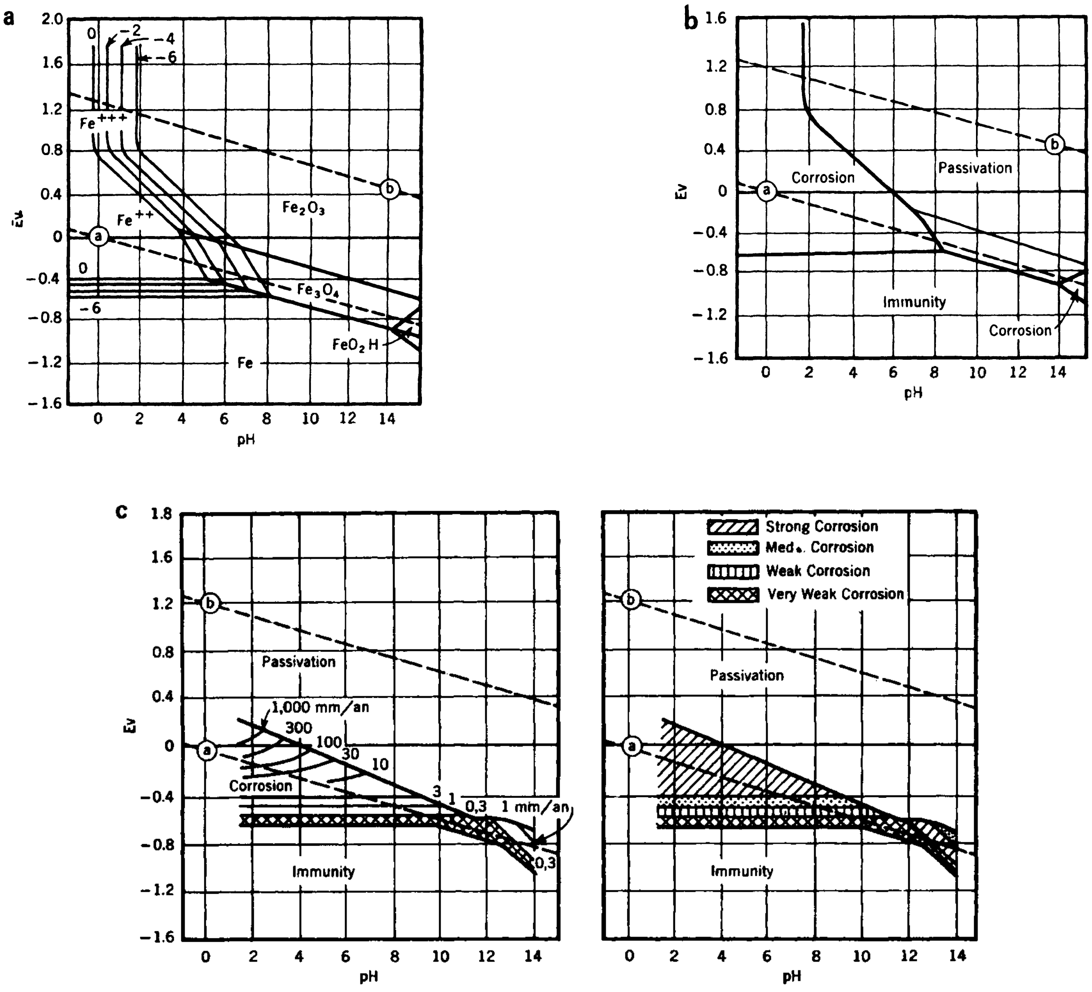

Figure 10.3. (a) Equilibrium potential–pH diagram. (b) Theoretical conditions for iron. (c) Experimental conditions of corrosion, immunity and passivation for iron. Reproduced from Obrecht and Pourbaix,[8] courtesy of the American Water Works Association.

water system. At a pH of 6–7, it is completely uncorroded if the E value does not exceed +0.2. Above this E value and for a given pH value, the corrosion products are one or more of the following: Cu^+ (not shown) and Cu^{2+} ions, $Cu_2O_{(s)}$, and $CuO_{(s)}$. It should be noted also from Figure 10.6a that the immunity area for metallic copper extends well into the stability area of water, which is an additional reason for its thermodynamic stability. Figure 10.6b was drawn from carefully controlled laboratory experiments by Obrecht and Pourbaix,[8] where a "close correlation" was obtained between total corrosion and oxygen consumption. These data demonstrate that copper does corrode in the presence of oxygen, as predicted by Equation 34, Table 10.4.

This is considerable evidence that copper pipes corrode under conditions other than in the presence of dissolved oxygen. For example, acid conditions (pH <6.5) and in the presence of carbon dioxide acidity are extremely conducive for copper corrosion. This corrosion may be categorized as uniform or localized on the basis of visual inspection. Localized corrosion (pitting or pinholes) is a function of water type and the morphology of pits on the copper's surface. Table 10.5 is a summary of the significant characteristics of uniform corrosion and the three major types of pitting.[15,16]

Uniform corrosion of copper pipes is characterized by a loose, powdery blue-green scale or a tarnish similar to that of an old copper penny. High rates of uniform corrosion are most commonly associated with waters of low pH and alkalinity where films and/or scale can not form to protect the copper surface.

Localized copper corrosion occurs randomly in distribution systems and leads to the formation of pits or pinholes. This is a common problem where the water supply has a low pH value and a high CO_2 content. This type of corrosion can appear rapidly in newly plumbed copper pipes.

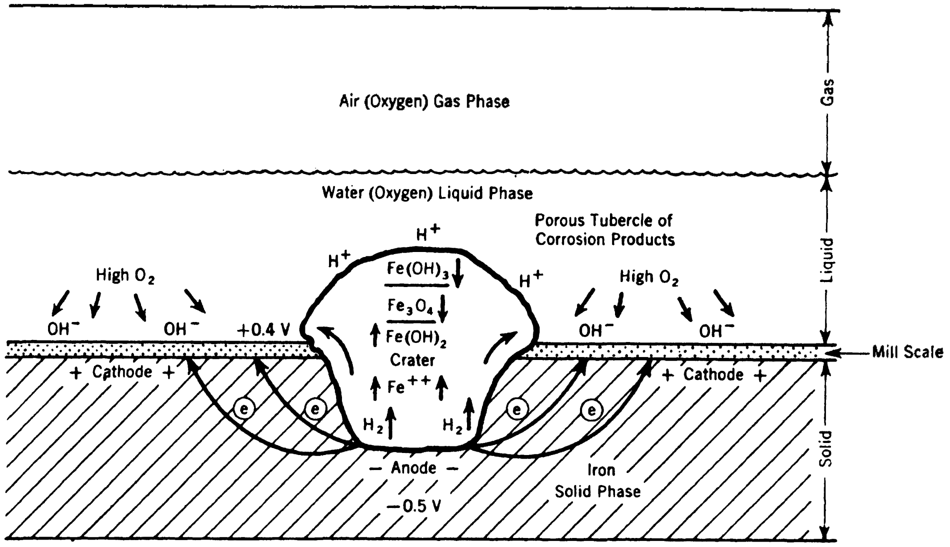

Figure 10.4. Pitting of iron by tuberculation and oxygen-concentration cells. Reproduced from Obrecht and Pourbaix,[8] courtesy of the American Water Works Association.

There are three distinctive types of pitting that involve cold, hot, and soft waters, as seen in Table 10.5.[15]

Several solid phases of copper corrosion products are involved in the three types of pitting. These are described in Table 10.5 and the appropriate chemical reactions are given in Table 10.6. Type I (cold water pits) corrosion is characterized by a film of reddish-brown glassy cuprite (Cu_2O) that is sandwiched between the pipe's surface and an exterior scale layer of basic copper salts such as malachite ($Cu_2OH_2CO_3$). Type I pits are usually formed in well waters of relatively high conductivity, hardness, alkalinity, and sulfate concentrations, and with low TOC. This type of pitting is, perhaps, the most common cause of copper pipe failures.[15]

Hot water pits (Type II) are characterized by a film of crystalline Cu_2O sandwiched between the pipe's surface and an exterior scale layer that frequently contains bronchanite ($Cu_4(OH)_6SO_4$) (Table 10.6). These pits are usually formed in waters with a pH <7, temperature >60°C, and a low HCO_3^-/SO_4^{2-} rate.[16] Hot water pitting apparently is much slower to form (years) than cold water pitting (months).

Soft water pits (Type III) are characterized by a film of crystalline Cu_2O sandwiched between the pipe's surface and an exterior scale layer that may contain either or both bronchanite and malachite. This type of pitting may be observed from the persistent release of insoluble corrosion products that may cause pipe blockage.[15] Soft waters with low conductivity, low alkalinity, and a relatively high pH value (>8.2) are conducive to type III pitting. This may be explained by the amphoretic dissolution of copper under alkaline pH values.[14]

An example of corrosion rates of copper in an accelerated experimental situation is seen in Figure 10.7.[8] These systems were employed to investigate the roles of oxygen and carbon dioxide in the corrosion of copper. As noted above, the chemistry of this type of copper corrosion is rather complex. "Carbon dioxide added to a pure copper-water system in the absence of oxygen did not cause copper corrosion."[8] However, when both oxygen and carbon dioxide were present in an experimental system (Figure 10.7) rather than oxygen alone (Figure 10.6b), an increase in corrosion rate was observed. For example, the total corrosion after six days was 0.65 mg Cu/cm^2 (Figure 10.7) for the $Cu\text{-}O_2\text{-}CO_2$ system, whereas it was 0.27 mg Cu/cm^2 (Figure 10.6b) for the $Cu\text{-}O_2$ system. In Figure 10.7, total corrosion was obtained from the summation of Cu in the precipitate (perhaps malachite), in the surface film (copper oxides), and the copper ions in solution.

Lead

Lead pipe and lead-based solders have been employed for many years in water distribution systems. Where its use is predominant in many areas of Europe and North America, lead pipe is used primarily for service and residential lines. Lead service lines are probably still in use in many places such as Chicago, New England, and New Jersey.[18,19] This is surprising in view of EPA's action level of 0.015 mg/L for lead.[2] Where the water is corrosive, lead concentrations can greatly exceed this action level.[18]

That lead plumbing is readily corroded is seen in the theoretical corrosion diagram in Figure 10.8[14] and Reaction 46, Table 10.7. The oxidation of elemental lead is thermody-

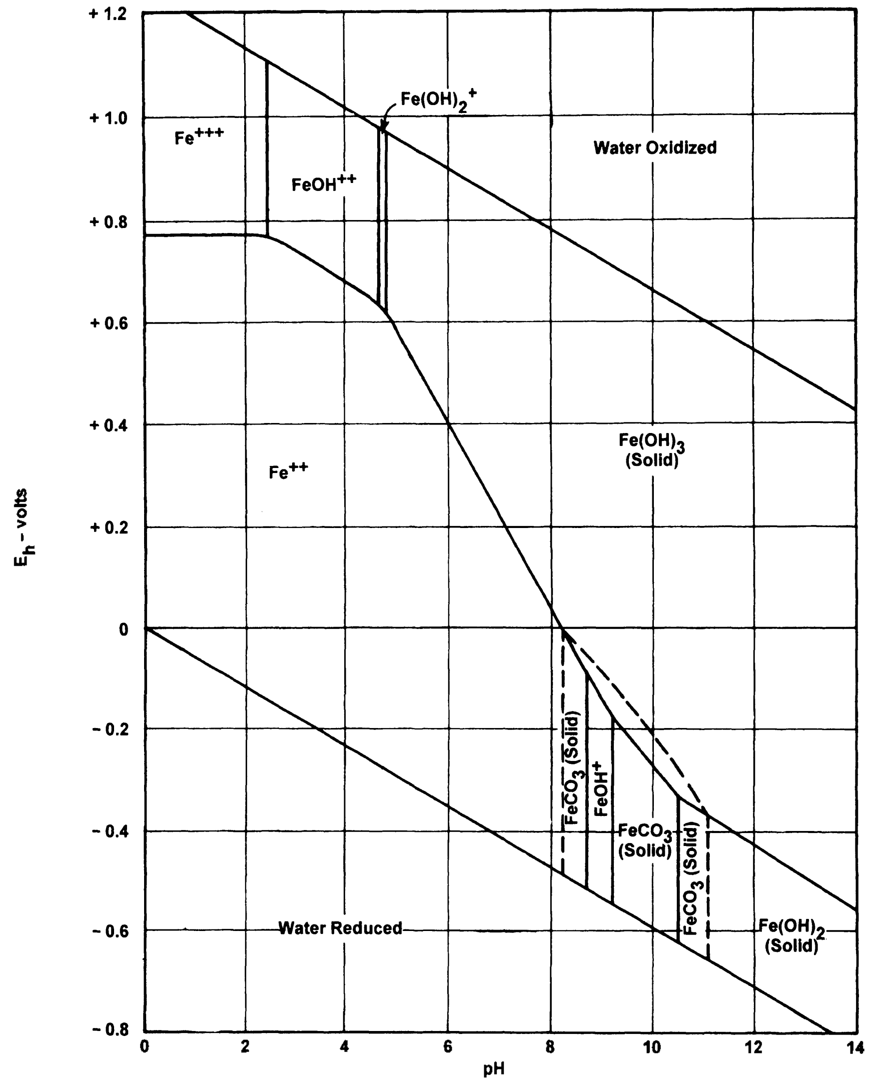

Figure 10.5. Stability fields of ferrous and ferric species for activity of 0.01 ppm dissolved iron. $[HCO_3^-]$ = 100 ppm (solid boundaries); or $[HCO_3^-]$ = 1000 ppm (dashed boundaries). Reproduced from Hem,[12] courtesy of the American Water Works Association.

Table 10.4. Some Corrosion and Precipitation Reactions for Copper at 25°C.

Reaction Number	Reaction	E°[a] (volts)	pE°
27	$Cu^+ + e = Cu_{(s)}$	+0.522	+8.81
28	$Cu^{2+} + 2e = Cu_{(s)}$	+0.3402	+11.4
29	$Cu^{2+} + e = Cu^+$	+0.158	+2.59
30	$Cu_2O_{(s)} + 2H^+ + 2e = 2Cu_{(s)} + H_2O$	+0.471	+15.97
31	$2Cu^{2+} + H_2O + 2e = Cu_2O_{(s)} + 2H^+$	+0.203	−6.88
32	$2CuO_{(s)} + 2H^+ + 2e = Cu_2O_{(s)} + H_2O$	+0.669	+22.7
33	$Cu_{(s)} + H^+ = Cu^{2+} + H_{2(g)}$	−0.337	−11.4
34	$O_{2(g)} + 4H^+ + 2Cu_{(s)} = 2H_2O + 2Cu^{2+}$	+0.892	+60.5

[a] From Pourbaix.[14]

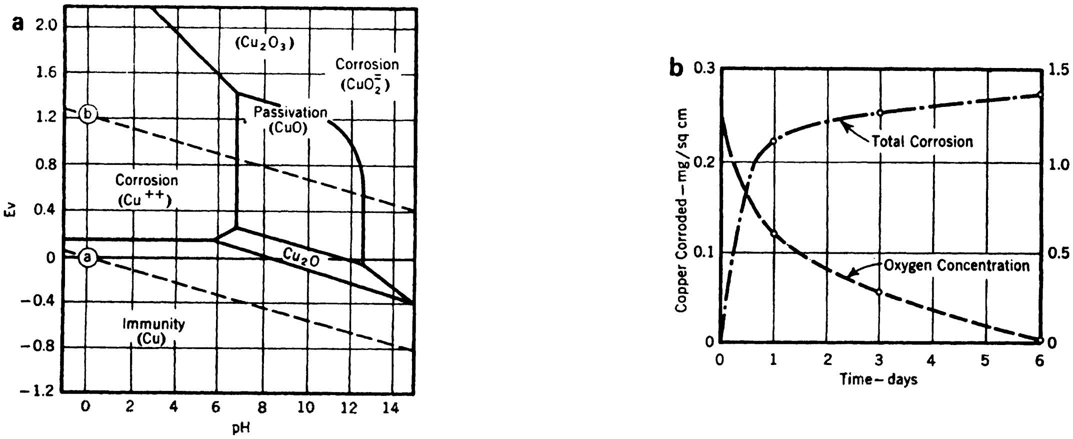

Figure 10.6. (a) Theoretical conditions for copper, 25°C. (b) Corrosion of high-purity copper in a closed system at 140°F (60°C) containing oxygen. Reproduced from Obrecht and Pourbaix,[8] courtesy of the American Water Works Association.

namically feasible in water to Pb^{2+}, $Pb^{2.67+}$, Pb^{4+} ions which, in turn, form the various oxides of lead: $PbO_{(s)}$, $Pb_{(3)}O_{4(s)}$, and $PbO_{2(s)}$. In the presence of CO_2 acidity, these compounds are fairly soluble, with the subsequent formation of the more insoluble lead carbonates or a lead hydroxy carbonate. For these reasons, lead must not be used for soft, acidic drinking waters, but may have some use in hard, scale-forming waters (see below). On the other hand, lead pipes may be banned entirely at some future date from use in public potable water systems. Additional electrochemical corrosion of lead in water may be found in Reference 20.

Plumbous ions, Pb^{2+}, are predominant, for the most part, in waters where they occur from corrosion reactions. In turn, these ions may form solid phases with such anions as OH^-, CO_3^{2-}, PO_4^{3-}, etc. Some precipitation reactions are given in Table 10.8 with their thermodynamic equilibrium constants at 25°C. One or more of these reactions may control the soluble concentration of lead in water. Also, some of these reactions are employed for treatment purposes in order to reach the action level of 0.015 mg/L for lead (see below). That these solid phases may affect corrosion reactions of lead is seen in Figure 10.9, where the carbonates form a "bridge" between the immunity area and the passivation area created by the stability of $PbO_{2(s)}$.

Zinc

The corrosion of galvanized pipe by aggressive potable waters continues to be a problem.[2,8] That zinc is corroded spontaneously is seen in Equation 63, Table 10.9. The theoretical graph is seen in Figure 10.10. Since the $Zn_{(s)}$-Zn^{2+} lies outside the water stability field, there is a rather "large" area for corrosion. It should be noted that the zinc corrosion reaction lies below the iron corrosion reaction (see Table 10.2); hence, it is "more" corrosive than iron. For galvanized pipes, this provides protection for the underlying iron. Passivation protection for zinc is provided by $ZnO_{(s)}$ (Equation 67, Table 10.9), or $Zn(OH)_{2(s)}$ as seen in Figure 10.10. This area of passivation may be expanded through formation of the insoluble $ZnCO_{3(s)}$ (not shown; see Equation 66, Table 10.9).

Asbestos-Cement Pipe

Much concern has been expressed by the USEPA[2] about release of asbestos fibers from corroding asbestos-cement (A/C) pipes. Occupational studies have indicated that inhaled asbestos is a human carcinogen. Also, an increased incidence of gastrointestinal cancer has been found in occupational groups who have been heavily exposed to asbestos. Evidence for a relationship between asbestos in drinking water and increased cancer risk is inconclusive. However, the EPA feels that there is justification to prevent the distribution of asbestos in drinking water.

The dissolution of asbestos-cement pipe in the deterioration of cement mortar linings of cast iron water mains yields a number of undesirable contaminants in the potable water. Such highly soluble components as free lime ($Ca(OH)_2$), calcium carbonates, silicates, and aluminosilicates are dissolved by aggressive water.[22] If the leaching is severe, walls of pipes can be weakened and mats of fibers can be dislodged. Such water quality characteristics as pH, alkalinity, hardness, and silica concentration determine its natural aggressive nature. Use of treatment chemicals that sequester calcium, zinc, iron, manganese, etc. can also contribute to leaching of A/C pipe.

The American Water Works Association[23,24] has established criteria for determining the quality of water that can be transported through A/C pipe without any adverse effects. An empirical indicator formula was developed for a

Table 10.5. Summary of Copper Corrosion Problems.[a]

Characteristic	Uniform Corrosion	Type I Pitting (Cold Water)	Type II Pitting (Hot Water)	Type III Pitting (Soft Water)
Pit shape	No pits	Deep and narrow	Narrower than type I	Wide and shallow
Problem	Blue or green water, high by-product release	Pipe failure	Pipe failure	Blue water, voluminous by-product releases, pipe blockage
Scale morphology on attacked surface	Tarnished copper surface or loose powdery scale	Underlying Cu_2O with overlying malachite, calcite, or other basic copper salts, occasionally CuCl underlies Cu_2O	Underlying Cu_2O with overlying bronchanite, some malachite	Underlying Cu_2O with overlying bronchanite, some malachite
Water quality	Soft water of low pH (<7.2)	Hard, cold, well waters between pH 7 and 7.8, high sulfate relative to chlorides and bicarbonate, high CO_2	Hot water, pH below 7.2, high sulfate relative to bicarbonate, occasional Mn deposits	Soft waters, pH >8.0
Initiating factors	None noted	Stagnation early in pipe life, deposits within pipe, including dirt or carbon films, high chlorine residuals, water softeners, alum coagulation	Higher temperatures, high chlorine residuals, alum coagulation, particles	Stagnation early in pipe life, pH>8.0, alum coagulation low chloride residuals
Ameliorating factors and treatment	Raise pH or increase bicarbonate	NOM, increase bicarbonate and pH	Lower temperatures, higher pH, increase bicarbonate and pH	NOM, avoid stagnation early in pipe life, increase hardness and alkalinity, elevate Cl_2 residual to >0.5 mg/L

[a] From Edwards et al.[15]

Table 10.6. Solid Phases of Copper from Corrosion Reactions.[a]

Reaction Number	Reaction	Solid	log Ks
35	$2Cu^+ + H_2O = Cu_2O_{(s)} + 2H^+$	Cuprite	1.55
36	$Cu^+ + Cl^- = CuCl_{(s)}$	Nantokite	6.76
37	$2Cu^+ + CO_3^{2-} = Cu_2CO_{3(s)}$	Cuprous Carbonate	—
38	$Cu^{2+} + CO_3^{2-} = CuCO_{3(s)}$	Cupric Carbonate	9.63[b]
39	$4Cu^{2+} + 6H_2O + SO_4^{2-} = Cu_4(OH)_6SO_{4(s)} + 6H^+$	Bronchanite	−15.3
40	$Cu^{2+} + 2H_2O = Cu(OH)_{2(s)} + 2H^+$	Cupric Hydroxide	−8.64
41	$Cu^{2+} + H_2O = CuO_{(s)} + 2H^+$	Tenorite	−7.62
42	$2Cu^{2+} + CO_3^{2-} + 2H_2O = Cu_2(OH)_2CO_{3(s)} + 2H^+$	Malachite	5.18[b]
43	$4Cu^{2+} + 4H_2O + 2CO_3^{2-} = 2CuCO_3{\bullet}Cu(OH)_{2(s)} + 4H^+$	Azurite	16.92
44	$H_4SiO_4 + Cu^{2+} = CuH_2SiO_{4(s)} + 2H^+$	Dioptase	−6.5
45	$3Cu^{2+} + 2PO_4^{3-} + 2H_2O = Cu_3(PO_4)_2{\bullet}2H_2O_{(s)}$	—	35.12[b]

[a] Modified from Edwards et al.[15]

[b] From Schock.[17]

water's aggressiveness toward the corrosion of A/C pipes. The so-called aggressiveness index (AI) is:

Formula	Comment	Type of A/C Pipe[a]
AI=pH+log(AH)[b]≥12.0	Nonaggressive	I or II
AI=pH+log(AH)= 10.0 to 11.9	Moderately aggressive	II
AI=pH+log(AH) 10.0	Highly aggressive	Neither

[a] Type I A/C pipe=not autoclaved, no limit on uncombined $Ca(OH)_2$. Type II A/C pipe=autoclaved, uncombined $Ca(OH)_2$ limited, resistant to all levels of soluble sulfates.

[b] A=alkalinity as mg/L as $CaCO_3$; H=Ca hardness as mg/L $CaCO_3$.

A study concerning the behavior of A/C pipe under various water quality conditions has been reported.[23] A summary of the data is seen in Table 10.10 where it is somewhat obvious that the "low" values of pH, alkalinity, and calcium hardness have a corrosive effect on A/C pipes. Asbestos fiber counts are also given for systems A–J cited in Table 10.10. Control of A/C pipe corrosion is given below.

ASSESSMENT OF CORROSION

All large water systems (>50,000 persons) are required to conduct corrosion control studies unless it can be demonstrated to the enforcement agency that corrosion control has been optimized.[2,3] Corrosion control studies must compare the effectiveness of pH and alkalinity adjustment, calcium adjustment, and addition, perhaps, of phosphate- or silica-based corrosion inhibitors (see below). These studies must be based on pipe rig/loop studies, metal coupon tests, partial system tests, or documented analogous treatment. Based on the results of these assessments of corrosion, large systems recommend an optimal control treatment to the enforcement agency.

Corrosion of plumbing metals is identified usually by *in situ* rate measurements. Rates of corrosion are expressed in mils (0.001/in.) penetration per year (MPY). Procedures for measurement of corrosion rates include: (a) weight-loss methods (coupon testing and loop studies) and (b) electrochemical methods. Weight-loss methods determine corrosion over long periods of time (months), whereas electrochemical methods may give instantaneous rates or rates over a short period of time.[6]

Coupon Weight-Loss Method

There are four important criteria for corrosion tests: (a) the metal sample must be representative of the metal piping, (b) the quality of the water to which the metal sample is exposed should be the same as that distributed in the plumbing system, (c) the flow velocity and stagnation times should be representative of those in the full-scale system, and (d) the test duration must allow for development of the pipe scales, which have an important effect on corrosion rate and on the quality of the water passing through the pipe system.[25] Table 10.11 gives some estimates of the time (months) required to determine the necessary information from tests with pipe inserts.[26] These times are only rough guidelines. Specific conditions may require other time periods. For example, corrosion tests for hot water systems may require less time. In test durations that are 12 months or longer, it may be desirable to analyze the coupons at 3-month intervals. Coupon weight-loss tests are excellent for measurement of general or uniform corrosion.[27]

There are several advantages and disadvantages of the coupon method.[4,27]

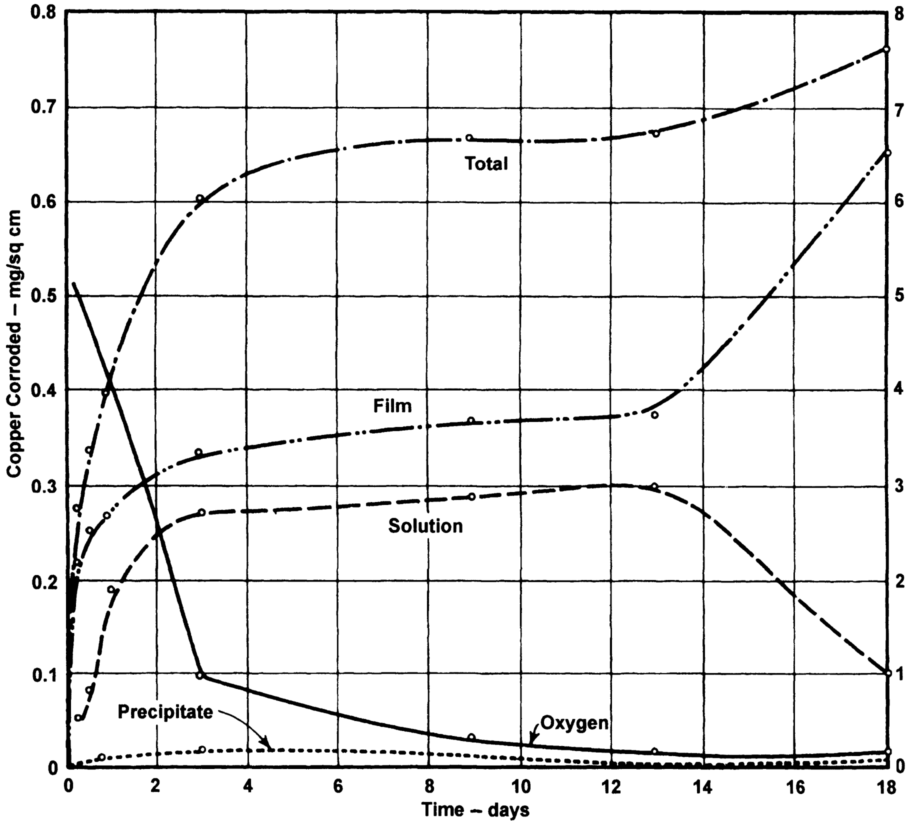

Figure 10.7. Effect of oxygen and $CO_{2(g)}$ on corrosion of pure copper. Closed system, 150°F (60°C), $[CO_{2(g)}]$ = 70 ppm. Reproduced from Obrecht and Pourbaix,[8] courtesy of the American Water Works Association.

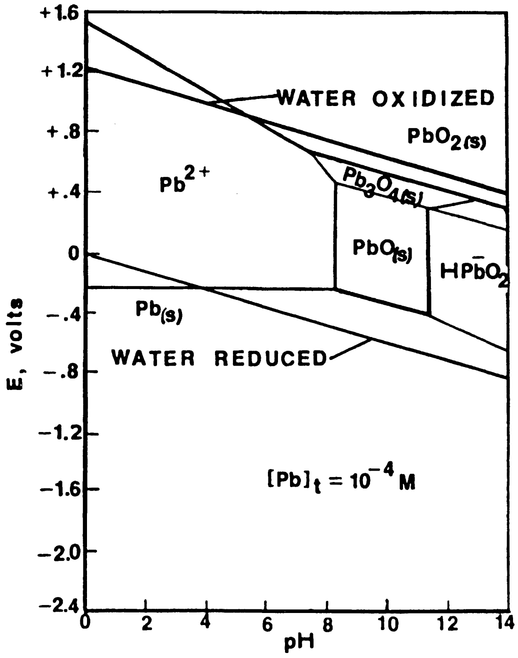

Figure 10.8. Potential-pH diagram for the Pb-H_2O system, 25°C. Reproduced from Pourbaix,[14] courtesy of Pergamon Press Ltd.

Table 10.7. Some Corrosion Reactions for Lead at 25°C.

Reaction Number	Reaction	E° (volts)	pE°
46	$Pb^{2+} + 2e = Pb_{(s)}$	–0.126[a]	–4.21
47	$PbO_{(s)} + 2H^+ + 2e = Pb_{(s)} + H_2O$	0.248[a]	8.41
48	$Pb_3O_{4(s)} + 2H^+ + 2e = 3PbO_{(s)} + H_2O$	0.972[a]	32.95
49	$3PbO_{2(s)} + 4H^+ + 4e = Pb_3O_{4(s)} + 2H_2O$	1.127[a]	76.4
50	$HPbO_2^- + 3H^+ + 2e = Pb_{(s)} + 2H_2O$	0.702[b]	23.75
51	$Pb_3O_{4(s)} + 2H_2O + 2e = 3HPbO_2^- + H^+$	–0.309[b]	–13.20
52	$PbCO_{3(s)} + 2H^+ + 2e = Pb_{(s)} + CO_{2(g)} + H_2O$	0.031[b]	1.05
53a	$PbO_{2(s)} + HCO_3^- + 3H^+ + 2e = PbCO_{3(s)} + 2H_2O$	1.55[b]	52.45

[a] From Reference 14.
[b] From Reference 18.

Table 10.8. Some Precipitation Reactions for Lead at 25°C.[a]

Reaction Number	Reaction	log K
53b	$Pb^{2+} + H_2O = PbO_{(s)} + 2H^+$	–12.65
54	$PbO_{(s)} + H_2O = HPbO_2^- + H^+$	15.36
55	$Pb^{2+} + H_2O + CO_{2(g)} = PbCO_{3(s)} + 2H^+$	–5.31
56	$Pb^{2+} + H_2CO_3 = PbCO_{3(s)} + 2H^+$	–3.87
57	$PbCO_{3(s)} = Pb^{2+} + CO_3^{2-}$	–13.11
58[b]	$Pb_3(OH)_2(CO_3)_{2(s)} = 3Pb^{2+} + CO_3^{2-}$	–46.78
59[b]	$Pb_3(OH)_2(CO_3)_{2(s)} + 2H^+ = 3Pb^{2+} + 2CO_3^{2-} + 2H_2O$	–18.0
60[c]	$Pb_5(PO_4)_3OH_{(s)} + H^+ = 5Pb^{2+} + 3PO_4^{3-} + H_2O$	–62.8
61	$Pb(OH)_{2(s)}$ FRESH = $Pb^{2+} + 2OH^-$	–14.93
62	$Pb(OH)_{2(s)}$ AGED = $Pb^{2+} + 2OH^-$	–19.85

[a] From References 14 and 19.
[b] Hydrocerussite.
[c] Hydroxypyromorphite.

Advantages

1. Provides information on the amount of material attacked by corrosion over a specified period of time and under specified operating conditions.
2. Coupons can be placed in actual distribution systems for monitoring purposes.
3. The method is relatively inexpensive.

Disadvantages

1. Rate determinations may take a long time (i.e., months, if corrosion rates are moderate or low).
2. The method will not indicate any variations in the corrosion rate that occurred during the test.
3. The specimen or coupon may not be representative of the actual material for which the test is being performed.
4. The reaction between the metal coupon and the water may not be the same as the reaction at the pipe wall because of friction or flow velocity, because the coupon is placed in the middle of the pipe section.
5. Removing the corrosion products without removing some of the metal may be difficult.
6. Analytical error may be significant due to the weighting procedure, which determines a small weight loss from a "heavy" coupon.

There are several other considerations and limitations to the coupon method:[25]

1. The insertion of flat metal coupons into a pipe may not have the same flow lines as those at the pipe wall. Consequently, scale formation and the action of inhibitors may not be representative.
2. Coupons may not be representative of the piping material.
3. Use of actual pipe sections may be more advantageous.

The preparation, handling, and examination of coupons are time-consuming and require precise operation. This should involve a trained laboratory technician or a corrosion specialist to provide reproducible results.[25]

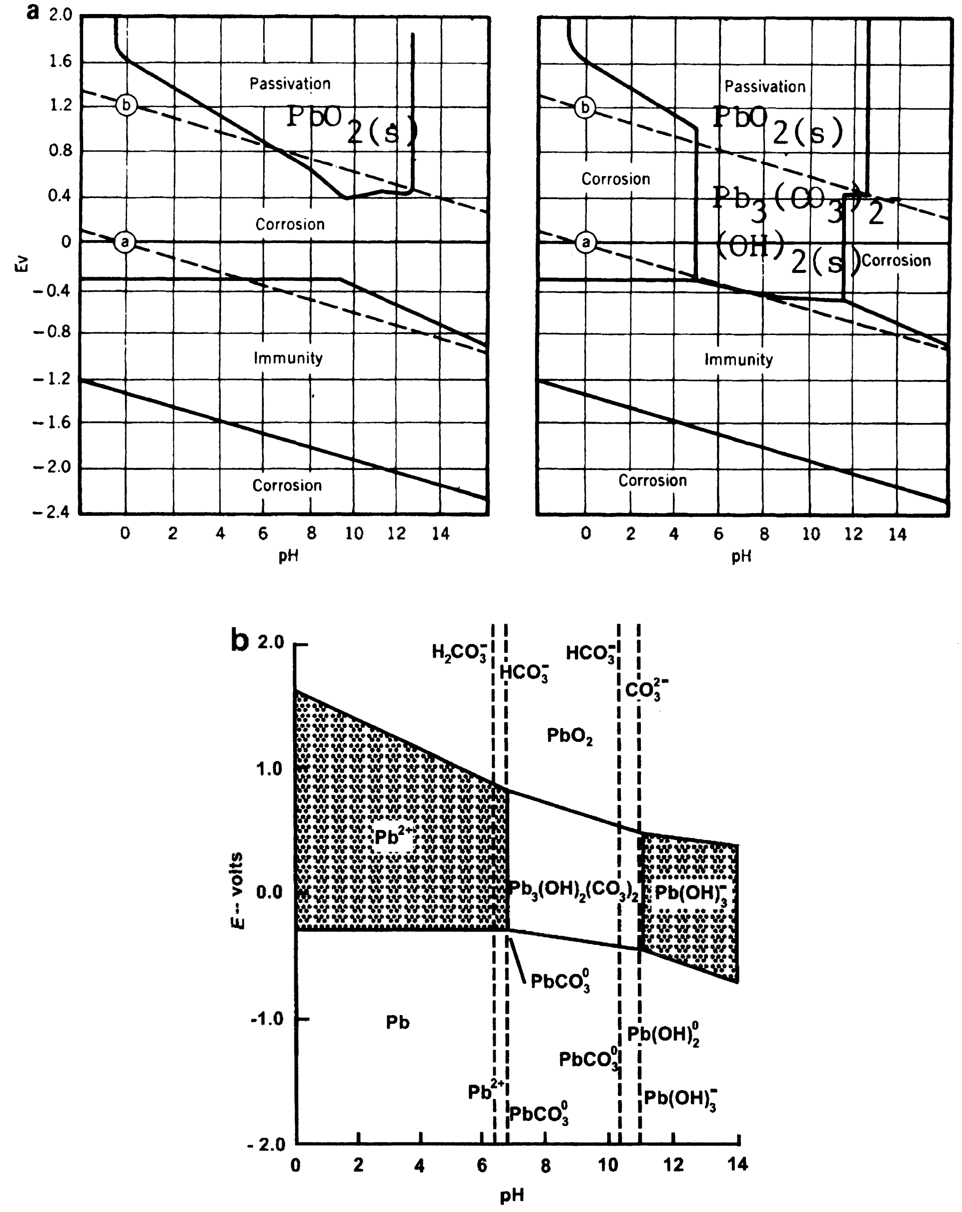

Figure 10.9. (a) Theoretical conditions for lead, 25°C in water (left) and 1 *M* $CO_{2(g)}$ (right). Reproduced from Obrecht and Pourbaix,[8] courtesy of the American Water Works Association. (b) Potential-pH diagram for $C_t = 10^{-3.7}$ *M* (20 mg/L as $CaCO_3$) and dissolved Pb(II) species at 10^{-6} *M* (0.21 mg/L). Ionic strength = 0.0, T = 25°C, areas of passivation and immunity are unshaded. Reproduced from Schock,[19] courtesy of the American Water Works Association.

"Coupon metal must be carefully degreased, etched, metal-stamped for identification, weighed, and stored in a sealed plastic wrapping in a desiccator to avoid atmospheric corrosion. The edges of a coupon are painted with epoxy, and gloves or tongs are used to handle a coupon so that skin moisture or oil will not mar its surface. Following coupon exposure and examination, the scale must be removed by brushing and using sequestered acids, before weight loss, pitting characteristics, and so forth can be determined. Again, the coupons must be thoroughly dry and stored in a desiccator. Control blanks are processed along with the exposed coupons in order to determine the weight loss or gain caused by the handling techniques, and these values are used to correct calculated corrosion rates."[6] Details of coupon or insert tests may be found in References 28, 29, and 30.

Table 10.9. Some Corrosion and Precipitation Reactions for Zinc at 25°C.[14]

Reaction Number	Reaction	E° Volts	pE°
63	$Zn^{2+} + 2e = Zn_{(s)}$	–0.763	–25.0
64	$ZnO_{(s)} + 2H^+ + 2e = Zn_{(s)} + H_2O$	–0.439	–14.0
65	$HZnO_2^- + 3H^+ + 2e = Zn_{(s)} + 2H_2O$	0.054	1.0
			log K
66	$Nz^{2+} + HCO_3^- = ZnCO_{3(s)} + H^+$		0.45[a]
67	$Zn^{2+} + H_2O = ZnO_{(s)} + 2H^+$		–10.96
68	$ZnO_{(s)} + H_2O = HZnO_2^- + H^+$		16.68
69	$\varepsilon\text{-}Zn(OH)_{2(s)} + H^+ = Zn^{2+} + 2H_2O$		11.54[b]
70	$ZnCO_{3(s)} = Zn^{2+} + CO_3^{2-}$		–10.00[b]
71	$Zn_5(OH)_6(CO_3)_{2(s)} + 6H^+ = 5Zn^{2+} + 2CO_3^{2-} + 6H_2O$		9.65[b]
72	$Zn_3(PO_4)_2.4H_2O_{(s)} = 3Zn^{2+} + 2PO_4^{3-} + 4H_2O$		–35.3[b]

[a] From Reference 21.
[b] From Reference 17.

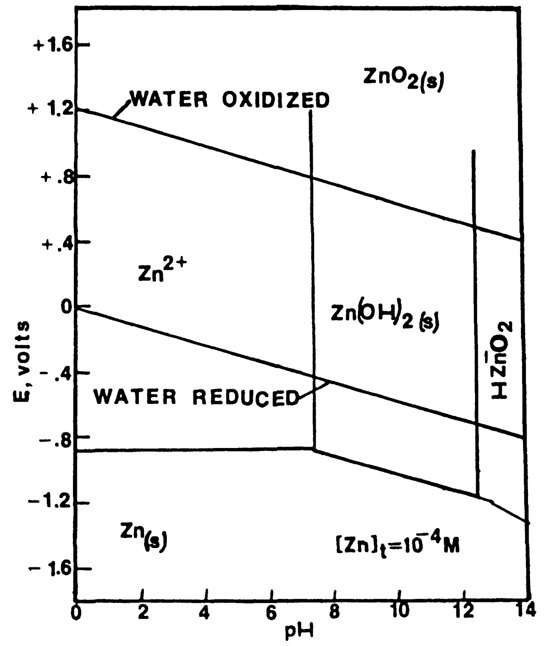

Figure 10.10. Potential-pH diagram for the system Zn-H_2O at 25°C. Reproduced from Pourbaix,[14] courtesy of Pergamon Press Ltd.

Loop System Weight-Loss Method

Use of a pipe loop in sections of pipes is another method for determination of water quality effects on material in the distribution system. The major advantage is that actual pipe is employed as the corrosion specimen. Water flow through the loop may be continuous or shut off periodically with a timer to simulate the flow pattern of a household. Pipe sections can be removed for measurement of weight-loss, and can be opened for visual inspection. This method is the Illinois State Water Survey (ISWS) method, which was adopted by the National Institute for Standards and Technology (NIST) Standard Method, D2688, Method C. It should be followed closely and carefully.

Advantages and disadvantages of the loop system are:[25]

Advantages

1. Actual pipe is used as the corrosion specimen.
2. Loops can be placed at several points in the distribution system.

Table 10.10. Corrosion of Asbestos Cement Pipes in Various Water Qualities.[a]

System	Initial Aggressiveness Index	pH	Alkalinity as $CaCO_3$ (mg/L)	Calcium Hardness as $CaCO_3$ (mg/L)	Consistently Quantifiable Fibers	Pipe Wall Deteriorated as Determined by Inspection
A	5.34	5.2	1.0	1.4	yes	yes
J	5.67	4.8	3.0	2.5	yes	yes
I	7.46	6.0	4.0	7.5	no	no
H	8.74	7.1	89.0	0.5	yes	yes
B	9.51	7.2	14.0	14.5	yes	yes
G	10.48	8.3	20.0	7.5	yes	[b]
C	11.56	7.5	88.0	82.0	no	[b]
D	12.54	7.8	220.0	250.0	no	[b]
E	12.74	9.4	50.0	44.0	no	[b]

[a] Reproduced from Buelow et al.,[23] courtesy of the American Water Works Association.
[b] Not inspected.

3. Loops can be set up in the laboratory to test the corrosive effects of different water qualities on pipe materials.
4. The method provides information on the amount of material attacked by corrosion over a specified period of time and under specified operating conditions.
5. The method is relatively inexpensive, as many corrosive effects can be examined visually.

Disadvantages

1. Determination of corrosive rates can take a long time (i.e., months, if corrosion rates are moderate or low).
2. The method does not indicate variations in the corrosion rate that occur during the test.

Some applications of loop system testing in References 31 (effect of Langelier Index), 32 (a modified ISWS procedure), and 33 (effect of buffer capacity, chlorine residual, and flow rate). Also, Reference 6 briefly discusses such other methods as: electrochemical rate measurements, immersion testing in the laboratory, chemical analyses, microscopic techniques, X-ray elemental analysis, and X-ray diffraction. Some examples of electrochemical rate measurements are found in References 34 and 35.

SOURCES OF CORROSION PRODUCTS

Obvious sources of iron and copper corrosion products are, of course, their plumbing materials. Soluble and insoluble products for Fe and Cu that initiate consumer complaints are sited above. Table 10.12 gives the most common symptoms and their possible causes. Not all complaints are necessarily caused by corrosion. Red water may be caused by incomplete removal of iron from the source water. However, corrosion is the major source of these complaints.

The lead and copper rule has been the impetus for several laboratory studies to investigate the sources of these two metals from plumbing materials and fixtures. Tin-lead (50-50) solder that is used as a joining compound for iron and copper pipes was researched in a laboratory corrosion study.[36] Source waters were two public supply wells. One water had a Langelier Index (see below) of −2.4, whereas the other LI value was −0.7. A copper pipe loop system was employed with three types of solder: 50-50 (tin-lead), 95-5 (tin-antimony), and a liquefied 50-50 formulation. Figure 10.11 shows typical results for the more corrosive well water. Lead was corroded from the copper plumbing that was soldered with the 50-50 and liquefied solders. Concentrations of Pb exceeded the 0.050 mg/L MCL in effect at that time (1984–1985), and the 0.015 mg/L action level in effect now.

The leaching of Pb, Cu, and Zn from brass fittings and water faucets has been investigated under field and laboratory conditions.[37,38] In the former study, six Illinois public water supplies were selected to research the influence of water source, treatment processes, corrosion control programs, and water quality on the corrosivity of water. Nineteen corrosion sites were selected from these six supplies whose water quality characteristics were variable. The LI values for some waters ranged from −2.6 to +0.9, whereas others ranged from +0.4 to +1.3. Figures 10.12 and 10.13 (field study) illustrate these observations: (a) Cu and Pb concentrations were greater in standing water samples than in running samples collected at the same site, and (b) the standing and running samples generally contained more Cu and Pb when collected from copper plumbing than from galvanized steel plumbing within the same water supply. The Pb and Cu concentrations exceeded the MCL or the secondary MCL in effect in 1986–87 in a significant number of

Table 10.11. Estimated Duration (Months) Required for Corrosion Tests.[26]

Material	Comparison of Uniform Corrosion Rates or Metal Leaching	Comparison of Inhibitors New Pipe	Comparison of Inhibitors Old Pipe	Pitting
Iron	12–24	3–6	12–24	12–24
Copper	3–6	1–3	3–6	12–36
Galvanized iron (zinc)	3–6	1–3	3–12	12–36
Lead	6–12	2–6	3–12	
Asbestos cement	18–24	3–12	12–18	
Mortar lining	24–36	12–24	24–36	

Table 10.12. Typical Customer Complaints Caused by Corrosion.[27]

Customer Complaint	Possible Cause
Red water or reddish-brown staining of fixtures and laundry	Corrosion of iron pipes or presence of iron in source water
Bluish stains on fixtures	Corrosion of copper lines
Black water lines	Sulfide corrosion of copper or iron
Foul taste or odors	By-products from microbial activity
Loss of pressure	Excessive scaling, tubercles building up from pitting corrosion, leaks in system from pitting or other types of corrosion
Lack of hot water	Buildup of mineral deposits in hot water system (can be reduced by setting thermostat to under 140°F)
Short service life of household plumbing	Rapid deterioration of pipes from pitting or other types of corrosion

water samples collected in the field study. It is interesting to note that sites 308, 309, 310, 311, and 312 yielded the highest Cu concentrations where the LI values ranged from –0.7 to 1.1 (Figure 10.12). These numbers suggest that these water supplies should not be corrosive (see below). Sites 301, 308, 312, 314, 315, 316, 318, and 319, Figure 10.13, showed the highest Pb levels in waters where the LI values ranged from –2.0 to +0.7 and from +0.4 to +1.3 (pH values in this group varied from 9.0 to 10.4). These "high" pH values may have been created by the application of SiO_2 (1–12 mg/L) for inhibition of corrosion. The authors of this study speculated that the effects of water chemistry adjustments or the addition of chemicals for controlling pipe corrosion might exacerbate the extent of metal leaching from brass fixtures (observed in dezincification studies). Some of these adjustments may be potentially effective treatment strategies for Cu and Pb corrosion control.[37]

A significant laboratory study was conducted for the leaching of Pb from 12 water faucets with various designs, materials of construction and manufacture.[38] Two sources of water were used for the leaching tests: distilled water (the aggressive source) and Cincinnati tap water (the nonaggressive source). It was found that newly cast brass faucets could contribute lead to drinking water in excess of the *proposed* (in 1988) no action level of 0.010 mg/L.[39] Also, 60–75% of the Pb leached from a faucet appeared in the first 125 mL of the collected water. The essential results from this study are found in Figures 10.14 and 10.15, where 24-hour distilled water (DT) 125 mL samples were collected from the cold water (CW) and hot water (HW) sides of each faucet and analyzed for Pb. Wide variations in Pb concentrations were found in both systems. For example, the highest value, 2.2 mg/L Pb, was recorded for the first sample (CW side) from faucet 3 on the second day. Faucets 1, 2, and 3—made of cast brass—produced the highest lead concentrations from both sides. A plastic faucet (#12) yielded undetectable levels of lead <1 mg/L. Samples collected from the CW side always contained higher lead levels than those collected from the HW side. In addition, water samples from the 24 hour tests were analyzed for Zn, Cd, Cr, Cu, and Fe. Of these elements, only zinc was detected in significant amounts. It is noted, also, in Figures 10.14 and 10.15 that several faucets yielded lead concentrations higher than the current action level of 0.015 mg/L.[2]

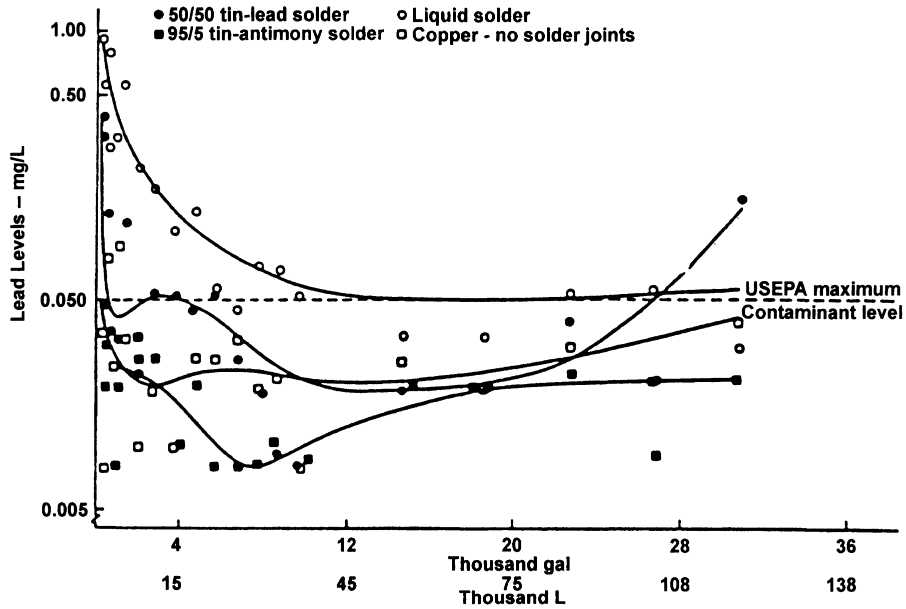

Figure 10.11. Lead levels in drinking water obtained from an aggressive groundwater source (well 3) after flow through plumbing configurations following an 18-h stagnation.[36]

INDICES OF CORROSION

That the electrochemical corrosion of metallic plumbing materials is a complex process is seen from the above discussion. This complexity has prevented the development of a method whereby the occurrence or nonoccurrence of corrosion can be predicted. The "complete" equation would have to include these chemical and physical factors: dissolved oxygen, pH, alkalinity, calcium, magnesium, particulates, organic compounds, buffer intensity, reducible metallic ions, total dissolved solids, such anions as chloride, sulfate, phosphate, and silicate, biological factors, and temperature. Many indices are available that have had limited success in the prediction of corrosion. Many have been misapplied and employed without recognition of their limitations. Generally, calcium carbonate saturation indices do not have any significant predictive value for the corrosion and leaching of lead, zinc, and copper from the many sources cited above.

Calcium Carbonate Saturation Indices

Several chemical indices indicate the corrosiveness of raw and finished water to metallic and A/C pipes. For the most part, they are derived from chemical equilibrium equations for the $CaCO_{3(s)}$ system. In turn, these indices are related to some symptom of corrosion, i.e., "red water" complaints due to the presence of iron by-products. Langelier[40,41] developed a saturation index (LSI) for corrosion protection by a thin film of $CaCO_{3(s)}$ on the interior walls of pipes. This index is calculated from readily obtainable analytical values and indicates the tendency of a natural or finished water either to deposit or dissolve calcium carbonate.

The fundamental reaction in the LSI of Langelier is:

$$CaCO_{3(s)} + H^+ = Ca^{2+} + HCO_3^- \qquad (73)$$

When equilibrium is reached:

$$K_{74} = \frac{[Ca^{2+}][HCO_3^-]}{[H^+]} \qquad (74)$$

Rearranging, taking logs, etc.:

$$pH_s = pCa^{2+} + pHCO_3^- + pK_{74} \qquad (74)$$

where pH_s = equilibrium pH value for Equation 73
pCa^{2+} = equilibrium calcium content
$pHCO_3^-$ = total alkalinity when the pH value is less than 9.5
pK_{74} = arithmetic difference between pK_2 (second protolysis constant for H_2CO_3) and pK_s (solubility product constant for $CaCO_{3(s)}$); i.e., $pK_{74} = pK_2 - pK_s$

Thus, the pH_s is a calculated value from the three terms on the right-hand side of Equation 74.

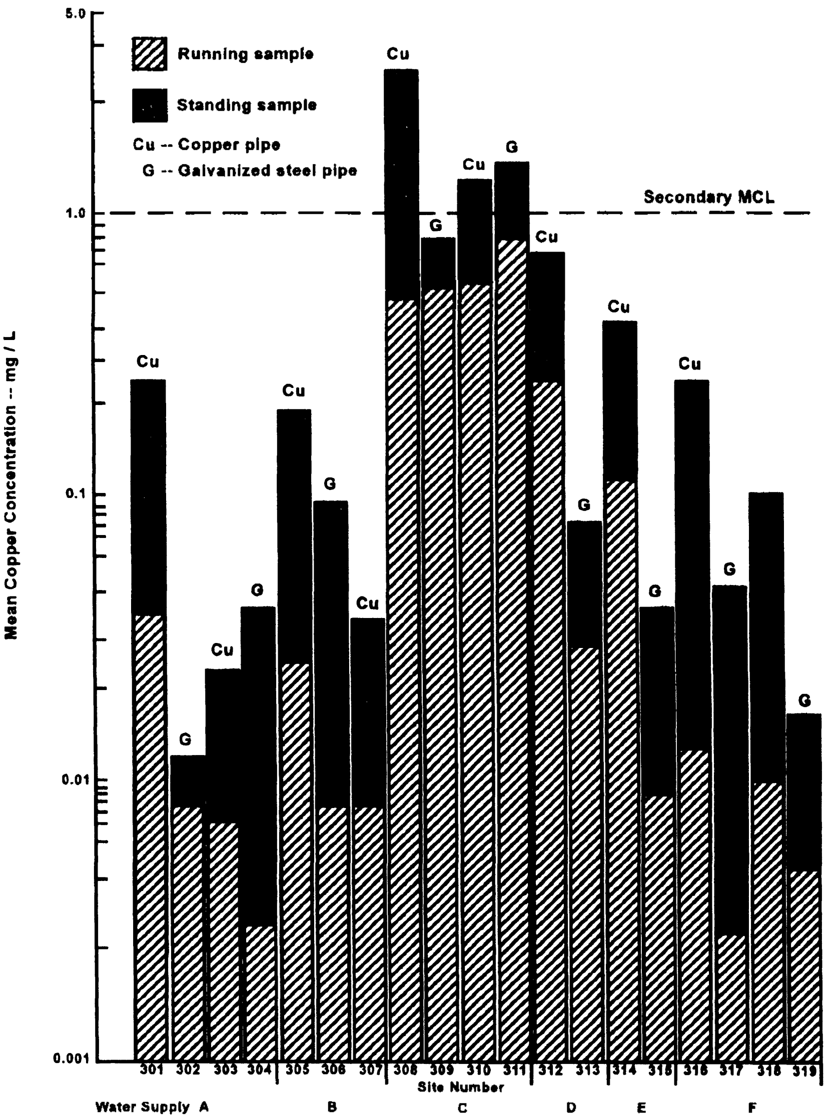

Figure 10.12. Mean concentrations of copper in standing and running water samples collected at each site during a two-year study.[37]

The saturation index is calculated from:

$$\mathrm{LSI} = \mathrm{pH_{ac}} - \mathrm{pH_s} \qquad (76)$$

where $\mathrm{pH_{ac}}$ = actual pH value of the water.

When $\mathrm{pH_{ac}}$ is less than $\mathrm{pH_s}$, negative LSI values are obtained, and the water tends to be corrosive. When the $\mathrm{pH_{ac}}$ is greater than the $\mathrm{pH_s}$, positive LSI values are obtained, and the water tends to be $\mathrm{CaCO_{3(s)}}$ scale forming. When the LSI value is 0, the water is in equilibrium with respect to Equation 73.

Occasionally, there is a need to "correct" Equation 75 for alkalinity due to carbonate above a $\mathrm{pH_{ac}}$ of 9.5 and hydroxyl ions above a $\mathrm{pH_{ac}}$ of 10.5. A definition of total alkalinity (TALK) in waters where the carbonates predominate is:

$$[\mathrm{TALK}] = [\mathrm{HCO_3^-}] + 2[\mathrm{CO_3^{2-}}] + [\mathrm{OH^-}] - [\mathrm{H^+}] \qquad (77)$$

For these situations, the following equation is employed:

$$\mathrm{pH_s} = -\mathrm{pK_{75}} + \mathrm{pCa^{2+}} + \mathrm{p}\left[\mathrm{alk} - [\mathrm{H^+}] - \frac{K_w}{[\mathrm{H^+}]}\right] + \log\left[1 + \frac{2K_2}{[\mathrm{H_s^+}]}\right] \qquad (78)$$

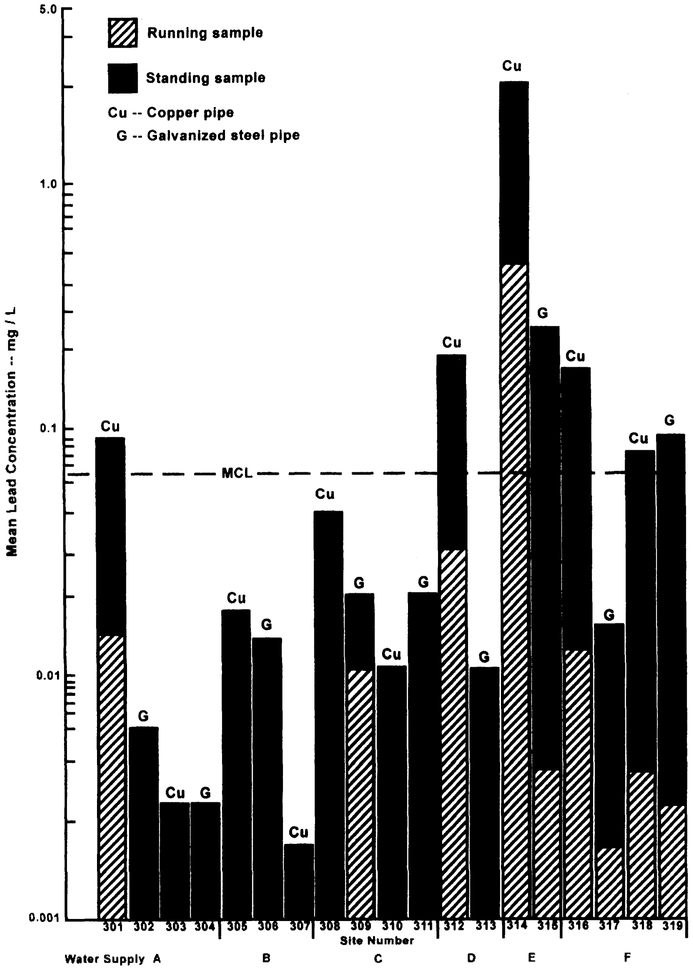

Figure 10.13. Mean concentrations of lead in standing and running water samples collected at each site during two-year study.[37]

Also, corrections should be made in Equations 74 and 78 for the ionic strength, I, of the water due to dissolved and charged ions. The concentration terms should read activities. For example:

$$K_s' = [Ca^{2+}]\gamma_{Ca^{2+}}[CO_3^{2-}]\gamma_{CO_3^{2-}} = (Ca^{2+})(CO_3^{2-}) \qquad (79)$$

where K'_s = thermodynamic infinite dilution solubility product constant for $CaCO_{3(s)}$.

The activity coefficients $\gamma_{Ca^{2+}}$ and $\gamma_{CO_3^{2-}}$ are calculated from the ionic strength of the water. In turn, it is necessary to know the ionic composition of the water in order to calculate the ionic strength. Since the ionic composition is infrequently known for raw or finished waters, there are several pragmatic and generalized methods for calculating I and γ (see Equation 94 and References 10 and 42). In Table 10.13, values of pK_1 and pK_2 are given for carbonic acid and of pK_s for calcium carbonate at various temperatures ranging from 0° to 80°C. Three equations are given in the footnotes of this table whereby these constants may be calculated at temperatures other than those tabulated.

Calculation of pH_s and Langeliers' Saturation Index

There are several techniques for calculation of the pH_s value and, subsequently, the LSI value. Rather complex stability diagrams were constructed initially by Langelier[40] to calculate pH_s from the appropriate variables in Equation 75. Generally, these diagrams are log-log plots of $[Ca^{2+}]$ and $[Mg^{2+}]$ vs. pH (25°C) for a series of total alkalinity curves. After the pH_s value is determined, then the LSI is calculated. These diagrams also may be used to determine the equilibrium concentration of Ca^{2+} at a specified pH_{ac}

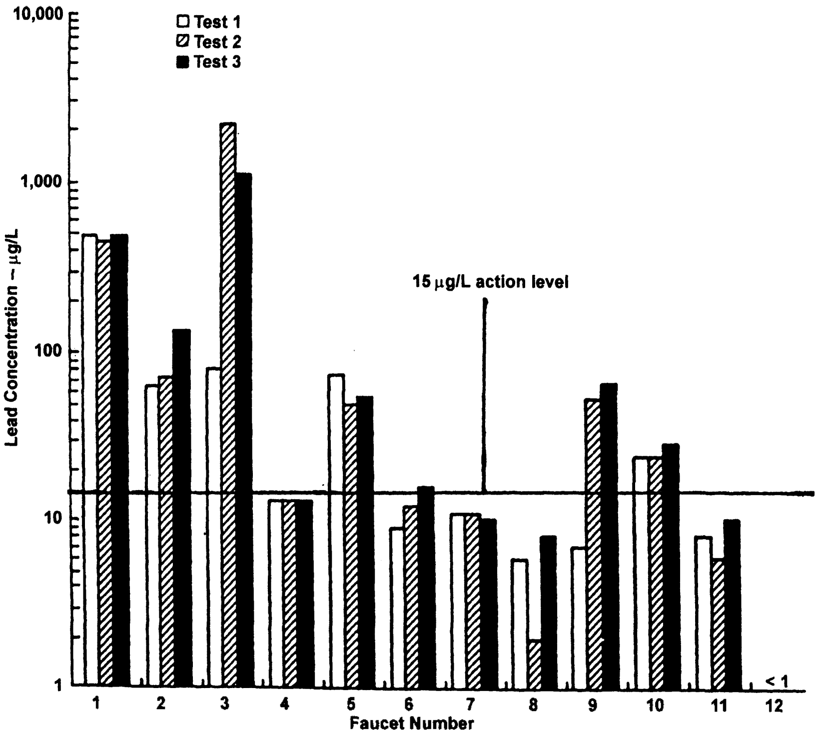

Figure 10.14. Lead leached from cold water side of faucets after one-day detention time (distilled water; 125 mL samples).[38]

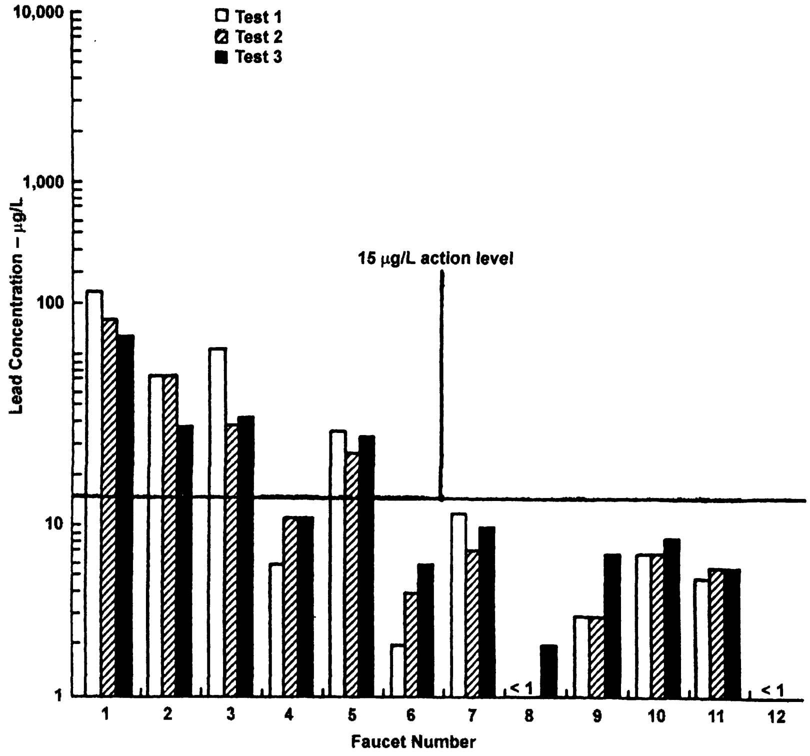

Figure 10.15. Lead leached from hot water faucets after one-day detention time (distilled water; 125 mL samples).[38]

Table 10.13. Thermodynamic Constants for Carbonic Acid and Calcium Carbonate at Various Temperatures and 0.00 Ionic Strength.[53]

Temperature (°C)	pK_1[a]	pK_2[b]	pK_{sc}[c] Calcite	pK_w[d]	A[e]
5	6.52	10.55	8.39	14.73	0.494
10	6.46	10.49	8.41	14.53	0.498
15	6.42	10.43	8.43	14.34	0.502
20	6.38	10.38	8.45	14.16	0.506
25	6.35	10.33	8.48	13.99	0.511
30	6.33	10.29	8.51	13.83	0.515
35	6.31	10.25	8.54	13.68	0.520
40	6.30	10.22	8.58	13.53	0.526
45	6.29	10.20	8.62	13.38	0.531
50	6.29	10.17	8.66	13.26	0.537
60	6.29	10.14	8.76	13.02	0.549
70	6.31	10.13	8.87		0.562
80	6.34	10.13	8.99		0.576
90	6.38	10.14	9.12		0.591

[a] $pK_1 = 356.3094 + 0.06091964\,T - 21{,}834.37/T - 126.8339 \log_{10}T + 1{,}684{,}915/T^2$ (273–373)

[b] $pK_2 = 107.8871 + 0.03252849\,T - 5{,}151.79/T - 38.92561 \log_{10}T + 563{,}713.9/T^2$ (273–373)

[c] $pK_{sc} = 171.9065 + 0.077993\,T - 2{,}839.319/T - 71.595 \log_{10}T$ (273–363)

[d] $pK_w = 4{,}471/T + 0.01706\,T - 6.0875$ (273–333)

[e] $A = 1.82 \times 10^6 (ET)^{-1.5}$ The parameter A is used to calculate pf_m. E = dielectric constant. T = degrees Kelvin.

and total alkalinity. Examples of these diagrammatic calculations are found in the first edition of this book.[46]

Calculation of pH_s may be performed also from the empirical method of Larson and Buswell:[47]

$$pH_s = A + B - \log[Ca^{2+}] - \log[TALK] \qquad (80)$$

where A is constant that reflects the temperature dependence of the difference of $pK_2 - pK_s$, B is the effect of ionic strength based on total dissolved residue, mg/L, and $[Ca^{2+}]$ and [TALK] are expressed as mg/L as $CaCO_3$. Tables 10.14a and b give the appropriate values of A and B as reported, corrected, and updated in Reference 48. The logarithmic values for $[Ca^{2+}]$ and [TALK] are computed on an appropriate calculator. Factor A is based on calcite in Table 10.14a. A-values are available also for the aragonite and vaterite forms of $CaCO_{3(s)}$ in Reference 48.

In the computations of pH_s and LSI, several important mathematical properties of these two corrosion constituents should be noted.[49] There are two possible values for $[H^+]_s$ and pH_s, since they evolve from a quadratic equation that was derived by Rossum and Merrill:[49]

$$[H^+]_s^2 + 2[H^+]_s K_2' = \frac{K_2'\,[Ca^{2+}]}{K_s'}\left(Alk[H^+]_s - K_w' + [H^+]_s^2\right) \qquad (81)$$

Rearranging:

$$[H^+]_s^2\left(1 - \frac{[Ca^{2+}]\,K_2'}{K_s'}\right) + [H+]_s\,K_2'\left(2 - \frac{[Ca^{2+}]\,Alk}{K_s'}\right) + \frac{K_W'\,K_2'}{K_s'}\,[Ca^{2+}] \qquad (82)$$

Solution for $[H^+]_S$ comes from the quadratic formula:

$$[H^+]_s = \frac{-B \pm \sqrt{B^2 - 4AC}}{2A} \qquad (83)$$

where

$$A = 1 - \frac{[Ca^{2+}]\,K_2'}{K_s'}$$

$$B = K_2'\left(2 - \frac{[Ca^{2+}]\,Alk}{K_s'}\right)$$

$$C = \frac{K_W'\,K_2'}{K_s'}\,[Ca^{2+}]$$

Table 10.14a. Constant A as a Function of Water Temperature.[48]

Water Temperature (°C)	A[a]
0	2.25
4	2.18
8	2.11
12	2.05
16	1.98
20	1.92
25	1.85
30	1.78
40	1.64
50	1.51
60	1.39
70	1.26
80	1.14

[a] At any temperature: $A = 2.24961 - 0.017853 \times T + 0.00008238 \times T^2 - 0.00000041 \times T^3$.

Table 10.14b. Correction Factor B[a] for Various Ionic Strengths and Four Temperatures[b].[48]

Ionic Strength[c]	TDS (mg/L)	4°C	16°C	25°C	50°C
0.0000	0	9.70	9.70	9.70	9.70
0.0003	10	9.74	9.74	9.74	9.74
0.0008	30	9.76	9.77	9.77	9.77
0.0013	50	9.78	9.78	9.79	9.79
0.0020	80	9.80	9.80	9.81	9.81
0.0026	100	9.81	9.82	9.82	9.82
0.0038	150	9.84	9.84	9.84	9.85
0.0050	200	9.86	9.863	9.86	9.87
0.0063	250	9.87	9.87	9.88	9.89
0.0075	300	9.89	9.89	9.89	9.90
0.0088	350	9.91	9.90	9.91	9.91
0.0100	400	9.91	9.91	9.92	9.93
0.0125	500	9.91	9.94	9.94	9.95
0.0150	600	9.95	9.95	9.96	9.97
0.0175	700	9.97	9.97	9.97	9.99
0.0200	800	9.98	9.98	9.99	10.00
0.0225	900	9.99	10.00	10.00	10.02
0.0250	1000	10.01	10.01	10.02	10.03

[a] For calcium analyses reported as mg Ca/L rather than mg $CaCO_3$/L, 0.30 should be subtracted from the values for B reported here.

[b] TDS is estimated by Langelier's approximation.[1,2] $TDS = 2.5 \times 10^5\ I$.

[c] $B = 9.7 + [(2.5 \times \sqrt{\mu})/(1.0 + 5.3 \times \sqrt{\mu} + 5.5\mu)]$, where the value of μ is 0.000025 × concentration of dissolved solids.

that yields a positive and a negative root for $[H^+]_s$. This may cause some confusion as to which value should be used. In order to maintain established conventions, for example, a + LSI for oversaturated waters, the lesser of pH_s must always be employed.[49] Another quirk of this mathematical situation is that for pH values above the HCO_3^--CO_3^{2-} equivalence point (circa pH 10.3 to 10.5), the negative root of the quadratic equation applies[50] and the LSI definition should be reversed to:

$$LSI_I = pH_s - pH_{ac} \tag{84}$$

where LSI_r is the reverse of Equation 76.

At these higher pH values, more of the alkalinity comes from the OH^- ion (Equation 78). This double notation of pH_s values can be obtained from the original Langelier diagrams.[40,41]

There are several difficulties with the LSI as a corrosion index:[16,17,48]

a. "Complexation of Ca^{2+} and HCO_3^- is not accounted for, although this is possible if the needed analytical data are available. In the presence of polyphosphates, the equations defining pH will overestimate calcium carbonate saturation unless correction factors are added to account for the complexation.
b. The crystalline form of $CaCO_{3(s)}$ has usually been assumed to be calcite. The presence of another form of $CaCO_{3(s)}$, aragonite, which has a higher solubility, has, however, been observed in several systems. The formation of other forms of $CaCO_{3(s)}$ may account for some of the observations of substantial supersaturation with respect to calcite.
c. A deposit of $CaCO_3(s)$ does not necessarily aid in preventing corrosion.
d. $CaCO_3$, if present in high enough concentrations, can also be deposited from waters with a negative LSI because of the localized high pH next to the pipe, which is generated by the cathodic reactions.
e. The preoccupation of many with maintaining a positive LSI has led to excessive deposition of $CaCO_{3(s)}$ and to significant decreases in the capacity of distribution systems to carry water."[6]
f. Oversaturation does not guarantee precipitation of $CaCO_{3(s)}$. A certain portion of oversaturation must be present before crystal nucleation can occur.
g. Phosphates and polyphosphates, certain naturally occurring organics and magnesium can inhibit $CaCO_{3(s)}$ precipitation from oversaturated waters.
h. Deposits of $CaCO_{3(s)}$ have been found in systems conveying undersaturated water. A locally oversaturated water may occur where high pH values are generated at the cathodic areas of corroding metal surfaces.

Since the LSI calculation is based upon the thermodynamic solubility constant of $CaCO_{3(s)}$, it can only predict whether precipitation or dissolution should occur. Unfortunately, it does not predict how much $CaCO_{3(s)}$ will precipitate or whether its structure will provide resistance to corrosion. The LSI value alone cannot predict how much $CaCO_{3(s)}$ will precipitate. For example, it was shown that an LSI of 0.9 is necessary to precipitate 10 mg/L of $CaCO_3$ at an alkalinity of 50 mg/L as $CaCO_{3(s)}$, but an LSI of only 0.2 is necessary for the same amount of precipitation if the alkalinity is 200 mg/L.[51]

Calcium Carbonate Precipitation Potential

The term calcium carbonate precipitation potential (CCPP) was employed by Merrill and Sanks[52] to denote the quantity of $CaCO_3$ that, theoretically, can be precipitated from oversaturated waters or dissolved by undersaturated waters. This concept is applied now for corrosion control, where it is necessary to calculate the quantity of $CaCO_3$ that *will* precipitate. Several sources have published procedures for calculation of CCPP.[49,52] An excellent summary of the equations needed for these calculations is presented here from Reference 6.

The essential equation for CCPP is:[49]

$$\mathrm{CCPP} = 50{,}000\,(\mathrm{TALK}_i - \mathrm{TALK}_{eq}) \qquad (85)$$

where CCPP is in units of mg/L $CaCO_3$ and subscripts i and eq, refer to the initial and equilibrium conditions, respectively. When $CaCO_3$ precipitates, the equivalents of Ca^{2+} precipitated must be equal to the equivalents of alkalinity precipitated. In such a system, the acidity (ACY) is conserved in this process so that $ACY_i = ACY_{eq}$.[49]

ACY_i may be computed from the relationship:[49]

$$\mathrm{ACY}_i = \left(\frac{\mathrm{TALK}_i + s_i}{t_i}\right) p_i + s_i \qquad (86)$$

where

$$p = \frac{2[H^+]_i + K_1}{K_1} \qquad (87)$$

$$s = [H^+]_i - \frac{K_w}{[H^+]_i} \qquad (88)$$

$$t = \frac{2K_2 + [H^+]_i}{[H^+]_i} \qquad (89)$$

When a condition of equilibrium is reached after precipitation, the alkalinity is related then to ACY_i:

$$\mathrm{TALK}_{eq} = \frac{t_{eq}}{p_{eq}}(\mathrm{ACY}_i - s_{eq}) - s_{eq} \qquad (90)$$

where the terms t_{eq}, p_{eq}, and s_{eq} correspond to those in Equations 87–89 with $[H^+]_i$ replaced by $[H^+]_{eq}$.

The $TALK_{eq}$ also can be related to the $[Ca^{2+}]_i$ and $TALK_i$ through:

$$2[Ca^{2+}]_i - \mathrm{TALK}_i = \frac{2K_s r_{eq}}{\mathrm{TALK}_{eq} + s_{eq}} - \mathrm{TALK}_{eq} \qquad (91)$$

in which:

$$r_{eq} = \frac{[H^+]_{eq} + 2K_2}{K_2} \qquad (92)$$

Combining Equations 91 and 92 gives the relationship:[49]

$$2[Ca^{2+}]_i - TALK_i = \frac{2K_s r_{eq} p_{eq}}{t_{eq}\,(ACY_i - s_{eq})} - \frac{t_{eq}\,(ACY_i - s_{eq})}{p_{eq}} + s_{eq} \qquad (93)$$

Values for $[Ca^{2+}]_i$ and $TALK_i$ are obtained from chemical analysis, whereas ACY_i is computed from Equation 86. The terms t_{eq}, s_{eq}, r_{eq}, and p_{eq} are functions of $[H^+]_{eq}$ and must be obtained through an iterative trial and error solution of Equation 93.[49] After calculation of $[H^+]_{eq}$, then $TALK_{eq}$ can be computed from Equation 90 and substituted into Equation 85 along with $TALK_i$ to obtain the CCPP.

Values of CCPP may be positive and denote oversaturation and the mg/L of $CaCO_3$ that should precipitate. A negative CCPP indicates undersaturation and how much $CaCO_3$ should dissolve.

Solution of Equation 93 for $[H^+]_{eq}$ requires a programmable calculator or PC spreadsheet software where a simple manual trial and error substitution is employed. The quantity $ACY_i - s_{eq}$, must always be greater than zero. It should be constantly checked when solving for $[H^+]_{eq}$.[49]

It must be noted that there is a difference between $[H^+]_s$ used with the Langelier saturation index and the $[H^+]_{eq}$ used with CCPP. $[H^+]_s$ is the hydrogen ion concentration of a water with a specific chemical composition that is in equilibrium with solid calcium carbonate. $[H^+]_{eq}$ is the final hydrogen ion concentration that occurs after initial water has either precipitated or dissolved $CaCO_3$ to reach saturation equilibrium. These latter two statements should be interpreted in the subjunctive of chemical thermodynamics.

Comparison of Methods for Calculating $CaCO_3$ Saturation Indices

In this section, three different methods are compared for their prediction of scale formation tendencies.[6] A hypothetical water has the following characteristics:

pH	8.35
Temperature	25°C
Ionic strength	0.012
TDS	480
Calcium	40 mg/L as Ca or 100 mg/L as $CaCO_3$
Magnesium	25 mg/L
Sodium	120 mg/L
Total alkalinity	100 mg/L (as $CaCO_3$)
Sulfate	150 mg/L
Chloride	163 mg/L

The first method utilizes Equation 80, which is the simplified procedure of Larson and Buswell.[47] Using the above values and the constants A for calcite and B from Tables 10.14a and b yields:

$$pH_s = 1.85 + 9.93 - 2 - 2 = 7.78$$

$$LSI = 8.35 - 7.78 = 0.57$$

The second method utilizes the quadratic Equation 82 of Rossum and Merrill,[49] which in turn requires several initial computations. For example, the equilibrium constants of K'_w, K'_2, and K'_s must be computed for the temperature and ionic strength (I) of the water. Reference 53 gives three formulas for calculation of I. However, the empirical relationship of Langelier[41] suffices for most waters:

$$I = 2.5 \times 10^{-5}\,[TDS] \qquad (94)$$

where the [TDS] is in mg/L.

After calculation of the appropriate activity coefficients from the ionic strength, the equilibrium constants for Equation 82 are: $K'_2 = 7.368 \times 10^{-11}$, $K'_w = 1.263 \times 10^{-14}$, and $K'_s = 9.413 \times 10^{-9}$. In turn, the concentrations of Ca^{2+} and TALK are: 9.980×10^{-4} *M* and 1.998×10^{-3} eq/L, respectively. The constant terms for the quadratic Equation 82 are: $A = 0.99999$, $B = -1.5463 \times 10^{-8}$, and $C = 9.8651 \times 10^{-20}$. Solving this equation with the quadratic formula (Equation 83) yields $[H^+]_s = 1.5457 \times 10^{-8}$ *M* (the more appropriate physical root). This $[H^+]_s$ is converted to $(H^+)_s$ via multiplication by its activity coefficient (0.893), which in turn yields a pH of 7.86. Consequently,

$$LSI = 8.35 - 7.86 = 0.49$$

The difference between this value and 0.57 may be due to differences in equilibrium constants and the assumption that all of the TALK is composed of the HCO ion.

The third method is based upon a computer program whose acronym is PHREEQE.[54] (Reference 53 gives the sources and addresses for several computer programs and diagrams for the calculation of $CaCO_3$ indices.) An LSI value of 0.47 was obtained from the PHREEQE program for the hypothetical water.[6] The author of this close result to the 0.49 obtained from Equation 82 argues that it is fortuitous and misleading. The reason given was that the PHREEQE computer model indicated a 13% availability of nonbound or "free" Ca^{2+} ion. The remainder was bound in ion pairs and complexes. Nevertheless, there is remarkable agreement between the three methods that calculated the LSI value. For routine assessment of the corrosive nature of water supplies, this author prefers Equation 80 because of its simplicity. It is certainly accurate enough to predict the tendency of a water to be corrosive or not.

Example Problem 10.1: Calculation of the Langelier Stability Index for Natural Waters

a. A groundwater in Salem County, New Jersey has the following water quality characteristics: pH=5.3, alkalinity=12 mg/L as $CaCO_3$, Ca^{2+}=62 mg/L as $CaCO_3$, temperature=16°C, and TDS=250 mg/L. Calculate the pH_s and the LSI.

   1. Use Equation 80 and Tables 10.14a and b for the appropriate constants:
      $pH_s = 1.98 + 9.87 - \log 62 - \log 12$
      $pH_s = 8.98$
   2. From Equation 76:
      $LSI = 5.3 - 8.98 = -3.68$

   This LSI value indicates that this water should have a severe tendency to corrode metallic plumbing.

b. A groundwater in Hunterdon County, New Jersey has these water quality characteristics: pH=8.4, alkalinity=145 mg/L as $CaCO_3$, Ca^{2+}=110 mg/L as $CaCO_3$, temperature=12°C, and TDS=258 mg/L.

   1. Use Equation 80 and Tables 10.14a and b for the appropriate constants:
      $pH_s = 2.05 + 9.87 - \log 110 - \log 145$
      $pH_s = 7.72$
   2. From Equation 76:
      $LSI = 8.4 - 7.72 = +0.68$

   This water should not be corrosive and should precipitate $CaCO_3$.

Example Problem 10.2: Calculation of the CCPP.

A computer spreadsheet and/or program is necessary to calculate the CCPP, since several of Equations 85–93 require iteration for their solution. Table 10.15 gives an example of a computerized calculation of the CCPP for a hypothetical water.[55] The terminology and symbols are consistent in this table with Equations 85–93. Lines 1–3 are the given water quality characteristics. Lines 4–7 are the equilibrium constants corrected for ionic strength and temperature. Lines 8–16 were calculated from the appropriate equations. Lines 17–21 were iterated and Line 22, the CCPP, was calculated from Equation 85 after the iterative values of $TALK_{eq}$ and $[H^+]_{eq}$ were obtained. In this example, the positive CCPP of 6.6 mg/L indicates oversaturation and the amount of $CaCO_3$ that should precipitate. Here again, the subjunctive thermodynamics limits interpretation of this CCPP model.

Other Indices

Ryznar[56] stated that "the saturation index, however, is not always reliable in predicting this (scale-forming or corrosion) because some waters with a positive index actually may be quite corrosive." It was stated also that "one reason for this is the fact that the Langelier index does not indicate how much calcium carbonate will deposit; whether a state of supersaturation will be present which will be great enough to produce a precipitate, and whether it is great enough to give a protective film." Whereupon, Ryznar proposed an empirical expression that was labeled the stability index (StI for convenience):

$$StI = 2pH_s - pH \tag{85}$$

In this system, the stability index will be positive for all waters. Two examples are:

Water A, 75°C	Water B, 75°C
pH_{ac} 6.5	pH_{ac} 10.5
pH_s 6.0	pH_s 10.0
SI +0.5	SI +0.5
StI +5.5	StI +9.5

According to Ryznar, water A will give an appreciable amount of $CaCO_{3(s)}$ scale, whereas water B will form a limited amount of scale and may be severely corrosive, especially at higher temperatures. Experimental data are given to support this interpretation (Figure 10.16). That waters with high pH values will form less scale and have positive StI values is consistent with the fact that $CaCO_{3(s)}$ solubility decreases with an increase in pH value and an increase of temperature.[10] These waters simply do not have the Ca^{2+} and CO_3^{2-} to form $CaCO_{3(s)}$.

The Ryznar index does not offer any significant advantages over the indices cited above for calculation of the state of $CaCO_3$ saturation or undersaturation. Rather, it is an empirical mathematical manipulation of the LSI that was developed from observations of corrosion rates and film formation in steel mains and heated water in glass coils.[6]

Caldwell and Lawrence[57,58] published a series of diagrams that are similar to Langelier's, one of which is seen in Figure 10.17. These diagrams can be used for both corrosion control and water softening by the lime-soda process (see Chapter 8). Two examples are cited for use of the C-L diagrams:

Table 10.15. Spreadsheet for Calculating CCPP.[55]

Determine CCPP
Given: pH = 8.6
Alk = 90 mg/L as $CaCO_3$
Cal = 100 mg/L as $CaCO_3$
Temp = 20°C

No.	Variable		Definition	Comments	Input	Output
1	Ca	=	Calcium, mol/L[a]	given	1.0E–03	
2	Alk_i	=	Alkalinity, equiv/L[a]	given	1.8E–03	
3	H_i	=	Hydrogen ion, mol/L[a]	given	2.5E–09	
4	K'_{sp}	=	Solubility constant, $CaCO_3$	see text	5.4E–09	
5	K'_w	=	Dissociation constant for water	see text	6.8E–15	
6	K'_1	=	1st Carbonic dissociation constant	see text	4.2E–07	
7	K'_2	=	2nd Carbonic dissociation constant	see text	4.2E–11	
8	R_{eq}	=	$(H_{eq} - 2^{*}K'_2)/K'_2$	calculated–92		3.0E+02
9	P_{eq}	=	$(2^{*}H_{eq} + K'_1)/K'_1$	calculated–87		1.1E+00
10	T_{eq}	=	$(2^{*}K'_2 + H_{eq})/H_{eq}$	calculated–89		1.0E+00
11	S_{eq}	=	$H_{eq} - K'_w/H_{eq}$	calculated–88		–5.2E–07
12	P_i	=	$(2^{*}H_i + K'_1)/K'_1$	calculated–87		1.0E+00
13	S_i	=	$H_i - K'_w/H_i$	calculated–88		–2.7E–06
14	T_i	=	$(2^{*}K'_2 + H_i)/H_i$	calculated–89		1.0E+00
15	Acy_i	=	$[(Alk_i + S_i)/T_i]^{*}P_i + S_i$	calculated–86		1.8E–03
16	Alk_{eq}	=	$T_{eq}/P_{eq}{}^{*}(Acy_i - S_{eq}) - S_{eq}$, mg/L[b]	calculated–90		83.4
17	$Term_1$	=	$2^{*}K'_{sp}{}^{*}R_{eq}{}^{*}P_{eq}/T/(Acy_i - S_{eq})$	calculated–93		1.9E–03
18	$Term_2$	=	$(Acy_i - S_{eq})^{*}T_{eq}/P_{eq}$	calculated–93		1.7E–03
19	H_{eq}	=	Equilibrium H, mol/L[c]	iterate	1.3E–08	
20	$Term_0$	=	$2^{*}Ca - Alk_i$	calculated–93		2.0E–04
21	Right	=	$Term_1 - Term_2 + S_{eq}$	calculated–93		2.0E–04
22	CCPP	=	$Alk_i - Alk_{eq}$, mg/L as $CaCO_3$[c]	calculated–85		6.6

[a] Convert given information into proper units of mol/L and equiv/L.

[b] Cover to mg/L by multiplying by 50,000.

[c] Iteration can be accomplished by several procedures. Manual iteration requires the user to input various values of H_{eq} until rows 20 and 21 converge. Another option in spreadsheets such as Lotus 123 and Microsoft Excel allows cells to be "dependent" on one another. In this case, rows 20 and 21 could be equated and the recalculate key used to iterate. Macros could also be written that would iterate using a loop command.

	Water C	Water D
Temperature (°C)	15.0	15.0
Total Dissolved Solids (mg/L)	96.0	115.0
pH	8.6	9.5
Ca^{2+} (mg/L as $CaCO_3$)	70.0	28.0
Alk (mg/L as $CaCO_3$)	37.0	70.0

When the values for pH, $[Ca^{2+}]$, and [alk] from water C are plotted on the C-L diagram (Figure 10.17), they form a triple point A. This is interpreted to be a water whose Ca^{2+} and CO_3^{2-} are in equilibrium. When these three values from water D are plotted, they do not form a triple point. Rather, three double points B, C, and D result. In order to determine the over- and undersaturation, the $[Ca^{2+}]$ at the intersection of the pH and alkalinity values, point C, is compared with the actual $[Ca^{2+}]$. If the measured $[Ca^{2+}]$ is greater than the graphical value, the water is oversaturated and $CaCO_{3(s)}$ should form. For this example, the actual $[Ca^{2+}]$ is 28 mg/L, whereas the graphical value is 6 mg/L. Undersaturation is denoted where the $[Ca^{2+}]_{ac} < [Ca^{2+}]_{graph}$. C-L diagrams are available at 2, 5, 15, and 25°C and at 40, 400, and 1200 mg/L TDS.

Summary of Methods for Calculation of $CaCO_3$ Saturation Indices

This summary is adapted from Method 2330, Calcium Carbonate Saturation, which was developed for the 18th edition of *Standard Methods.*[59] Reference 53 contained essentially the same information. There are two general categories of $CaCO_3$ saturation indices: (a) those that determine whether a water has a tendency to precipitate or to dissolve $CaCO_3$ (i.e., the LSI), and (b) those that estimate the quantity of $CaCO_3$ that can be precipitated from an oversaturated water, and the amount that can be dissolved by an undersaturated water (i.e., the CCPP).

The reader is reminded that several water quality characteristics must be measured to calculate the $CaCO_3$ satura-

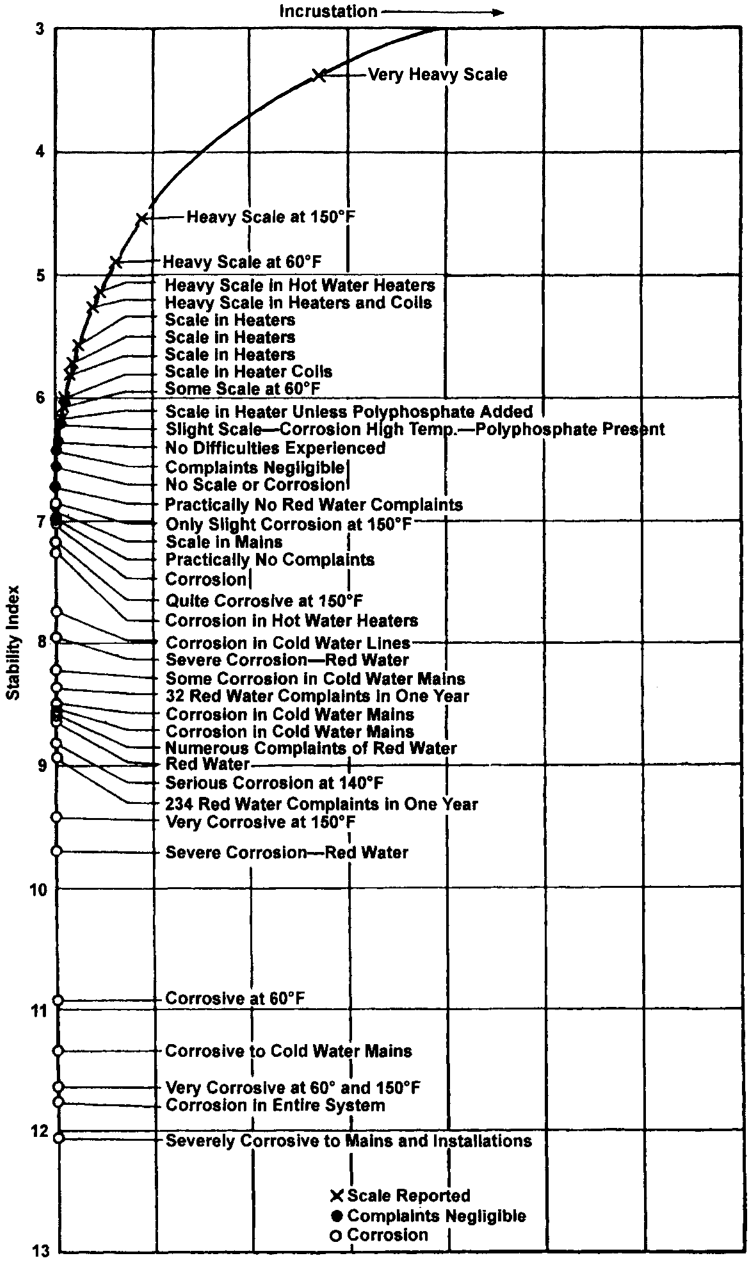

Figure 10.16. Field observations of Ryznar's stability index. Reproduced from Ryznar,[56] courtesy of the American Water Works Association.

tion indices.[53] Minimum requirements are: total alkalinity, total Ca^{2+}, pH, total dissolved solids, and temperature. The I must be calculated or estimated from conductivity or TDS measurements via one of these equations:

$$I = 1/2\Sigma[X_i]Z_i^2 \text{ (preferred)} \qquad (96)$$

$$I = 1.6 \times 10^{-5}C \text{ (second choice)} \qquad (97)$$

$$I = TDS/40{,}000 \text{ (third choice)} \qquad (98)$$

where $[X_i]$ = concentration of component i, molar, Z_i=charge of species i and C=conductivity, μmho/cm.

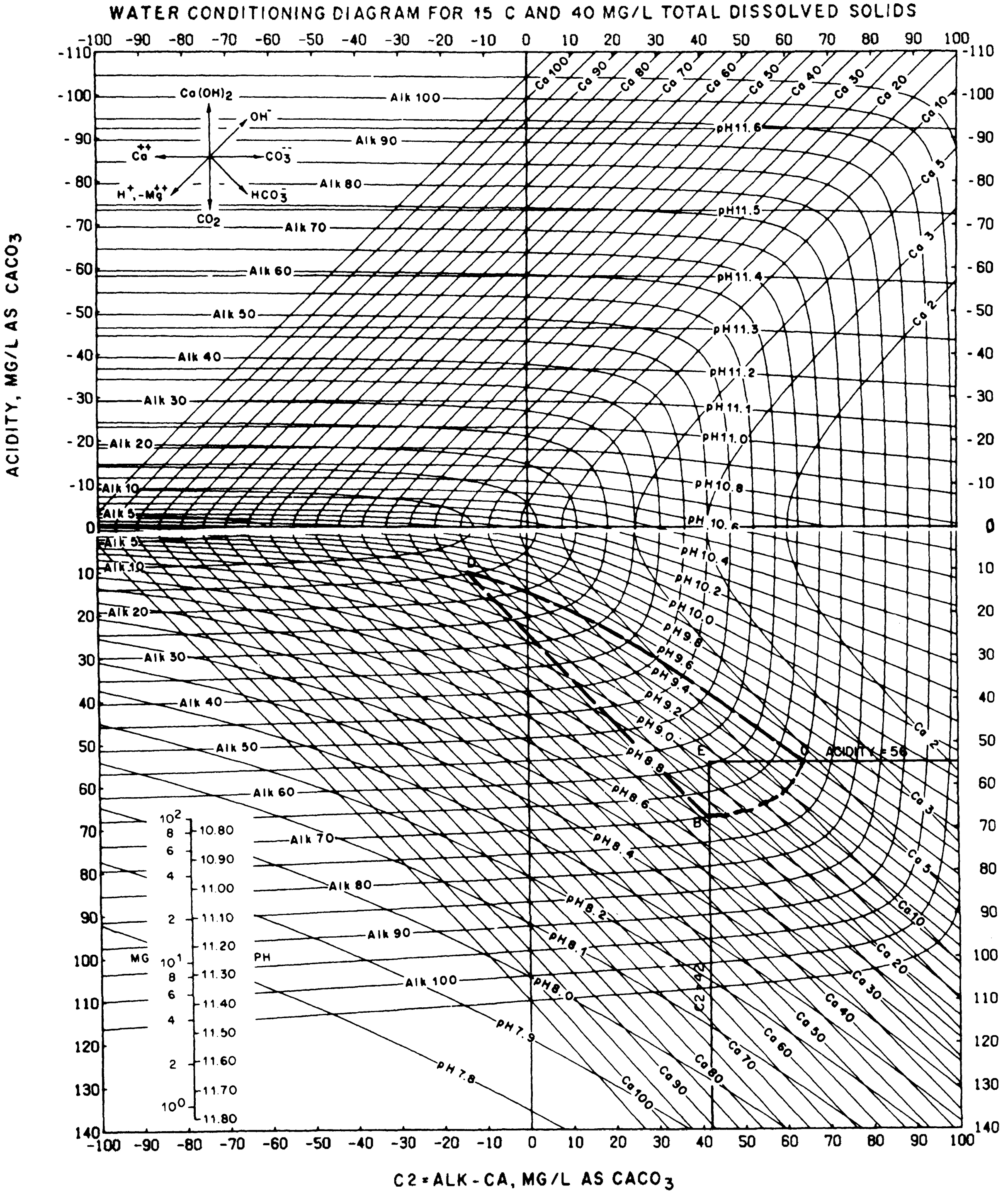

Figure 10.17. Caldwell-Lawrence water conditioning diagram for corrosion control. Reproduced from Caldwell and Lawrence,[57] courtesy of the American Chemical Society.

The pH should be measured at the system's water temperature with a temperature-compensated meter. When pH and alkalinity are measured, the CO_2 exchange between sample and the atmosphere must be minimized. Laboratory techniques are available for pH measurements that minimize the effect of CO_2 exchange.[60]

Manual calculations, diagrams, experimental systems, and computer programs are available for pH_s, LSI, and CCPP determinations. Sample calculations are given above and in References 53 and 59. Table 10.16 gives the state-of-the-art in graphs and computer software employed to calculate the $CaCO_3$ indices. It is taken from Reference 59, which was published in 1992. The reader should consult the various footnotes in order to obtain the current and updated computer programs.

CORROSION CONTROL STRATEGIES

Thermodynamically, it is impossible to eliminate corrosion of metallic plumbing completely. This is observed in the equilibrium potential-pH diagrams in Figure 10.3.[8] Rather, corrosion control involves reduction and/or inhibition of the rate at which metals corrode. Specific water quality and pipe material are the major factors that promote corrosion.[61] Consequently, a corrosion control strategy in one system may not work in another.

There are three basic approaches to corrosion control:[4] (a) modify the water quality so that it is less corrosive to the pipe material, (b) place a protective barrier or lining between the water and the pipe, and (c) use pipe materials and design the system so that it is not corroded by a particular water.

According to the manual for operators,[4] corrosion control can be achieved by: (a) select proper system materials and design systems adequately, (b) modify water quality, (c) use inhibitors, (d) provide cathodic protection (Figure 10.3), and (e) use corrosion-resistant linings, coatings, and paints. The reader is directed to Reference 6 for item (a), whereas (b)–(e) are discussed below.

Modification of Water Quality

Corrosion control via modification of water quality can be characterized by two general approaches to the inhibition of lead and copper dissolution:[55] (a) form a precipitate in the system that deposits onto the pipe wall to create a protective coating, or (b) create a chemical environment in which the pipe material and the water interact in such a way that metallic compounds are formed on the pipe's surface. The latter creates a film of less soluble material. These two items provide the conceptual framework for corrosion control, as seen in Table 10.17.[55]

The difference in these two approaches is the mechanism by which the protective film is formed, for example *precipitation* of a relatively insoluble compound $CaCO_3$, for example, onto the pipe wall by adjustment of the water chemistry. *Passivation* of the pipe material occurs through the formation of such less soluble compounds as carbonates and phosphates that adhere to the pipe wall. These two mechanisms are also operative for corrosion control of such nonmetallic pipe materials as asbestos-cement (AC) pipe.

In Table 10.17, *alkalinity* and *pH adjustment* refer to the modification of pH and/or alkalinity (a surrogate for dissolved inorganic carbon [DIC]) that induces the formation of less soluble compounds with the pipe materials. The *passivation* mechanism is involved in this type of corrosion control. *Calcium adjustment* refers to the modification of the $CaCO_3$ system's equilibrium so that a tendency for precipitation of this compound results. This method of corrosion control depends upon *precipitation* as the means of protecting distribution systems. *Corrosion inhibitors* refer to the application of specially formulated chemicals characterized by their ability to form metal complexes that reduce corrosion. *Passivation* is the mechanism of corrosion control of the metallic surface. The common *corrosion inhibitors* include orthophosphates, polyphosphates, polyorthophosphate blends, and silicates.

Alkalinity and pH Adjustment

That $[H^+]$ plays an important role in the corrosion of metallic plumbing was seen above in Reactions 10.21(Fe), 10.34(Cu), 10.47(Pb), and 10.64 (Zn). These reactions suggest that, at high concentrations of H^+, corrosion is enhanced. On the other hand, a decrease in $[H^+]$ (i.e., increase in pH) retards or inhibits the rate of corrosion (Figure 10.3) via several chemical mechanisms. An increase in the pH value increases the $[OH^-]$, which in turn decreases the solubility of metals that have relatively insoluble hydroxides, basic carbonates, and oxides. If carbonate alkalinity is present, raising the pH value to circa 10.0 will increase the amount of CO_3^{2-} ion in solution. This will control the solubility of such metals as Cu and Pb that have insoluble basic carbonates. This is the role of pH in the *passivation* mechanism of corrosion control.

The solubility of $CaCO_{3(s)}$ is governed by a complex relationship of $[H^+]$, dissolved inorganic carbon (DIC), CO_2 acidity, and ionic strength. In order to deposit a protective scale of $CaCO_{3(s)}$ on the interior pipe surfaces, the pH value of the water must be slightly higher than the pH value required for its precipitation when the requisite amounts of DIC and $[H^+]$ are present. It must be emphasized that pH adjustment alone is not sufficient to control corrosion in water where the DIC concentrations are low.

Table 10.18 is a summary of the various chemicals that are employed in corrosion control treatment for pH/alkalinity and calcium adjustments. Selection of the appropriate chemical is dictated by such local conditions as cost, shipment, and personal preference.

Table 10.16. Graphs and Computer Software That Can Be Used to Calculate $CaCO_3$ Saturation Indices[a].[59]

Item[b]	$CaCO_3$ Indices		Approximate Temperature Range (°C)	Approximate Limit of Ionic Strength	Ion Pairs Considered?	Alk_0 Considered?[c]	Minimum Equipment Required
	Basis for Calculation of SI	CCPP					
1. Caldwell-Lawrence diagrams	pH_{sa}	P,D	2–25	0.030	No	No	Diagrams
2. ACAPP	RS	P,D	−10–110	6+	Yes	Yes	IBM-compatible PC, 512K bytes of RAM, MS DOS or PC DOS v. 2.1 or higher
3. DRIVER	RS	P	7–65	2.5	Yes	Yes	Mainframe computer
4. INDEX C	pH_{sa}, pH_{sb}	P,D	0–50	0.5	No	No	Hewlett-Packard 41C calculator, with three memory modules
5. LEQUIL	RS	No	5–90	0.5	Yes	Yes	IBM-compatible PC, 512K bytes of RAM, Lotus 1-2-3 or work-alike, PC DOS or MS DOS v. 2.0 or higher
6. MINTEQAI	RS	P,D	0–100	0.5	Yes	Yes	IBM-compatible PC, 512K bytes of RAM, PC DOS v. 3.0 or higher, 10 megabyte hard disk drive, math coprocessor useful but not required
7. PHREEQE Standard	RS	P,D	0–100	0.5	Yes	Yes	IBM-compatible PC, known to work with 512K RAM PC DOS or MS DOS v.2.11 or higher. Also available for mainframe computers
For high-salinity waters	RS	P,D	0–80	7–8	Yes	Yes	IBM-compatible PC, 640K RAM recommended, with math coprocessor, MS DOS v.3.2 or higher
8. SEQUIL	RS	P,D	7–65	2.5	Yes	Yes	IBM-compatible PC, 512K bytes of RAM, MS DOS or PC DOS v.2.1 or higher
9. SOLMINEQ.88	RS	P,D	0–350	6	Yes	Yes	IBM-compatible PC, 640K RAM, math coprocessor, PC DOS or MS DOS v.3.0 or higher. Also available for mainframe computer.

10. WTRCHEM	pH_{sa}	P,D	0–100	0.5	No	No	Any PC equipped with a BASIC interpreter, 5K RAM
11. WATEQ4F	RS	No	0–100	0.5	Yes	Yes	IBM-compatible PC, known to work with 512K RAM, PC DOS or MS DOS v.2.11 or higher.

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[a] SI = saturation index
CCPP = $CaCO_3$ precipitation potential
pH_{sa} = alkalinity-based pH
pH_{sb} = bicarbonate-based pH
P = calculates amount of $CaCO_3$ theoretically precipitated
D = calculates amount of $CaCO_3$ theoretically dissolved
RS = relative saturation
PC = personal computer
RAM = random access memory

[b] 1. Loewenthal and Marais[3] provide 10.2- by 11.4-cm diagrams, with documentation; Merrill[5] provides 10.2- by 16.5-cm diagrams, with documentation.
2. Radian Corp., 8501 MoPac Blvd., P.O. Box 201088, Austin, TX 78720-1088 Attn: J.G. Noblett (software and documentation).
3. Power Computing Co., 1930 Hi Line Dr., Dallas, TX, 74207 (software and documentation[6]).
4. Brown and Caldwell, P.O. Box 8045, Walnut Creek, CA 94596-1220 Attn: D.T. Merrill (software and documentation).
5. Illinois State Water Survey, Aquatic Chemistry Section, 2204 Griffith Dr., Champaign, IL 61820-7495 Attn: T.R. Holm (software and documentation).
6. Center for Exposure Assessment Modeling, Environmental Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Athens, GA 30613 (software and documentation).
7. U.S. Geological Survey, Water Resources Division, MS 420, 345 Middlefield Rd., Menlo Park, CA 94025 Attn: K. Nordstrom (provides software for personal computer version of standard code); National Water Research Institute, Canada Centre for Inland Waters, 867 Lakeshore Rd., Burlington, Ontario, Canada L7R 4A6 Attn: A.S. Crowe (provided software and documentation[8,9] for personal computer version of both standard and high-salinity codes); U.S. Geological Survey, Books and Open File Report Section, Box 25425, Federal Center, Denver, CO 80255 (provides documentation[8,10] for mainframe and personal computer versions of standard code).
8. Power Computing Company, 1930 Hi Line Dr., Dallas, TX 74207 (software and documentation[11]).
9. U.S. Geological Survey, Water Resources Division, MS 427, 345 Middlefield Rd., Menlo Park, CA 94025 Attn: Y.K. Kharaka (software and documentation[12]).
10. D.T. Merrill, Brown and Caldwell, P.O. Box 8045, Walnut Creek, CA 94596-1220 (code listing and documentation).
11. U.S. Geological Survey, Water Resources Division, MS 420, 345 Middlefield Rd., Menlo Park, CA 94025 Attn: K. Nordstrom (software). Books and Open File Report Section, Box 25425, Federal Center, Denver, CO 80225 (documentation[13]).

[c] Codes differ in the species included in Alk_0.

Table 10.17. Conceptual Framework for Corrosion Control Approaches.[55]

Control Mechanism	Passivation		Precipitation
Treatment Approach	pH/Alkalinity Adjustment	Corrosion Inhibitor	Calcium Adjustment
Key Water Quality Parameters	pH, Alkalinity, TDS, Temperature	pH, Alkalinity, Metals, Hardness, Temperature	Calcium, pH, Alkalinity, TDS, Temperature
Appropriate Chemical Feed Systems	Lime Soda Ash Sodium Bicarbonate Caustic Soda Carbon Dioxide	Orthophosphate Silicates Polyphosphate Ortho-Polyphosphate	Lime Soda Ash Sodium Bicarbonate Caustic Soda Carbon Dioxide

Passivation Control of Lead and Copper Corrosion

Lead and copper can form insoluble carbonates (Reactions 10.57 and 10.37) and, more likely, their basic carbonates, $Pb_3(CO_3)_2(OH)_2$ (Reaction 10.58), and $Cu_2CO_3(OH)_2$ (Reaction 10.42) that minimize corrosion rates and dissolution of these metals in water distribution systems. An important question is whether or not the solubility of these solid phases can achieve the action levels of Pb, $10^{-7.14}$ M (0.015 mg/L) and Cu $10^{-2.04}$ M (1.3 mg/L). Obviously, CO_3^{2-} ions must be available in the water supply for these precipitations to occur. If there is a carbonate deficiency, then soda ash (Na_2CO_3) or sodium bicarbonate ($NaHCO_3$) are the preferred chemicals. They adjust the pH value also.

The formation of effective Pb and Cu carbonate films depends upon pH and DIC. Figure 10.18 shows the relationship of titrated alkalinity to DIC at several pH values.[62] This graph assumes that alkalinity comes principally from the OH^- ion and the carbonate system. The DIC content, in mol/L, is obtained directly from the measured *in situ* pH value and total alkalinity in equivalents/L. DIC, mol/L, can be converted to mg C/L by multiplying by 12,011. In turn, mg C/L can be converted to mg $CaCO_3$/L by multiplying by 8.331. Total alkalinity in equivalents/L can be derived from mg $CaCO_3$/L by dividing by 50,044.5. Figure 10.18 is at a temperature of 25°C and an ionic strength of 0.005. Graphs at other ionic strengths are found in Reference 63, and a tabular format is given in Reference 55 at several temperatures and ionic strengths.

Theoretical solubility diagrams of the various carbonates and hydroxy carbonates of Pb and Cu can be utilized to assess the potential value of passivation techniques for control of their solubility levels in water distribution systems. Figure 10.19 presents a family of solubility contour diagrams for $PbCO_{3(s)}$ and $Pb_3(CO_3)_2(OH)_{2(s)}$ at 25°C and an ionic strength of 0.005. In order to read the graph, the x-axis is the DIC content, whereas the y-axis is the pH value of the treated water. DIC is calculated from the total alkalinity as described above. Each contour line in Figure 10.19 represents the log of mg Pb/L. The action level of Pb, 0.015 mg/L or $10^{-1.82}$, is not seen on this diagram. "Low" solubilities of Pb are indicated by the darkened area that falls into the $Pb_3(CO_3)_2(OH)_{2(s)}$ domain, where the pH values are in the 9–10 range and the DIC is less than 20 mg C/L. "High" solubilities of Pb fall into the $PbCO_{3(s)}$ domain at pH values less than 8.5 and DIC contents greater than 36 mg C/L.

The solubilities of Pb seen in Figure 10.19 are predicted values based on the thermodynamic solubility constants of $PbCO_{3(s)}$ and $Pb_3(CO_3)_2(OH)_{2(s)}$. As such, they are ideal values based on ideal conditions. It is implied in Figure 10.19 that the action level of 0.015 mg/L for Pb cannot be achieved only by precipitation of the later solid phase. Certainly, some additional chemical controls must be employed to control Pb levels. These considerations are discussed thoroughly in Reference 62 as well as other complications of any program for lead control in water distribution systems. For example, there is the tendency for occasional high lead values—i.e., "spikes"—to occur. These are caused usually by particles of corrosion products of lead pipe, solder, or brass.[62]

That the solubility of Cu can be controlled below its action level of 1.3 mg/L is seen in Figure 10.20.[17] This diagram assumes that CuO (terrorite) is the predominant solid phase in the pH range of 9 to 10, where it is more insoluble in water than $Cu_2(OH)_2CO_{3(s)}$ (malachite). At pH values less than 7.8, malachite would be the controlling solid phase over terrorite.[15] In any event, the action level for Cu is easily achieved by pH and alkalinity adjustment.

Calcium Adjustment for Control of Lead and Copper Corrosion

Formation of a $CaCO_3$ precipitate may be utilized to coat the interior walls of metallic pipes, which should reduce their corrosion. A finished water slightly supersaturated with Ca^{2+} and CO_3^{2-} at a specified pH value must be delivered into the distribution system where the precipitation of $CaCO_{3(s)}$ occurs. This supersaturated condition must be available

Table 10.18. Summary of Chemicals Typically Used in pH/Alkalinity and Calcium Adjustment Corrosion Control Treatment.[55]

Chemical	Use	Composition	Alkalinity Change	Notes
Caustic Soda, NaOh	Raise pH. Convert excess CO_2 to alkalinity species	93% purity liquid bulk. Colder climates, bulk storage at <50% purity to prevent freezing	1.55 mg/L $CaCO_3$ alkalinity per mg/L as NaOH	pH control is difficult when applied to poorly buffered water
Lime, $Ca(OH)_2$	Raise pH. Increases alkalinity and calcium content	95–98% purity as $Ca(OH)_2$. 74% Active ingredient as CaO. Dry storage with slurry feed	1.21 mg/L $CaCO_3$ alkalinity per mg/L as $Ca(OH)_2$	pH control is difficult when applied to poorly buffered water. Slurry feed can cause excess turbidity. O&M intensive
Sodium Bicarbonate, $NaHCO_3$	Increases alkalinity with little increase in pH	98% purity. Dry storage with solution feed	0.60 mg/L $CaCO_3$ alkalinity per mg/L as $NaHCO_3$	Good alkalinity adjustment choice, but very expensive
Soda Ash, Na_2CO_3	Increases alkalinity with moderate increase in pH	95% purity. Dry storage with solution feed	0.90 mg/L $CaCO_3$ alkalinity per mg/L as Na_2HCO_3	More pH increase caused as compared to $NaHCO_3$, but less costly
Carbon Dioxide, CO_2	Lowers pH. Converts excess hydroxyls to bicarbonate and carbonate species	Pressurized gas storage. Fed either through education or directly	None	Can be used to enhance NaOH or lime feed systems

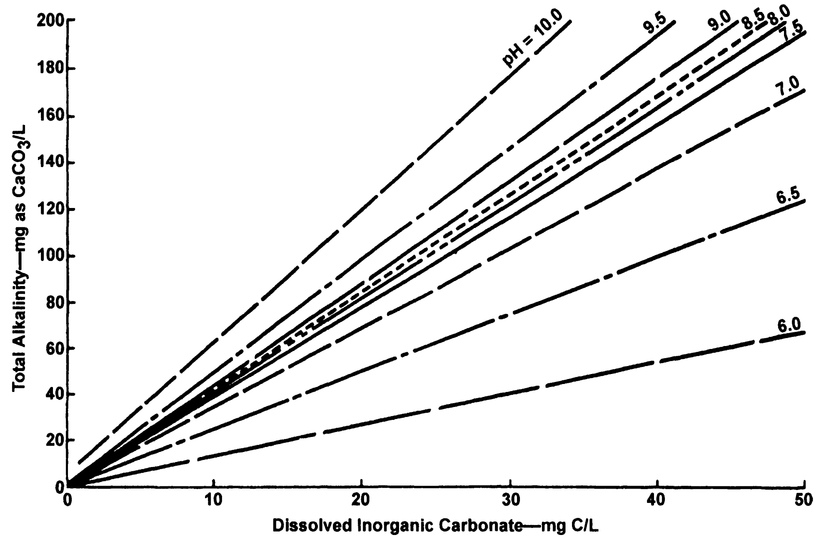


Figure 10.18. Relationship between DIC concentration and total alkalinity for different pH values (temperature—25°C; ionic strength—0.005; in the range of approximately 1 pH unit either side of the midpoint between the pH-pK values [about pH 8.3], DIC in mg C/L is approximately one-fourth of the total alkalinity in mg $CaCO_3$/L).[62]

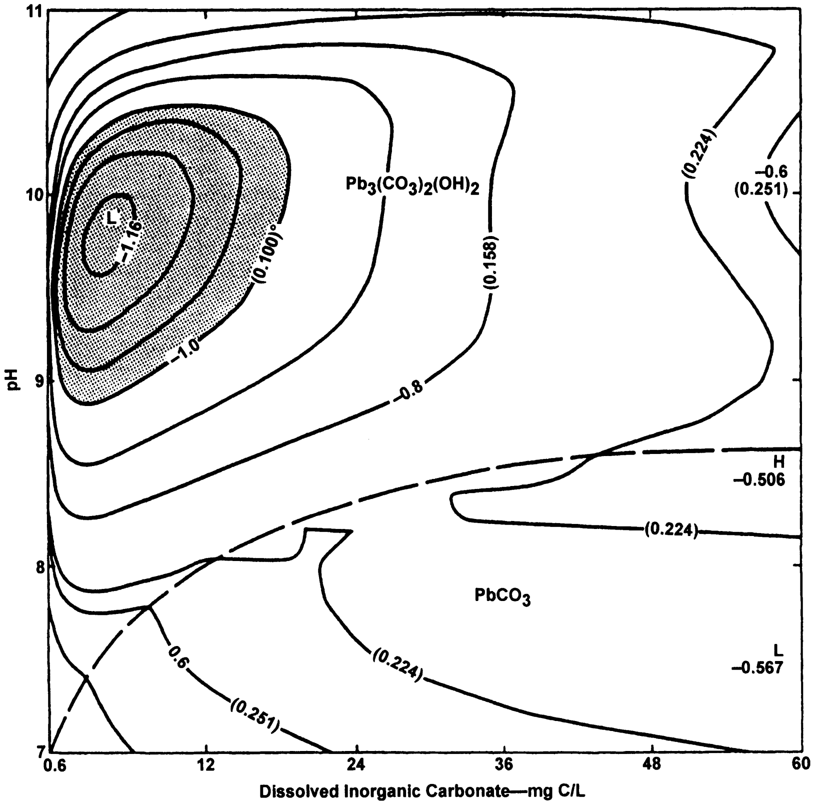


Figure 10.19. Contour diagram of Pb(II) solubility in a system containing only water and DIC [temperature—25°C; ionic strength—0.005; control by either $PbCO_3$ or $Pb_3(CO_3)_2(OH)_2$ is assumed; the contours are for log (mg Pb/L); the current AL of 0.015 mg Pb/L would be at the −1.82 line; the contour interval is 0.05 log units; "H" or "L" represents local high or low points; zone in which the theoretical lead solubility is <0.1 mg/L is darkened; concentrations in mg Pb/L are given in parentheses for some lines].[62]

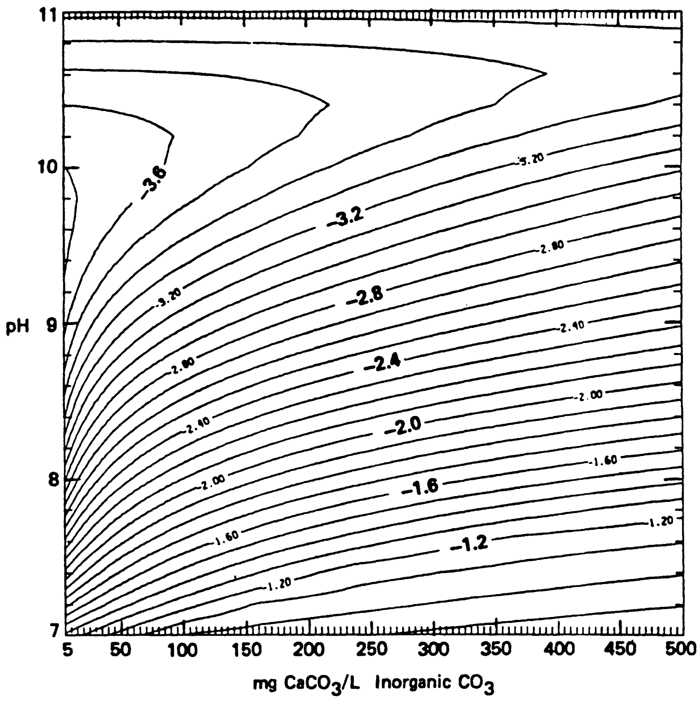


Figure 10.20. Contour diagram of copper (II) solubility in the system copper (II)-water-carbonate at 25°C and I = 0.005 mol/L. All points lie below the AL of 1.3 mg/L (0.114 in diagram units). The contour interval is 0.1 log units.[17]

throughout the distribution system. In addition, techniques for the prediction of the potential formation of $CaCO_{3(s)}$ must be reliable (see discussion of LSI and CCPP above). These are the two key factors for providing corrosion control protection by calcium carbonate adjustment. Needless to state, the formation of scale buildup must be controlled, whereby the hydraulic capacity of the distribution system is not affected unduly.

A major difficulty associated with calcium adjustment lies in the precise determination of the degree of $CaCO_3$ precipitation in the treated water. Many indices (see above) have been proposed to predict and describe the $CaCO_3$ equilibrium system. Such indices may not be adequate to predict the efficiency of calcium adjustment. However, they may be useful to estimate, initially, the water quality conditions to precipitate $CaCO_3$. In the opinion of Reference 55, the CCPP index may be the most useful for this purpose.

The treatment practice of calcium adjustment is not simply supplementation of the water with the appropriate chemicals for precipitation of $CaCO_3$. If soluble Pb^{2+} is in the system, then there will be the competition of this ion for the CO_3^{2-}, which results in the formation of $PbCO_{3(s)}$ and/or $Pb_3(CO_3)_2(OH)_{2(s)}$ (Figure 10.19). Furthermore, waters with a "high" DIC are theoretically capable of dissolving as much, or more, lead as waters with less DIC at lower pH values.[62] It may be possible that some systems with "high" DIC contents have precipitated $CaCO_3$ films, or have developed mixed Ca and Pb lead solids inside their pipes. To date, however, no study has reported the formation of such a film that could be identified by X-ray diffraction or infrared spectroscopy. Consequently, this protection remains speculative.[62]

Corrosion Inhibitors

Corrosion can also be controlled by the addition of various chemicals to the water that form a protective film on the interior surface of the pipe. These chemicals are commonly called *inhibitors*. They attempt to reduce corrosion or limit the metal's solubility. Here again, corrosion is suppressed, but not entirely eliminated. There are three types of chemical inhibitors that are approved for use in potable water systems: chemicals that cause $CaCO_{3(s)}$ scale formation (discussed above), inorganic phosphates, and sodium silicate.

There are a plethora of commercially available chemical inhibitor formulations. Caution must be employed in the selection of these products. Since these chemicals are added directly to the drinking water, they are subject in most states to the American National Standards Institute (ANSI)/National Sanitation Foundation (NSF) Health Effects Standard 60. Consequently, these products must be certified or approved by the primary agent prior to use in a potable water system. Each public water system (PWS) should contact

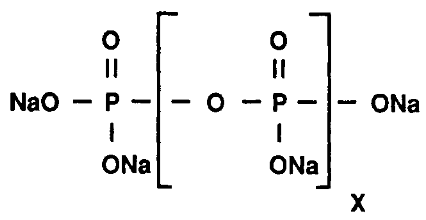
Table 10.19. Molecularly Dehydrated Phosphates.[64]

$Na_2O:P_2O_5$	Compound	Chain Length	Form
3:1	Na_3PO_4 Trisodium phosphate	0	crystalline
2:1	$Na_4P_2O_7$ Tetrasodium pyrophosphate	2	crystalline
5:3	$Na_5P_3O_{10}$ Sodium tripolyphosphate	3	crystalline
1.1:1	$(NaPO_3)_n$ Sodium polyphosphate	12–14	glass

their state agency to obtain the requirements for product certification.

There are three fundamental requisites for any successful chemical inhibitor:[6]

1. Initial treatment uses two or three times the normal inhibitor concentration. This builds up the protective film as rapidly as possible.
2. The inhibitor must be fed continuously and at the optimal concentration. Dissolution of the protective film must not occur.
3. Water flow rates must be sufficient to transport the inhibitor continuously to all parts of the distribution system. This is essentially for formation and maintenance of the protective film.



X = 0 Orthophospate
X = 1 Pyrophosphate
X = 2 Tripolyphospate
X = 12-14 Polyphosphate

Figure 10.21. Condensed inorganic polyphosphates.[64]

Inorganic Phosphates

There are several types of phosphates available for corrosion control. These include: linear and cyclic polyphosphates, orthophosphates, glassy polyphosphates, bimetallic phosphates, and zinc phosphates. The term polyphosphate, as applied to water utilities, refers to commercially available condensed phosphates.[64] The range of materials within this classification is broad, and extends from the simple diphosphate to linear long-chain polymeric structures consisting of about 21 repeating O-P units. Only linear polyphosphates are employed in water utilities.[64] Other compounds are the cyclic structures (metaphosphates) and the branched chains (ultraphosphates).

The crystalline orthophosphate and condensed phosphates employed in PWS are the: disodium phosphates (Na_2HPO_4), tetra potassium pyrophosphate ($K_4P_2O_7$), and sodium tripolyphosphates ($Na_5P_3O_{10}$).[64] That the $Na_2O:P_2O_5$ ratio defines the average chain length is seen in Table 10.19. The linear chain structure of these phosphates is seen in Figure 10.21, where the X symbol represents the polymeric group.

Lead can form several orthophosphate solids that are, apparently, less soluble than basic lead carbonate over a wide range of pH values.[62] The most likely solid phase to form is hydroxypyromorphite ($Pb_5[PO_4]_3OH$) in accord with Reaction 60. Another possibility is tertiary lead orthophosphate ($Pb_3(PO_4)_2$). Figure 10.22 shows a contour diagram for a thermodynamic system that contains 0.5 mg PO_4/L of orthophosphate. The shaded area in this diagram defines the 0.1 mg Pb/L equilibrium solubility zone. The action level—0.015 mg/L for lead—is not seen on this diagram. The formation of lead orthophosphate films depends on the DIC concentration (must be "low"), $[H^+]$, temperature, and orthophosphate content. These phosphate films may not form as rapidly as the basic lead carbonate solids. Consequently, a longer time frame may be needed to evaluate the effectiveness of a phosphate control program.[62]

The effect of various levels of orthophosphate and total alkalinity on lead solubility at a pH of 8.0 is seen in Figure 10.23.[62] (This reference also has similar graphs for pH values of 6.5, 7.0, 7.5, 8.5, and 9.0.) Since carbonates compete with orthophosphates for control of lead solubility, lower levels, generally, are found in waters with lower DIC contents. For example, the optimum pH value for orthophosphate film formation is about 8.0 when the DIC content is less than 1 mg C/L (Figure 10.23). An increase in the orthophosphate dosage will lower this optimum pH value, which will remain >7 "for virtually all but the highest DIC concentrations and orthophosphate dosages that could be encountered."[62]

The ideal combination of a pH value of 7.6, an orthophosphate content >4.5 mg PO_4/L, and DIC values in the 5–10 mg C/L range could attain an equilibrium level of lead of 0.01 mg Pb/L.[62] This reference speculates that "adequate lead control can probably be obtained over a wider range of orthophosphate, DIC, and pH conditions." On the other hand, a decrease in the pH value upon initiation of orthophosphate

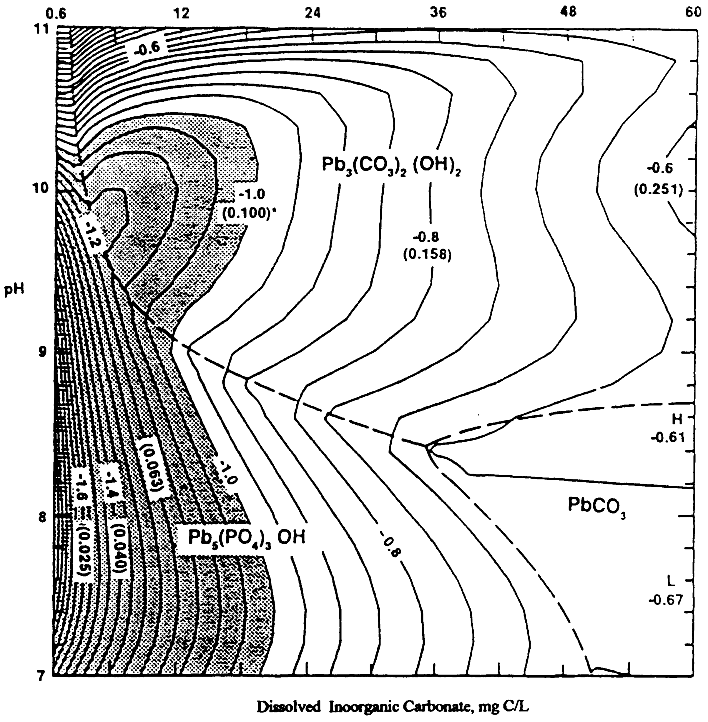


Figure 10.22. Contour diagram of Pb(II) solubility at different pH values and different DIC concentrations in the presence of 0.5 mg PO_4/L of orthophosphate [temperature—25°C; ionic strength—0.005; control by $PbCO_3$, $Pb_3(CO_3)_2(OH)_2$, or $Pb_5(PO_4)_3OH$ is assumed; the contours are for log(mg Pb/L); the contour interval is 0.05 units; the current AL of 0.015 mg Pb/L is at the –1.82 line; "H" or "L" represents local high or low points; the zone in which theoretical lead solubility is <0.1 mg/L is darkened; concentrations in mg Pb/L are given in parentheses for some lines].[62]

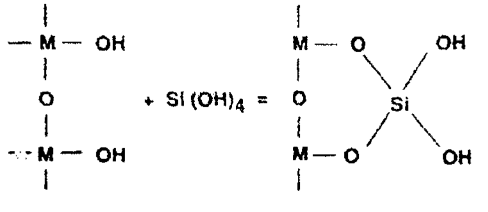
treatment may destabilize an existing basic lead carbonate film. This could result in higher lead levels by dissolution of an existing film during formation of the replacement film.

Another consideration in waters that are "hard" from Ca^{2+} is the possibility that a calcium orthophosphate solid phase may form. For example, $Ca_5(PO_4)_3OH$ (hydroxyapatite) is thermodynamically stable at contents of H^+, orthophosphate, and Ca^{2+} in hard waters that have had their pH values increased through treatment.

Inorganic Silicates

Soluble silicates have been employed for more than 70 years to protect metals from the corrosive effects of water.[65] They may be classified as corrosion inhibitors since a protective film may be formed onto various metal surfaces. These silicates are produced by fusing high purity silica sand and Na_2CO_3 (or K_2CO_3) at temperatures of 1000–1500°C. An amorphous glass is produced that can be dissolved in water to produce silicate solutions sometimes referred to as "waterglass." In solution, the silica is present in a solubility equilibrium between monomeric and polymeric anionic species (Figure 10.24). Ratio and silicate concentration are important factors that influence which species are present in solution. The silica monomer predominates at concentrations typical for corrosion control.[66] The proportion of silica and alkali in a sodium silicate is usually expressed as the weight ratio of SiO_2/Na_2O, which ranges from 1.60 to 3.22. Typical ratios employed in municipal water treatment are 2.00 or 3.22 (25–30% S_iO_2).

There is some experimental evidence that soluble silicates are reactive with cationic metals and metal surfaces.[67] A schematic of this reaction is:



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According to this reaction, the anionic $S_iO_3^{2-}$ species is adsorbed onto the metal pipe surface at the anodic areas and forms a thin, monomolecular film. Silicates have enjoyed some success in the inhibition of the corrosion of iron pipes.

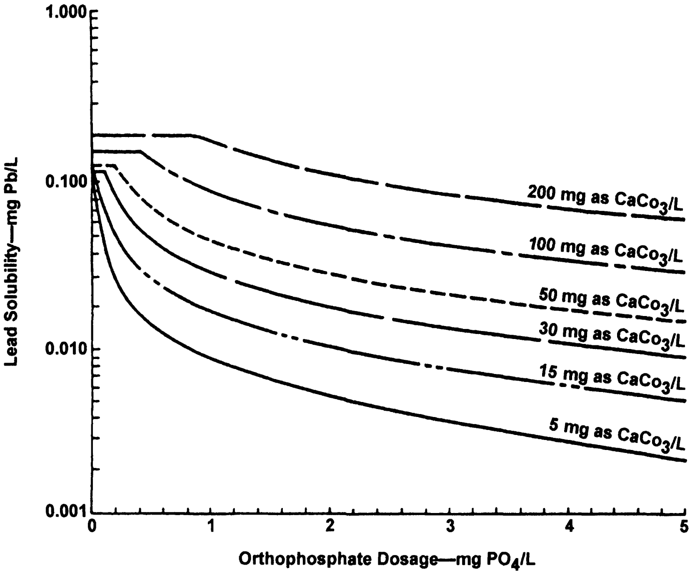
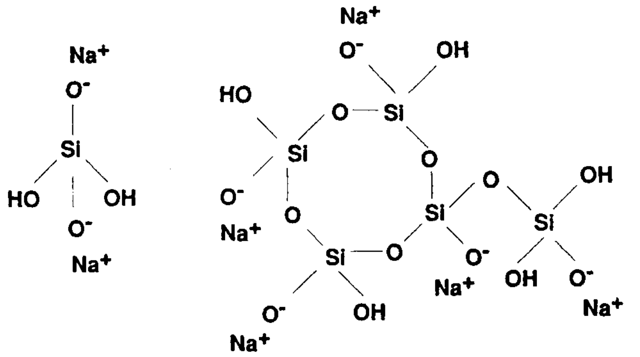


Figure 10.23. Variation in lead solubility for different total alkalinities and orthophosphate dosages at pH 8.0, assuming the formation of $PbCO_3$, $Pb_3(CO_3)_2(OH)_2$, or $Pb_5(PO_4)_3OH$ (temperature—25°C; ionic strength—0.005).[62]



monomer

branched ring

Figure 10.24. Two silica structures found in sodium silicate solutions.[66]

Their ability to inhibit the corrosion of lead and copper is somewhat debatable.[62]

Treatment Technologies for Corrosion Inhibitors

Chemical characteristics of the raw water determine the strategy for corrosion control of metallic pipes. The major parameters are pH, total alkalinity, calcium hardness, total dissolved solids or conductivity, and temperature. Each PWS should have these characteristics determined on a daily basis. Also, it would be extremely helpful to have some historical data. Other useful parameters would be dissolved oxygen, iron, manganese, lead, and copper. Presence of these metals is, of course, symptomatic of corrosion and inefficient treatment. Water quality data should be collected from the raw, finished, and distributed supplies.

An understanding of the treatment processes at PWS and their effect on water chemistry is an important aspect of the interpretation of the water quality data and selection, and subsequent evaluation of corrosion control treatments. A graphical presentation is found in Reference 55. Three regions of pH values (low, moderate, and high) are given with alternative treatment approaches that may be viable on the basis of the alkalinity and calcium contents shown in each block (low, moderate, and high). The graphs provide general guidelines on water quality conditions that involve alternative treatment approaches. It is not intended to serve as the sole basis for selection and/or elimination of the various treatments. It is an excellent side-by-side comparison of the quality condition under which these treatments should be effective. Corrosion inhibitors certainly have a role under a wide range of water quality conditions.

Phosphates

Distinction should be made between the application of orthophosphates and polyphosphates for corrosion control. Historically, the latter have been employed to control corrosion in cast iron systems and to prevent scale formation. To date, very little evidence has been presented to demonstrate the effectiveness of polyphosphates for control of lead corrosion. In fact, there are some studies that showed polyphosphates were not only ineffective in reducing lead levels, but they could actually increase levels by complexation and solubilization of protective films on the pipe.[62,68]

Iron and manganese stabilization can be accomplished with polyphosphates with an initial feed of 5–10 mg/L for several weeks that is followed by a maintenance dosage of 1–2 mg/L thereafter.[69] A ratio of 2:1 inhibitors to iron or manganese is usually effective at pH values circa 7.0. Occasionally, a higher ratio may be needed when the water is heavily chlorinated or the pH is above 7.5.[69] Control of $CaCO_3$ scale rarely requires more than 1 mg/L of polyphosphate.

It appears that orthophosphate can reduce lead solubility in low- and high-alkalinity waters. This premise is based upon the formation of such solid phases as $Pb_5(PO_4)_3OH$ (hydroxypyromorphite) (Figures 10.22 and 10.23). A "few" mg/L of orthophosphate should be sufficient at pH values in the 7–9 range. The chemical limitations of orthophosphate treatment were discussed above.

There are commercial formulations of orthophosphate that contain zinc. These products have no additional benefit in reducing lead solubility when compared to orthophosphate alone.[70] Zinc/orthophosphate is used primarily in waters where the potential for formation of $CaCO_3$ scale is low. These waters are usually soft and slightly acidic, hence corrosive.

Zinc/orthophosphate corrosion control programs are capable of suppressing attack on carbon steel, have some efficiency toward cast iron, mild inhibition toward copper, and are capable of suppressing the release of asbestos fibers from the AC pipe.[70]

Figure 10.25 shows a "decision tree" that involves a sequence of decisions for the selection of treatment alternatives for corrosion control. This "tree" involves treatment options from among pH, DIC, and orthophosphate.[62,63] The underlying principle behind Figure 10.25 is that the chemical models discussed above are useful guides to the impact of water chemistry on corrosion control. However, the optimum levels of chemical controls should be determined through feedback from specific pilot and monitoring programs at a given PWS. These chemical models also suggest conditions under which lead leaching can increase by searching for truly optimum conditions. Optimization is an iterative process at the present time and must be monitored carefully. Passive film formation on lead and most other metals is reversible, so that continuous feeding of inhibitors and maintenance of water quality conditions are necessary for lead control. The strategy behind Figure 10.25 begins by dividing the systems according to the level of DIC. Details of this strategy are given in Reference 62.

Silicate

According to the commercial literature, silicate treatment has been effective for the corrosion control of a variety of metals: lead, copper, cast iron and ferrous metals, steel, galvanized steel, bronze, red and yellow brass, and nickel alloys.[66] Relatively high dosages—24 mg/L above the background—of silicate are required during the first 30 to 60 days of treatment. This should form the initial protective coating. Thereafter, the silicate dosage is reduced incrementally in 30-day periods to maintenance doses in the 4–8 mg/L range.

Unfortunately, there is very little enthusiasm in the technical literature for inhibition of corrosion by silicates. Several pipe loop experiments were conducted by the USEPA with soft, low-alkalinity waters at a pH of 8.2 over a period of 8 to 9 months with dosages of 10 and 20 mg/L S_iO_2. Some research in England with low alkalinity waters showed little improvement in lead concentrations with 10 mg/L S_iO_2.[71] More laboratory and field studies apparently are needed to determine the true efficacy of silicates in corrosion control.

Case Studies of Corrosion Control

Several case studies of corrosion control are given in this section in chronological order, for the most part. This will give the reader a historical perspective of corrosion control techniques prior to the advent of the lead and copper rule. Also, some studies are reviewed that were conducted in response to this rule.

Boston, Massachusetts

Water supplied to the Boston metropolitan area has been relatively corrosive to lead, copper, and iron pipes.[72] Their water supply is slightly acidic (pH=6.7), soft (12 mg/L as $CaCO_3$), and low in alkalinity (8 mg/L as $CaCO_3$). Contamination of the drinking water by Pb was a concern because lead pipe was used widely in Boston from the late 1800s and the early 1900s. These pipes were durable enough to be in service into the late 1970s. Before corrosion control, the average lead concentrations at the consumer's tap were consistently well above the 0.05 mg/L

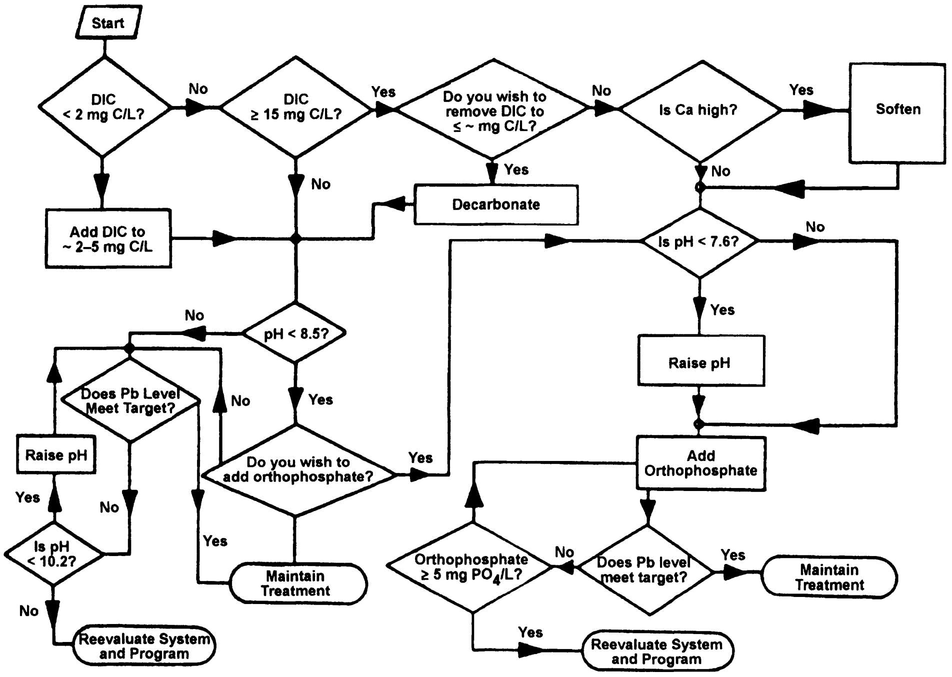


Figure 10.25. Conceptual decision tree for the selection of treatment options from among pH, DIC, and orthophosphate.[62]

standard that was in effect at that time (the 1970s). In 1976, a six-month trial utilized zinc orthophosphate at an initial passivation dosage of 13 mg/L (for several weeks), a maintenance dosage of 3.2–4.5 mg/L, and no pH adjustment. The lead level was not reduced below 0.05 mg/L. Subsequently, NaOH was added to increase the pH value to 8.5, whereupon lead contents were lowered from an average of 0.128 mg/L to 0.035 mg/L. Copper levels were reduced "significantly" as well.

Scotland

Scottish water supplies are soft and acidic, with a pH value of about 6.3.[73] Medical studies revealed unacceptable elevated contents of lead in human blood that were correlated statistically with excessive levels of lead in drinking water. The EEC standard of 0.100 mg/L for lead plumbing systems was in effect at that time. Initially, several of the public supplies employed a pH adjustment with $Ca(OH)_2$ to values in the 7.8 to 9.0 range. Subsequently, lead levels in the finished waters decreased to less than 0.100 mg/L, with a majority less than 0.05 mg/L. However, there were some waters from areas around Glasgow that continued to contain elevated levels. It was decided, then, to supplement the pH adjustment with NaH_2PO_4 at dosages approximating 2 mg/ P/L. This treatment produced finished waters with mean lead concentrations less than 0.025 mg/L. Lead levels in human blood samples were lowered also.

Ohio

Control of copper pipe corrosion was effected through the addition of soda ash (Na_2CO_3) for elevation of the pH value to the 8.1 to 8.3 range.[74] This case study is interesting wherein the groundwater supply has substantial hardness (656 mg/L as $CaCO_3$), alkalinity (298 mg/L as $CaCO_3$), and a pH value of 7.1. A portion of this water is softened with sodium zeolite and blended with unsoftened water to produce a distribution water with a hardness in the range of 250 to 300 mg/L as $CaCO_3$. Despite this treatment, corrosion occurred in domestic cold water copper plumbing systems. Most of the failures occurred in the drawn temper type M distribution lines, with some occurring in annealed type L service lines. It was thought that the dissolved CO_2 content of 18 to 28 mg/L as CO_2 and dissolved O_2 from an aeration treatment were the responsible factors for the copper corrosion. Subsequent treatment of the water with soda ash eliminated this corrosion.

Virginia

A recent monitoring and control experiment under the Lead and Copper Rule was reported from the City of Newport News, Virginia.[75] Their Department of Public Utilities is a regional water supplier in southeastern Virginia that reaches a population of approximately 350,000 persons. Their program included: (a) lead service line replacement, (b) corrosion control treatment, and (c) at-the-tap monitor-

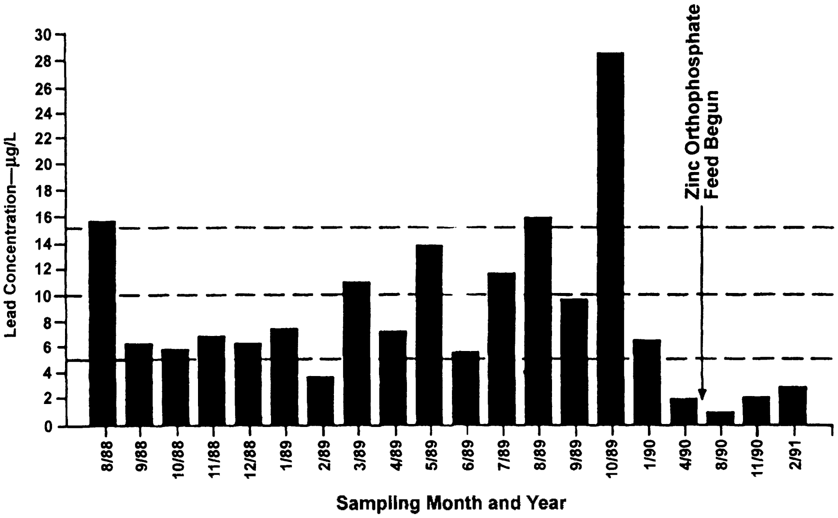


Figure 10.26. Average tap lead levels in standing samples and the effect of the zinc orthophosphate corrosion inhibition program.[75]

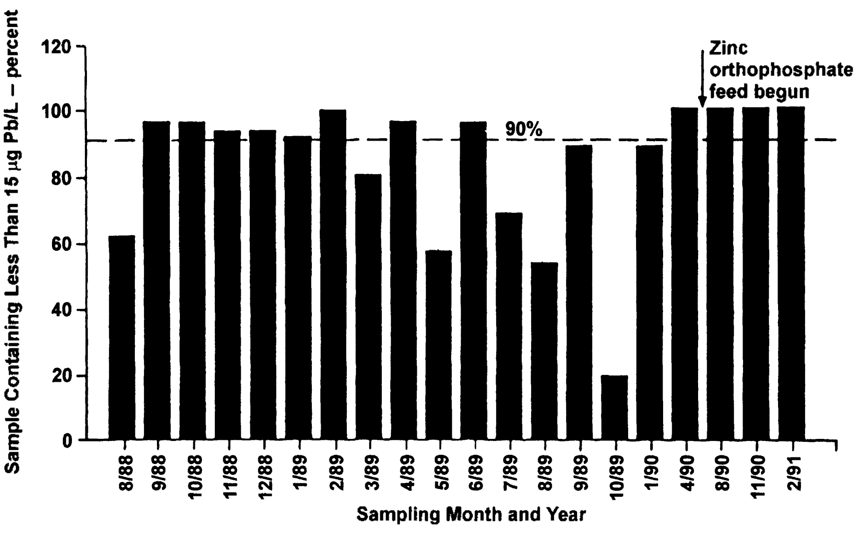


Figure 10.27. Percentage of standing samples containing less than 15 µg/L of lead.[75]

ing. Completion of the lead service lines occurred in 1989 after its initiation in 1985. The corrosion control was started in 1987 with an investigation of several treatment strategies which included various means of pH adjustment to achieve a more positive Langelier Index and the feeding of various phosphate-based corrosion inhibitors.

First, the merits and effects of raising the finished water's pH value from 7 to 8 were evaluated. This change in pH increased the THMFP by approximately 25% and TTHMS by 40%. Since this would violate the USEPA's THM standard at that time (late 1980s), pH adjustment was judged to be impractical as a means of controlling lead levels while free chlorine is used for disinfection. Consequently, this utility concluded that zinc orthophosphate was the corrosion inhibitor of choice. Full-scale treatment with this compound began in June 1990 when it replaced sodium hexametaphosphate. A bulk-liquid product (a 3:1 orthophosphate to zinc formulation) was employed at zinc levels of 0.20 mg/L or less in the distribution systems. The results of this corrosion control program are seen in Figures 10.26 and 10.27, where the success is obvious. Unfortunately, this report did not give any supporting water quality data for the corrosion control program.

Other Case Studies

Reference 63 has a tabulated historical review of lead treatment programs, as well as a detailed description of lead control strategies.

Reference 76 is a report of a research project that investigated the corrosion rates of copper, milled-steel, and zinc-galvanized pipe coupons as a function of the chemical characteristics of Seattle, Washington tap water with and without 1 or 5 mg/L orthophosphates.

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Chapter 11

Removal of Pathogenic Bacteria, Viruses, and Protozoans

11

Removal of Pathogenic Bacteria, Viruses, and Protozoans

PURPOSES

Waterborne Diseases

The primary purpose for disinfection of drinking and bathing waters is, of course, prevention of waterborne diseases. Modern practice of disinfection began, perhaps, with chlorination of the waters from Boonton Reservoir of the Jersey City Water Works in 1908.[1] Despite these 88 years of disinfection of public and other water supplies, Lippy[2] states: "The disturbing trend toward more frequent occurrence of outbreaks of waterborne diseases should serve as a warning to all who share in the responsibility for delivery of a safe and potable water." The major bacteria, enteric viruses, and protozoans are given in Table 11.1 as the potential waterborne disease-causing organisms.[3]

For the two-year period, 1991–1992, 17 states and territories reported 34 outbreaks associated with water intended for drinking.[4] The outbreaks caused illnesses in an estimated 17,464 people. In contrast, during 1971–1978, 43 states and Puerto Rico reported 224 outbreaks that affected 48,193 individuals and included 2 deaths.[5] These data suggest a decline in waterborne diseases. However, there have been some unusual and rare occurrences, as seen by outbreaks of *Cryptosporidium* in 1991 and 1992. Within the 34 outbreaks, a protozoal parasite (*Giardia lamblia* or *Cryptosporidium*) was identified as the causative agent in seven outbreaks, with four associated with the former organism. Three outbreaks of cryptosporidiosis resulted in illness in an estimated 3,551 persons in Oregon and Pennsylvania. Figure 11.1 shows a summary of waterborne diseases and their trends for the period 1971–1992.[4]

Additional surveys of waterborne disease outbreaks include 1946–1960,[6] 1971–1974,[7] 1975–1976,[8] waterborne giardiasis in the United States,[9] viruses in water supplies,[10–12] and the necessity of controlling bacterial populations in potable water.[13]

Indicator Organisms and Pathogenic Bacteria

Perhaps the classic paper of Kehr and Butterfield[14] established the relation between the indicator coliform organisms and enteric pathogens. Much of their data were collected from domestic sewage surveys conducted by the London Metropolitan Water Board during the years 1927–1938. The occurrence of *Salmonella* organisms was sought in these surveys. Kehr and Butterfield plotted the available data in order to establish some sort of a relationship between reported isolations and the normal prevalence of typhoid fever in various communities. They used log-log plot (for convenience) of the ratio of *Eberthella typhosa* (now *S. typhosa*) per 10^6 coliforms per mL vs. the typhoid fever morbidity rate. The plots showed direct relationship between the morbidity rates and the ratios that might be expected in polluted river waters and sewage. These ratios were the approximate minimum ratios to be expected in domestic sewage and surface waters polluted by sewage from reasonably large populations. This assumed, of course, that cases of typhoid fever and typhoid carriers exist as providers of *Salmonella* organisms in the sewage.

Additional evidence may be cited from fecal coliform correlations with *Salmonella* occurrence. This is seen in Table 11.2, where data collected from numerous stream and estuarine surveys are grouped into fecal coliform density ranges that bracket recommended limits (for 1970) for recreational waters and public water supply intakes.[15] These data suggest a sharp increase in the frequency of *Salmonella* detection when fecal coliform densities are greater than 200/100 mL of fresh water. Also, *Salmonella* isolations (positive occurrences) should occur with nearly a 100% frequency when the fecal coliform density exceeds 2000/100 mL. For estuarine waters, the 1–70 range of fecal coliform has application to shellfish waters. In this range, only 6.7% of 184 *Salmonella* examinations were positive. In polluted estuarine waters with fecal coliforms ranging from 201 to

Table 11.1. Potential Waterborne Disease-Causing Organisms.

Name of Organism or Group	Major Reservoirs and Major Disease	Primary Sources
Bacteria		
Salmonella typhi	Typhoid fever	Human feces
Salmonella paratyphi	Paratyphoid fever	Human feces
Other salmonella	Salmonellosis	Human and animal feces
Shigella	Bacillary dysentery	Human feces
Vibrio cholerae	Cholera	Human feces
Enteropathogenic *E. coli*	Gastroenteritis	Human feces
Yersinia enterocolitica	Gastroenteritis	Human and animal feces
Campylobacter jejuni	Gastroenteritis	Human and animal(?) feces
Legionella pneumophila and related bacteria	Acute respiratory illness (legionellosis)	Thermally enriched waters
Mycobacterium tuberculosis	Tuberculosis	Human respiratory exudates
Other (atypical) mycobacteria	Pulmonary illness	Soil and water
Opportunistic bacteria	Variable	Natural waters
Enteric Viruses		
Enteroviruses		
Polioviruses	Poliomyelitis	Human feces
Coxsackieviruses A	Aseptic meningitis	Human feces
Coxsackieviruses B	Aseptic meningitis	Human feces
Echoviruses	Aseptic meningitis	Human feces
Other enteroviruses	Encephalitis	Human feces
Reoviruses	Mild upper respiratory and gastrointestinal illness	Human and animal feces
Rotaviruses	Gastroenteritis	Human feces
Adenoviruses	Upper respiratory and gastrointestinal illness	Human feces
Hepatitis A virus	Infectious hepatitis	Human feces
Norwalk and related GI viruses	Gastroenteritis	Human feces
Protozoans		
Acanthamoeba castellani	Amoebic meningoencephalitis	Soil and water
Balantidium coli	Balantidosis (dysentery)	Human feces
Cryptosporidium	Cryptosporidiosis	Human and animal feces
Entamoeba histolytica	Amoebic dysentery	Human feces
Giardia lamblia	Giardiasis (gastroenteritis)	Human and animal feces
Naegleria fowleri	Primary amoebic meningoencephalitis	Soil and water
Algae (blue-green)		
Anabaena flos-aquae	Gastroenteritis	Natural waters
Microcystis aeruginosa	Gastroenteritis	Natural waters
Alphanizomenon flos-aquae	Gastroenteritis	Natural waters
Schizothrix calciola	Gastroenteritis	Natural waters

>2,000,000/100 mL, recovery of *Salmonella* did not reach the 100% proportions observed in fresh water. These observations are illustrated further by a bacterial quality study at several water plant intakes along the Missouri River. When fecal coliforms exceeded 2000/100 mL, *Salmonella,* poliovirus types 2 and 3, and echovirus types 7 and 33 were detected.[16]

Another major relation between indicator organisms and *Salmonella* is survival in fresh waters. These enteric organisms are not expected to survive for a considerable period of time in an unfavorable environment. An important consideration would be that the length of survival of the indicator organism and the pathogen should be approximately the same. Studies were conducted on the relative persistence of selected indicator organisms and a *Salmonella* strain in 52 urban stormwater samples.[17] Survival curves are seen in Figure 11.2 for selected enteric bacteria. It appears that fecal coliforms and *S. typhimurium* have approximately the same length of survival or rate of death in stormwater stored at 20°C. Similar survivals are expected in lakes, streams, rivers, etc., receiving these organisms. Kehr and Butterfield[14] and Heukelekian and Schulhoff[18] reported similar relation-

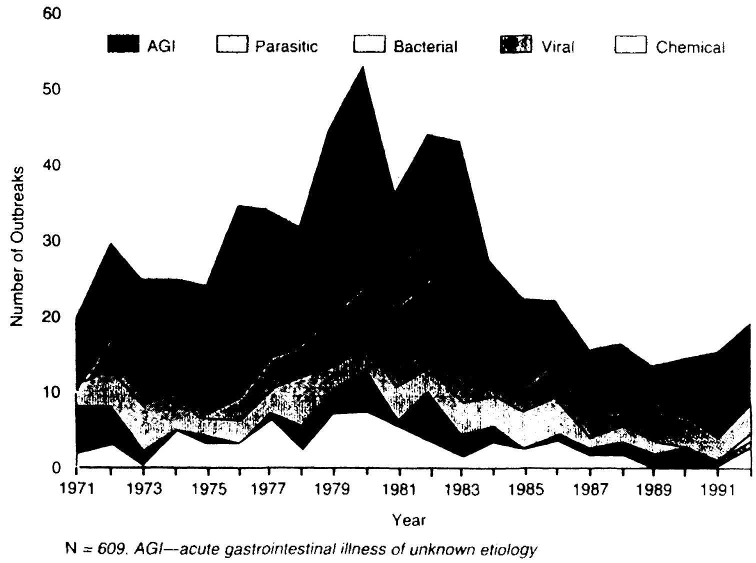

Figure 11.1. Waterborne disease outbreaks by year and etiologic agent for 1971–1992.[4]

Table 11.2. Fecal Coliform Correlations with *Salmonella* Occurrence.[a]

Source	Fecal Coliform Density (per 100 mL)	*Salmonella* Detection: Total Examinations	Positive Occurrence: Number	Positive Occurrence: %
Fresh water	1–200	29	8	27.6
	201–2000	27	19	85.2
	>2000	54	53	98.1
Estuarine Water	1–70	184	12	6.5
	71–200	74	21	28.4
	201–2000	91	40	44.0
	>2000	75	45	60.0

[a] Reproduced from Geldreich,[15] courtesy of the American Water Works Association.

ships for the survival of pathogens and indicator organisms in natural waters.

An indicator organism should provide evidence of recent fecal contamination from warm-blooded animals. The general criteria for an indicator organism are:[3]

1. The indicator should always be present when the pathogenic organism of concern is present, and absent in clean, uncontaminated water.
2. The indicator should be present in fecal material in large numbers.
3. The indicator should respond to natural environmental conditions and to treatment processes in a manner similar to the pathogens of interest.
4. The indicator should be easy to isolate, identify, and enumerate.
5. The ratio of indicator/pathogen should be high.
6. The indicator and pathogen should come from the same source (GI tract).

Statements above cite the two major arguments for the use of nonpathogenic enteric organisms to indicate the possible occurrence of pathogenic enteric bacteria. These are (a) the statistical correlations among coliform density, *Salmonella* density, and typhoid death rate, and (b) the survival factor in natural waters. There are, however, several limitations to this practice, thoroughly discussed in Hoadley and Dutka.[19]

CHEMISTRY OF DISINFECTION

Disinfection of water can be traced back to about 2000 B.C., where two medical maxims in Sanskrit advised that water should be exposed to sunlight and filtered through

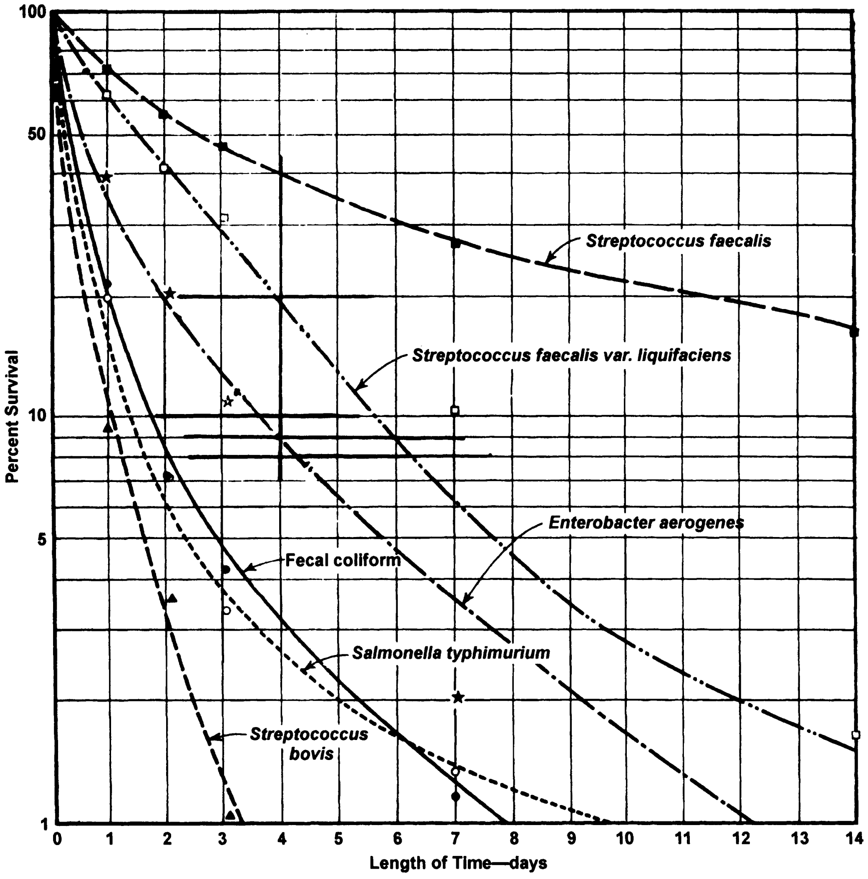

Figure 11.2. Persistence of selected enteric bacteria in sterilized stormwater stored at 20°C. Reproduced from Geldreich,[15] courtesy of the American Water Works Association.

charcoal and that "foul water" be treated by boiling and "by dipping seven times into it a piece of hot copper and then filtering it."[1] There are also many references to boiling water and storage in silver flagons in ancient civilizations. Other early efforts of water disinfection were the use of copper, silver, and electrolysis. The first American patent on chlorination of water was given to Albert R. Leeds, on May 22, 1888. This led eventually to the first large-scale chlorination of a public water supply in the United States at the Boonton Reservoir of the Jersey City Water Works in 1908.[1]

Types of Disinfectants

There are several means and types of disinfectants available for municipal and domestic water and swimming pool waters. It should be emphasized that these waters are disinfected for the destruction of pathogenic and indicator organisms. It is not necessary for the waters to be sterilized to achieve the complete absence of microorganisms. Some of the more specific disinfection processes for water are: (a) physical treatment by means of storage or the application of heat; (b) irradiation by ultraviolet light; (c) metal ions; for example, copper and silver; (d) strong acids and bases; i.e., pH adjustment; (e) surface active agents; for example, the quaternary ammonium compounds; and (f) chemical oxidants, such as Cl_2, Br_2, I_2, O_3, ClO_2, $KMnO_4$, FeO_4^{2-}, and organohalogen compounds.[20] Many of these are, of course, not suitable for the large-scale disinfection of public drinking water. For this water, Fair et al.[21] have established criteria for a potential disinfectant:

1. Ability of the disinfectant to destroy the kinds and numbers of organisms present within the contact time available, the range of water temperatures encountered, and the anticipated fluctuations in composition, concentration, and condition of the water being treated.
2. Ready and dependable availability of the disinfectant at reasonable cost and in a form conveniently, safely, and accurately applied.
3. Ability of the disinfectant, in concentrations employed, to accomplish the desired objectives with-

out rendering the water toxic or objectionable, aesthetically or otherwise, for the purposes it is intended.

4. Ability of the disinfectant to persist in residual concentrations as a safeguard against recontamination where this might be important (such as potable-water distribution systems).
5. Adaptability of practical, duplicable, quick, and accurate assay techniques for determining disinfection concentration, for operating control of the treatment process, and as a measure of disinfecting efficiency.

Chlorine meets these criteria, and the widespread practice of chlorination is essentially synonymous with disinfection.

Chemical Oxidants

Bromine. Br_2 is a dark, reddish-brown halogen that exists as a liquid at atmospheric pressure. It is about 3.2 times heavier than water, has a melting point of 7.3°C, and has a boiling point of 58.78°C. Its solubility in water at 20°C is 2.1×10^{-1} M (33.56 g/L). According to Laubusch,[20] bromine is a good germicidal agent and can be detected in water rather easily. Bromine and monobromamine (NH_2Br) have been reported[22] to be nearly equal in germicidal properties, and essentially equal to chlorine at comparable pH values. It is used primarily in disinfecting swimming pool and industrial waters.[20] It could be used, perhaps, in emergency situations for drinking water.

Chlorine. See chlorination section below.

Iodine. This halogen, I_2, is a volatile, purplish-black, crystalline solid, which sublimates slowly at normal atmospheric conditions. It has a melting point at 114°C and a boiling point at 183°C. Its solubility in water is 1.33×10^{-3} M (0.337 g/L). Here again, I_2 is an excellent disinfectant for drinking water, but is limited to emergency situations because of its obvious "iodine" taste. In the 1940s, research was conducted with such halogen compounds as Halazone for use as a field disinfectant in military operations. By 1945, Globaline (tetraglycine hydroperiodide) had been developed and demonstrated to be effective for the disinfection of enteric bacteria, amoebic cysts and cercariae of schistosoma with one or two tablets per quart and a 10-min contact period.[20] In turn, this led to a number of studies on the efficacy of I_2 as a disinfectant for public drinking waters. Some of these studies are presented below. It is used also for disinfecting swimming pool waters.

Ozone. This oxidant is a faintly blue, pungent smelling, unstable (in water) gas. It is an allotrophic form of oxygen in which three atoms are combined to form the molecule O_3. Because of the instability it is usually generated onsite. Some of the properties of ozone are: boiling point, −112.4°C and melting point, −193 ± 0.5°C. Its solubility in water is 0.494 cm^3/cm^3 of water at 0°C and 1 atm.[23] Ozone was discovered in 1783 by the Dutch scientist Van Marum. It is interesting to note that research was conducted late in the 19th century for municipal water treatment in Germany, Holland, and France.[20] Ohmller[24] reported that O_3 was effective in the destruction of typhoid and cholera bacteria at a semicommercial plant at Martinikenfeld in 1891. Several other investigations led to the installation of ozone treatment at water plants in Paris, Lille, and Nice, France (1898–1904). By 1933 about 90 MGD of water was treated by O_3 in Paris. France still uses this treatment more than any other country. In the United States, O_3 was employed by the city of Philadelphia for taste and odor control as well as disinfection.[20] Today, ozone disinfection has been given serious consideration in order to avoid formation of the halogenated hydrocarbons (see Chapter 2). Some studies on the effectiveness of ozone as a disinfectant are cited below. The two major disadvantages of ozone treatment are: electric energy costs of generation are extremely high, and its instability in water does not leave a residual for protecting the distribution system.

Other. Other chemical oxidants for disinfection are: ClO_2, $KMnO_4$, FeO_4^{2-}, H_2O_2, and peroxone (a combination of O_3 and H_2O_2). Here again, their use is limited to specific treatments for destroying microorganisms. If these oxidants are used for such other purposes in water treatment as taste and odor control, and iron and manganese removal, there will be an incidental effect of disinfection.

Alternate Disinfectants

Heat Treatment. It is common knowledge that boiling water for 15–20 min is sufficient for destruction of the pertinent microorganisms. This treatment is limited to emergency situations and is frequently recommended by utilities in such cases. There are continuous-flow water pasteurizers for small supplies, i.e., domestic applications.[25]

Irradiation. The ultraviolet method of disinfection requires the exposure of a thin film of water, ~120 mm thick, to one or more quartz mercury vapor arc lamps that emit radiation in the range between 240 and 295 nm. The operational aspects are: a wavelength of 253.7 nm, flow rate of 750 gal/hr, a 4.2 sec contact time, and a flow depth of 3/8 in.[26] Some of the advantages of this process of sterilization are: chemical treatment is avoided; contact times are short; it is extremely effective for the destruction of coliform organisms; and no tastes and odors are produced. Its disadvantages are: it is not very effective against spores, cysts and viruses; it requires pretreatment for turbidity removal; it has no residual disinfection capability; and the accompanying electrical energy costs may be high. Here again, ultraviolet irradiation is limited to small-scale water supplies.

Metal Ions. The bactericidal properties of such metal ions as Cu^{2+}, Ag^{+}, and Hg_2^{2+} have been known for many centuries.[20] Their effectiveness is noted at "low" concentrations. There have been numerous publications since 1869 or so on the disinfection properties of silver, etc. The algicidal properties of copper are well known also. Most of the research and applications of metallic disinfection have been with silver. There are reports of European and Russian uses of silver in village water supplies.[20] Some of the advantages are: "low" disinfectant concentrations and long residual bactericidal activity. Disadvantages are: pretreatment of the water is required for removal of turbidity, organic color, etc.; cysts and spores are resistant; cold temperatures lower germicidal activity; long contact times are required; and the treatment is costly. There may be some emergency and small-scale applications for disinfection by silver.

Chlorination

Semantics and Practices

Plain or simple chlorination is the application of chlorine to an untreated water supply as it enters into a distribution system, either municipal or domestic. The intent is disinfection, and no other treatment is required. Pre- and postchlorination are addition of chlorine before and after any other water treatment. Rechlorination is the addition of chlorine to the finished water at one or more points in the distribution system. The intent is to assure disinfection. Combined residual chlorination is the application of chlorine to water with a subsequent reaction with ammonia (NH_3) to yield and to maintain the chloramines NH_2Cl and $NHCl_2$ throughout the distribution system. Thus, the chlorine is combined with ammonia to produce two chloramines that also have disinfectant properties. Assurance of disinfection is the intent.

Free residual chlorination is the application of chlorine to water to produce a residual of hypochlorous acid, HOCl, and/or hypochlorite ion, OCl^-. No ammonia or chloramines are present. Thus, the residual chlorine in the water is "free" from any combined residual. It is necessary to satisfy the "chlorine demand" of the water in order for chlorine to be "free" for disinfection. This is frequently labeled "free available chlorine."

Breakpoint chlorination is the continuous addition of chlorine to water to a point or dosage whereby all of the chlorine demand has been "satisfied" and all of the ammonia has been oxidized, which leaves a "free" residual of chlorine. The quantitative aspects are given below. The primary intent is, of course, disinfection, but there are some other benefits. Control of tastes and odor may be one. To achieve the breakpoint, it is frequently necessary to practice "superchlorination."

Superchlorination is the addition of an extraordinary quantity of chlorine to water to achieve disinfection, taste and odor control, iron and manganese removal, etc. Chlorine dosages are several orders of magnitude greater than the 1.0 mg/L quantity for disinfection.

In accord with *Standard Methods,*[27] chlorine (oxidant) demand is "the difference between the added oxidant dose and the residual oxidant concentration measured after a prescribed contact time and at a given pH and temperature." Since chlorine is a nonselective oxidant, almost any substance in water in a reduced valence state will react and consume chlorine. These substances may be NH_3, CN^-, organics, Fe^{2+}, Mn^{2+}, S^{2-}, SO_3^{2-}, etc. The chlorine demand presumably must be satisfied before disinfection is achieved. Such variables affecting the chlorine demand are pH, temperature, contact time, and desired free residual. These must be stated. Knowledge of the chlorine demand from laboratory tests yields data that are readily converted to operational practice.

In accord with *Standard Methods,*[27] chlorine (oxidant) requirement is "the oxidant dose required to achieve a given oxidant residual at a prescribed contact time, pH, and temperature" for a specific result. The latter may be an iron or manganese residual, taste and odor level, or a bacterial count. It is, however, usually associated with a desired disinfection result requiring a specific chlorine residual.

Dechlorination is the partial reduction of chlorine residuals, usually by sulfur dioxide or activated carbon, prior to entry into the distribution system.

Physical and Chemical Properties

In its elemental form, chlorine is a greenish-yellow gas that is readily compressed into a clear, amber-colored liquid which, in turn, solidifies at atmospheric pressure at about −102°C.[28] Gaseous chlorine forms a soft ice following contact with water at 9.5°C and at atmospheric pressure. This is chlorine hydrate, $Cl_2{\bullet}8H_2O$, so-called "chlorine ice." Chlorine has an atomic number of 17 and an atomic weight of 35.457. Molecular chlorine (Cl_2) has a weight of 70.914. Some of the physical properties of gaseous and liquid chlorine are given in Table 11.3. A solubility curve for Cl_2 in water is seen in Figure 11.3.

Chlorine Compounds

Several chlorine-containing compounds are available for disinfection of water (Table 11.4). Selection of the appropriate compound depends on the type of water facility. Gaseous chlorine is, today, employed exclusively for the large volumes of municipal and industrial waters. Small-scale facilities, domestic and small communities, frequently apply calcium or sodium hypochlorite. Large public swimming pools use gaseous chlorine, whereas smaller public

Table 11.3. Physical Properties of Gaseous and Liquid Chlorine.[28]

Gas	
Density at 34°F and 1 atm (lb/ft^3)	0.2006
Specific gravity at 32°F and 1 atm	2.482[a]
Liquefying point at 1 atm [°F (°C)]	–30.1 (–34.5)
Viscosity at 68°F (cP)	0.01325[b]
Specific Heat (Btu/lb-°F)	
At constant (1 atm) pressure and 59°F	0.115
At constant volume, 1 atm pressure and 59°F	0.085
Thermal conductivity at 32°F (Btu/hr-ft^2-°F-ft)	0.0042
Solubility in water (Figure 11.4) at 58°F [lb/1000] gal (g/L)]	60.84 (7.297)
Liquid	
Critical temperature [°C (°F)]	144 (291.2)
Critical Pressure (psia)	1118.36
Critical density [g/L (lb/ft^3)]	573 (35.77)
Density at 32°F (lb/ft^3)	91.67
Specific gravity at 68°F	1.41[c]
Boiling (liquefaction) point at 1 atm [°C(°F)]	–34.5 (–30.1)
Freezing point [°C (°F)]	–100.98 (–149.76)
Viscosity at 68°F (cP)	0.342[d]

[a] Specific gravity of air=1.

[b] Approximately the same as saturated steam between 1 and 10 atm.

[c] Specific gravity of water=1.

[d] Approximately 0.35 times that of water at 68°F.

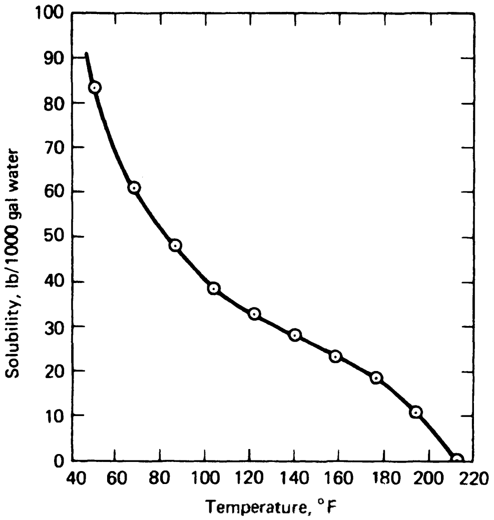

Figure 11.3. Solubility of chlorine in water. Reproduced from White,[28] using the data of Winkler,[29] courtesy of the Van Nostrand-Reinhold Company.

and private pools apply either the hypochlorites or the chlorine derivatives of isocyanuric acid.

The term "available chlorine content" was employed in the early days of chlorination as a method of comparing the disinfection power of the various chlorinated compounds. Gaseous Cl_2 was thought to be entirely "available" for the disinfection reactions. It is, simply stated, a measurement of the oxidizing power expressed in terms of an equivalent quantity of chlorine. It is determined analytically by titration of the I_2 released by the chlorine compound from an acidic solution of KI. It is expressed as the percentage by weight of the original chlorine, 70.914. For example:

$$Cl_2 + 2I^- = 2Cl^- + I_2 \qquad (1)$$

Since one mole of chlorine releases one mole of iodine:

$$\%AC = \frac{nMWCl_2}{MW\ compound} \times 100 = \frac{1 \times 70.914}{70.914} = 100\% \qquad (2)$$

where AC = available chlorine
n = number of moles of released I_2
MW = molecular weight

Another example:

$$OCl^- + H_2O + 2I^- = Cl^- + 2OH^- + I_2 \qquad (3)$$

$$\%AC\ of\ NaOCl = \frac{70.914}{74.5} = 95.2\%$$

$$\%AC\ of\ HOCl = \frac{70.914}{52} = 136.4\%$$

Table 11.4. Percent Available Chlorine of Various Chlorine Materials.[a]

Material	Available Chlorine, %
Cl_2, Chlorine	100 (by definition)
Bleaching Powder (chloride of lime, etc.)	35–37
$Ca(OCl)_2$, Calcium Hypochlorite	99.2
Commercial Preparations	70–74
NaOCl, Sodium Hypochlorite (unstable)	95.2
Commercial Bleach (industrial)	12–15
Commercial Bleach (household)	3–5
ClO_2, Chlorine Dioxide	263.0
NH_2Cl, Monochloramine	137.9
$NHCl_2$, Dichloramine	165.0
NCl_3, Nitrogen Trichloride	176.7
$HOOCC_6H_4SO_2NCl_2$ (Halazone)	52.4
NClCONClCONCl CO, Trichloroisocyanuric Acid	91.5
CONClCONClCONH, Dichloroisocyanuric Acid	71.7
CONClCONClCON Na, Sodium Dichloroisocyanurate	64.5

[a] Reproduced from Laubusch,[20] courtesy of the McGraw-Hill Book Company.

Hydrolysis and Protolysis of Chlorine

When gaseous chlorine is dissolved in water, the hydrolysis reaction occurs rapidly:[30,31]

$$Cl_2 + H_2O = H^+ + Cl^- + HOCl \tag{4}$$

The hydrolysis constant for this reaction is:

$$K_H = \frac{[H^+][Cl^-][HOCl]}{[Cl_2]} \tag{5}$$

The equilibrium constant values are:

	0°C	15°C	25°C	35°C	45°C	Ref.
$K_H \times 10^4$ (M^2/l^2)	1.46	2.81	3.94	5.10	6.05	31
$K_H \times 10^4$ (M^2/l^2)	1.56	3.16	4.48			30
$K_H \times 10^4$ (M^2/l^2)	1.45		4.47	5.68		31

The extent of chlorine hydrolysis is controlled by the $[H^+]$ in Equation 4. At pH values >3 and with $[Cl_2]_t$ <100 mg/L, very little molecular Cl_2 is present.

That the rate of hydrolysis is extremely rapid was determined by Morris[32] and Shilov and Solodushenkov.[33] The latter investigators found the hydrolysis essentially to be complete in less than 1 sec at 1°C. Morris,[32] by means of kinetic considerations, found the reaction mechanism to be:

$$Cl_2 + OH^- = HOCl + Cl^- \tag{6}$$

and the rate of hydrolysis conforms to:

$$-\frac{d[Cl_2]}{dt} = \left[\frac{k_1[Cl_2]K_w}{H^+}\right] - k_2[HOCl][Cl^-] \tag{7}$$

The rate constant, k_1, is on the order of 3.4×10^{14} at 1.2°C.

Equation 4 shows that, for each mole of Cl_2, there is formed one mole of HCl, a "strong" acid, and one mole of hypochlorous acid (HOCl), a "weak" acid. It should be noted that superchlorination of water will reduce the natural alkalinity in substantial quantities. For example, 1 mg/L Cl_2 produces the acidic equivalent of 1.41 mg/L of alkalinity as $CaCO_3$. Both HCl and HOCl were considered in this calculation. Since HOCl is a "weak" acid, it protolyzes in the Brønsted sense:

$$HOCl + H_2O = H_3^+O = OCl^- \tag{8}$$

The protolysis constant for HOCl has been reported by Morris[34] and several other investigators. Table 11.5 shows the pK_a values for HOCl for the temperature range from 0–35°C. K_a is a function of temperature via this equation:[34]

$$\ln K_a = 23.184 - 0.0583T - \frac{6908}{T} \tag{9}$$

where T is expressed in the Kelvin scale (K = °C +273.15). It is, of course, the $[H^+]$ that determines the extent of Equation 8 and the predominance of [HOCl] or $[OCl^-]$ at a given pH value. For disinfection purposes, it is extremely important to know the distribution of chlorine between HOCl and OCl^- because they have considerably different capabilities for destruction of microorganisms. Figure 11.4 shows the percentage dissociation of HOCl over the pH range of

Table 11.5. pK_a for Hypochlorous Acid at Even Temperature Intervals.[a]

Temp (°C)	pK_a	pK_a (Caramazza)	pK_a (others)
0	7.825	7.82	7.72 (S and K)
5	7.754		7.63 (K and H)
10	7.690	7.72	
15	7.633	7.65	7.58 (B and D)
20	7.582		7.55 (A and M)
25	7.537	7.53	7.53 (H)
30	7.497		
35	7.463	7.50	

[a] Reproduced from Morris,[34] courtesy of the American Chemical Society.

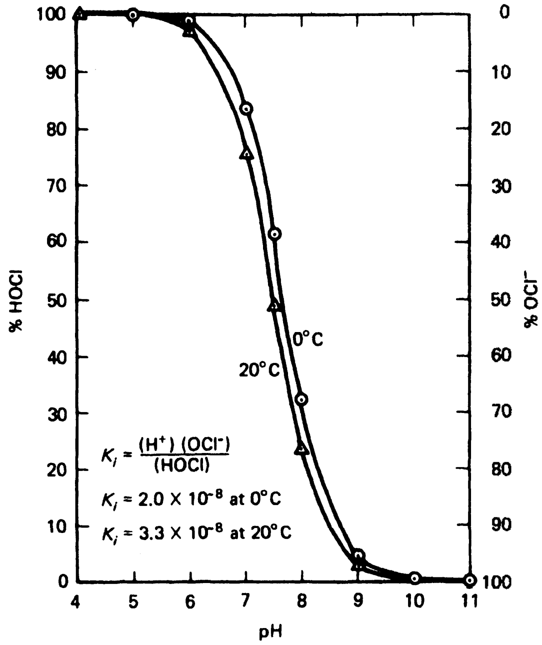

Figure 11.4. Protolysis of hypochlorous acid at 0 and 20°C. Reproduced from White,[28] courtesy of the Van Nostrand-Reinhold Co.

4–11 at 0° and 20°C. The K_a values cited in the graph are the earlier ones from Morris.[34]

Oxidation States of Chlorine

Table 11.6 shows the oxidation states of chlorine and the free energies of formation for the dissolved and gaseous species. Some of the relevant reduction reactions (10–17) involving these species are given in Table 11.7 at 25°C. The E-pH stability diagram for the $Cl_{2(g)}$–$H_2O_{(l)}$ system at 25°C is seen in Figure 11.5. It is obvious that, as an oxidant in water, Cl_2 is not stable.

Chloramination

Reactions with Ammonia

In aqueous systems, chlorine reacts with ammonia (NH_3) to form the chloramines:

$$\underset{\text{monochloramine}}{NH_3 + HOCl = NH_2Cl + H_2O} \tag{18}$$

$$\underset{\text{dichloramine}}{NH_2Cl + HOCl = NHCl_2 + H_2O} \tag{19}$$

$$\underset{\substack{\text{trichloramine}\\ \text{(nitrogen trichloride)}}}{NHCl_2 + HOCl = NCl_3 + H_2O} \tag{20}$$

The ammonia occurs from natural decomposition of organic N compounds or denitrification reactions catalyzed by various microorganisms. Also, NH_3 may be added to water before (preammoniation) to prevent tastes and odors by phenols (see Chapter 3) or after (postammoniation) addition of chlorine. The latter practice is the combined residual chlorination described above. In any event, NH_3 contributes to the chlorine demand of the water. Figure 11.6 shows a graphic illustration of the "breakpoint" reaction where only NH_3 is involved. The breakpoint curve results from Reactions 18–20 whose products, the chloramines, are dependent on: pH value, relative concentrations of HOCl and NH_3 reaction time, and temperature. Monochloramine usually is the only chloramine observed when pH values are greater than 8, and when the molar ratio of HOCl to NH_3 is 1:1 or less. At pH values less than 3, only trichloramine ordinarily is detected.

Kinetics of Formation Reactions

The rate of monochloramine formation was reported by Weil and Morris.[37] It is an extremely rapid reaction and extremely sensitive to changes in the [H$^+$]. Within the pH range of most water supplies, the reaction is usually 90% complete in one minute or less. As seen in Figure 11.7, the reaction rate is at its maximum at pH 8.5. The production of $NHCl_2$ is optimized in the pH range of 7–9 and at a HOCl:NH_3 ratio of 3:1 to 5:1 (by weight). At higher HOCl:NH_3 ratios or at lower pH values, di- and trichloramines are formed. Formation of monochloramine accounts for the chlorine residual in Figure 11.6 up to the "peak" of the curve.

It should be noted that Reaction 11.18 could occur also between ionic molecules: $NH_4^+ + OCl^-$, between ionic and neutral molecules: $NH_4^+ + HOCl^-$ or $NH_3 + OCl^-$. Weil and Morris[37] favor the neutral reaction mechanism because it

Table 11.6. Oxidation States of Chlorine.[a]

Oxidation Number (Z)	Considered	Not Considered	DG_f° (kcal/mol)	Name, Color, Crystalline System
−1	Cl^-		−31.350	Chloride ion, colorless
0	Cl_2		1.650	Dissolved chlorine
+1	HClO		−19.110	Hypochlorous acid, colorless
+1	ClO^-		−8.900	Hypochlorite ion, colorless
+3	$HClO_2$		0.070	Chlorous acid, colorless
+3	ClO_2^-		2.740	Chlorite ion, colorless
+5	ClO_3^-		−0.620	Chlorate ion, colorless
+7	ClO_4^-		−2.470	Perchlorate ion, colorless
−1	HCl		−22.769	Hydrogen chloride, colorless
0	Cl_2		0	Chlorine, greenish-yellow
+1	Cl_2O		22.400	Chlorine monoxide, hypochlorous anhydride, brownish
+2		ClO		Chlorine oxide
+4	ClO_2		29.500	Chlorine dioxide, orange-yellow
+6		ClO_3		Chlorine trioxide, brown
+7		Cl_2O_7		Chloric heptoxide, perchloric anhydride, colorless
+8		ClO_4		Chlorine tetroxide, colorless

[a] Reproduced from Pourbaix,[35] courtesy of Pergamon Press, Ltd.

Table 11.7. Some Reduction Reactions of Chlorine at 25°C.[35]

Reaction Number	Reaction	E° (V)
10	$Cl_2 + 2e = 2Cl^-$	+1.395
11	$HOCl + H^+ + 2e = Cl^- + H_2O$	+1.494
12	$OCl^- + 2H^+ + 2e = Cl^- + H_2O$	+1.715
13	$ClO_3^- + 6H^+ + 6e = Cl^- + 3H_2O$	+1.451
14	$ClO_4^- + 8H^+ + 8e = Cl^- + 4H_2O$	+1.389
15	$ClO_{2(g)} + 4H^+ + 5e = Cl^- + 2H_2O$	+1.511
16	$Cl_{2(g)} + 2e = 2Cl^-$	+1.359
17	$ClO_{2(g)} + 2H^+ + 3\ e = ClO^- + H_2O$	+1.374

fits their kinetic data reasonably well. An increase in rate of the reaction as the pH value is increased in acid range is explained by a greater fraction of the analytical ammonia present as the free base (pK_a=9.2 for NH_4^+). Similarly, a decrease in the rate in the alkaline pH range can be attributed to ionization of the HOCl (pK_a=7.537). It is interesting to note that, at the pH of maximum rate (Figure 11.7), approximately 80% of the analytical chlorine is OCl^-. In any event, the rate of the ammonia reaction is:

$$v = k_1 [NH_3] [HOCl] \gamma_{NH_3} \gamma_{HOCl} / \gamma_x \qquad (21)$$

where v = velocity of reaction
k_1 = rate constant
γ = activity coefficients (γ_x is for the activated complex)

At 25°C, the second-order rate constant k_1 between the uncharged molecule is 5.1×10^6 L/mol-sec.[38]

The specific formation rate of dichloramine is considerably slower than the formation of monochloramine, except at pH values less than 5.5. Specific rates are given in Table 11.8a for the formation of the three chloramines.[39] Since dichloramine forms more slowly than monochloramine at nearly neutral pH values, $NHCl_2$ does not constitute a large percentage of the available chlorine unless the water is quite acid or where the molar ratio of Cl_2:NH_3 is greater than 1.0. The relative percentages of di- and monochloramine for equimolar Cl_2 and NH_3 and for 25% excess NH_3 are seen in Figure 11.8.[40] In waters with pH <4, or where Cl_2 concentrations are considerably in excess of NH_3, trichloramine is formed. Since NCl_3 is formed from $NHCl_2$ (Reaction 11.20), the reaction occurs only under conditions in which the dichloramine is reasonably stable. Therefore, NCl_3 is the only chloramine at pH <3. Also, it may be formed when Cl_2:NH_3 molar ratios are >2. However, NCl_3 occurs in diminishing proportions as the pH value is increased from 3 to 7.5. Above the latter value, no NCl_3 is observed, regardless of the Cl_2:NH_3 ratio.[41]

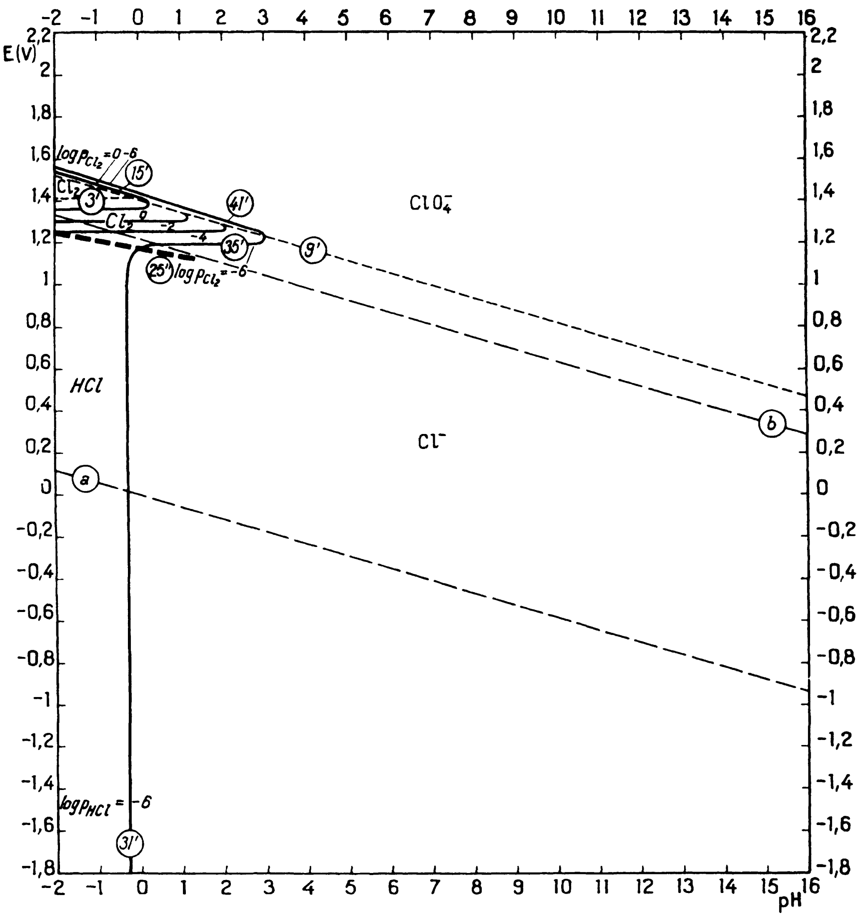

Figure 11.5. Potential-pH equilibrium diagram for the system Cl_2-H_2O at 25°C, for solutions containing 1 g-atom Cl/L. Equation numbers refer to original text. Reproduced from Pourbaix,[35] courtesy of Pergamon Press Ltd.

In Figure 11.6, the breakpoint become significant in the pH range of 6–9. When the Cl_2:NH_3 molar ratios are 0 to 1, NH_2Cl is formed. This creates the peak seen in Figure 11.6. At molar ratios >1, $NHCl_2$ is formed, but it decomposes rapidly in accord with, perhaps, Reaction 23 (see below). Therefore, when the molar ratio exceeds 1 and up to about 1.65, the chlorine residual decreases until the breakpoint occurs after the NH_3 has been converted mainly to N_2 and some NO_3^-.[42] After the breakpoint, the chlorine residual exists as free available chlorine; that is, HOCl and OCl^-.

Stoichiometry of Breakpoint Chemistry

It is appropriate to examine the stoichiometry of the breakpoint chlorination phenomenon. Figure 10.10 shows another schematic diagram of breakpoint chlorination.[42] It is based on the classical studies of Griffin and Chamberlain,[43] Griffin,[44] and Palin.[45] In Figure 11.9a, the residual oxidizing chlorine increases proportionately with chlorine dosage until the molar ratio of Cl_2:NH_3 reaches 1. This is up to point A. As seen in Figure 11.9b, very little, if any, combined nitrogen was oxidized in this range. Once the ratio exceeds 1, there is a decrease in residual oxidizing chlorine with the concurrent increase in chlorine dosage (points A to B, Figure 11.9a). At point B—the "breakpoint"—essentially all of the oxidizing chlorine is reduced, and all of the NH_3-N is oxidized (Figure 11.9b). An appropriate reaction is understood. Beyond point B, free chlorine residual exists. According to Wei and Morris,[42] "the development of the breakpoint results from a redox reaction between aqueous chlorine and ammonia with location of the breakpoint indicating the stoichiometry of the reaction." The molar ratio of reduced chlorine to oxidized nitrogen, equal to about 1.65 at the breakpoint, shows that the major oxidation of the ammonia is to gaseous nitrogen, which requires a ratio equal to 1.5. The excess over 1.5 is accounted for by a small side formation of nitrate as shown by Palin.[45] Except for the formation of NO_3^-, the stoichiometry is explained by two reactions:

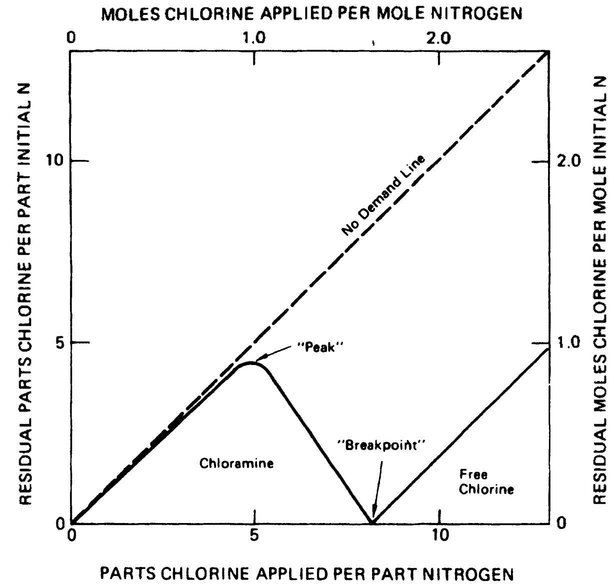

Figure 11.6. Diagrammatic representations of completed breakpoint reaction.[36]

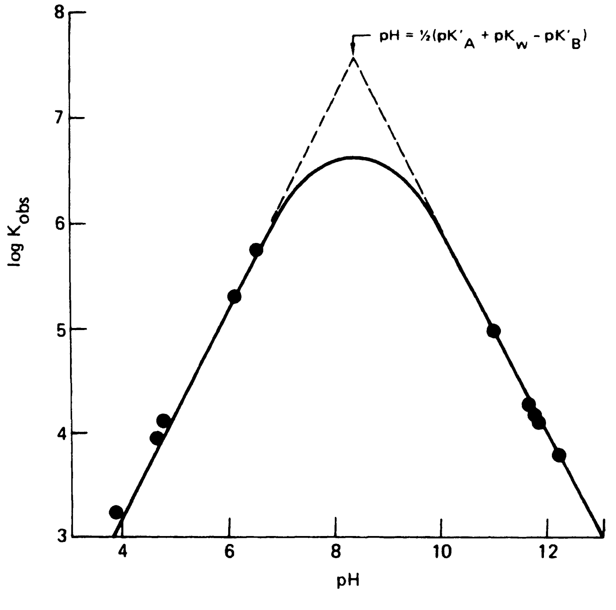

Figure 11.7. Variation in rate of chloramine formation with pH calculated with log K_n = 8.48.[36]

$$HOCl + NH_3 = NH_2Cl + H_2O \qquad (18)$$

and

$$2NH_2Cl + HOCl = N_2 + H_2O + 3H^+ + 3Cl^- \qquad (22)$$

Although the stoichiometry of the breakpoint comes from the addition of reactions 18 and 22, this may not be the precise mechanism.[45] It, however, is not a major consideration in the dynamics of the breakpoint process.

According to Wei and Morris,[42] "it is the first hour of reaction that is most significant in terms of practical application of the breakpoint process, for disinfection of water supplies must almost always be accomplished within that period." This first hour of the Cl_2–NH_3 reaction was studied in great detail by Wei and Morris.[42] The experimental

Table 11.8a. Comparison of Specific Rates for Chloramine Formation at 20°C.[a]

	Reaction Number	$k(M^{-1}\text{-sec}^{-1})$	General Expression for k (L/mol-sec)
NH_2Cl	18	5.6×10^{6}[b]	$k=9.7 \times 10^{8} \exp(-3000/RT)$
pH 3.2	—	4.9[c]	
pH 2.3	—	0.6[c]	
$NHCl_2$	19	2.7×10^{2}[d]	$k=7.6 \times 10^{7} \exp(-7300/RT)$
NCl_3			
pH 2.3	—	14.9	$k=1.15 \times 10^{3} \exp(-2500/RT)$
pH 3.2	—	3.4	$k=2.62 \times 10^{4} \exp(-5200/RT)$
pH 3.97	—	1.6	$k=7.83 \times 10^{4} \exp(-6270/RT)$
pH 4.53	20	2.0	$k=3.43 \times 10^{5} \exp(-7000/RT)$

[a] Reproduced from Sanuinsin and Morris.[39]
[b] Calculated assuming reaction between neutral molecules.
[c] Extrapolated K_{obs}.
[d] Rate for nonacid-catalyzed reaction.

Table 11.8b. Summary of Dynamic and Equilibrium Constants for the Aqueous Chlorine-Ammonia System.[48]

Reaction	Constant	General Expression	25°Value
18	k_{18}	$6.6 \times 10^{8} \exp(-1510/T)$	4.2×10^{6}
30	k_{30}	$1.38 \times 10^{8} \exp(-880/T)$	2.1×10^{-5}
33	k_{33}	$0.209 \exp(-7290/T)$	5.0×10^{-12}
19	k_{19}	$3.0 \times 10^{5} \exp(-2010/T)$	3.5×10^{2}
31	k_{31}		7.6×10^{-7}
—	K		2.2×10^{-9}
20	k_{20}	$2.0 \times 10^{5} \exp(-3420/T)$	2.1
32	k_{32}	$5.1 \times 10^{3} \exp(-5530/T)$	4.5×10^{-5}
—	K	$2.6 \times 10^{-2} \exp(-2110/T)$	2.1×10^{-5}

conditions were: (a) three pH values: 6.7, 7.0, and 7.2 (phosphate buffer); (b) four temperatures: 5, 10, 15, and 20°C; and (c) a varying of the reactant concentrations of NH_3–N from 0.25 to 1.5 mg/L; however, the molar ratio of Cl_2:NH_3 was held constant at 1.8 in order to leave some free chlorine after completion of the breakpoint.

Typical kinetic curves are seen in Figure 11.10. It is seen that formation of NH_2Cl is "rapid" (<1 min). Also, formation and decomposition of $NHCl_2$ are rapid, the latter of which is a first-order process. In each curve in Figure 11.10, a maximum $[NHCl_2]$ is observed for which temperature affects the magnitude and rate of decomposition. $NHCl_2$ is more persistent at the lower temperatures of 10 and 5°C. The overall effect of pH on the breakpoint process as it is decreased from 7.2 to 7.0 to 6.7 is: (a) to increase the "hump" (magnitude) of the $NHCl_2$ curve; (b) to delay appearance of the hump on the time ordinate, i.e., it takes longer for the hump to form; and (d) to increase the persistence of $NHCl_2$. These observations are consistent with previous works of Morris et al. (see Figure 11.7 and Wei and Morris[37]).

Figure 11.11 summarizes the effect of initial $[NH_3]$ on $NHCl_2$ formation at pH 7.0. Since the formation of $NHCl_2$ is a second-order reaction, its maximum concentration should occur sooner on the time ordinate and with a larger magnitude. This is seen in Figure 11.11. Also, the rate of decomposition of $NHCl_2$ is faster as the $[NH_3]_0$ is increased.

Table 11.9 summarizes the experimental data of the stoichiometry of the Cl_2–NH_3 reaction in Column 6. The R values are those obtained after 60 min of reaction and at the breakpoint. There was no significant effect of $[H^+]$ on the R value within the limited pH range, 6.7 to 7.2. Wei and Morris[42] seem to think that there is an effect of temperature with an R value of 1.72 at 20°C and 1.66 at 5°C. This may or may not be significant statistically.

The point in time at which $NHCl_2$ reaches its maximum concentration, i.e., the "hump", apparently governs the overall kinetics of the breakpoint. The kinetic pattern of this reaction indicates that $NHCl_2$ is a true intermediate in the breakpoint reaction. Since the formation of $NHCl_2$ by Reaction 19 is a second-order reaction[46] and its decomposition by Reaction 23 is a first-order reaction, the former is favored over the latter. Evidence for this statement is seen in Figure 11.10.

Another factor in the breakpoint reaction, especially in the last few minutes, is the resurgence of free chlorine. This may occur from:

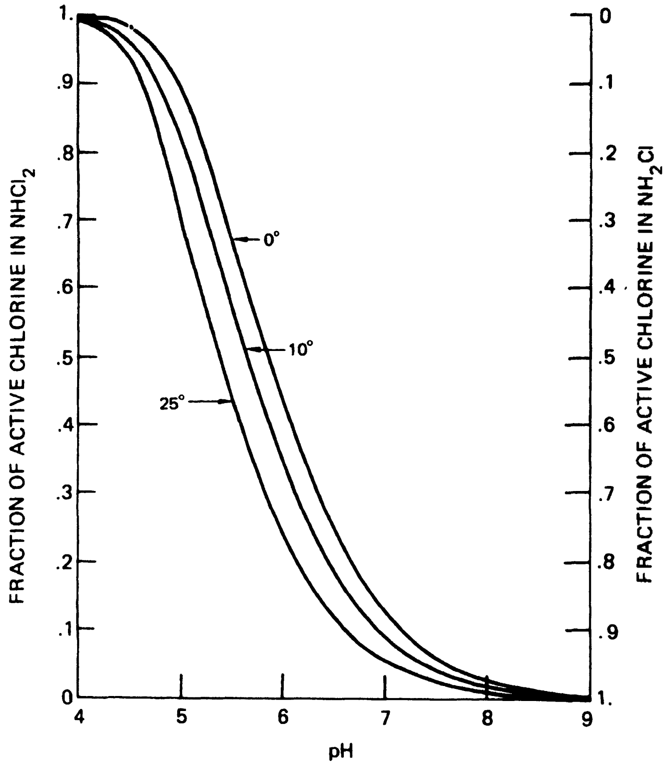

Figure 11.8. Proportions of monochloramine (NH_2Cl) and dichloramine ($NHCl_2$) formed in water chlorination with equimolar concentrations of chlorine and ammonia.[36,40]

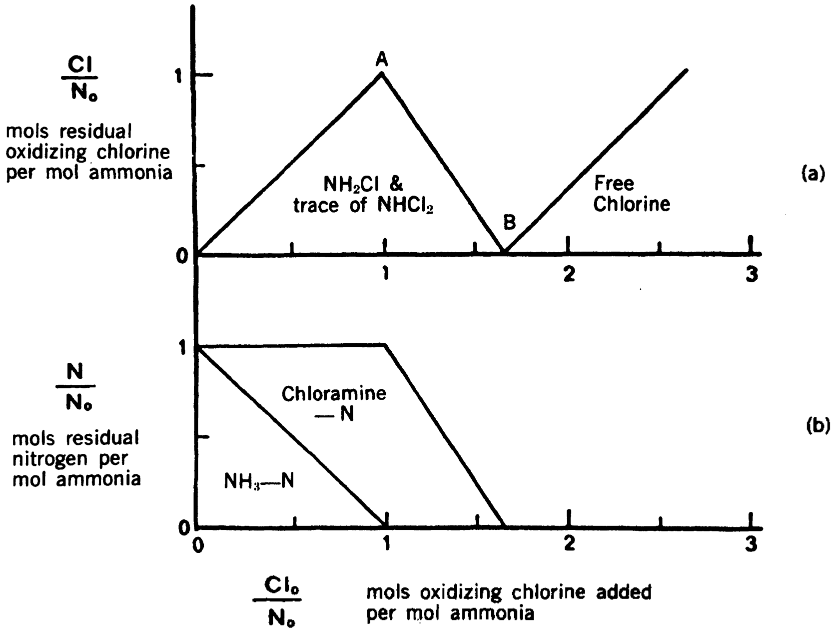

Figure 11.9. Schematic diagram of breakpoint chlorination. Reproduced from Wei and Morris.[42]

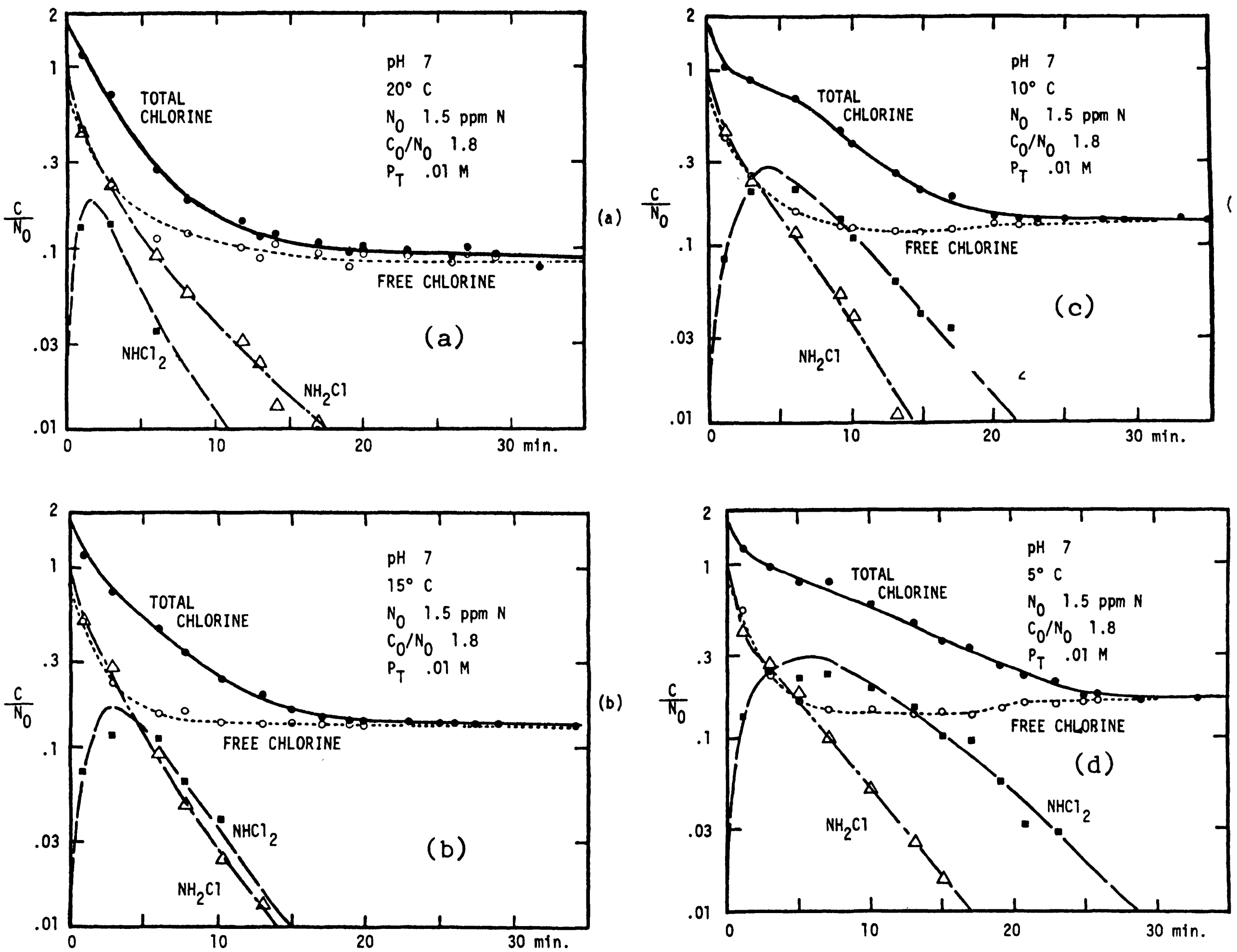

Figure 11.10. Chlorination of ammonia. Conditions: pH 7, N_0 = 1.5 mg/L N, C_0/N_0 = 1.8, P_t = 0.01 *M*, (a) 20°C, (b) 15°C, (c) 10°C, and (d) 5°C. Reproduced from Wei and Morris.[42]

$$2NHCl_2 + H_2O = N_2 + 3H^+ + 3Cl^- + HOCl \quad (23)$$

This resurgence of HOCl has been observed also by Palin.[45] It affects the kinetic process as well as the stoichiometry. Also, it fits the experimental data whereby a molar ratio of 1.5 of Cl_2:NH_3 yields N_2 as a decomposition product in the breakpoint.

Kinetics of Decomposition Reactions

Wei and Morris[42] reported that the decomposition of $NHCl_2$ in aqueous solutions is in accord with first-order kinetics wherein the specific rate is more than proportional to the $[OH^-]$ (also, see below). NOH is, perhaps, an intermediate in the decomposition of $NHCl_2$. Other competing reactions for NOH are:[41]

$$NOH + NH_2Cl = N_2 + H_2O + H^+ + Cl^- \quad (24)$$

$$NOH + NHCl_2 = N_2 + HOCl + H^+ + Cl^- \quad (25)$$

$$NOH + 2HOCl = NO_3^- + 3H^+ + 3Cl^- \quad (26)$$

Saguinsin and Morris[39] reported the formation and decomposition of NCl_3 under a variety of conditions. That the kinetics of the formation reaction is much slower than formation of NH_2Cl or $NHCl_2$ was given in Table 11.8. Values of the specific rate are seen in Figure 11.12, where it is a function of the $[H^+]$ at a given temperature. The formation reaction is not strongly dependent on the pH until a value of 3.2 is reached. When the ratio of formation of the three chloramines is compared (Table 11.8) at 20°C, the specific

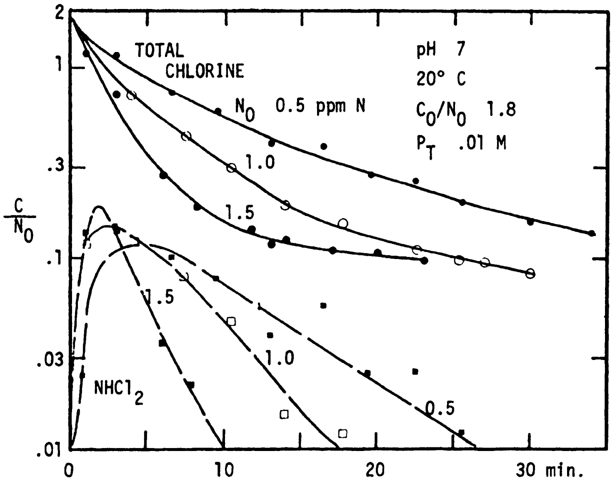

Figure 11.11. Effect of initial ammonia concentration on chlorination of ammonia at pH 7, 20°C, C_0/N_0 = 1.8, P_t = 0.01 *M*. Reproduced from Wei and Morris.[42]

Table 11.9. Comparison of Stoichiometric Ratios.[a]

Temp.	**N_o**				
pH	**(°C)**	**(mg/L N)**	**C_o/N_o**[b]	**C_f/N_o**[c]	**R**[d]
6.7	20	1.0	1.8	0.09	1.71
	15	1.0	1.8	0.10	1.70
	10	1.0	1.8	0.11	1.69
	5	1.0	1.8	[e]	[e]
7.0	20	1.0	1.8	0.07	1.73
	15	1.0	1.8	0.10	1.70
	10	1.0	1.8	0.11	1.69
	5	1.0	1.8	0.13	1.67
7.2	20	1.0	1.8	0.07	1.73
	15	1.0	1.8	0.08	1.72
	10	1.0	1.8	0.12	1.68
	5	1.0	1.8	0.12	1.68
7.0	20	1.5	1.8	0.19	1.71
	15	1.5	1.8	0.13	1.67
	10	1.5	1.8	0.14	1.66
	5	1.5	1.8	0.16	1.64
6.7	20	0.25	1.8	[e]	[e]
	20	0.5	1.8	[e]	[e]
7.0	20	0.5	1.8	[e]	[e]
7.2	20	0.5	1.8	[e]	[e]
	20	1.5	1.8	0.07(–)	1.73(+)
7.04–7.24	20	0.25	1.7	[e]	[e]
7.05–7.25	20	0.5	1.7	0.17	1.53
7.16–7.22	20	1.0	1.7	0.17	1.53

[a] Reproduced from Wei and Morris.[42]

[b] C_o/N_o=molar ratio of initial chlorine to initial ammonia.

[c] C_f/N_o=molar ratio of final free chlorine to initial ammonia.

[d] R=stoichiometric ratio as a molar ratio of chlorine reduced to ammonia oxidized. R=C_o/N_o – C_f/N_o.

[e] Data are not available because the reaction had not reached completion at the time the experiment was terminated.

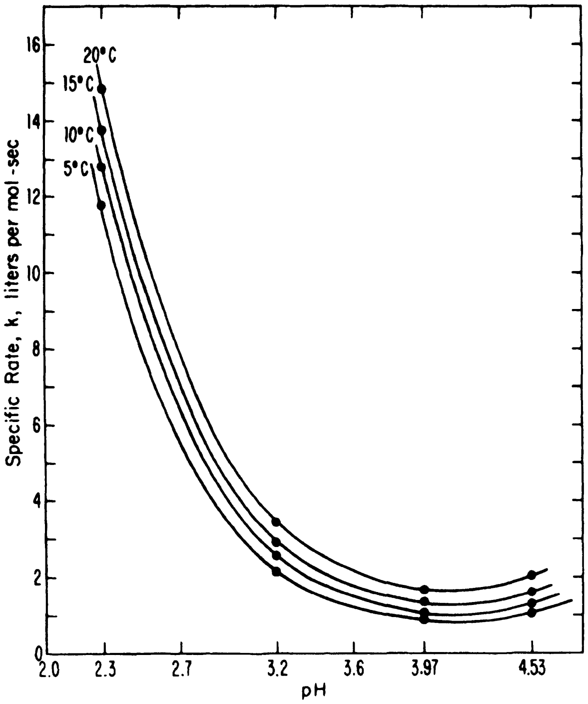

Figure 11.12. Specific rates of NCl_3 formation as a function of pH and temperature. Reproduced from Saguinsin and Morris.[39]

rate for NH_2Cl is approximately 10^4 times that for $NHCl_2$, and about 10^6 times that for NCl_3, based on a direct reaction between HOCl and the uncharged amine. At the lower two pH values, 2.3 and 3.2, the effect of Cl_2 on the kinetics of the formation reaction must be considered also. There was a tenfold increase in the reaction rate in the presence of $5 \times 10^{-4}\,M\,Cl^-$.

That the decomposition of NCl_3 in neutral and slightly alkaline solutions is a first-order process is seen in Figure 11.13a. Here again, the pH value, or, in this reaction, the $[OH^-]$, is the factor accelerating the decomposition. This is seen in Figure 11.13b. The decomposition was dependent directly on the $[OH^-]$, since a linear relation was observed between the specific rate constant and $[OH^-]$. Either one of these two reactions may be operative:

$$NCl_3 + H_2O \overset{OH^-}{=} NHCl_2 + HOCl \qquad (27)$$

$$NCl_3 + OH^- = NHCl_2 + OCl^- \qquad (28)$$

Reaction 11.27 is OH^--catalyzed, and Reaction 28 is a direct reaction with OH^-. See below for hydrolytic decomposition reactions.

Saunier and Selleck[47] reported a rather comprehensive investigation into the kinetics of breakpoint chlorination in continuous-flow systems via a pilot plant. Three types of chlorine contact chambers were employed: (a) a pipe reactor whose flow characteristics approached those of a plug flow reactor (PFR), (b) a tubular reactor, and (c) a tank reactor whose mixing characteristics approached those of an ideal continuous-flow, stirred-tank reactor (CSTR). Tap water was employed in which the molar ratio of chlorine to ammonia-N was held in the 1.6 to 2.78 range. The major variables in this were the $[H^+]$ and the Cl_2:NH_3-N molar ratio. Reaction times were <1 hr in which the formation and disappearance of the three chloramines were followed. The essential results were:

1. The major oxidation products of ammonia were N_2 and NO_3^-. The proportion of NH_3-N converted to NO_3^- "appeared to be independent of reaction pH" (6.65 to 9.2).
2. The maximum speed of the oxidations of mono- and dichloramine occurred at a pH of almost 7.5. These reactions were slower at pH values <7 and >8.
3. NCl_3 appeared very early in the reaction and reached its greatest content at a pH of about 7, in the PFR experiments. This observation is at variance with other researchers.
4. The oxidation of mono- and dichloramine occurred within a matter of minutes to unknown intermediate nitrogen compounds. According to Saunier and Selleck, the eventual appearance of N_2 and NO_3^- required substantially longer reaction times; i.e., several hours. No explanations were given for this observation. Evidence from these experiments indicate that the principal oxidation product may be NO_3^- formed from this reaction:

$$NH_4^+ + 4HOCl = NO_3^- + 4Cl^- + 6H^+ + H_2O \qquad (29)$$

Kinetics of Hydrolysis Reactions

The reverse of Reactions 18–20 represent the hydrolysis of the three chloramines and their regeneration. Consequently, it is important to note the rates of these reverse reactions in relation to the rates of the forward reactions. In turn, the rate constants may be combined to form equilibrium constants for the three reactions that determine their overall direction. These hydrolytic reactions, in the forward direction, are:

$$NH_2Cl + H_2O = NH_3 + HOCl \qquad (30)$$

$$NHCl_2 + H_2O = NH_2Cl + HOCl \qquad (31)$$

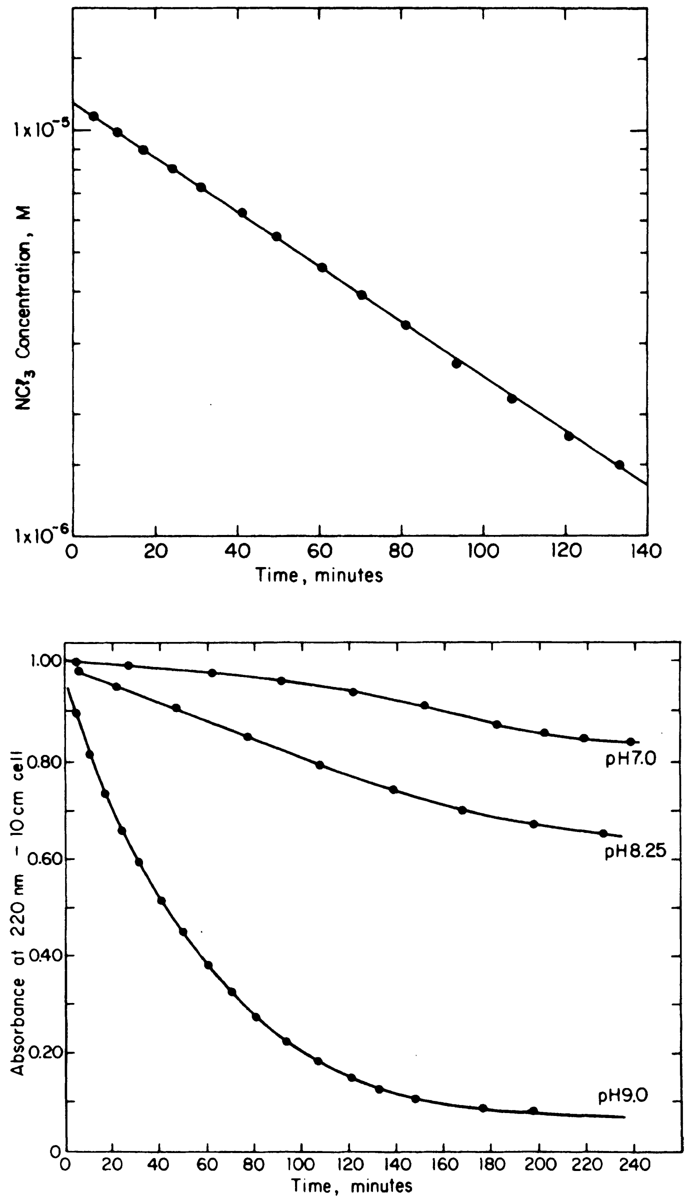

Figure 11.13. (a) Rate of decomposition of 1.15 x 10^{-5} *M* NCl_3 at 20°C and pH 9. (b) Effect of pH on the rate of decomposition of 1.2 x 10^{-5} *M* NCl_3 at 20°C. Reproduced from Saguinsin and Morris.[39]

$$NCl_3 + H_2O = NHCl_2 + HOCl \qquad (32)$$

The rate constants for Reactions 30–32 are found in Table 11.8b, as well as revised rate constants for Reactions 18–20.[48]

The equilibrium constants in Table 11.8b were computed from the ratio of the forward rate constant to the reverse rate constant. For example:

$$k_{eq} = \frac{K_{29}}{k_{18}} = \frac{2.1\times10^{-5}}{4.2\times10^{6}} =$$

$$5.0\times10^{-12} = \frac{[NH_3]\,[HOCl]}{[NH_2Cl]\,[H_2O]} \qquad (33)$$

Consequently, the equilibrium constants for Reactions 29–31 indicate that the formation of the chloramines greatly

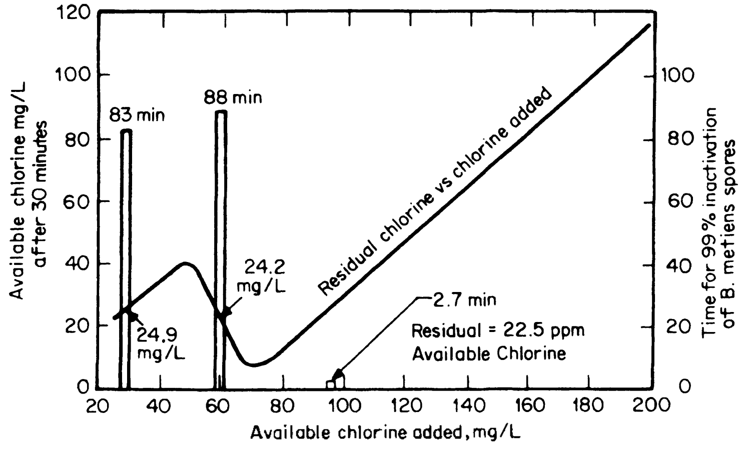

Figure 11.14. Effect of increased chlorine dosage on residual chlorine and germicidal efficiency: pH 7.0, 20°C, NH_3 10 mg/L.[49]

exceeds their decomposition by hydrolysis. The degree of hydrolysis of NH_2Cl (Reaction 29) ranges from 0.1 to 1% for pH values near neutrality, and for concentrations in the range of 1–10 mg/L as Cl_2.[47a] An excess of ammonia depresses the hydrolysis greatly.

Miscellaneous

In an investigation on the effect of NH_3 on the germicidal efficiency of chlorine in neutral solutions, the effect of chlorine speciation on disinfection efficiency was demonstrated via a breakpoint graph.[49] Figure 11.14 shows that as the chlorine dose is increased, the total chlorine residual (after 30 minutes) increases until a quantity of 50 mg/L is reached (the "hump"). Thereafter, the residual chlorine decreases to a low value (the "dip"), whereupon it subsequently increases in a linear manner. The times required to inactivate 99% of *Bacillus metiens* spores is noted by these points in Figure 11.14. For these points, the total available chlorine is approximately identical at 22 to 24 mg/L with a 32-fold difference in microbial sensitivity. The first two points represent chloramines, whereas the third point denotes the effect of free available chlorine beyond the "dip" or breakpoint. This effect of chlorine species on disinfection efficiency is discussed below.

Bromination

Bromine was applied for disinfection of water by Henderson in 1935[50] and by Hildesheim for swimming pool water in 1936.[51] Since these times, bromine has been used mainly for swimming pool disinfection.

Physical Properties

Bromine, Br_2, is a dark brownish-red, heavy liquid.[28] A heavy, brownish-red vapor with a sharp, penetrating and suffocating odor is yielded by this liquid at room temperature. Liquid bromine is extremely corrosive and destructive to organic tissues. It has an atomic number of 35, a molecular weight of 159.808, and a specific gravity of 3.12. Bromine is unique in that it is the only nonmetallic element that is a liquid at room temperature. It is produced by the oxidation of bromine-rich brines (0.05 to 0.6% Br^-) with chlorine. Bromine is then stripped with air or steam and is collected as liquid Br_2.

An interhalogen compound, bromine chloride is produced by mixing equal molar quantities of pure bromine and chlorine.[52] It condenses to a liquid below 5°C at 1 atm pressure or above 30 psig at 25°C. In the liquid phase, 80% or more of the liquid is bromine chloride, and the rest is Br_2 and Cl_2. In the gaseous phase, about 40% of the BrCl dissociates to Br_2 and Cl_2 at 25°C. BrCl is used occasionally for disinfection of water. The physical properties of bromine and bromine chloride are given in Table 11.10.[53]

Hydrolysis and Protolysis Reactions

Bromine and bromine chloride hydrolyze rapidly:

$$Br_2 + H_2O = HOBr + H^+ + Br^- \tag{34}$$

$$BrCl + H_2O = HOBr + H^+ + Cl^- \tag{35}$$

In both cases, hypobromous acid is formed. The equilibrium constant for Reaction 34 is 5.8×10^9 at 25°C[53] and for Reaction 35, 7.21×10^{-5} at 25°C (calculated from free energy data in Latimer[54]). The extent of hydrolysis to HOBr is controlled by $[H^+]$. For a solution containing ≥ 10 mg/L Br and a pH of 6.3, 1% of the analytical bromine is Br_2. At lower bromine concentrations or higher pH values, HOBr is the predominant form. This acid is "weak" in the Brønsted sense:

Table 11.10. Physical Properties of Bromine Chloride Compared to Bromine.[a]

	BrCl	Br_2
Mol wt	115.37	159.83
% bromine	69.27	100.0
Fp, (°C)	–66.0	–7.27
Bp (°C)		
760 mm	5.0	58.78
226 mm	–30.0	25.0
100 mm	–56.0	6.0
10 mm		–32.0
5 atm	48.0	
10 atm	70.0	139.8
Density (g/cm^3)		
15°	2.352	3.1396
20°	2.339	3.1226
25°	2.324	3.1055
30°	2.310	3.0879
lb/gal, 25°C	19.3	25.8
Vapor density, (g/L), std conditions		
(0°C, 1 atm)	5.153	7.139
Latent heat of fusion, (cal/g)	17.6	15.8
Latent heat of vaporization, (cal/g),	53.2	44.9
bp 25°	30.0	46.2
Heat capacity, (cal/°K-mol), 298°K	8.38	18.09
Entropy (cal/°K-mol), 298°K	57.34	36.38
Dipole moment, D	0.56	0.0

[a] Reproduced from Kanyaer and Shilan,[53] courtesy Tekhvol. Institute of USSR.

$$HOBr + H_2O = H_3^+O + OBr^- \qquad (36)$$

The protolysis constant for HOBr, at 25°C, is 2×10^{-9}.[55] Consequently, the pH value must exceed 8.7 before OBr^- predominates.

Oxidation States of Bromine

The relevant oxidation states of bromine in aqueous solutions are: 0, Br, –I, Br^-, and +I, OBr.[35] Some reduction reactions (Equations 37–39) of bromine are given in Table 11.11. An E-pH stability diagram is seen in Figure 11.15 where Br^- is the preferred oxidation state in water. Consequently, Br_2, HOBr and OBr^- are easily reduced.

Reactions with Ammonia

Bromine and bromine chloride react with NH_3 to form bromamines:[56,57]

$$NH_3 + HOBr = NH_2Br + H_2O \qquad (40)$$

$$NH_2Br + HOBr = NHBr_2 + H_2O \qquad (41)$$

$$NHBr_2 + HOBr = NHBr_3 + H_2O \qquad (42)$$

According to Galal-Gorchev and Morris,[56] NH_2Br predominates in alkaline solutions at "high" N:Br ratios; $NHBr_2$ is the major form in the pH range 6–9 with N:Br ratios about 5–20, and NBr_3 predominates in more acidic solutions. Nitrogen tribromide can occur in mixtures up to pH 8 when two to three moles of bromine per mole of ammonia are permitted to react.

The formation and subsequent decomposition of the bromamines apparently are extremely rapid.[57] When a mixture of NH_3-N and Br_2, a 2:3 molar ratio, was allowed to react at pH of 6, the following was observed:

Constituent	1 min (10^{-4} M Br_2)	12 min (10^{-4} M Br_2)
Dibromamine	0.75	0.25
Tribromamine	0.69	0.27

There is concurrent formation and decomposition of the two bromamines. When the pH value was held at 7.0 and at 20°C, the second-order rate constant for the decomposition of $NHBr_2$ was observed to be 17.5 L/M-sec. This gives a half-life of 4.2 min for a 32 ppm solution. The temperature-dependence of this decomposition was: $K=1.38 \times 10^7 e^{-7510/RT}$ L/M-sec. The kinetics of decomposition of NBr_3 are dependent on the $[H^+]$ and the molar ratio of NH_3-N:Br_2. When the pH is 6 and the molar ratio is 0.333:1, the decomposi-

Table 11.11. Some Reduction Reactions of Bromine at 25°C.[35]

Reaction Number	Reaction	E° (V)
37	$Br_2 + 2e = 2Br^-$	+1.087
38	$HOBr + H^+ + 2e = Br^- + H_2O$	+1.331
39	$BrO^- + 2H^+ + 2e = Br^- + H_2O$	+1.589

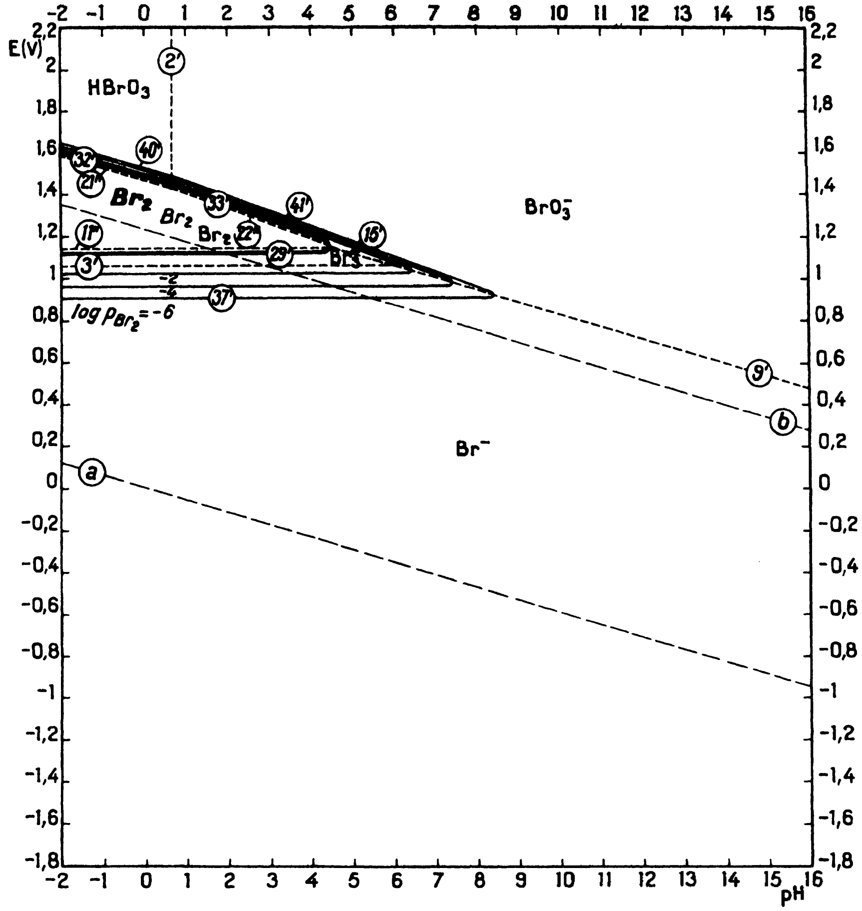

Figure 11.15. Potential-pH equilibrium diagram for the system Br_2-H_2O at 25°C, for solutions containing 1 g-atom Br/L. Equation numbers refer to the original text. Reproduced from Pourbaix,[35] courtesy of Pergamon Press Ltd.

tion rate is apparently third-order, with an observed rate constant of 9.5×10^3 L^2/M^2-sec (20°C). When the pH is increased to 7 and the molar ratio to 0.5:1, the rate constant is increased to 1.2×10^5 L^2/M^2-sec (20°C).

According to Johnson and Overby,[57] kinetic data have shown that at pH values of 6, 7, and 8, a breakpoint occurs for bromine at a N:Br mole ratio of 2:3. In the presence of excess Br_2, NBr_3 is the most stable species, whereas $NHBr_2$ is most stable in the presence of excess NH_3 (Figure 11.16). High pH values decrease the stability of both bromamines.

In addition, a breakpoint occurs when there is 17 mg/L Br_2 and 1 mg/L NH_3-N, which is the point of minimum bromamine stability. The apparent breakpoint reaction is:[58]

$$3HOBr + 2NH_3 = N_2 + 3HBr + 3H_2O \qquad (43)$$

At or near neutral pH values, NH_2Br may form ammonia bromide, which in turn dissociates into ammonia and the Br^+ ion:[59]

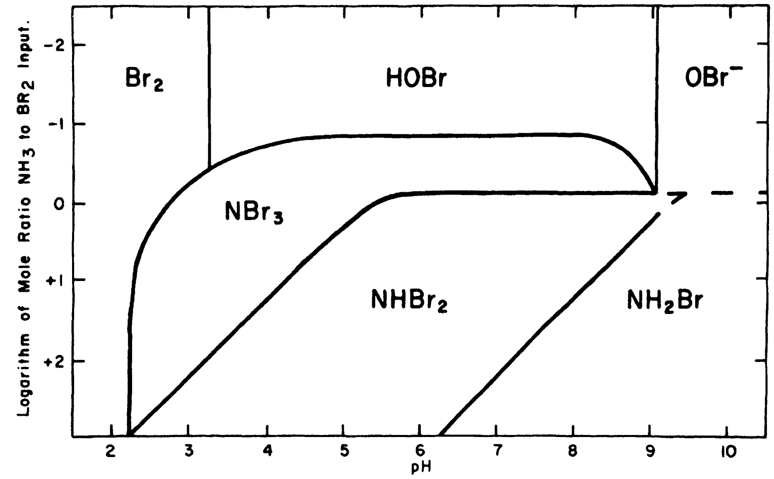

Figure 11.16. Principal species of bromine and bromamine predominating after 1–2 min at various pH and ammonia-to-bromine ratios. Lines represent equal equivalent concentrations. Hypobromous acid separation from bromine given for 10^{-3} *M* bromine. Reproduced from Johnson and Overby,[57] courtesy of the American Society of Civil Engineers.

$$NH_2Br + H^+ = NH_3Br^+ \tag{44}$$

$$NH_3Br^+ = NH_3 + Br^+ \tag{45}$$

According to Johanneson,[59] the NH_2Br and NH_3Br^+ are present in equal quantities at pH 6.5. These two reactions may account for the excellent germicidal efficiency of NH_2Br.

Iodination

Iodine, I_2, has a long history and record as a disinfectant for skin wounds and mucous surfaces of the human body. It is used, also, as a strong and universal sanitizing compound in hospitals and microbiology laboratories. The use of iodine for disinfection of drinking water, swimming pools, and wastewaters has not been extensive. There are, however, some occasions, especially small-scale treatments and emergency situations, when it is utilized.[36]

Physical Properties

Iodine has an atomic weight of 126.92 and a molecular weight of 253.84. It is the only halogen that is solid at room temperature, and it sublimates. It is a blackish-gray solid with a specific gravity of 4.93.

Iodine Compounds

One of the major uses of iodine-containing compounds is field sterilization of water, especially in military situations. During World War II, a series of studies led to the development of Globaline and other tablets for disinfection of small or individual supplies for the U.S. Army.[60] Table 11.12 gives several of these tablets and their iodine contents. The disinfective superiority of these iodine tablets over such chlorine-containing tablets as Halazone is discussed below.

Hydrolysis and Protolysis Reactions

Iodine hydrolyzes to form hypoiodous acid and hydroiodic acid:

$$I_2 + H_2O = HOI + H^+ + I^- \tag{46}$$

whereupon

$$K_H = \frac{[HOI]\,[H^+]\,[I^-]}{[I_2]} \tag{47}$$

K_H at 25°C is 3×10^{-13} M^2/L^2 (Reference 61). Consequently, the extent of hydrolysis of I_2 is less than Cl_2 and Br_2 and is controlled, of course, by $[H^+]$.

Hypoiodous acid is "weak" in the Brønsted sense:

$$HOI + H_2O = H_3^+O + OI^- \tag{48}$$

with the protolysis constant = 4.5×10^{-13} at 25°C.[61] It is only slightly stronger than pure water as an acid. It is interesting to compare the effect of $[H^+]$ on the hydrolysis and protolysis of I_2 and HOI with Cl_2 and HOCl. This comparison is seen in Table 11.13. It is noted, for example, that at a pH value of 8, 78.5% of Cl_2 is OCl^-, whereas 88% of I_2 is in the HOI form, and the remaining 12% is I_2. An iodate ion can be formed:

Table 11.12. Characteristics of Some Polyiodides.[a]

Commercial Name	Chemical Name	Formula	Active Iodine (%)	Solubility (g/L) at 25°C	Iodine Vapor Pressure[b] at 25°C Iodine (10^3 mm)	Relative[c] Stability
	Tetramethylammonium triiodide	$(CH_3)_4NI_3$	55.8	0.25	0.9	
Globaline	Tetraglycine hydroperiodide	$(NH_2CH_2COOH)_4HI \cdot 1.25I_2$	42.3	380.0	1.3	50
Potadine	Potassium tetraglycine triiodide	$(NH_2CH_3COOH)_4KI_3$	35.3	Large	0.5 (est)	95
Hexadines	Aluminum hexaurea sulfate triiodide	$Al[CO(NH_2)_2]_6SO_4I_3$	29.4	590.0	0.4	100
Hexadinen	Aluminum hexaurea dinitrate triiodide	$Al[CO(NH_2)_2]_6(NO_3)_2I_2$	28.5	390.0	0.12	

[a] Reproduced from Morris et al.,[60] courtesy of the American Chemical Society.

[b] Determined by equilibration of solid with CCl_4 and titration of dissolved iodine, assuming validity of Henry's law.

[c] Percentages of initial iodine remaining after 50 days when thin layers of powdered materials (<100 mesh) were maintained at 60°C for this period.

$$3HOI + 2OH^- = HIO_3 + 2H_2O + 2I^- \quad (49)$$

Formation of iodic acid is catalyzed by the OH^- ion and the occurrence of IO_3^- at alkaline pH values is significant since this anion has no disinfection properties.[63]

Oxidation States of Iodine

Iodine has 12 oxidation states, of which 2 are relevant to aqueous systems (–I and +I). Some reduction reactions (Equations 50–53) are seen in Table 11.14. The E–pH stability diagram is seen in Figure 11.17 where the iodide ion, I^-, is the stable species in most of the graph. I_2 predominates, for the most part, under acid conditions and above an E value of +0.6.

Reactions with Ammonia

McAlpine[64] reported some experiments with the reaction of I_2 with NH_3. This reaction is suggested:

$$I_2 + 2NH_3 = NH_2I + NH_4^+ + I^- \quad (54)$$

An average k_{eq} of 1.8 was determined when the molar ratio of NH_3 to I_2 was on the order of 4000:1. This is extremely unlikely in treated waters.

Other Chemical Disinfectants

Ozone

In addition to the physical properties cited above, ozone is frequently called a "powerful" oxidant, that is, it is unstable in water according to:

$$O_{3(g)} + 2H^+ + 2e = H_2O + O_{2(g)};\ E^o = +2.076\ V \quad (55)$$

or

$$O_{3(g)} + 6H^+ + 6e = 3H_2O;\ E^o = +1.511\ V \quad (56)$$

The E^o values for these two reactions exceed the one for $O_{2(g)}$, +1.228 V; consequently, its instability and its strong oxidative properties in water are noted. Ozone must be generated onsite by an electrical discharge in air or streams of oxygen. This produces in practice 1–2% O_3 when air is used, and 3–5% when pure $O_{2(g)}$ is used. It is moderately soluble in water—0.494 cm^3/cm^3 at 0°C. Ozone has a half-life of about 40 min in pure distilled water at pH 7.6 and 14.6°C. At pH 8.5, the half-life is 10 min.[65]

Table 11.13a. Effect of pH on the Hydrolysis of Iodine.[a,b]

	Content of Residual (%)		
pH	I_2	HIO	IO^-
5	99	1	0
6	90	10	0
7	52	48	0
8	12	88	0.005

Table 11.13b. Effect of pH on the Hydrolysis of Chlorine.

	Content of Residual (%)		
pH	Cl_2	HOCl	OCl^-
4	0.5	99.5	0.0
5	0	99.5	0.5
6	0	96.5	3.5
7	0	72.5	27.5
8	0	21.5	78.5
9	0	1.0	99.0

[a] Reproduced from Black et al.,[62] courtesy of the American Water Works Association.

[b] Total iodine residual, 0.5 ppm.

Table 11.14. Some Reduction Reactions of Iodine at 25°C.[35]

Reaction Number	Reaction	E^o (V)
50	$I_2 + 2e = 2I^-$	+0.621
51	$I^+ + 2e = I^-$	+0.946
52	$HOI + H^+ + 2e = I^- + H_2O$	+0.987
53	$OI^- + 2H^+ + 2e = I^- + H_2O$	+1.313

Ferrate

The ferrate ion, FeO_4^{2-}, has received some attention as a disinfectant. In this ion, iron has an oxidation state of VI, which is unstable in water, as seen in these reactions:[35]

$$FeO_4^{2-} + 8H^+ + 3e = Fe^{3+} + 4H_2O = 1.7\ V \quad (57)$$

$$FeO_4^{2-} + 5H^+ + 4e = HFeO_2^- + 2H_2O = 1.001\ V \quad (58)$$

Here again, the instability of FeO_4^{2-} in water and the acceptance of 3 and 4 moles of electrons makes this ion an oxidizing disinfectant. It is prepared electrochemically from scrap iron. Aqueous ferrate solutions have a violet color similar to $KMnO_4$.

Chlorine Dioxide

There are occasions in drinking water treatment for the application of ClO_2 as a disinfectant (see below). It is a

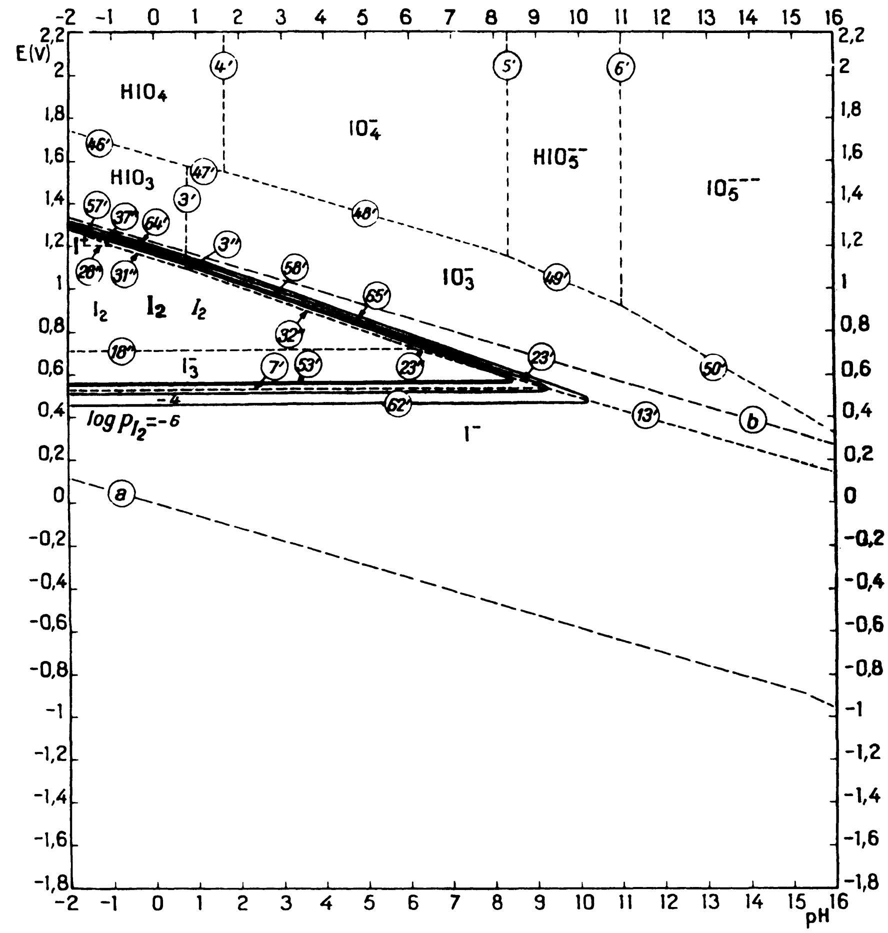

Figure 11.17. Potential-pH equilibrium for the system I_2-H_2O at 25°C, for solutions containing 1 g-atom I/L. Equation numbers refer to original text. Reproduced from Pourbaix,[35] courtesy of Pergamon Press Ltd.

neutral compound of chlorine in the +IV oxidation state. It has a boiling point of 11°C at atmospheric pressure. The liquid is denser than water, whereas the gas is denser than air.[66] It is "extremely" soluble in water.[28]

The chlorine in ClO_2 is 52.6% by weight. Since the chlorine atom undergoes a reduction with 5 electrons:

$$ClO_{2(g)} + 4H^+ + 5e = Cl^- + 2H_2O \qquad (15)$$

the equivalent available chlorine content is 52.6 × 5 = 263% (Table 11.4). This reaction suggests that ClO_2 theoretically has about 2.5 times the oxidizing power of chlorine. However, this oxidation capacity is rarely, if ever, utilized in water treatment practice for disinfection and/or oxidation of organic matter. Rather, ClO_2 is reduced to chlorite in its reaction with most substances in water:

$$ClO_{2(g)} + 2H^+ + 3e = ClO^- + H_2O \qquad (17)$$

Under alkaline conditions, the following disproportionation reaction into chlorite (ClO_2^-) and chlorate (ClO_3^-) occurs:[67,68]

$$2ClO_2 + 2OH^- = H_2O + ClO_3^- + ClO_2^- \qquad (59)$$

Since this reaction is catalyzed by OH^- ions, the half-life of aqueous ClO_2 solutions deceases rapidly with an increase in pH values. Even at neutral pH values, the half-life of 10^{-4} to 10^{-2} *M* solutions of ClO_2 can lose its stability within 0.5 hours.

A unique chemical property of ClO_2 is that it does not react with NH_3 in water. Consequently, the efficacy of this chlorine compound has been investigated as a disinfectant.

EFFECTIVENESS OF DISINFECTION

The primary purpose of disinfecting drinking water is, of course, to destroy and eliminate pathogenic organisms responsible for waterborne diseases. Sterilization is not necessary, nor is it desirable to have killed all microorganisms. It is impractical to do so. An assessment of a reduction in the concentration of microbes is sufficient protection against the transmission of pathogens.

Biocidal efficacy of disinfectants is evaluated, usually, through laboratory studies using indicator organisms or the pathogens themselves. As such, there is a need to control many variables that affect the effectiveness of the disinfection process. Among these variables are contact time, pH, temperature, and halogen demand. (Note that the halogens, particularly chlorine, are used predominantly in drinking water. However, disinfection and chlorination are not necessarily synonymous.) In laboratory studies, these variables can be carefully controlled. In treatment practice, however, it is much more difficult to do so, especially in distribution systems.

A major factor affecting an evaluation of the efficacy of a particular disinfectant is the test microorganism.[36] There is a wide variation in susceptibility among bacteria, viruses, and protozoa (cyst stage), as well as among genera, species, and strains of these microbes. Furthermore, the vast majority of the literature on water disinfection is concerned with use of model organisms instead of the pathogens. The hypothesis is that the reaction of the model to a disinfectant is the same as the pathogen. Defense of this approach is argued in Reference 36. A model and/or indicator microorganism should follow these criteria:[69]

1. Be present whenever the pathogens concerned are present.
2. Be present only when the presence of pathogens is an imminent danger (i.e., they must not be able to proliferate to any greater extent in the aqueous environment).
3. Occur in much greater numbers than pathogens.
4. Be more resistant to disinfectants and to the aqueous environment than pathogens.
5. Grow readily on relatively simple media.
6. Yield characteristic and simple reactions enabling, as far as possible, an unambiguous identification of the group.
7. Be randomly distributed in the sample to be examined; or it should be possible to obtain a uniform distribution by simple homogenization procedures.
8. Grow widely independent of other organisms present when inoculated in artificial media (i.e., the indicator bacteria should not be seriously inhibited in their growth by the presence of other bacteria).

As mentioned earlier in this chapter, bacteria of the coliform group, especially *Escherichia coli*, have proved useful as indicator organisms and disinfection models for enteric bacterial pathogens. However, they are not very good indicators and models for nonbacterial pathogens. The bacterial viruses of *E. coli* are used also as disinfection models for enteric viruses.

There is also the question of responses to disinfectants by laboratory cultures and their counterparts in natural waters. There is considerable evidence that "naturally occurring" bacteria in swimming pools, for example, are one to two times more resistant to disinfectants than cultured bacteria.

All of this points to two major areas of concern and interpretation of disinfection studies:

1. Is there a sufficient and an accurate correlation of the responses to disinfection by model microorganisms with those of pathogens?
2. Are the responses to disinfectants in treatment plant practice the same as, or, at least, similar to, those obtained in the laboratory?

A major factor in disinfection studies and practices is the relation between contact time and disinfectant dosage to effect a specified or equal destruction of microorganisms. An empirical equation has been developed for these two variables:[28]

$$T = kC^b \tag{60}$$

where T = contact time, usually in minutes
C = disinfectant dosage, used in mg/L
k = a proportionality constant for a given organism, pH value, and temperature
b = the slope of a log-log plot of T vs. C

Typical plots are seen in Figure 11.18, where most of the lines have a slope or b value of −1. Since b is negative, the curve is hyperbolic, whereupon:

$$T = k/C \tag{61}$$

or

$$k = CT \tag{62}$$

where k is a constant that can be used conveniently to compare disinfectants, organism response, etc., as long as the percentage kill is 99.6 to 100% and the slope is −1. Frequently, b is called the coefficient of dilution.[71] When b >1, the efficiency of the disinfectant decreases rapidly as it is diluted; when b <1, time of contact is more important than dosage; and when b=1, C and T are weighted equally. The reports of disinfectant effectiveness that follow should be read with Equation 60 in mind.

Free Chlorine (HOCl and OCl^-)

One of the early researches was conducted by Butterfield et al.,[72] who studied percentages of inactivation as a func-

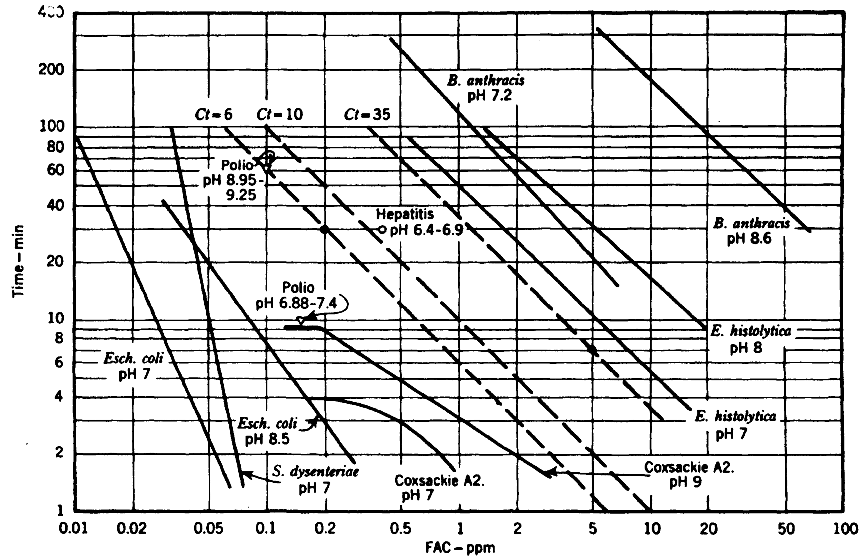

Figure 11.18. Disinfection vs. free available chlorine residuals. Time scale is for 99.6–100% kill. Temperature was in the range 20–29°C, with pH as indicated. Reproduced from Baumann and Ludwig,[70] courtesy of the American Water Works Association.

tion of time for *E. coli, Enterobacter aerogenes, Pseudomonas aeruginosa, Salmonella typhi,* and *Shigella dysenteriae.* Various concentrations of free chlorine were utilized at pH values ranging from 7.0 to 10.7 and in two temperature ranges: 2–5°C and 20–25°C. This classical study dealt with the action of disinfectants on pathogens. In general, the primary factors affecting the bactericidal efficacy of free chlorine are:[36]

1. the time of contact between the bacteria and the bactericidal agent, i.e., the longer the time, the more effective is the chlorine disinfection process;
2. the temperature of the water in which contact is made, i.e., the lower the temperature, the less effective is the chlorine disinfecting activity; and
3. the pH of the water in which contact is made, i.e, the higher the pH, the less effective is chlorination.

Early Studies

The results of Butterfield's free available chlorine research are summarized in Table 11.15. (It should be noted here that the 2–5°C temperature range is employed to slow the kinetics of disinfection and also to simulate the winter operation of treatment plants.) From these data, HOCl is more effective than OCl$^-$, and the higher temperatures, 20–25°C, lowered the contact time and chlorine dosage for 99–100% kill of *E. coli.* This comparison is seen also

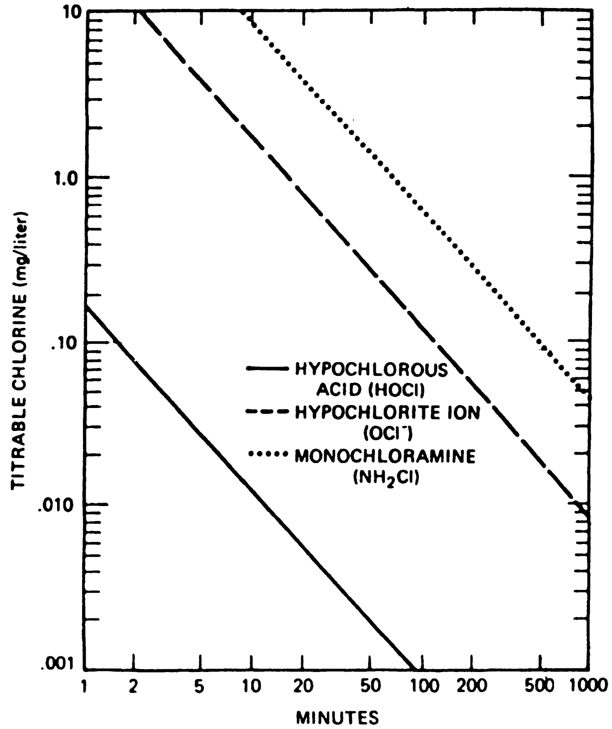

Figure 11.19. Comparison of germicidal efficiency of hypochlorous acid, hypochlorite ion and monochloramine for 99% destruction of *E. coli* at 2–6°C.

Table 11.15a. Effect of pH and Temperature on Contact Time (min) for 100% Kill of *E. coli*.[72]

pH	Dosage (mg/L)		Contact Time (min)	
	2–5°C	20–25°C	2–5°C	20–25°C
7.0	0.04	0.04	3	1
8.5	0.14	0.07	10	10
9.8	0.72	0.06	10	20
10.7	0.30	0.40	60	10

Table 11.15b. Effect of pH and Temperature for 100% Kill of *E. coli*, Contact Time=K, Cl_2 Dosage (mg/L) for 100% Kill, 10 min Exposure.

pH	2–5°C	20–25°C
7.0	0.03	0.04
8.5	0.14	0.07
9.8	0.72	0.30
10.7		0.40

Table 11.15c. Effect of Species, 5 min Exposure, pH 7, 20–25°C.

Species	Cl_2 Dosage for 100% Kill (mg/L)
A. aerogenes	0.08
S. typhosa	0.06
Sh. dysenteriae	0.05
E. coli	0.03
Ps. pyocyaneus	0.03

in Figure 11.19. That there is some genera dependency is seen also in Table 11.15. *Salmonella typhi* required twice as much chlorine as *E. coli*, but the absolute quantities of 0.06 and 0.03 mg/L, respectively, are minute compared to the overall chlorine demand of a water.

Another early laboratory study of the effectiveness of chlorine was reported by Chang[73] for disinfection of the cyst of *Entamoeba histolytica*. The time-concentration effects are seen in Figure 11.20, where as long as 120 min is required for destruction of 30–75 cysts/cm^3 of water. It is interesting to note the convergence of the curves representing $Cl_{2(g)}$, HOCl, and chloramines at 120 min. It appears that the type of chlorine disinfectant is a significant factor at contact times of less than 60 min in the destruction of cysts of *E. histolytica*.

Clarke and Kabler[74] and Clarke et al.[75] reported the results of laboratory studies on the inactivation of purified coxsackievirus and type 3 adenovirus, respectively, by chlorine. The time-concentration relationships are given in Figure 11.21 for the two temperatures and two pH values. (It should be noted here that, at pH 7.0, HOCl is 80% of the $[Cl_2]_t$ (see Figure 11.4); therefore, any disinfection at this pH value is not entirely accomplished by HOCl.) The b values for Equation 60 are:

- pH 9, 3–6°C, b = 1.07 ± 0.26
- pH 7, 3–6°C, b = 0.72 ± 0.07
- pH 9, 27–29°C, b = 0.63 ± 0.10

Somewhat similar results were reported for inactivation of type 3 adenovirus in water.[75] The data in Table 11.16a were plotted to be linear for the log-log relation of time and concentration of disinfectant. The b values were:

- pH 9, 25°C, b = 1.46
- pH 9, 4°C, b = 1.04
- pH 7, 4°C, b = 0.66

The pH 7, 25°C data apparently were curvilinear and were similar to the pH 7.27, 29°C curve in Figure 11.21. Table 11.16b shows the concentrations of HOCl and OCl^- required to destroy some pathogenic microorganisms. *E. coli* and *S. typhosa* require about the same $[Cl_2]$ and contact time for their demise.

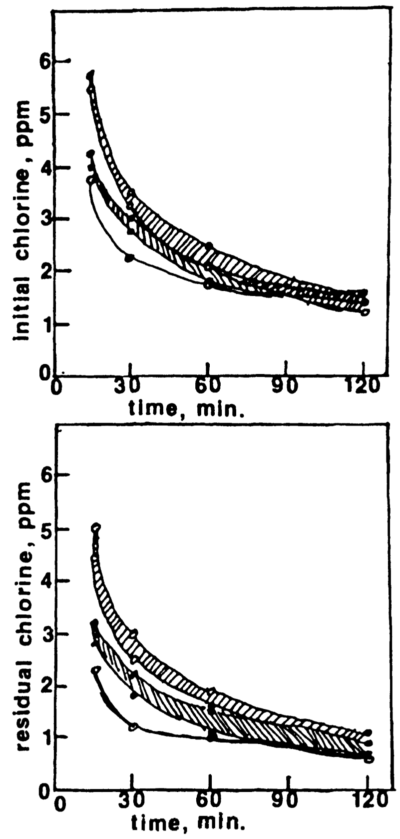

Figure 11.20. Comparison of lethal residual concentrations of the solution of hypochlorite, chloramines, and gaseous chlorine for killing *E. histolytica* cysts in tap water under similar conditions. T = 18°C, cyst density = 30–75/cm^3, total organic nitrogen = 0.1–0.2 ppm, pH 6.8 to 7.2. Solid circles = high test hypochlorite, open circles = chloramines, dotted circles = gaseous chlorine. Reproduced from Chang.[73]

Laboratory studies were conducted for the effect of chlorine over the pH range of 6–10 on five types of polioviruses and two types of coxsackieviruses, all of which are enteric.[76] The results are summarized in Table 11.17. These data clearly show that HOCl, at pH 6, is at least four times as effective as OCl^-, at pH 9. Also, there are considerable differences in response of the various types of viruses to chlorine. This is especially the case at the lower temperatures of 1-5°C.

A comparative study of the inactivation of an animal virus and *E. coli* by HOCl and OCl^- was conducted through laboratory experiments.[77] Figure 11.22 shows the time-concentration relationships for a 99% inactivation of the enteric microorganisms. Hypochlorous acid was more effective for disinfection of *E. coli* than for the poliovirus I. However, this was reversed for OCl^- (Figure 11.22b). That OCl^- is more effective than HOCl for inactivation of the poliovirus I is seen in Figure 11.22c. This is contrary to the work of Clarke and Kabler.[74] Figure 11.22d shows that HOCl is about 50 times more effective than OCl^- against *E. coli*. This result has been reported by others[71] where the argument is in the arithmetic of the HOCl:OCl^- effectiveness ratio.

These studies were extended to two DNA phages, T2 and T5, two RNA phages, f2 and MS2, *E. coli* and two animal viruses, poliovirus 1 and coxsackievirus.[78] Their graphic results are seen in Figures 11.23 and 11.24. The two DNA phages were more responsive to HOCl than *E. coli*, whereas the other viruses require more free chlorine for their destruction. All of the viruses and phages required less OCl^- than *E. coli*. Nearly all of the slopes or b values for Equation 60 were 1.0, which is interpreted as a first-order inactivation mechanism.

That chlorine inactivates various viruses, and that [H^+] is a factor was reported by Engelbrecht et al.[79] Table 11.18 summarizes their data, giving the times and the chlorine concentrations needed for 99% inactivation of the viruses at pH values of 6.0, 7.8, and 10.0. These results indicate that there is a significant difference in the time required for the 99% inactivation at pH 6 (HOCl) and 10 (OCl^-). This is, of course, similar to the results with *E. coli*. Engelbrecht et al.[79] agree with the results of Scarpino et al.[78] for the coxsackievirus A9 at pH 10 (OCl^-). However, their results disagree at pH 6 (HOCl). Engelbrecht reported that 0.3 min was required for 99% inactivation with about 0.5 mg/L free chlorine, whereas Scarpino reported that 3 min were required. In any event, there is an obvious species dependency for disinfection of bacteria and viruses by free chlorine.

Late Studies

Since promulgation of the Surface Water Treatment Rule (SWTR) (see Chapter 1) and proposal of the Enhanced Surface Water Treatment Rule (ESWTR), considerable attention has been given to the disinfection of water supplies infected with *Giardia* cysts and *Cryptosporidium* oocysts. Most of the traditional chemical disinfectants have been evaluated for their efficacy to disinfect these cysts.[80,81]

Animal models are employed to determine the viability of the above cysts after exposure to various concentrations of disinfectants and exposure times. For example, the Mongolian gerbil, *Meriones unguiculatus*, was used to determine viability of the cysts of *Giardia duodenalis* following exposure to chlorine.[80] Cysts were exposed to varying concentrations of chlorine for different periods of time at temperatures of 0.5, 2.5, and 5°C at pH values of 6, 7, and 8. Chlorine residuals were measured at the end of the specified contact time, and five gerbils were inoculated with an appropriate number of cysts from the dechlorinated systems. Disinfectant efficacy was noted by the number of infected animals per group compared to the controls. In turn, these data were transferred to log-log plots of free chlorine versus time similar to Figure 11.18. Then, Equation 11.62 was uti-

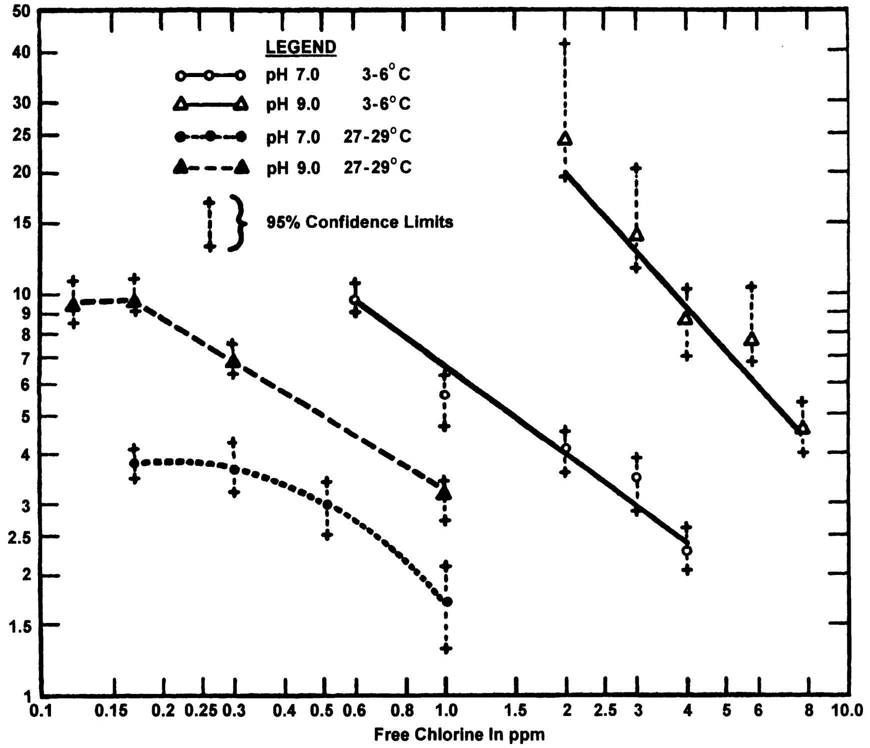

Figure 11.21. Time (min) required to inactivate 99.6% of coxsackievirus in water by chlorine. Reproduced from Clarke and Kabler,[74] courtesy of the American Society of Hygiene.

Table 11.16a. Time Required by Free Chlorine to Inactivate Approximately 99.8% of Purified Type 3 Adenovirus in Water.[a]

pH	Temperature (°C)	Free Chlorine (ppm)	Time Required (sec)
8.8–9.0	25	0.1	120–140
		0.2	40–50
		0.5	8–16
8.8–9.0	4	0.1	180
		0.2	80–110
		0.5	30–40
6.9–7.1	25	0.1	8–16
		0.2	8–16
		0.5	<8
6.9–7.1	4	0.1	18–25
		0.2	8–20
		0.5	<10

lized to calculate CT values for each of the temperature and pH values. The effects of these two variables is clearly seen in Table 11.19, where HOCl (pH 6.0) is more effective than OCl^- (pH 8.0).[80] Also, there appears to be a significant temperature effect, with the lower values requiring higher CT numbers. Chlorine dosages ranged from 0.5 to 4.0 mg/L, which is well within the range of water treatment processes. However, contact times were as high as 12.5 hours with, for example, OCl^- at a pH = 8.0, 2.5°C.

Purified *Cryptosporidium parvum* oocysts were exposed to O_3, ClO_2, Cl_2, and NH_2Cl.[81] Excystation and mouse infectivity were evaluated comparatively to assess oocyst vi-

Table 11.16b. Approximate Time Required by Free Chlorine to Achieve >99% But <100% Kill of Various Microorganisms in Water.[a]

Organism	pH	Temperature (°C)	Range of Free Chlorine (ppm)	Time
E. coli	7.0	25	0.08–0.12	<60 sec
A. aerogenes				60 sec
S. typhosa				60 sec
Type 3 Adenovirus				<16 sec
Coxsackievirus A2				240 sec[b]
E. histolytica Cysts				150min[b]
B. anthrax Spores				360 min[b]
E. coli	7.0	4	0.08–0.10	< 60 sec
S. typhosa				<60 sec
Type 3 Adenovirus				22 sec
Coxsackievirus A2				40 min[b]
E. histolytica Cysts				630 min[b]
B. anthrax Spores				24 hr[b]
E. coli	8.5	25	0.08–0.14	180 sec
S. typhosa	8.5	25		180 sec
Type 3 Adenovirus	9.0	25		130 sec
Coxsackievirus A2	9.0	25		10 min[b]
E. coli	8.5	4	0.14	300 sec
S. typhosa	9.8	4	0.40	10 min
Type 3 Adenovirus	9.0	4	0.14	130 sec
Coxsackievirus A2	9.0	4	1.0	45 min[b]

[a] Reproduced from Clarke et al.,[75] courtesy of the American Society of Hygiene.

[b] Values obtained by extrapolation or interpolation.

Table 11.17. Time Required for 99.9% (or Greater) Inactivation by Free Residual Chlorine.[a]

Temperature	Virus Strain	Concentration of Free Chlorine (ppm)	Time at pH (min) 6	7	8	9	10
25–28°C	Polio 1 (Mahoney)	0.01–0.10		16			
		0.11–0.20			5		
		0.21–0.30	2	3	4	8	30
	Polio 1 (487)	0.21–0.30		4			
	Polio 1 (MK 500)	0.21–0.30	4	6	12	16	>30
	Polio 2	0.11–0.20		2			
	Polio 3	0.11–0.20		2	8	16	
	Coxsackie B1	0.21–0.30		8	4	8	
		0.31–0.40		2			
	Coxsackie B5	0.21–0.30	2	1	2	8	16
1–5°C	Polio 1 (Mahoney)	0.11–0.20		8			
		0.21–0.30	4	8			16
	Polio 1 (MK 500)	0.21–0.30		30	120		
	Polio 2	0.01–0.10		60			
		0.11–0.20		30			
		0.21–0.30		16			
	Polio 3	0.11–0.20		30			
	Coxsackie B5	0.21–0.30		16	30		

[a] Reproduced from Kelley and Sanderson,[76] courtesy of the American Public Health Association.

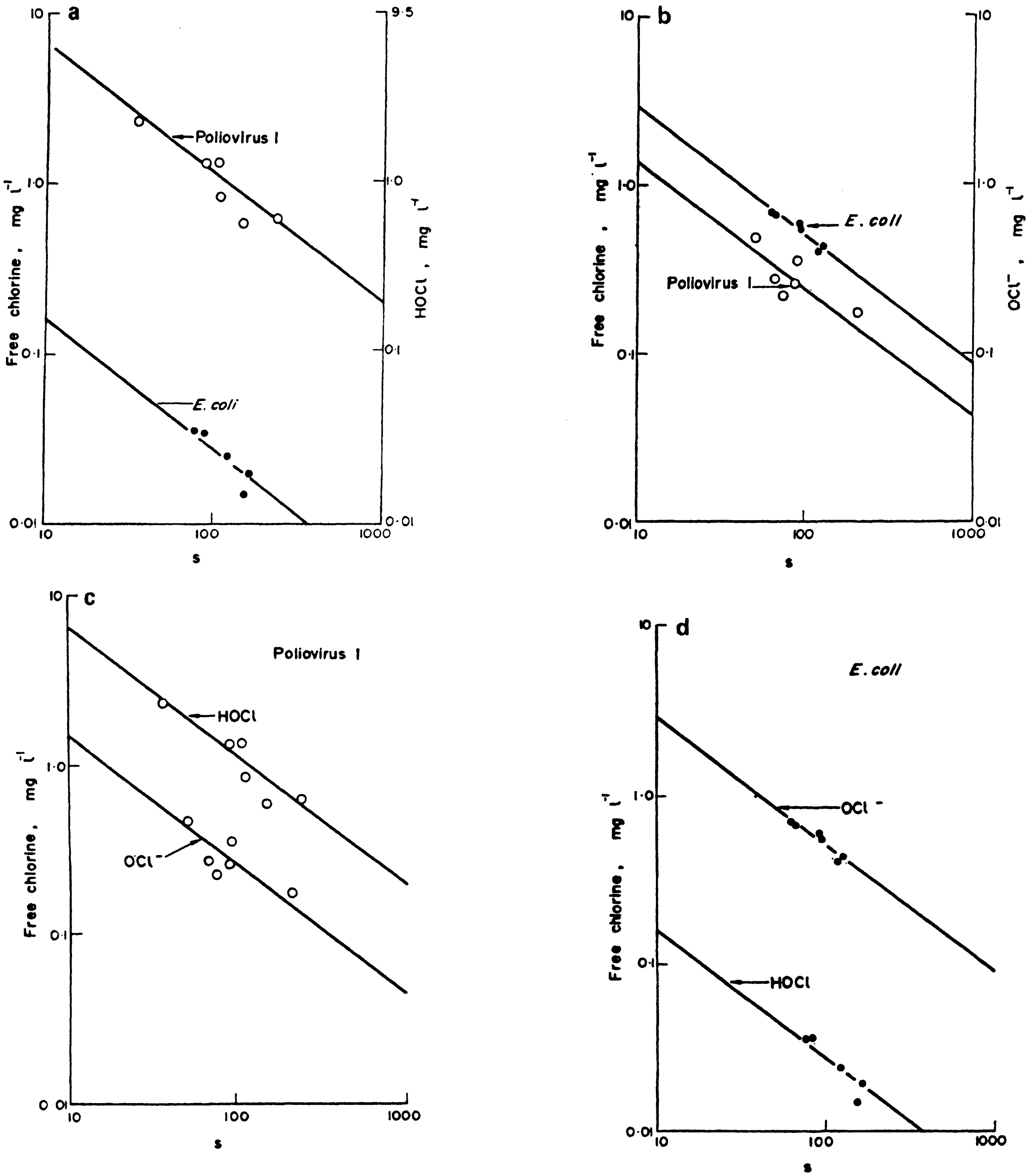

Figure 11.22. Concentration-time relationship for 99% inactivation of (a) poliovirus 1 and *E. coli* by HOCl at pH 6 and 5°C; (b) poliovirus and *E. coli* by OCl^- at pH 10 and 5°C; (c) poliovirus 1 by HOCl and OCl^- at 5°C; (d) *E. coli* by HOCl and OCl^- at 5°C. Reproduced from Scarpino et al.,[77] courtesy of the International Association on Water Pollution Research.

ability. O_3 and ClO_2 were more effective in the inactivation of the oocysts than Cl_2 and monochloramines. This evaluation is seen by comparing the exposure times and the percentages of excystation in Figures 11.25a–d for the four disinfectants. Greater than 90% inactivation, measured by infectivity, was achieved by treating oocysts with 1.0 mg/L O_3 for 5 minutes. Exposure to 1.3 mg/L ClO_2 yielded 90% inactivation after one hour, whereas 80 mg/L of Cl_2 and 80 mg/L NH_2Cl required approximately 90 minutes for 90% inactivation. These data indicate that *C. parvum* oocysts are

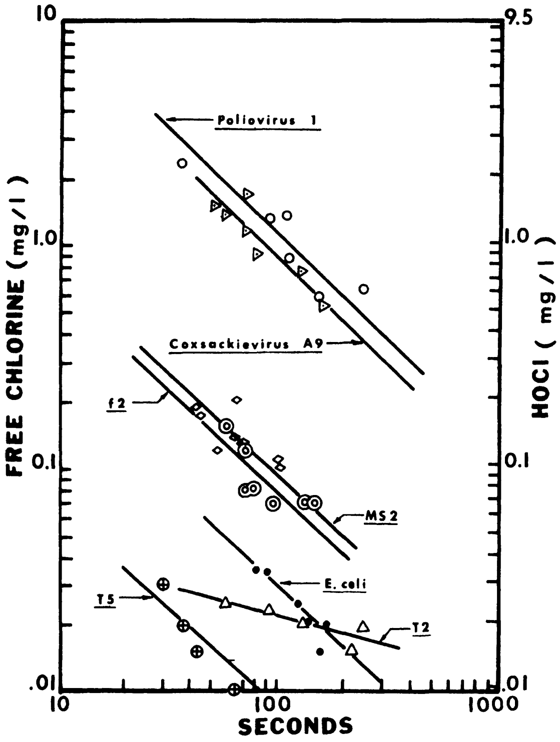

Figure 11.23. Concentration-time relationship for 99% inactivation of animal and bacterial viruses, and the reference bacterium *E. coli* ATCC 11229, by hypochlorous acid at 5°C and pH 6. Reproduced from Scarpino et al.[78]

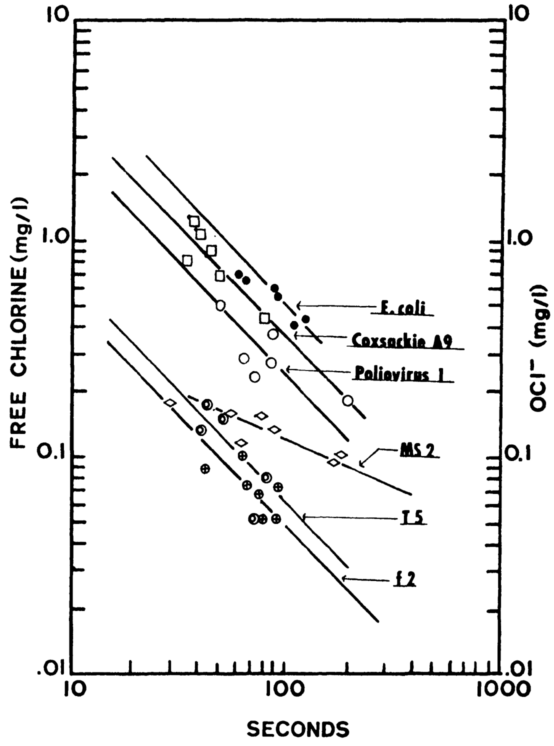

Figure 11.24. Concentration-time relationship for 99% inactivation of animal and bacterial viruses, and the reference bacterium *E. coli* ATCC 11229, by hypochlorite ion at 5°C and pH 10. Reproduced from Scarpino et al.[78]

30 times more resistant to O_3 and 14 times more resistant to ClO_2 than *Giardia* cysts exposed to these disinfectants under the same conditions.

Chloramines

Butterfield and Wattie[82] were among the first investigators to report the bactericidal properties of the chloramines at pH values ranging from 6.5 to 10.5 and in two temperature ranges, 2–5°C and 20–25°C. A summary of their results is given in Table 11.20a, where the chloramine dosage and contact times required for 100% kill of *E. coli* are noted. Dichloramine is more effective than monochloramine, since lesser dosages and lower contact times were required at pH values of 7.0 and 6.5. To obtain a 100% kill with the same contact time required about 25 times as much chloramine as free chlorine. For the same kill with equal quantities of chlorine and chloramine, approximately 100 times the exposure period is required for the latter disinfectant. That there is little genera difference is also seen in Table 11.20a. *E. coli* and *A. aerogenes* were slightly more resistant at pH 7.0.

Another early report was given by Kelly and Sanderson,[83] who researched the effect of combined chlorine on polio- and coxsackieviruses. At 25°C and a pH value of 7.0, a concentration of at least 9.0 ppm was necessary for inactivation of polioviruses with a contact period of 30 min and of 6 ppm over 60 min; 0.5 ppm required seven hr of contact. No data were available from this study to distinguish the effectiveness of mono- and dichloramine.

At 15°C, a 99% kill of *E. coli* was effected in about 20 min using 1.0 ppm NH_2Cl at a pH value of 9.0.[84] There was some evidence from this study also that *E. coli* was less resistant to NH_2Cl than several animal viruses.

The rates of disinfection of test organisms by $NHCl_2$ in demand-free phthalate buffer at pH 4.5 and 15°C was reported.[85] Figure 11.26 shows the comparisons that were made among two enteroviruses, poliovirus I and coxsackievirus A9, the bacteriophage øX-174, and *E. coli*. These data suggest that, at 15°C, poliovirus I was 17 times more resistant than the coxsackievirus A9, 83 times more resistant than øX-174 and 1700 times more resistant than *E. coli* to dichloramine. It was observed also that dichloramine was a more effective disinfectant than monochloramine in these experimental systems.

Table 11.21 summarizes the various types of chlorine dosages required for 99% inactivation of *E. Coli* and poliovirus I. Reference 36 cites the individual studies in this table.

Table 11.18. Time Required for 99% Inactivation by Free Residual Chlorine at 5.0 ± 0.2°C.[a]

pH	Concentration of Free Chlorine (mg/L)[b]	Virus Strain	Minutes for 99% Inactivation	Rank Ordering
6.00	0.46–0.49	Coxsackie A9 (Griggs)	0.3	1
6.00	0.48–0.49	Echo 1 (Farouk)	0.5	2
6.00–6.02	0.48–0.51	Polio 2 (Lansing)	1.2	3
6.00–6.03	0.38–0.49	Echo 5 (Noyce)	1.3	4
6.00	0.47–0.49	Polio 1 (Mahoney)	2.1	5
6.00–6.06	0.51–0.52	Coxsackie B5 (Faulkner)	3.4	6
		Coxsackie A9 (Griggs)	ND[c]	
7.81–7.82	0.47–0.49	Echo1 (Farouk)	1.2	1
		Polio 2 (Lansing)	ND[c]	
7.79–7.83	0.48–0.52	Echo 5 (Noyce)	1.8	3
7.80–7.84	0.46–0.51	Polio 1 (Mahoney)	1.3	2
7.81–7.82	0.48–0.50	Coxsackie B5 (Faulkner)	4.5	4
10.00–10.01	0.48–0.50	Coxsackie A9 (Griggs)	1.5	1
1.00–10.40	0.48–0.51	Echo 1 (Farouk)	96.0	6
9.89–10.03	0.48–0.50	Polio 2 (Lansing)	64.0	4
9.97–10.02	0.49–0.51	Echo 5 (Noyce)	27.0	3
9.99–10.40	0.50–0.52	Polio 1 (Mahoney)	21.0	2
9.93–10.05	0.50–0.51	Coxsackie B5 (Faulkner)	66.0	5

[a] Data from Engelbrecht et al.[79]

[b] Range of measured free chlorine residual in the test reactor at the termination of each of three separate experiments.

[c] ND=not determined.

Table 11.19. Interpolation of CT Values for Temperatures 0.5°C to 5.0°C, pH 6.0 to 8.0[a].[80]

Degrees Centigrade	pH				
	6.0	6.5	7.0	7.5	8.0
0.5	185	237	289	316	342
1.0	174	227	280	302	324
1.5	164	217	271	288	305
2.0	153	207	261	274	287
2.5	142	197	252	260	268
3.0	143	188	234	252	270
3.5	144	180	216	244	273
4.0	144	171	197	237	275
4.5	145	163	179	229	278
5.0	146	154	161	221	280

[a] If the temperature or pH of the water is between the interpolated values given, use the value for the lower temperature and the higher pH.

The sensitivity of *Entamoeba histolytica* cysts to chloramines is given in Table 11.22.[86] These pathogenic cysts were exposed to free chlorine and inorganic chloramine for 10 minutes under varied conditions of concentration and pH values. For example, at pH 8.0, 3 mg/L free chlorine inactivated 99% of the cysts, whereas 8 mg/L chloramine was required to reach the same level of inactivation. That chloramines are reasonably effective for the inactivation of *E. histolytica* cysts is seen in Table 11.22.

Chlorine Dioxide

There has been much interest and research into the efficacy of ClO_2 as a disinfectant for bacteria and viruses since the early 1940s.[86] Ridenour and Ingols[87] were among the early investigators to report that ClO_2 was at least as effective as Cl_2 against *E. coli* after 30 min with equivalent concentrations apparently over the pH range of 6–10. The results of other studies in the 1940s and 1950s are questionable because their method of preparing ClO_2 invariably included

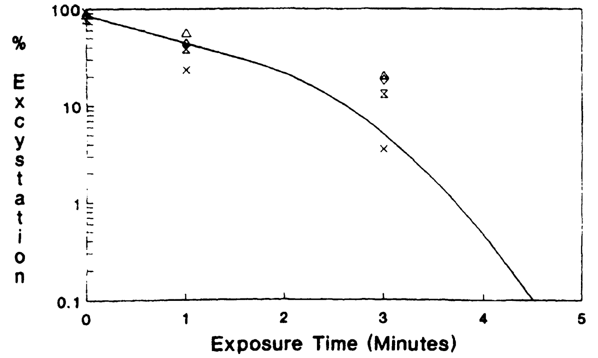

Figure 11.25a. Decline in mean percent excystation of *Cryptosporidium* oocysts exposed to 1 ppm of ozone at 25°C. Symbols show results of independent trials.[81]

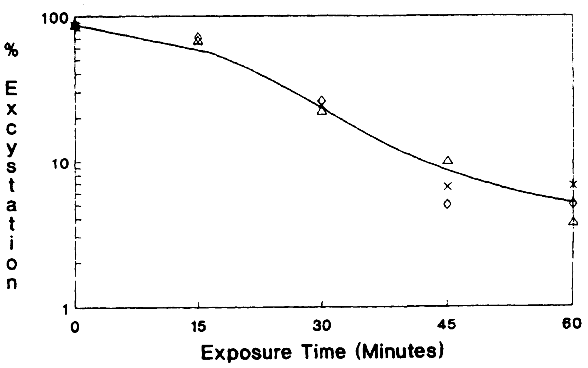

Figure 11.25b. Decline in mean percent excystation of *Cryptosporidium* oocysts after exposure to 1.3 ppm of chlorine dioxide (measured as parts per million of ClO_2) at 25°C. Symbols show results of independent trials.[81]

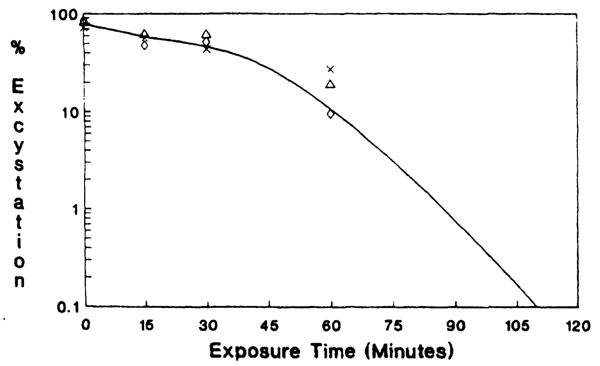

Figure 11.25c. Decline in mean percent excystation of *Cryptosporidium* oocysts after exposure to 80 ppm of chlorine (measured as parts per million of Cl_2) at 25°C. Symbols show results of independent trials.[81]

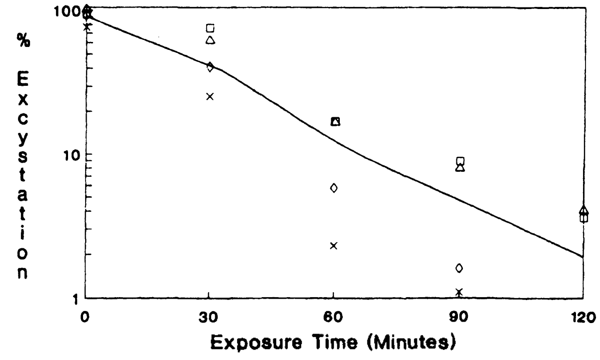

Figure 11.25d. Decline in mean percent excystation of *Cryptosporidium* oocysts exposed to 80 ppm of monochloramine at 25°C. Symbols show results of independent trials.[81]

the production of Cl_2.[36] Analytical procedures employed in those years could not distinguish between ClO_2 and other oxychloro species.

The analytical problems apparently were overcome in the 1960s, enabling Benarde et al.[88] to compare the bactericidal effectiveness of Cl_2 with ClO_2 at pH values of 6.5 and 8.5. At the lower pH value, both compounds inactivated a fresh strain of *E. coli* in less than 60 sec, with Cl_2 (or HOCl) being slightly more effective. However, at the higher pH value, ClO_2 was much more effective than Cl_2. A 0.25 mg/L dosage of ClO_2 effected a 99% destruction of *E. coli* in 15 sec, whereas 5 min were required for Cl_2. Another study by Benarde et al.[89] showed the usual temperature effects on the rate of disinfection in the 30–5°C range. For 99% inactivation of *E. coli* with 0.25 mg/L ClO_2, 190, 74, 41, and 16 sec were required at 5, 10, 20, and 30°C, respectively.

ClO_2 destruction of viruses and bacteria in water at 15°C and pH 7 was determined.[90] Figure 11.27 shows the concentration-time relationships for 99% disinfection of poliovirus I, coxsackievirus A9, and *E. coli*. From the relative positions of the curves in Figure 11.27, poliovirus was 8.9 times and the coxsackievirus was 2.3 times more resistant than *E. coli* to ClO_2. Each curve had a slope of approximately 1, indicating a first-order kinetic disinfection reaction (see kinetics discussion below). The plots in Figure 11.27b show that ClO_2 is a more effective viricide at pH 9 than at pH 7 or 4.5.

Under conditions where chlorine in the form of HOCl is unlikely to appear (>pH 7.0 or in the presence of NH_3), results indicate that ClO_2 is superior to Cl_2 in the inactivation of bacteriophage f_2, coliphage, and for coxsackievirus B3, echovirus 7, Herpes simplex viruses 1 and 2, Newcastle

Table 11.20a. Effect of pH and Temperature on Contact Time for 100% Kill of *E. coli* by Chloramines.[82]

pH	NH_2Cl[a] (%)	Dosage (mg/L)		Contact Time (min)	
		2–5°C	20–25°C	2–5°C	20–25°C
6.5	35.0		0.3		60.0
7.0	51.0	0.6	0.3	180.0	90.0
7.8	84.0		0.3		180.0
8.5	98.0	1.8	0.6	20.0	120.0
9.5	100.0	1.8	0.9	90.0	180.0
10.5	100.0		1.5		180.0

Table 11.20b. Effect of Species.[a]

Genera	Chloramine Dosage (mg/L)[b]		
	pH 7.0	pH 8.5	pH 9.5
E. coli	1.2	1.8	1.8
A. aerogenes	1.5	1.8	1.8
S. typhosa	0.9	1.8	1.8
Sh. dysenteriae	0.9	1.8	1.8
Ps. pyocyaneus	0.9	1.8 (98)[c]	1.8 (99.2)[c]

[a] For 100% kill at 20–25°C, 20 min contact time.
[b] Estimated, balance is $NHCl_2$.
[c] Percent kill.

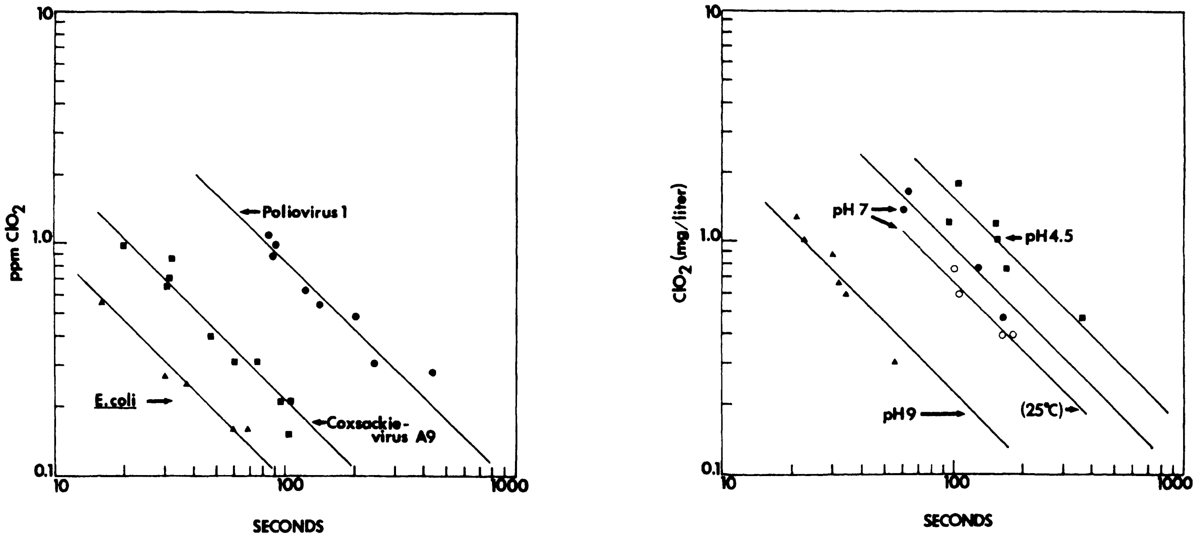

Figure 11.26. (a) Concentration-time relationship for 99% destruction or inactivation of poliovirus 1, coxsackievirus A9 and *E. coli* by chlorine dioxide at 15°C and pH 7.0. (b) Effect of pH on inactivation of poliovirus 1 at 21°C and pH 4.5, 7, and 9, and at 25°C and pH 7. Reproduced from Cronier et al.[90]

disease virus, phage øX-174, Sendaivirus, and Vaccinia virus.[68]

Bromine and Bromine Chloride

Bromine or combined bromine compounds have been rarely used to disinfect drinking water. Their reasonably good potential as disinfectants is seen below. These are confined, however, to small-scale or emergency situations and to swimming pools.[58]

An early study by Tanner and Pitner[91] indicated that 0.15 mg/L HOBr was needed for a "complete kill" in 30 min, whereas 0.6 mg/L was needed for *S. typhi*. Spores of *Bacillus subtilis* required >150 mg/L of Br_2.

Table 11.21. Dosages of Various Chlorine Species Required for 99% Inactivation of *E. coli* and Poliovirus 1.[36]

Test Microorganism	Disinfecting Agent	Concentration (mg/L)	Contact Time (min)	CT	pH	Temperature (°C)
E. coli	Hypochlorous acid (HOCl)	0.1	0.4	0.04	6.0	5
	Hypochlorite ion (OCl^-)	1.0	0.92	0.92	10.0	5
	Monochloramine (NH_2Cl)	1.0	175.0	175.0	9.0	5
		1.0	64.0	64.0	9.0	15
		1.2	33.5	40.2	9.0	25
	Dichloramine ($NHCl_2$)	1.0	5.5	5.5	4.5	15
Poliovirus 1	Hypochlorous acid (HOCl)	1.0	1.0	1.0	6.0	0
		0.5	2.1	1.05	6.0	5
		1.0	2.1	2.1	6.0	5
		1.0	1.0	1.0	6.0	15
	Hypochlorite ion (OCl^-)	0.5	21.0	10.5	10.0	5
		1.0	3.5	3.5	10.0	15
	Monochloramine (NH_2Cl)	10.0	90.0	900.0	9.0	15
		10.0	32.0	320.0	9.0	25
	Dichloramine ($NHCl_2$)	100.0	140.0	14,000.0	4.5	5
		100.0	50.0	5,000.0	4.5	15

Table 11.22. Concentrations of Prereacted Inorganic Chloramines Resulting in 99% Inactivation of *Entamoeba histolytica* Cysts in Relatively Demand-Free Systems[a].[86]

Chloramine Concentration (mg/L)	Estimated Composition of Chloramines		pH	Temperature (°C)	Contact Time (min)	Density of Cysts (cysts/mL)
	Monochloramine (%)	Dichloramine (%)				
5.0	40	60	5.0	30	10	1600–2000
8.0	95	5	7.0	30	10	1600–2000
8.4	100	0	9.0	30	10	1600–2000
2.0	95	5	7.0	27	25	200

[a] Studies carried out under chlorine-demand-free conditions or under conditions where chlorine demand is negligible.

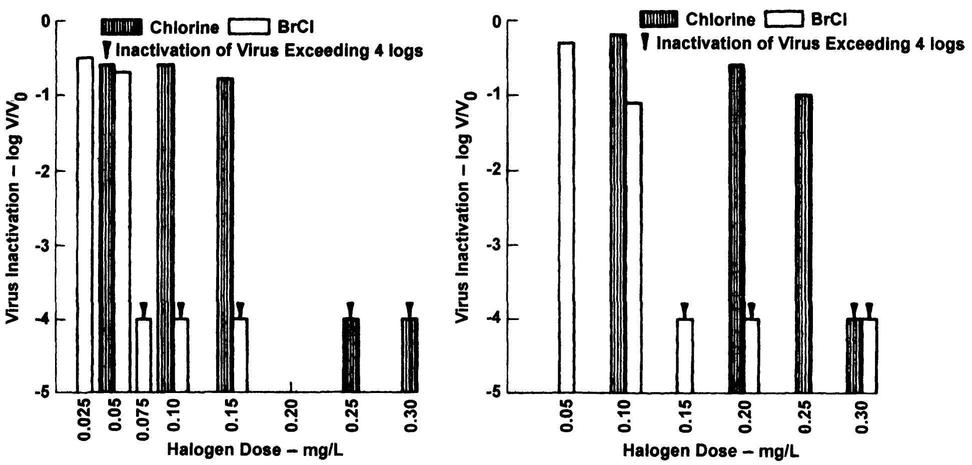

Figure 11.27. Stability and minimum concentration of BrCl and Cl_2 required to effectively inactivate poliovirus, with premixing times of 4 min (left) and 10 min (right). Reproduced from Keswick et al.,[96] courtesy of the American Water Works Association.

Table 11.23. Effect of Ammonia on Bromine Concentrations Required for 99% Inactivation of *Bacillus subtilis* Spores at 20 mg/L, pH 7, 25°C[a].

Ammonia (mg NH_3-N/L)	10-min Residual (mg/L)[b]	Contact Time (min)	CT[c]
0	20	14	280
1	16	19	304
2	2	>100	>200
10	8	85	680
30	9	70	630
100	14	18	252
1000	19	14	266

[a] Reproduced from Wyss and Stockton,[93] as reported in Reference 37.
[b] Initial bromine concentration 20 mg/L.
[c] Concentration of bromine times contact time.

The effect of formation and decomposition of the bromamines on the efficacy of bacterial destruction was discussed by Johannesson.[92] A dosage of 0.28 mg/L of NH_2Br (as Br_2) effected a 99% inactivation in less than 1 min, whereas the same content of N-bromodimethylamine [$N(CH_3)_2Br$] required 12 min.

Wyss and Stockton[93] reported the effect of HOBr and bromamines on spores of *Bacillus subtilis* at pH 7 and 25°C. This was accomplished simply by addition of increasing quantities of NH_3 to a 20 mg/L solution of bromine. Table 11.23 shows the results of this experiment, wherein a 99% kill was recorded for each [NH_3]. Hypobromous acid is the predominant compound when [NH_3]=0. At the 1 mg/L NH_3 level, NBr_3 is predominant. Between 10 and 30 mg/L, $NHBr_2$ is present, which is less stable and less effective than HOBr. At 100 and 1000 mg/L NH_3, NH_2Br predominates and is apparently as effective as NBr_3 and HOBr when the CT values are compared.

Reoviruses and polioviruses have received considerable attention in bromine disinfection studies. The effect of HOBr on single vs. aggregated particles at pH 7 and 2°C has been studied by several investigators.[36] The degree of aggregation had a marked effect on the observed inactivation rates. For example, reoviruses, as single particles, required only 1 sec for a 1000-fold decrease in their numbers at pH 7, 2°C and 0.46 mg/L HOBr as Br_2.[94] For the same degree of inactivation, the time was doubled for aggregated particles.

The inactivation of single poliovirus particles in buffered, distilled water and constant residual contents has been studied by Floyd et al.[94] for six species of the bromines. Table 11.24 shows the calculated CT values needed to yield the 99% inactivation by the six species whose concentrations were near 1 mg/L as Br_2. These researchers also demonstrated that $NHBr_2$, NBr_3, and HOBr were less efficient at higher contents, whereas the OBr^- became more effective as its concentration was increased. This observation is opposite to the OCl^-/HOCl system.

The chemistry and disinfectant properties of interhalogens and halogen mixtures—BrCl, ICl, and IBr—were reported by Mills.[95] For example, Poliovirus II(Sabin), with 10 ppm NH_3 present, was sterilized in <5 min using 4.0 ppm BrCl (as Cl_2), whereas equivalent chlorine concentrations failed to kill all of the viruses within 60 min.

The comparative disinfection efficiency of BrCl and Cl_2 for poliovirus is seen in Figure 11.28.[96] Experiments were conducted at pH 6 to enable a comparison between HOBr and HOCl. Several concentrations of BrCl and Cl_2 were prepared in a phosphate buffer and mixed for 4 and 10 min before 1 mL of purified poliovirus (10^5–10^6 PFU/mL) was added and allowed to react at 25°C for 15 min. Figure 11.27 shows that the minimum dose of BrCl required effectively to inactivate more than 99.99% of the virus was 0.075 mg/L, 4 min premix, and 0.15 mg/L for the 10 min premix. The Cl_2 dosages were 0.25 and 0.30 mg/L for the same premix periods. These results suggested that BrCl (HOBr) is two to three times more effective than Cl_2 (HOCl) for inactivation of poliovirus.

That Br_2 and/or $HOBr/OBr^-$ is an effective bactericide and viricide in laboratory studies has been discussed above. It is more effective than Cl_2 in the presence of NH_3 and is reasonably active over a wide range of pH values. However, a major disadvantage of Br_2 as a drinking water disinfectant is its reactivity with ammonia and other amines encountered in the treatment of drinking water.[36]

Iodine

Iodine has had a history as an antiseptic for skin wounds and mucous surfaces of the body and as a sanitizing agent in hospitals and laboratories.[36] The use of I_2 as a disinfectant of drinking and swimming pool waters has been limited due to a variety of reasons. It has been found useful for small-scale and emergency situations.

Some of the early research into the efficacy of iodine as a drinking water disinfectant was conducted by Chang and

Table 11.24. Exposure (CT)[a] to Various Bromine Compounds Required for 99% Inactivation of Poliovirus 1, Mahoney.[b]

Chemical Form	CT[a]	Temperature (°C)	pH
Dibromamine ($NHBr_2$)	1.2	4	7.0
Nitrogen Tribromide (NBr_3)	0.19	5	7.0
Bromine (Br_2)	0.03	4	5.0
Hypobromite Ion (OBr^-)	0.01	2	10.0
Hypobromous Acid (HOBr)	0.24	2	7.0
Hypobromous Acid	0.21	10	7.0
Hypobromous Acid	0.06	20	7.0

[a] Concentration of compound times contact time.

[b] Reproduced from Floyd et al.,[94] as reported in Reference 36.

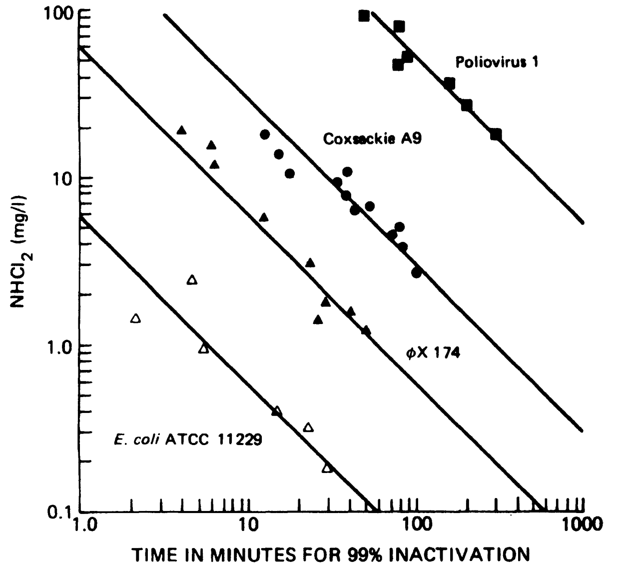

Figure 11.28a. Inactivation of various microorganisms with dichloramine ($NHCl_2$) at pH 4.5 and 15°C. Reproduced from Esposito et al.,[85] as reported in Reference 36.

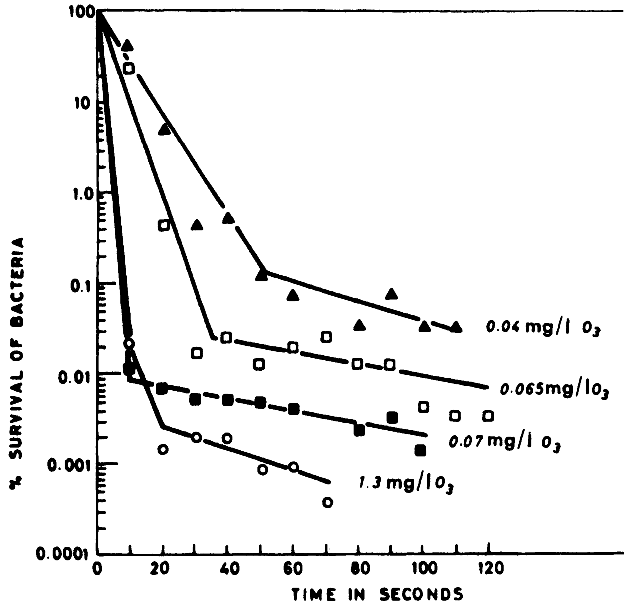

Figure 11.28b. Inactivation kinetics of *E. coli* by various concentrations of ozone at 1°C. Reproduced from Katzenelson et al.,[102] courtesy of the American Water Works Association.

Morris,[97] Morris et al.,[60] and Chang.[61] Chang and Morris[97] determined the usefulness of I_2 as an emergency disinfectant for drinking water. I_2 concentrations of 5–10 mg/L were found to be effective against all types of waterborne pathogenic organisms (enteric bacteria, amoebic cysts, cercariae, leptospira and viruses) within 10 min at room temperature. Germicidal activity is maintained over the pH range 3–8 in the presence of a variety of natural water contaminants (organic color, loess, clay minerals, NH_3, urea, etc.). Typical results are given in Table 11.25.[97] Iodine was also reasonably effective against the cysts of *Entamoeba histolytica*. The concentration-time relation (Equation 62) was on the order of 200, 130, and 65 for 3, 10, and 23°C, respectively. The b value from the log-log plot was 1.5, which is the more or less typical CT relationship. This work led to the development of the iodine tablets: Globaline, Potadine and Hexadine S&N, for use as field disinfectants in military situations.[60] In a later study, Chang[61] reported the CT relationship for destruction of coxsackievirus B1 at 25°C by elemental iodine. In this case, b=0.96 and C^bT=58.5.

The effect of $[I_2]$, pH, contact time and temperature on 13 enteric bacteria in a laboratory study was reported.[98] The pH effect at 2–5°C was demonstrated when some bacterial species required 3–4 times as much I_2 for inactivation (≈99.9% kill) at pH 9 than at pH 7.5. A summary of this work appears in Table 11.26, where *E. coli* is the model organism. This apparently is the best available information on the I_2 disinfection of bacteria.[36]

Table 11.25. Destruction of Various Types of Bacteria by Iodine.[a,b]

	Geometric Mean No. of Survivors per 100 mL after:			
Organism	**5 min**	**10 min**	**20 min**	**30 min**
E. coli (22 tests)	6.6	2.4	1.6	1.3
Sal. typhosa (8 tests)	1.4	<1.0	<1.0	<1.0
Sh. dysenteriae (9 tests)	1.6	1.0	1.0	<1.0
Sal. schöttmuelleri (9 tests)	21.0	5.1	2.7	2.1
Vibrio cholera (6 tests)	<1.0	<1.0	<1.0	<1.0
Mixed *coli aerogenes* flora of sewage, intial count 5000/mL (3 tests)	1.7	1.3	1.3	1.6

[a] Reproduced from Chang and Morris,[97] courtesy of the American Chemical Society.

[b] Cambridge tap water (10% seawater added for *V. cholera* tests; 10% filtered Cambridge sewage added for *coli-aerogenes* tests). Iodine dosage 7–8 ppm; residuals after 10 min, 5–7 ppm; residuals after 30 min, 4–6.5 ppm. Temperature, 25°C, pH values range from 4.5 to 8.1; low values obtained by addition of citric acid, high values by addition of $NaHCO_3$. Initial no. of organisms, 10^6/mL.

Table 11.26. Concentrations of Iodine and Contact Times Necessary for 99% Inactivation of *Escherichia coli*.[a]

Iodine (mg/L)	Contact Time (min)	CT[b]	pH	Temperature (°C)
1.3	1	1.3	6.5	2–5
0.9	2	1.8	6.5	
1.3	1	1.3	7.5	
0.7	2	1.4	7.5	
0.8	1	0.8	7.5	
0.6	2	1.2	7.5	
0.8	1	0.8	8.5	
0.9	2	1.8	8.5	
1.8	1	1.8	9.1	
1.2	2	2.4	9.1	
0.35	1	0.35	6.5	20–25
0.20	2	0.40	6.5	
0.45	1	0.20	7.5	
0.30	2	0.60	7.5	
0.45	1	0.45	8.5	
0.40	2	0.80	8.5	
0.45	1	0.20	9.1	
0.30	2	0.60	9.1	

[a] Reproduced from Chambers et al.,[98] as reported in Reference 36.

[b] Concentration of iodine times contact time.

Several studies have been conducted on the efficacy of I_2 destruction of viruses. These studies are summarized in Table 11.27 (see Reference 36 for original references). The viruses are, of course, more resistant to disinfection than are the negative cells of bacteria. This is reflected in the CT values in Table 11.26 and 11.27. In addition, at pH 6, I_2 is nearly as effective a viricide as HOCl.

Many studies have been reported on cyst inactivation by iodine.[36] Direct comparison of the results, however, is difficult because of a wide variety of experimental systems.

As a disinfectant in water, iodine is similar in many respects to Cl_2 and Br_2. Free I_2 is an effective bactericide over a relatively wide range of pH values. Field studies with small public water systems have shown that 0.5 to 1.0 mg/L of I_2 can be maintained in distribution systems, and that the magnitude of the residual is enough to produce safe drinking water with no apparent adverse effects on human health.[36] I_2 is effective against bacteria and cysts, although its effectiveness is reduced at "high" pH values ~9–10. Its current use is restricted to emergency disinfection of field water supplies.[99]

Table 11.27. Concentrations of Iodine and Contact Times Necessary for 99% Inactivation of Polio and f_2 Viruses with Flash Mixing.[36]

Test Microorganism	Iodine (mg/L)	Contact Time (min)	CT[a]	pH	Temperature (°C)
f_2 Virus	13.0	10.0	130	4.0	5
f_2 Virus	12.0	10.0	120	5.0	
f_2 Virus	7.5	10.0	75	6.0	
f_2 Virus	5.0	10.0	50	7.0	
f_2 Virus	3.3	10.0	33	8.0	
f_2 Virus	2.7	10.0	27	9.0	
f_2 Virus	2.5	10.0	25	10.0	
f_2 Virus	7.6	10.0	76	4.0	25–27
Poliovirus 1	30.0	3.0	90	4.0	
f_2 Virus	64.0	10.0	64	5.0	
f_2 Virus	4.0	10.0	40	6.0	
Poliovirus 1	1.25	39.0	49	6.0	
Poliovirus 1	6.35	9.0	57	6.0	
Poliovirus 1	12.7	5.0	63	6.0	
Poliovirus 1	38.0	1.6	60	6.0	
Poliovirus 1	30.0	2.0	60	6.0	
f_2 Virus	3.0	10.0	30	7.0	
Poliovirus 1	20.0	1.5	30	7.0	
f_2 Virus	2.5	10.0	25	8.0	
f_2 Virus	2.0	10.0	20	9.0	
f_2 Virus	1.5	10.0	15	10.0	
Poliovirus 1	30.0	0.5	15	10.0	

[a] Concentration of iodine times contact time.

Ozone

In recent times, ozone (O_3) has been mentioned frequently as an alternative disinfectant for Cl_2 in drinking water in order to avoid formation of the low-molecular-weight halogenated hydrocarbons. However, it has been researched for efficacy of disinfection since the 1950s, when Fetner and Ingols[100] reported the bactericidal activity of O_3 against *E. coli* at 1°C. Table 11.28 shows the survival of *E. coli* in several O_3 contents and contact times, at pH 6.8 and 1°C. Ozone appears to have an "all or none" effect, as seen in the sharp demarcation between the 0.42 and 0.53 mg/L dosages. There is apparently a critical value above which O_3 is effective and below which it is not. Table 11.28 also shows the survival of *E. coli* in chlorinated waters where the optimum dosage lies between 0.27 and 0.35 mg/L. The two disinfectants are nearly equal on a weight basis.

A somewhat different result was reported by Wuhrmann and Meyrath,[101] who found that 99% of *E. coli* was inactivated in 21 sec with 0.0125 mg/L O_3, 62 sec with 0.0023 mg/L, and 100 sec with 0.0006 mg/L at pH 7 and 12°C. The higher temperature used by Wuhrmann and Meyrath undoubtedly was responsible for the faster disinfection. Another "rapid inactivation" was reported by Katzenelson et al.,[102] who observed that an initial residual O_3 concentration of 0.04 mg/L, in demand-free water, disinfected approximately 3 logs (i.e., 99%) of *E. coli* in 50 sec, whereas a concentration of 1.3 mg/L achieved the same effect in 5 sec at 1°C and pH 7.2, as seen in Figure 11.28.

Broadwater et al.[103] also observed the "all or none" response of *E. coli*, *B. megaterium*, and *B. cereus* to various concentrations of O_3 up to 0.71 mg/L at 28°C (pH not reported). With a constant contact time of 5 min, no inactivation of vegetative cells of *E. coli* or *B. megaterium* occurred until the initial concentration of O_3 was 0.19 mg/L, whereupon they were all nearly destroyed. An initial O_3 content of 0.12 mg/L was needed for disinfection of *B. cerus*. These values of O_3 content are slightly lower than those of Fetner and Ingols at 1°C.[100] A greater [O_3] was needed to inactivate the spores of *B. megaterium* and *B. cereus*, 2.29 mg/L within 5 min.

A dosage of 0.5 mg/L O_3 was required at 25°C for the inactivation of *E. coli*, *Staphylococcus aureus*, *S. typhimurium*, *Shigella flexmeri*, *Pseudomonas fluorescens*, and *Vibrio cholerae*.[104] All were reduced by 7.5 logs in 15 sec.

The inactivation of poliovirus I and coliphage T_2 at 5°C and pH 7.2 by O_3 was investigated.[102,105] That the kinetics of this disinfection are rapid is seen in Figure 11.29. There is an apparent two-stage action of O_3. The first stage occurs in less than 8 sec with a virus kill of 99 to 99.5%. The second stage lasts from 1 to 5 min, during which residual viruses are disinfected. It is interesting to note than an increase

Table 11.28. Survival Percentages of *E. coli* in Different Concentrations of Ozone and Chlorine in Solution After Various Contact Times at pH 6.8 and 1°C.[a]

Initial Concentration (mg/L)	Period of Exposure (min)						
	1	2	4	8	16	32	64
Ozone							
1.00	<1.0	<1.0	<1.0	<1.0			
0.75	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	
0.63	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	
0.53	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	
0.42	75.0	<1.0	71.0	<1.0	73.0	46.0	
0.31	96.0	97.0	74.0	70.0	92.0		
0.21	33.0	82.0	99.0	99.0	79.0	69.0	
Chlorine							
1.10	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
0.52	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
0.35	1.5	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
0.27	2.0	1.5	1.6	1.2	1.0	<1.0	<1.0
0.25	24.0	10.0	12.0	13.0	8.0	7.0	5.0
0.17	70.0	53.0	39.0	24.0	15.0	4.0	<1.0
0.10	87.0	66.0	64.0	46.0	46.0	45.0	40.0

[a] Reproduced from Fetner and Ingols,[100] courtesy of the *Journal of General Microbiology*.

of [O_3] beyond 0.2 mg/L did not affect the rate or the percentage of kill. Some of these microorganisms apparently are resistant to ozonation. Later experiments suggested that single-particle viruses were destroyed in the first stage and the slower second stage was due to clumps of viruses. These experiments were conducted with O_3-demand-free water.

Inactivation of >99.9% for vesicular stomatitis virus, >99.99% for encephalomyocarditis, and 99.99% for GDV11 virus in 15 sec with an O_3 residual of approximately 0.5 mg/L were obtained by Burleson.[104]

A wide range of ozone dosages, contact times, and percentages of inactivation is noted above. Most of these studies were conducted in ozone-demand-free waters. However, this variable may account for some of the differences in the required ozone content. On the other hand, natural waters will have these demands. The pH value is apparently not a factor between 6 and 8.5, whereas temperature is, with faster rates occurring at the higher values. Table 11.29 brings all of this together, where CT relationships are noted. It is seen that the CT product varies over a broad range from 10^{-3} to 4.2×10^{-1}. In addition to the variables cited above, there are difficulties with the ozone analytical method and nonuniformity of microorganisms from one laboratory to another. Another difficulty with O_3 is its relatively short half-life in water, 10–40 min. Consequently, it is necessary to add another disinfectant to maintain an inactivation capability in a water distribution system. Additional kinetics studies of O_3 disinfection are discussed below.

The effects of O_3 and storage temperature on the survival of *Giardia lamblia* cysts (human giardiasis) and *Giardia muris* (a parasite of mice) were the focus of a laboratory study prior to the promulgation of the SWTR.[106] The viabilities of the cysts were similar over a period of 25 days of storage in the range of –6° to 37°C. The optimum temperature for their long-term survival was approximately 5°C. The contact times needed to achieve 2 logs of inactivation of *G. lamblia* cysts with 0.15 mg/L O_3 at a pH of 7 are 1 and 4 minutes at 25°C and 5°C, respectively. *G. Muris* cysts were 1.5 and 3.5 times more resistant to O_3 than *G. lamblia* cysts at 25° and 5°C, respectively. CT values were computed from the experimental data and are given in Table 11.30 for a 99% inactivation. Note that the SWTR requires a 99.9% inactivation (see Chapter 1).

Comparative Studies of the Halogens and Ozone

In many instances, it is difficult to evaluate and compare the disinfection efficacy of the various agents cited above. Several studies are available, however, in which the experimental conditions were held constant, thereby allowing a direct comparison to be made.

An early study was reported by Kruse et al.[107] that compared the effectiveness of Cl_2, Br_2, I_2 and their amines as viricides and bactericides for water and wastewater. From the results of this study, it was seen that iodamines are more effective than bromamines and chloramines for both viruses and bacteria. Chloramine apparently is not viricidal within 30 min. Iodine was a more effective viricide than bromine and chlorine at pH 7 and 8. At pH 6, chlorine is the most effective agent. This undoubtedly is due to the predominance of HOI at pH 7 and 8, whereas HOCl is predominant at pH 6.

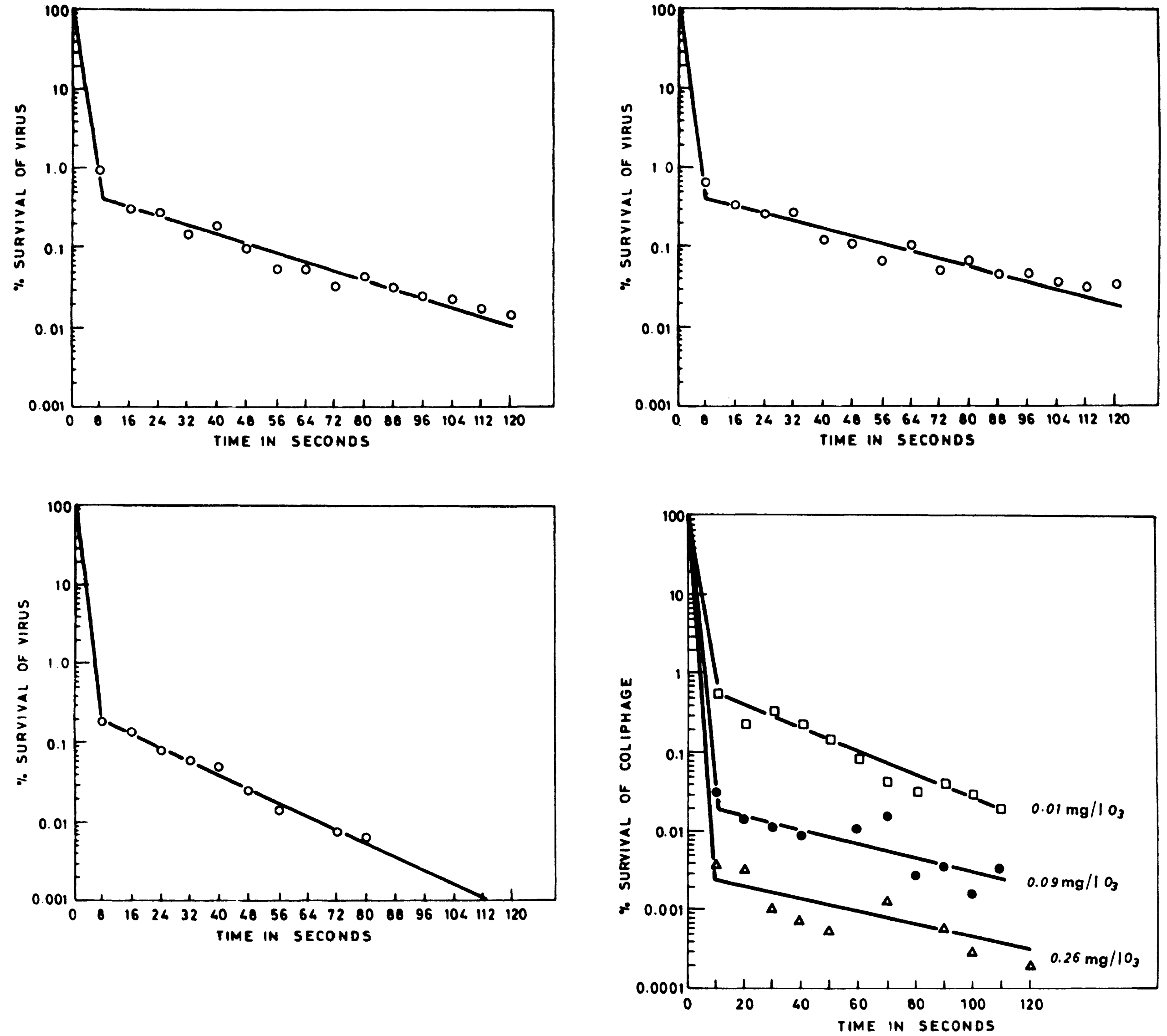

Figure 11.29. Inactivation kinetics of (a) poliovirus 1 by 0.3 mg/L ozone at 5°C; (b) poliovirus 1 by 0.8 mg/L ozone at 5°C; (c) poliovirus 1 by 1.5 mg/L ozone at 5°C; (d) coliphage T_2 by various concentrations of ozone at 1°C. Reproduced from Katzenelson et al.[105]

A quantitative comparative study of the cysticidal properties of Cl_2, Br_2, and I_2 was conducted by Stringer et al.[108] Table 11.32 shows the contact times required for a 90% inactivation of amoebic cysts by the three halogens at pH values of 6.0, 7.0, and 8.0, at 30°C. At pH 8.0, for example, iodine is not as effective as bromine and chlorine. However, bromamine appears to be more effective at pH 8.0 than the iodamines and chloramines. Also, the halamines are generally less effective than the free halogens in cysticidal activity.

From the studies of Cronier et al.,[90] Figure 11.30 shows a comparison of the inactivation efficacies of ClO_2, HOCl, OCl^-, NH_2Cl, and $NHCl_2$, for poliovirus at 15°C. On a weight basis, chlorine dioxide is as efficient a viricidal agent as HOCl.

The biocidal efficiencies of alternative disinfectants to chlorine were reported by Hoff and Geldreich.[109] Citing the research of others, the order of decreasing efficiency is: ozone, chlorine dioxide, free chlorine, and chloramines, while the order of stability in water is the reverse of efficiency. An increase of pH value (in the range of 6–9) has a beneficial effect on ClO_2, a detrimental effect on free chlorine, and little effect on ozone or chloramine efficacies. As

Table 11.29. Concentration of Ozone and Contact Time Necessary for 99% Inactivation of *E. coli* and Poliovirus 1.[36]

Test Microorganism	Ozone (mg/L)	Contact Time (min)	CT[a]	pH	Temperature (°C)
E. coli	0.07	0.083	0.006	7.2	1
	0.065	0.33	0.022	7.2	1
	0.04	0.50	0.02	7.2	1
	0.01	0.275	0.027	6.0	11
	0.01	0.35	0.035	6.0	11
	0.0006	1.7	0.001	7.0	12
	0.0023	1.03	0.002	7.0	12
	0.0125	0.33	0.004	7.0	12
Polio 1	<0.3	0.13	<0.04	7.2	5
	0.245	0.50	0.12	7.0	24
	0.042	10.0	0.42	7.0	25
	<0.03	0.16	<0.005	7.0	20

[a] Concentration of ozone times contact time.

Table 11.30. Concentration-Time Data for 99% Inactivation of *Giardia* Cysts with Ozone at pH 6.[106]

	Giardia lamblia			*Giardia muris*		
Temperature (°C)	C (mg/L)	T (min)	CT (mg-min/L)	C (mg/L)	T (min)	CT (mg-min/L)
25	0.15	0.97	0.15	0.18	1.3	0.24
	0.082	1.9	0.16	0.10	2.2	0.22
	0.034	5.5	0.19	0.080	3.4	0.27
				0.034	8.2	0.28
			0.17[a]			0.25[a]
	0.48	0.95	0.46	0.70	2.5	1.8
	0.20	3.2	0.64	0.40	5.0	2.0
	0.11	5.0	0.55	0.31	6.4	2.0
				0.21	9.6	2.0
			0.55[a]			1.9[a]

[a] Average CT value at a given temperature.

Table 11.31. Contact Times Necessary for Low Residual Bromine, Chlorine, and Iodine in Water at 30°C to Effect 90% Inactivation of Cysts from Simian Stools.[a,b]

		Contact Time Required (min) by 10-min Halogen Residual Concentration								
		0.5 mg/L			1.0 mg/L			2.0 mg/L		
	pH	Br_2	Cl_2	I_2	Br_2	Cl_2	I_2	Br_2	Cl_2	I_2
Buffered Water	6.0	10	10	20	4	4	10	3	3	5
	7.0	12	14	40	8	12	20	4	5	7
	8.0	15	20	ND[c]	10	15	80	5	10	20
Buffered Water in Presence of Excess Ammonia	6.0	10	65	20	8	35	10	4	22	5
	7.0	30	120	40	10	55	20	7	35	7
	8.0	35	ND	ND	13	80	80	9	50	20

[a] Reproduced from Stringer et al.[108]

[b] The proportions of the molecular species present in the test system depend on the halogen, the pH and the presence or absence of ammonia.

[c] ND=not determined.

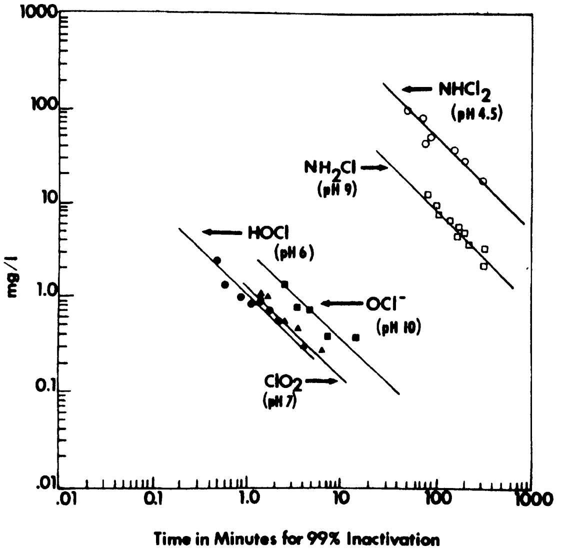

Figure 11.30. Comparison of the relative inactivation of poliovirus 1 by HOCl, OCl^-, NH_2Cl, $NHCl_2$, and ClO_2 at 15°C and different pH values. Reproduced from Cronier et al.[90]

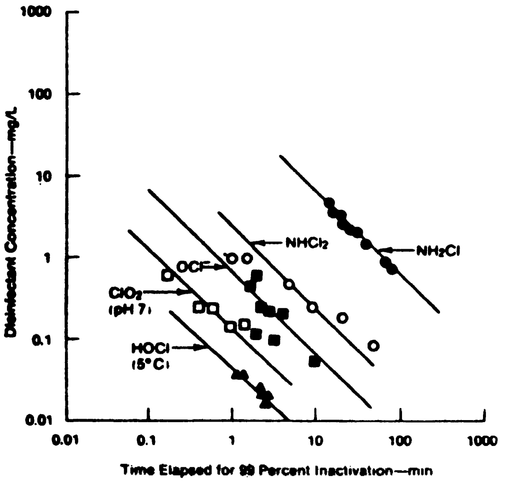

Figure 11.31. Inactivation of *E. coli* ATCC 11229 by free and combined chlorine species and chlorine dioxide at 15°C. Reproduced from Scarpino et al.,[78] and Esposito et al.,[85] courtesy of the American Society of Microbiology.

Table 11.32. Concentrations of Ferrate (FeO_4^{2-}) and Contact Times Necessary for 99% Inactivation of *E. coli, Streptococcus faecalis* and f_2 Virus.[a]

Test Microorganism	Ferrate Dosage (mg/L)	Contact Time (min)	CT[b]	pH	Temperature (°C)
E. coli	1.2	4.6	5.52	7.0	20
		6.0	2.5	15.0	
Streptococcus faecalis	1.2	365.0	438.0	7.0	20
		6.0	4.0	24.0	
f_2 Virus	1.2	3.7	4.4	6.0	20
		6.0	1.5	9.0	

[a] Reproduced from Waite,[111] as reported in Reference 36.
[b] Concentration of ferrate vs. contact time.

seen in Figures 11.30 and 11.31, neither order of efficiency nor degree of difference between the disinfectants is the same for both poliovirus and *E. coli*. These two figures summarize, in general, the state-of-the-art for the major disinfectants in water to date.

Comparative studies were conducted to examine the efficacy of O_3, ClO_2, Cl_2, and NH_2Cl for disinfection of *Cryptosporidium parvum* oocysts.[81] These results are discussed above and are seen in Figures 11.25a–d.

Other Disinfectants

Ferrate

That the oxidation state of Fe(VI) in the ferrate ion FeO_4^{2-} is easily reduced was discussed above. Several studies have been conducted on the efficacy of this oxidant as a disinfectant.[36] A pure culture of *E. coli* was inactivated at pH 8.0 with [FeO_4^{2-}] ranging from 1.2 to 6.0 mg/L.[110] A 99% disinfection was observed at 6.0 mg/L, pH 8.0 and 27°C within 8.5 min. Waite[111] extended these studies to include enteric pathogens and gram-positive bacteria and also evaluate the effects of pH and temperature. The rate of *E. coli* inactivation by ferrate was increased as the pH value was decreased from 8.0 to 6.0. However, the benefit of this higher rate is offset by a greater rate of ferrate decomposition. *S. typhimurium* and *Shigella flexneri* were inactivated in a manner similar to *E. coli* (Table 11.32). However, considerably higher dosages (>12 mg/L) were needed to inactivate *Streptococcus faecalis*. Concentrations of 12 and 60

Table 11.33. Concentrations and Contact Times Necessary for Potassium Permanganate to Effect 99% Inactivation of a 48–hr *E. coli* Lactose Broth Culture.[a]

Temperature (°C)	pH	Contact Time (min)					
		1 mg/L	2 mg/L	4 mg/L	8 mg/L	12 mg/L	16 mg/L
0	5.9	45	ND[b]	ND	ND	10	5
	7.4	[c]	ND	ND	ND	[c]	115
	9.2	ND	ND	ND	ND	ND	ND
20	5.9	95	45	15	15	10	5
	7.4	[c]	ND	[c]	80	80	25
	9.2	ND	ND	ND	ND	ND	[c]

[a] Reproduced from Cleasby et al.,[112] as reported in Reference 36.

[b] ND=no data reported.

[c] Inactivation in 120 min was less than 90%.

mg/L required 5 and 15 min, respectively, for 99% inactivation at pH 8.0.

The disinfection efficacy of ferrate is summarized in Table 11.32, where dosage is given rather than a residual because of rapid decomposition in aqueous solution. The CT values, therefore, should be interpreted as relative to the test microorganism and for ferrate itself when compared to other disinfectants. Rates of inactivation of *E. coli* with ferrate appear to be on the same order of magnitude as NH_2Cl.[110] Considerably more research is needed before ferrate is employed in water treatment.[36]

Potassium Permanganate

That this oxidant has some disinfection capability is seen in Table 11.33.[112] There are occasions when $KMnO_4$ is used for Fe and Mn removal, taste and odor control, etc. There will consequently be some disinfection incidental to the intended treatment. It is doubtful that $KMnO_4$ should be used as the principal disinfectant. The dosages cited in Table 11.33 are within those used in actual practice. According to Cleasby et al.,[112] the major factor influencing the effectiveness of $KMnO_4$ is the $[H^+]$. The lowest contact times were obtained at pH 5.9 rather than at 7.4 or 9.2. Because the oxidation product is $MnO_{2(s)}$, a brown-black solid, any use of $KMnO_4$ would be limited to pretreatment.

Ultraviolet Light

Electromagnetic radiation, in wavelengths from 240 to 280 nm, is an effective agent for disinfection of bacteria and other microorganisms in water. An emission of ultraviolet radiation occurs at a wavelength of 253.7 nm from a low-pressure mercury arc. This disinfectant can be used for small-scale systems that range from home supplies to small communities. Ultraviolet disinfection also could be used in an emergency situation. The dose, D, of electromagnetic radiation that is applied to a water is measured as the intensity of radiant energy input, I_o, at the lamp surface or at some given distance from the lamp multiplied by the time, T, of exposure in seconds:

$$D = I_o T \tag{63}$$

where I_o is expressed as $\mu W/cm^2$ (W=watt). The reader is directed to Reference 36 for the engineering configurations of ultraviolet radiation systems.

Several laboratory studies have been conducted on the efficacy of UV radiation for the disinfection of *E. coli, Salmonella,* and *Shigella* species, *Streptococcus faecalis,* and an assortment of viruses.[36] Table 11.34 gives the UV energy necessary to inactivate various microorganisms.[113] These values are, of course, the energies required for disinfection of the microorganisms under the experimental conditions employed. Energy values may vary with design and configuration of a specific UV system. It is important to have the water flow rate (i.e., contact times), water depth, and the raw water turbidity. If the latter is present, then it must be removed before exposure to the UV radiation. Also, UV disinfection leaves no residual. Another disinfectant must be used if a residual is desired in the system.

Oocysts of *Cryptosporidium parvum,* suspended in sterile demineralized water, were exposed to UV radiation, 15,000 μW/sec, for different periods of time.[114] When the exposure time was less than 150 min, the reduction in infection incidence was 36% and less. Infectivity was eliminated totally only upon exposure to UV light for 150 and 180 min.

Miscellaneous Compounds

Other disinfectants used in water treatments are: the chlorosulfamates, $NHClSO_3^-$ and $NCl_2SO_3^-$, for swimming pools,[115] silver, Ag^+, for use in home treatment systems and swimming pools,[36] the chloroisocyanurates for swimming pools,[116] and ultraviolet radiation for disinfecting bacteria and other microorganisms in small water systems.[36]

Table 11.34. Ultraviolet Energy Necessary to Inactivate Various Organisms.[a]

Test Microorganism	Lethal Dose (μW•s/cm^2)
Escherichia coli	360
Staphylococcus aureus	210
Serratia marcescens	290
Sarcina lutea	1,250
Bacillus globiggli spores	1,300
T3 coliphage	160
Poliovirus	780
Vaccinia virus	30
Semliki Forrest virus	470
EMC virus	650

[a] Data from Morris,[113] as reported in Reference 36.

Summary

Tables 11.35, 11.36, and 11.37 bring together the major disinfection methods for drinking water and the comparative efficacy of the disinfectants. The biocidal activities of these disinfectants are compared through the CT product that is required to achieve a particular degree of inactivation under similar conditions of temperature, [H$^+$], etc. The lower the CT value, the more effective is the disinfection by a particular agent.

KINETICS OF DISINFECTION

Chick's Law

Chemical destruction of the microorganisms cited above ideally should occur as a reaction between a single organism and the disinfectant. Also, the disinfectant should remain unchanged in chemical composition as well as in concentration throughout the period of contact. The water should contain no interfering substances. Under these conditions, the rate of disinfection is a function of contact time, disinfectant concentration, and water temperature. The number of microorganisms may or may not affect this process.

Much of the kinetics of disinfection follows the time-rate of kill described by Chick's law of disinfection.[118] This law states that y, the number of organisms destroyed per unit time, is proportional to N, the number of organisms remaining, with the initial number being N_0 (nomenclature follows Fair et al.[21]):

$$\frac{dy}{dt}k(N_0 - y) \tag{64}$$

where k is the rate constant (time^{-1}). Integration between the limits of y=0, t=0, and y=y at time t yields:

$$\ln\frac{N}{N_0} = -kt \tag{65}$$

or

$$\frac{N}{N_0} = e^{-kt} \tag{66}$$

Consequently, a plot of log N/N_0 vs. time gives a straight line with a slope of $-k \log e = -k'$, and an intercept of 1 (or 100%) at time 0. For a reaction time of 1, $k't=0.4343$, the surviving fraction is 0.368 or 36.8%. Other reaction times may be calculated from Equation 66. For example, a 99.995% kill is achieved with 10 reaction times. Chang[119] and others have indicated that disinfection is a first-order rate process. In other aspects of the quantitative assessment of germicidal efficiency, the reader is referred to the specific lethality coefficient presented by Morris[120] and the multi-Poisson distribution model, or the "multihit" concept described by Wei and Chang.[121]

Equation 66 was later modified by Watson[122] to relate the rate constant of inactivation, k, to the disinfectant concentration C:

$$k = k'C^b \tag{67}$$

In Equation 67, b is termed the coefficient of dilution (see Equation 60), and k is presumed to be independent of C and microorganism concentration. Combining Equations 67 and 66 leads to the Chick-Watson relation:

$$\frac{N}{N_0} = e^{k'c^b t} \tag{68}$$

Departures from Chick's law are frequent and common in laboratory experiments and treatment plant practice. Rates of kill may increase or decrease rather than remain constant with time. Explanations are offered for departures from Chick's law, but no proof is given. In order to linearize these data, empirical coefficients are added to the t term in Equation 66:[21]

$$\frac{N}{N_0} = e^{kt^m} \tag{69}$$

An example is given in Figure 11.32, where linearization is achieved with m=2. When m>1, the rates of kill rise in time, whereas when m<1, the rates of kill decrease with time. This modification of Equations 66 and 68 was reported by Hom[127] (see below).

Temperature of Disinfection

It is well known that temperature affects the rate of disinfection. This was seen in many of the studies cited above. In accord with the rate laws, a diffusion-controlled disin-

Table 11.35. Summary of Major Possible Disinfection Methods for Drinking Water.[36]

Disinfection Agent[a]	Technological Status	Efficacy in Demand-Free Systems[b]			Persistence of Residual in Distribution System
		Bacteria	Viruses	Protozoan Cysts	
Chlorine[c]	Widespread use in U.S. drinking water				Good
As hypochlorous acid (HOCl)		++++	++++	++	
As hypochlorite ion (OCl^-)		+++	++	NDR[d]	
Ozone[c]	Widespread use in drinking water outside United States, particularly in France, Switzerland and Quebec	++++	++++	++++	No residual possible
Chlorine dioxide[c,e]	Widespread use for disinfection (both primary and for distribution system residual) in Europe, limited use in United States to counteract taste and odor problems and to disinfect drinking water	++++	++++	NDR[d]	Fair to good (but possible health effects)
Iodine	No reports of large-scale use in drinking water				Good (but possible health effects)
As diatomic iodine (I_2)		++++	+++	+++	
As hypoiodous acid (HOI)		++++	++++	+	
Bromine	Limited use for disinfection of drinking water	++++[f]	++++[f]	+++[f]	Fair
Chloramines	Limited present use on a large scale in U.S. drinking water	++	+	+	Excellent

[a] The sequence in which these agents are listed does not constitute a ranking.

[b] Ratings:++++, excellent biocidal activity; +++, good biocidal activity;++, moderate biocidal activity;+, low biocidal activity; ±, of little or questionable value.

[c] By-product production and disinfectant demand are reduced by removal of organics from raw water prior to disinfection.

[d] Either no data reported or only available data were not free from confounding factors, thus rendering them not amenable to comparison with other data.

[e] MCL=1.0 mg/L because of health effects.

[f] Poor in the presence of organic material.

Table 11.36. Comparative Efficacy of Disinfectants in the Production of 99% Inactivation of Microorganisms in Demand-Free Systems[a],[36]

	E. coli			Poliovirus 1			*Entamoeba histolytica* Cysts		
Disinfection Agent	**pH**	**Temperature (°C)**	**CT[b]**	**pH**	**Temperature (°C)**	**CT[b]**	**pH**	**Temperature (°C)**	**CT[b]**
Hypochlorous Acid	6.0	5	0.04	6.0	0	1.0	7.0	30	20
				6.0	5	2.0			
				7.0	0	1.0			
Hypochlorite Ion	10.0	5	0.92	10.5	5	10.5		NDR[c]	
Ozone	6.0	11	0.031	7.0	20	0.005	7.5–8.0	19	1.5[d]
	7.0	12	0.002	7.0	25	0.42			
Chlorine Dioxide	6.5	20	0.18	7.0	15	1.32			
	6.5	15	0.38	7.0	25	1.90		NDR[c]	
	7.0	25	0.28						
Iodine	6.5	20–25	0.38	7.0	26	30.0	7.0	30	80.0
	7.5	20–25	0.40						
Bromine		NDR[c]		7.0	20	0.06	7.0	30	18.0
Chloramines									
Monochloramine	9.0	15	64.0	9.0	15	900.0		NDR[c]	
	9.0	25	40.0	9.0	25	320.0			
Dichloramine	4.5	15	1.5	4.5	15	5,000.0		NDR[c]	

[a] Conditions closest to pH 7.0 and 20°C were selected from studies discussed in the text. Values for other conditions and agents appear in the text along with discussions of the cited studies.

[b] Concentration of disinfectant (mg/L) times contact time (min).

[c] Either no data reported or only available data were not free from confounding factors, thus rendering them not amenable to comparison with other data.

[d] This value was derived primarily from experiments that were conducted with tap water; however, some parallel studies with distilled water showed essentially no differences in inactivation rates.

Table 11.37. CT Products for 99% Inactivation of Various Microorganisms by Free Chlorine at 5°C, pH 6.0.[117]

Microorganism	Chlorine Concentration (mg/L)	Time (min)	CT
E. coli	0.1	0.4	0.4
Poliovirus 1	1.0	1.7	1.7
E. histolytica[a] cysts	5.0	18.0	90.0
G. lamblia[b] cysts	1.0	50.0	50.0
	2.0	40.0	80.0
	4.0	20.0	80.0
	8.0	9.0	72.0
G. lamblia[c] cysts	2.5	30.0	75.0
G. lamblia[b] cysts	2.5	100.0	250.0[a]
G. muris cysts	2.5	100.0	250.0[a]

[a] Extrapolated data.
[b] Cysts from asymptomatic carriers.
[c] Cysts from symptomatic carriers.

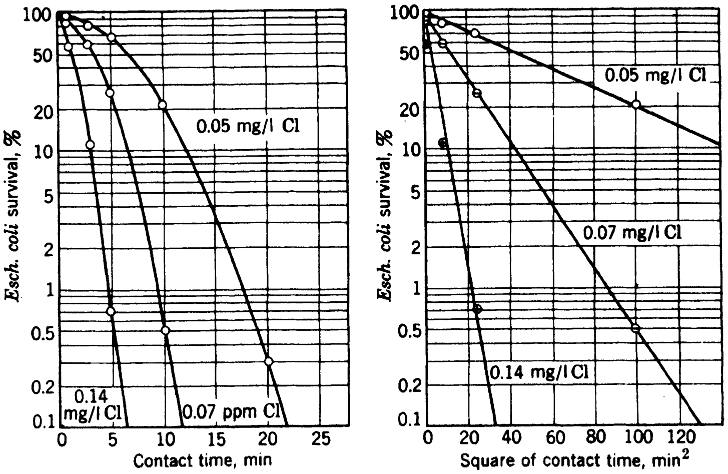

Figure 11.32. Length of survival of *E. coli* in pure water at pH 85 and 2–5°C. Reproduced from Fair et al.,[21] courtesy of John Wiley & Sons, Inc.

fection reaction—or, perhaps, an enzyme-disinfectant reaction—will show temperature effects in conformance with the van't Hoff-Arrhenius relationship, for which it is convenient to write:

$$\log \frac{t_1}{t_2} = \frac{E_a(T_2 - T_1)}{2.303RT_1T_2} \qquad (70)$$

where T_1, T_2 = absolute temperatures (°K)
t_1, t_2 = times required for equal percentages of kill at fixed contents of disinfectant
E_a = activation energy (cal)
R = the ideal gas law constant, 1.9872 cal/mol deg

When $T_2 - T_1 = 10$, the ratio of t_1/t_2 is called Q_{10}, which is helpful in comparing destruction rates of various disinfectants and microorganisms. Equation 70, at water temperatures near 20°C, becomes:

$$\log Q_{10} = \log \frac{t_1}{t_2} = \frac{E_a}{39{,}000} \qquad (71)$$

Fair et al.[21] fitted the data of Butterfield[72] into Equation 71 and calculated E_a and Q_{10} values (Table 11.38).

Early Studies

One of the early kinetic studies concerning disinfection of water was the iodine destruction of amoebic cysts by

Table 11.38. Temperature Dependence of Disinfecting Concentrations of Aqueous Chlorine and Chloramines in the Destruction of *E. coli* in Clean Water.[a]

Type of Chlorine	pH	E_a (cal)[b]	Q_{10}
Aqueous Chlorine	7.0	8,200[c]	1.65[c]
	8.5	6,400	1.42
	9.8	12,000	2.13
	10.7	15,000	2.50
Chloramines	7.0	12,000	2.08
	8.5	14,000	2.28
	9.5	20,000	3.35

[a] Reproduced from Fair et al.,[21] courtesy of John Wiley & Sons, Inc.

[b] The higher the value of E_a, the slower the reaction.

[c] The rate of reaction at pH 7.0 is relatively so fast that these values are probably unreliable. The magnitudes of E_a throw some light on the nature of the disinfecting process for the chlorine species released in water.

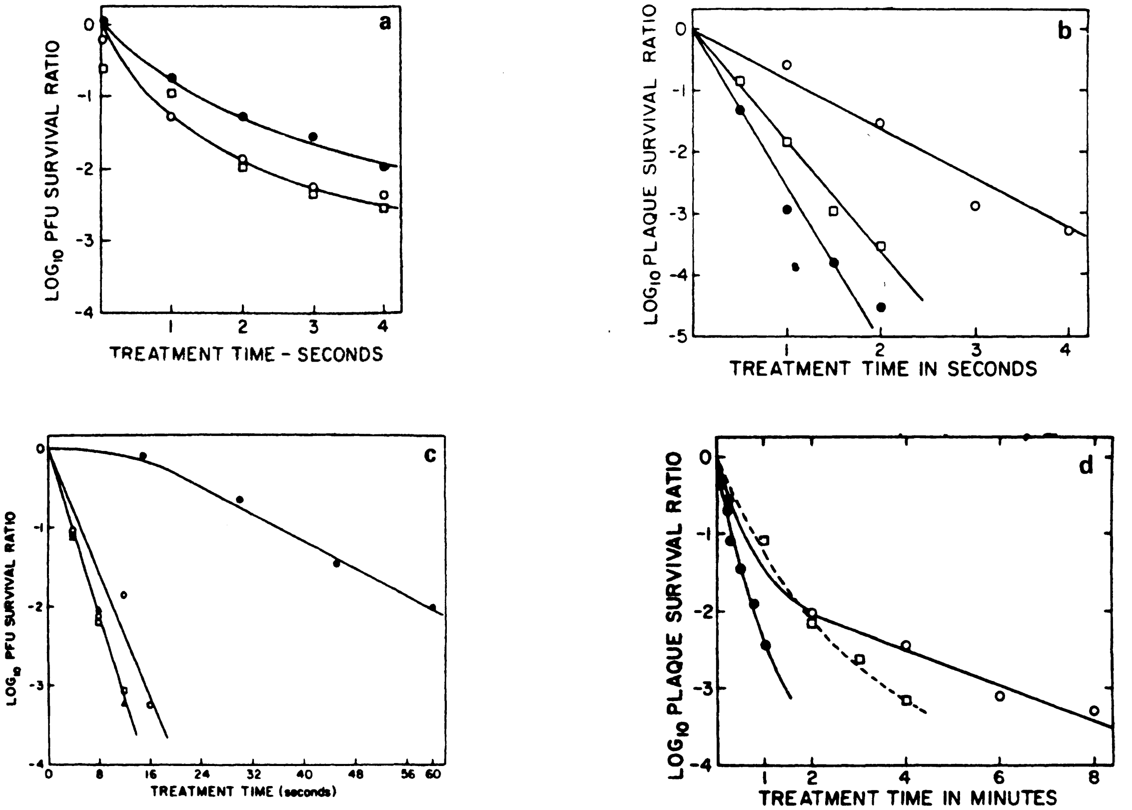

Figure 11.33. Kinetics of inaction of poliovirus at 4°C by (a) OBr⁻ at pH 10 (●—● = 2 μ*M*, □—□ = 6 μ*M*, ○—○ = 12 μ*M*); (b) Br_2 at pH 5 in the presence of 0.3 *M* NaCl (○—○ = 4.7 μ*M*, □—□ = 12.9 μ*M*, ●—● = 21.6 μ*M*); (c) NBr_3 (●—● = 3.2 μ*M*, ○—○ = 12 μ*M*, □—□ = 27 μ*M*, △—△ 49 μ*M*); (d) $NHBr_2$ (○—○ = 2.9 μ*M*, □—□ = 13.8 μ*M*, ●—● = 39 μ*M*); data points at 39 μ*M* represent two experiments, one with samples taken up to 15 sec, and samples taken at 15–60 sec). Reproduced from Floyd et al.,[94] courtesy of the American Chemical Society.

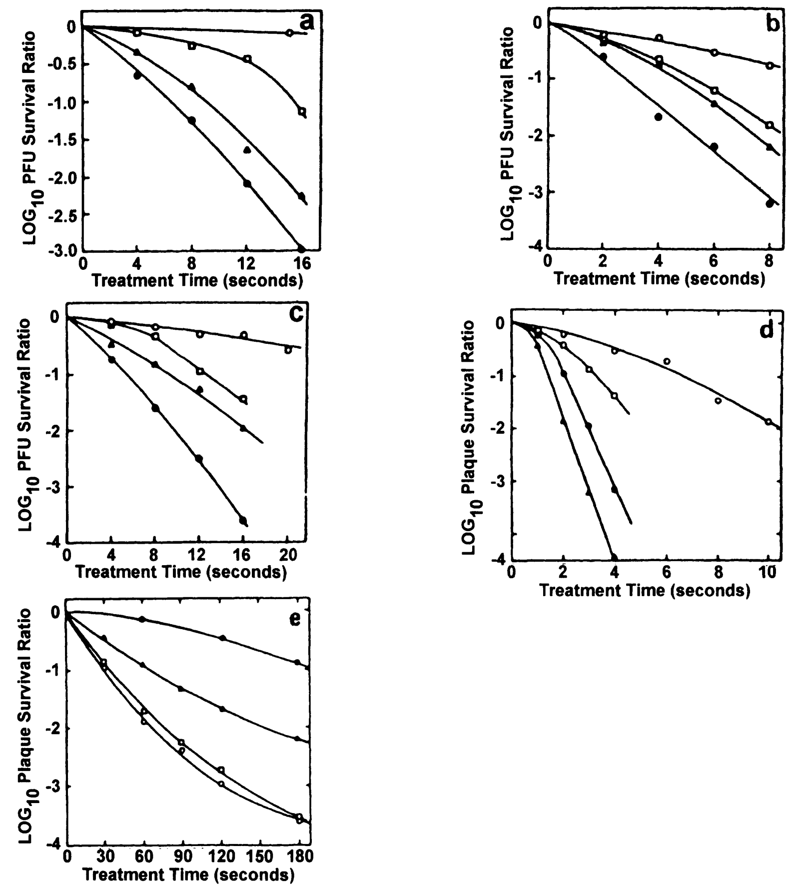

Figure 11.34. Inactivation of poliovirus single particles (a) at 2°C by HOCl, pH 6.0, ○ = 1.4 μ*M*, □ = 10 μ*M*, Δ = 22 μ*M*, ● = 40 μ*M*; (b) at 20°C by HOCl, pH 6.0, ○ = 2.2 μ*M*, □ = 11 μ*M*, = 22 μ*M*, ● = 35 μ*M*; (c) at 10°C by HOCl, pH 6.0, ○ = 1.5 μ*M*, □ = 11 μ*M*, Δ = 20 μ*M*, ● = 41 μ*M*; (d) at 30°C by HOCl, pH 6.0, ○ = 1.4 μ*M*, □ = 10 μ*M*, ● = 20 μ*M*, Δ = 42 μ*M*; (e) at 20°C by OCl$^-$, pH 10.0, ● = 3.5 μ*M*, = 7.5 μ*M*, □ = 15 μ*M*, ○ = 30 μ*M*. Reproduced from Floyd et al.,[124] courtesy of the American Chemical Society.

Chang and Morris.[97] The CT products are given above for three temperatures, 3°, 10°, and 23°C. An activation energy of 9500 cal was obtained when the temperature was varied and the contact time was held constant. The cysticidal action of iodine was dependent less on temperature than HOCl (E_a=13,000 cal).[97] The Q_{10} value for the I_2-amoebic cyst system was 1.65.

The kinetics of inactivation of single poliovirus particles were investigated in water with various species of bromine.[94] Figure 11.33 shows the usual semilogarithmic and first-order plot of the inactivation of pH 10, where OBr^- predominates. The inactivation rate typically was quite rapid initially, whereupon it decreased with time. Figure 11.33b gives the kinetics of inactivation of the poliovirus with Br_2 contents of 4.7, 12.9, and 21.6 μ*M* (0.75, 2.06, and 3.46 mg/L). These results were linear and did not curve with time as did OBr^-. The reaction rates were –0.8, –1.81, and –2.5 $\log_{10}$/sec, respectively, for the three Br_2 contents. These rates were slower than the initial ones for OBr^- but were approximately 10 times greater than for HOBr.[123] Figures 11.33c and d show the kinetics of inactivation of a poliovirus by NBr_3 and $NHBr_2$, respectively. The latter kinetics were definitely slower than NBr_3, Br_2, and OBr^-. Note that the time scale on Figure 11.33d is in minutes, whereas the others are in seconds. In summary, the initial rate for OBr^-, the linear rates of Br_2, NBr_3, and HOBr,[123] and the initial rate of $NHBr_2$, all at 10 μ*M*, are 3.85, 1.55, 0.15, 0.16, and 0.013 $\log_{10}$/sec, respectively. The CT values for these bromine species are given in Table 11.24.

Some kinetic aspects of the inactivation of poliovirus by HOCl and OCl^- were reported by Floyd et al.,[124] who used virus preparations in which no less than 99% of the virus were free single particles. Figure 11.34 shows a reasonably consistent and similar mode of inactivation by HOCl regardless of temperature. Note that the time scales on Figures 11.34a and b are twice the ones on Figures 11.34c and

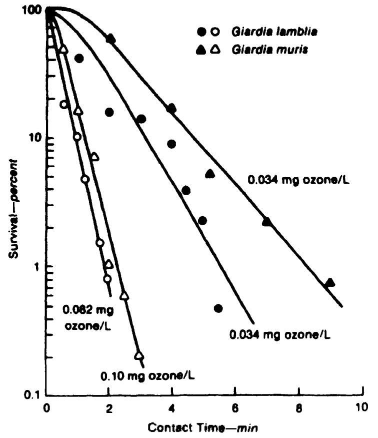

Figure 11.35a. Inactivation of *Giardia* cysts with ozone at pH 7 and 25°C.[106]

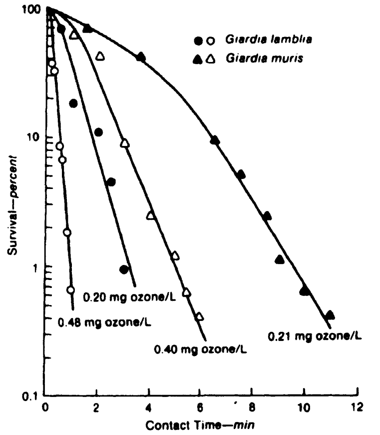

Figure 11.35b. Inactivation of *Giardia* cysts with ozone at pH 7 and 5°C.[106]

d. The results for virus inactivation with OCl^- are seen in Figure 11.34e. These reaction rates were considerably slower than with HOCl. All of these curves indicate that the inactivation rate is concentration-dependent, with the exception of the 15 and 30 μ*M* of OCl^-. Neither rate constants nor activation energies were calculated.

Comparisons may be made now between the rates of inactivation of the poliovirus by various bromine and chlorine species. The rates shown by HOBr and HOCl are quite similar: 22 μ*M* HOBr at 2°C reduced the plaque survival level to 10^{-3} in 16 sec,[124] whereas it required 40 μ*M* HOCl to produce essentially the same results (see Figure 11.35). However, there are considerable differences when OCl^- and OBr^- are compared with each other and with HOCl and HOBr. The OBr^- is more effective than HOBr, whereas HOCl is far more efficient that OCl^-. The relative rates are in the order: $OBr^- > HOBr > HOCl > OCl^-$.[124]

Late Studies

Some kinetics of O_3 disinfection of *Giardia lamblia* and *Giardia muris* cysts were reported prior to the advent of the SWTR.[106] A typical set of survival curves for these two *Giardia* is given in Figure 11.35a and b. These curves, which are semilog plots of percentage survival against contact time, generally consist of an initial log followed by an essentially linear region and, as such, are similar to Figure 11.32 for the disinfection of *E. coli* with Cl_2. When the cysts were exposed to 0.034 mg/L O_3 at pH 7 and 25°C, *G. muris* was consistently more resistant than *G. lamblia* (Figure 11.35a). *G. muris* required more than 0.1 mg/L O_3 to achieve the inactivation with *G. lamblia* at 0.082 mg/L O_3. At 5°C and pH 7, *G. muris* cysts were consistently more resistant than *G. lamblia* cysts.

Another pre-SWTR study examined the kinetics of inactivation of *Naegleria* and *Giardia* cysts by O_3 in water.[125] Four O_3 concentrations were employed for the disinfection of *N. Gruberi* cysts at pH values ranging from 5 to 9, and at temperatures ranging from 5° to 30°C. A typical semi-log plot of the fraction of cysts surviving, N/N_o, against contact time is seen in Figure 11.36a. O_3 dosages ranged from 0.28 to 1.14 mg/L, whereupon the contact times were lowered as the concentration was increased. Similar results were obtained for the inactivation of *G. muris* cysts by O_3 concentrations of 0.054, 0.14, and 0.25 mg/L at 15°C and pH 7.0 (Figure 11.36b). The values generated from these survival curves were utilized subsequently to construct log-log plots of $[O_3]$ (c) in mg/L against time (t) required to obtain 99% inactivation. At each pH and temperature, these plots were essentially linear, wherein the data were in close agreement with the Chick-Watson relationship (Equation 68). In this study, the b values for *N. Gruberi* averaged 1.0 for pH 5–9 and 25°C, and 1.1 for pH 7 over 5° to 30°C temperatures. Similarly, the b values for *G. muris* averaged 1.2 for a temperature of 25°C over the pH range of 5 to 9, and 1.1 for pH 7 over 5° to –25°C temperatures.

The kinetics of inactivation of *Cryptosporidium parvum* by O_3 was performed in ozone demand-free 0.05 *M* phosphate buffer (pH 6.9) in bench-scale batch reactors at 7° and 22°C.[126] These kinetics deviated from the simple first-order Chick-Watson model (Equation 68) and were better described by a nonlinear Hom model:[127]

$$\log \frac{N}{N_o} = -k\,C^b t^m \tag{72}$$

where m is an empirical constant (Equation 69). In the simple Chick-Watson model, where b=1.0, the CT product is a constant for each level of inactivation irrespective of contact time or concentration. In the Hom model, b and m values

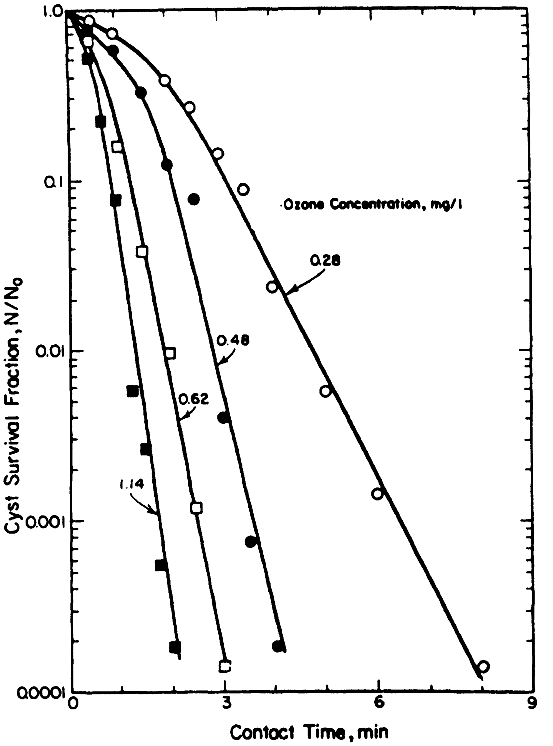

Figure 11.36a. Inactivation of *N. gruberi* cysts with ozone at 25°C and pH 5.

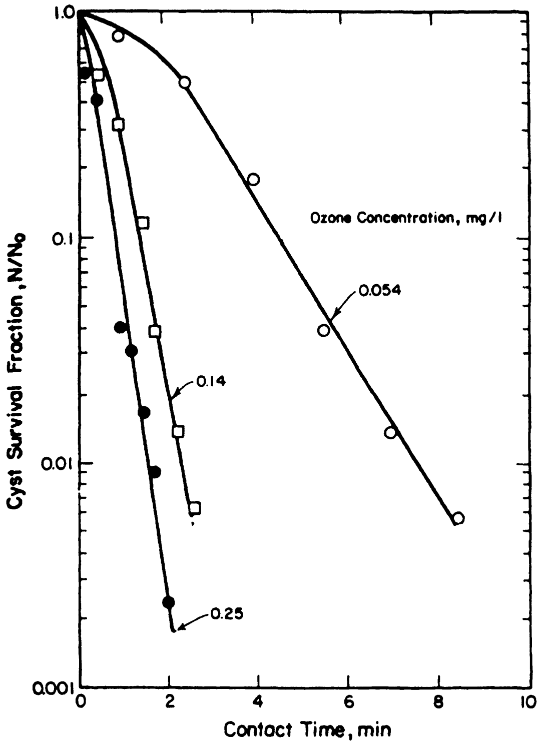

Figure 11.36b. Inactivation of *G. muris* cysts with ozone at 15°C and pH 7.

are not unity. Rather, the concentration and contact time change in a nonlinear manner according to:

$$C^b t^m = K \tag{73}$$

where K is a constant for a given microorganism at the desired level of inactivation, and incorporates the kinetic rate constant k in Equations 66 and 69. For this study, the constants in Equation 72 were evaluated and presented as:

$$\text{at } 7^\circ\text{C} \log \frac{N}{N_0} = -0.29C^{0.68}t^{0.95} \tag{74}$$

$$\text{at } 22^\circ\text{C} \log \frac{N}{N_0} = -0.82C^{0.23}t^{0.64} \tag{75}$$

In Table 11.39, the required contact times, the conventional linear CT values, and the nonlinear $C^b t^m$ values are given for a 99% inactivation of *C. parvum* at 7° and 22°C by O_3. For the latter, constant values of 6.9 and 2.4 were obtained for the two temperatures. Certainly, the Hom model (Equation 72) describes the nonlinear kinetics of O_3 disinfection of *C. parvum* better than the conventional CT model. These data illustrate the differences in the design conditions for O_3 contact time and the integrated O_3 residual when compared with the simple CT values for the same disinfection conditions. For example, in Table 11.39, an integrated O_3 residual of 0.25 mg/L required a contact time of 6.6 min (22°C) for a 99% inactivation (simple CT = 1.7 mg min/L). When this residual is doubled to 0.50 mg/L, the required contact time drops to 5.2 min for a 99% inactivation (simple CT = 2.6 mg min/L). Inasmuch as the contact time was not decreased by 50% when the $[O_3]$ was doubled in the latter system, this observation has design implications. The designer of an O_3 disinfection system needs to decide whether or not the cost of providing extra contact time can be justified by the savings in O_3 generation. For 99.9% inactivation of *C. parvum*, the $C^b t^m$ values were 10.3 and 3.7, respectively, for 7° and 22°C.[126]

Figure 11.37 summarizes some of the significant kinetic studies in the 1980s for the chlorine and ozone disinfection of bacteria, viruses, and parasitic cysts.[128] For the most part, these log-log plots were derived from the Chick-Watson model (Equation 11.68) where the constant, k′, is a function of the organism, pH, temperature, form of disinfectant, and extent of activation. Deviations from the Chick-Watson model are discussed above. In any event, the plots in Figure 11.37 do show the relative efficacies of the disinfectants, and the responses of the various organisms.

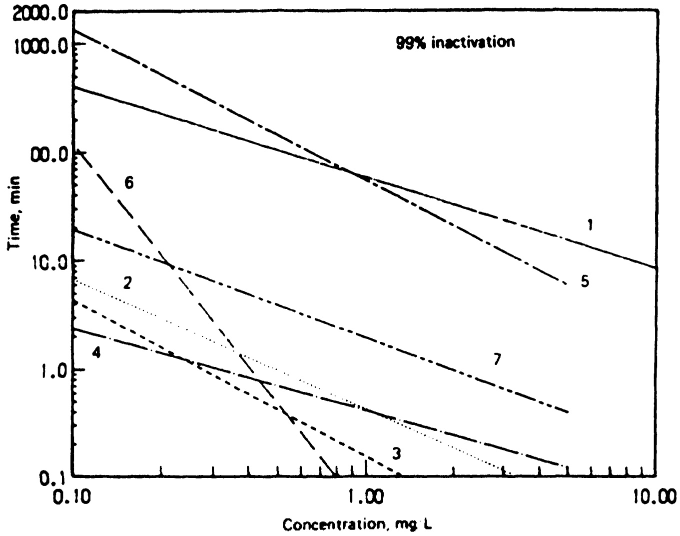

Figure 11.37. Concentration-time relationships for 99% inactivation of various microorganisms by various disinfectants. (1) *Giardia lamblia;* free chlorine, 5°C, pH 6.[129] (2) *E. coli;* free chlorine, 2 to 5°C, pH 8.5.[130] (3) *E. coli;* free chlorine, 20 to 25°C, pH 8.5.[130] (4) Poliovirus 1 (Mahoney); free chlorine, 2°C, pH 6.[130] (5) *E. coli;* combined chlorine, 3 to 5°C, pH 7.[130] (6) Poliovirus 1 (Mahoney); ozone, 20°C, pH 7.2.[131] (7) *Giardia muris;* ozone, 5°C, pH 7.[125]

Table 11.39. Summary of Ozonation Design Criteria Required to Achieve 99% Inactivation of *Cryptosporidium* Oocysts.[126]

Integrated Ozone Residual (mg/L)	Required Contact Time (min)		Conventional Linear CT		Nonlinear C^nT^m	
					n=0.68, m = 0.95	n=0.23, m = 0.64
	7°C	22°C	7°C	22°C	7°C	22°C
0.25	20.6	6.6	5.1	1.7	6.9	2.4
0.50	12.5	5.2	6.3	2.6	6.9	2.4
0.75	9.4	4.5	7.0	3.3	6.9	2.4
1.00	7.6	4.0	7.6	4.0	6.9	2.4
1.25	6.5	3.7	8.1	4.6	6.9	2.4
1.50	5.7	3.5	8.6	5.2	6.9	2.4
1.75	5.1	3.3	8.9	5.8	6.9	2.4
2.00	4.6	3.1	9.3	6.3	6.9	2.4
2.25	4.3	3.0	9.6	6.8	6.9	2.4
2.50	4.0	2.9	9.9	7.2	6.9	2.4
2.75	3.7	2.8	10.2	7.7	6.9	2.4
3.00	3.5	2.7	10.4	8.1	6.9	2.4

Mechanisms of Activity

The mechanisms of disinfection by chlorine and other oxidants have received considerable discussion and speculation over the decades of research.[36] It seems reasonable to require disinfectants to penetrate the cell wall of the target organism and subsequently to react with one or more of the enzyme systems therein. An early reference to a mechanism of disinfection is an observation by Chang[73] that there was a greater uptake of chlorine by cysts of *E. histolytica* at a "low" pH value than at a "high" pH. It was hypothesized that uncharged HOCl was able to penetrate into this organism. There was considerable support for this hypothesis by several investigators.[36] Later, Kulikovsky et al.[132] implicated permeability damage to bacterial spores as a mechanism of chlorine inactivation. Studies with *E. coli* have shown that Cl_2 causes leakage of cytoplasmic material with protein existing first, followed by RNA and DNA into the suspending menstruum.

Several studies have indicated that disinfection of bacteria was due to enzyme inhibition.[36] Green and Stumpf[133] and Knox et al.[134] suggested that the destruction of bacteria by Cl_2 was caused by inhibiting the mechanism for glucose oxidation. The specific reaction was an oxidation of the sulhydryl group associated with the aldolase enzyme. Another study reported that Cl_2 significantly inhibits both O_2 uptake and oxidative phosphorylation.[36] Chang[119] concurred with the hypothesis that the quick disinfection of vegetative bacteria by Cl_2 was caused by extensive destruction of metabolic enzyme systems. Also, there was some speculation about the inactivation of viruses, which are generally more resistant to Cl_2 than bacteria. Chang suggested that denaturation of the capsid protein of viruses was responsible. Venkobachar[135] reported some data that show the total dehydrogenase activity of intact *E. coli* cells was affected by Cl_2 doses, which in turn correlated well with percent survivals. It was shown that the succinic dehydrogenase activity in crude extracts of *E. coli* was affected by Cl_2. Also, the effect of chlorine on thiol groups in the crude extract was studied. A reduction in these thiol groups suggested that they are vulnerable to oxidation. Haas and Engelbrecht[136] determined the uptake of radioactive chlorine by coliforms, acid-fast bacteria, and yeasts. The Freundlich adsorption model was able to describe the uptake of chlorine. *Candida parapsilosis* and *Mycobacterium fortuitum* exhibited more uptake of Cl_2 at pH 7 than at pH 9.14. This study confirmed that the inactivation of vegetative microorganisms was from the cell-associated chlorine. Generally, the association of chlorine with virus disinfection parallels the biocidal efficacy of HOCl, OCl^-, and NH_2Cl.[128] There are exceptions, however, from the report that some viruses are more sensitive to free chlorine at high pH (OCl^-) than at low pH (HOCl).[77]

As mentioned above, once chlorine enters the cell of the living organism, it may participate in a number of reactions. For example, in bacteria, respiratory, transport and nucleic acid activity are adversely affected.[128] In bacteriophage f_2, the mode of inactivation appears to be a disruption of the viral nucleic acid.[137] With poliovirus, however, the protein coat, and not the nucleic acid, appears to be the critical site for inactivation of free chlorine.[128] The mechanism of bacterial disinfection by O_3 appears to be some sort of a physiochemical damage to deoxyribonucleic acid,[138] whereas for poliovirus, the inactivation appears to be nucleic acid damage.[131] The mode of inactivation of microorganisms by UV radiation is well characterized by specific deleterious changes in their nucleic acid.[128]

The mechanism of inactivation of *E. coli* by NH_2Cl was reported from laboratory studies.[139] This disinfectant did not severely damage the cell envelope of the bacterium or affect nucleic acid function. Apparently, there was inhibition of typical protein-associated biological activities, e.g., bacterial transport, respiration, and substrate dehydrogenation at normal disinfection concentrations.

DISINFECTION REQUIREMENTS OF THE SWTR AND ESWTR

All public water systems are required to filter their surface waters and those groundwaters that are under the influence of surface water (see Chapter 1). Filtration can be avoided if the PWS can meet certain criteria related to source water quality and site-specific conditions. One of these criteria is the utilization of disinfection to avoid filtration. Under the SWTR, a system must practice disinfection and achieve 99.9 and 99.99% inactivation of *Giardia* cysts and viruses, respectively. This must be demonstrated by the system each day it delivers water to consumers by meeting CT values (see below) in the rule. Under the proposed enhanced surface water treatment rule (ESWTR) (see Chapter 1), deficiencies in the SWTR for the removal of *Giardia* cysts and viruses are addressed. Also, treatment control of *Cryptosporidium* is proposed.

Calculation of CT Value

Succinctly, the contact time, T, used in the calculation of CT values is the time it takes water to move between the disinfection application point to the point where the residual is measured.[140,141] Times for water flow through pipes, basins, and reservoirs must be calculated and included in CT.

Flow Through Pipes

The time that water is in contact with the disinfectant when it is flowing through pipes is calculated on the basis of uniform plug flow. It is assumed that water moves in a uniform manner between two points in a pipe. This contact time is calculated from:

$$T = \frac{\text{internal volume of pipe}}{\text{peak hourly flow rate through pipe}} \tag{76}$$

Flow Through Reservoir

Water does not flow through reservoirs (including tanks and basins) in a uniform manner. Rather, there is a wide range of residence times of water in reservoirs that depends on a variety of factors: shape, inlet and outlet design and location, and baffling. The contact time used to calculate the CT for a reservoir is the detention time at which 90% of the water passing through the reservoir is retained within the reservoir. In other words, it is the time it takes 10% of the water to pass through the reservoir. This contact time is designated as T_{10}. This value for a reservoir may be determined experimentally by tracer studies or theoretically by approximation. The reader is directed to References 140 and 141 for all of the engineering details to obtain T_{10} values. Three simple examples will suffice here.[140]

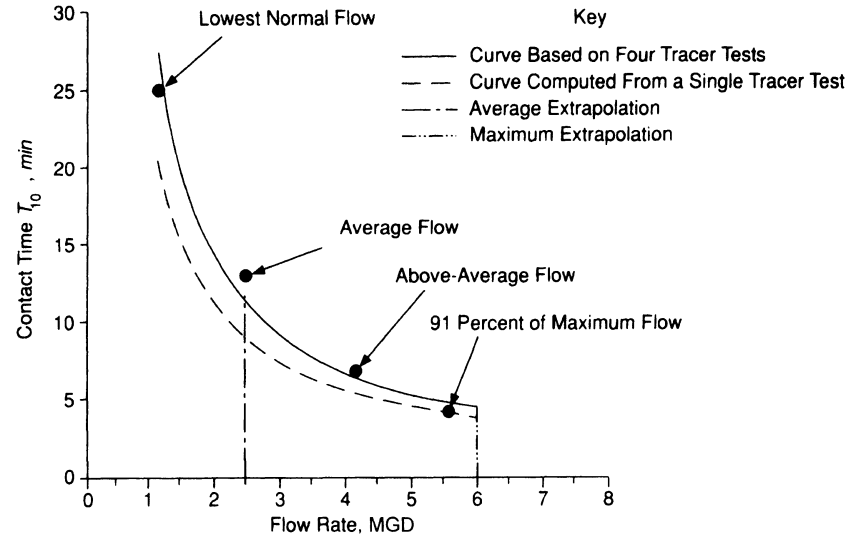

Figure 11.38. Contact time vs. flow in a basin.[140]

Method A: Generally, contact time between water and disinfectant in a reservoir will be longer at low flow rates and shorter at high flow rates. It is suggested that each water system run a tracer study with Cl^- or F^- ions for each reservoir for at least four different flow rates: lowest normal flow, average flow, above-average flow, and at least 91% of maximum flow. The results of these tracer studies are used to plot a curve for each reservoir (Figure 11.38) from which the contact time for any plant flow rate can be selected.

Method B: At least one tracer test must be conducted if a system has the ability to conduct four studies. The single test is conducted at a flow rate of at least 91% of the highest flow rate experienced in the reservoir. This gives a conservative estimate of the contact time. Subsequently, the T_{10} values for flow rates other than the tracer test are calculated from:

$$T_{10\,(\text{operational})} = \frac{Q\ (\text{tracer test})}{Q\ (\text{operational})} \times T_{10\,(\text{tracer test})} \qquad (77)$$

A simple example would be: given the T_{10} (tracer test) value of 4 minutes at a Q (tracer test) of 5.6 MGD, what is the T_{10} (operational) value at an operational flow rate of 1.5 MGD? A T_{10} operational value of 15 minutes can be obtained from Figure 11.38 or from:

$$T_{10}(1.5\text{ MGD}) = \frac{5.6\text{ MGD}}{1.5\text{ MGD}} \times 4 = 15\text{ min}$$

Method C: T_{10} values may be calculated by the theoretical method when there are extenuating circumstances for the PWS to conduct tracer tests. This method involves the use of a rule-of-thumb fraction of the value of T_{10} in relation to the theoretical time T of detention that is based on the design of the reservoir. There are several significant design characteristics that determine the ratio of T_{10} to T: length to width ratio, degree of baffling within the reservoir, and the effect of inlet baffling and outlet configuration. Almost all reservoirs have some areas where there is dead space (i.e., no flow). Also, there are some areas with flows close to plug flow and some areas of mixed flow. Here again, the reader is referred to References 140 and 141 for the engineering details for determination of T_{10} via the theoretical method.

Examples of CT Calculations

Two example calculations from Reference 140 shall suffice here to illustrate the CT concept.

Example 11.1: The System as a Single Section

For this example, a PWS (A) has a single point of disinfection whereupon the entire treatment train is considered to be a single section (Figure 11.39). A 3-log inactivation of *Giardia* cysts has been mandated. The detention time from the chlorine feed point to the first customer had been determined previously by a series of tracer studies that produced a curve similar to Figure 11.38.

Data

Metered peak hourly flow = 200 gpm
Water temperature = 15°C
Water pH = 7.5
Free Cl_2 residual at first house = 1.4 mg/L
T_{10} (detention time) = 80 min

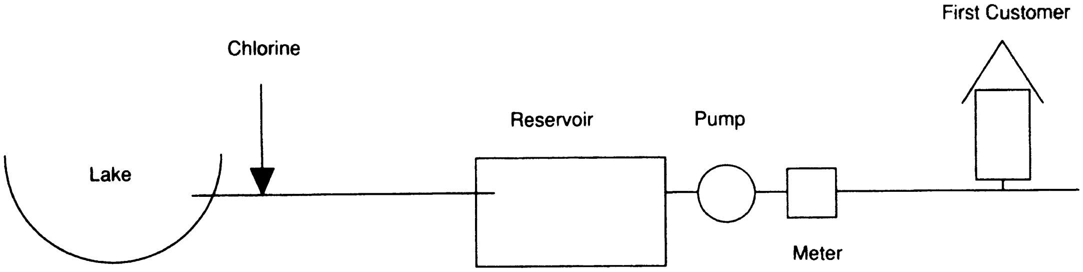

Figure 11.39. Flow diagram of system A.[140]

Calculation

For this hourly flow, the CT value is

$$C \times T = 1.4 \times 80 = 112$$

Using the appropriate CT table (see below) for the conditions cited above, the required minimum CT is 94. Consequently, this PWS meets the requirements for this day and this peak hourly flow. Since these CT values vary with flow, their calculation will be required frequently.

Example 11.2: A System with Multiple Points of Disinfection

Systems that add a disinfectant at more than one location must use a profiling method as follows:

1. Measure the disinfectant residual C at the end of each section of detention in the treatment process.
2. Use the detention time T for each section at the peak hourly flow for the day, as determined in previous tracer studies or calculations.
3. Calculate the CT_{calc} for each section.
4. Determine the CT value required for 3-log *Giardia* cyst inactivation $CT_{99.9}$ from the appropriate table.
5. Calculate the inactivation ratio for each section. This number is, in essence, the portion of the total treatment that is being accomplished in that section.

$$\text{inactivation ratio for the section} = CT = \frac{CT_{calc}}{CT_{99.9}} \tag{78}$$

6. The sum of the inactivation ratios for all sections determines the overall level of disinfection being provided.

Table 11.40 shows the relationship between inactivation ratio, log inactivation, and percent inactivation. For nonfiltering systems that are required to meet 3-log *Giardia* cyst inactivation by disinfection alone, the sum of the inactivation ratios must be equal to or greater than one. Filtering systems that are only required to attain a partial inactivation by disinfection need only meet the inactivation ratio specified by their states.

Table 11.40. Relationship Between Inactivation Ratio, Log Inactivation, and Percent Inactivation.[141]

Inactivation Ratio $CT_{calc}/CT_{99.9}$		Log Inactivation		Percent Inactivation
0.17	=	0.5 log	=	68.0
0.33	=	1.0 log	=	90.0
0.50	=	1.5 log	=	96.8
0.67	=	2.0 log	=	99.0
0.83	=	2.5 log	=	99.7
1.00	=	3.0 log	=	99.9
1.33	=	4.0 log	=	99.99

For this example, a PWS (B) serves a population of 6000 from a lake located 10 miles from the city. There are two 0.2 MG reservoirs located along the 12-in. transmission main from the lake to the distribution system (Figure 11.40). Table 11.41 summarizes the appropriate data needed to calculate the inactivation ratios.

Calculations

Section 1.

$$\begin{aligned} \text{pipe detention time} &= \frac{\text{internal volume}}{\text{flow rate}} \\ &= \frac{\pi \times r^2 \times \text{length}}{Q} \\ &= \frac{12{,}434\ \text{ft}^3}{139\ \text{ft}^3/\text{min}} = 89\ \text{min} \end{aligned} \tag{79}$$

Tank detention time, from tracer studies, is 116 min. Total detention time through section 1 is 89 + 116 = 205 min.

$$\begin{aligned} CT_{calc} &= \text{disinfectant residual C} \times \text{time T} \\ &= 0.1\ \text{mg/L} \times 205 = 20.5\ \text{mg/L-min} \end{aligned}$$

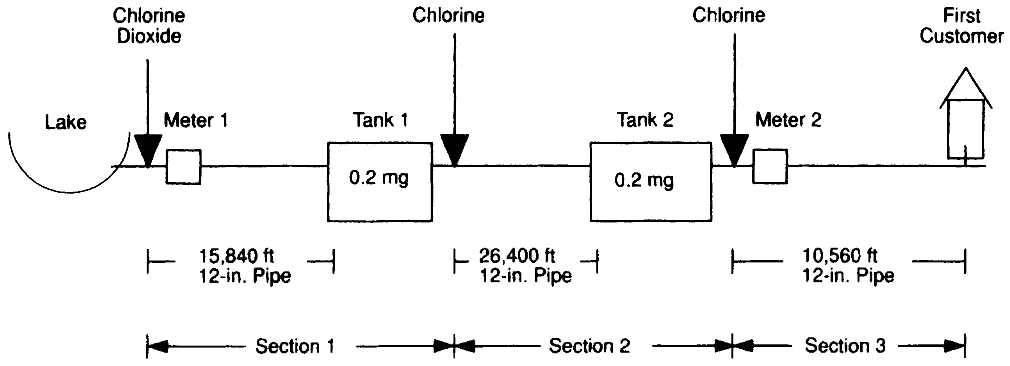

Figure 11.40. Flow diagram of system B.[140]

Table 11.41. System B: Data Collected for a Typical Day.[141]

	Section 1	Section 2	Section 3
Length of pipe (ft)	15,840	26,400	10,560
Flow (MGD)			
Pipe	1.5	2.0	2.0
Tank	2.0	2.0	
Contact time (min)			
Pipe	89	111	45
Tank	116	114	0
Total	205	225	45
Disinfectant	chlorine dioxide	chlorine	chlorine
Residual (mg/L)	0.1	0.2	0.4
Temperature (C)	5	5	5
pH	8	8	8

From the appropriate table for a 3-log inactivation of *Giardia* cysts, the required CT value is 26 mg/L-min. The inactivation ratio for section 1 is calculated from Equation 78 = 20.5/26 = 0.79.

Sections 2 and 3. The detention times for the pipelines and tank 2 are calculated in the same manner as above. The required $CT_{99.9}$ for chlorine inactivation of *Giardia* cysts at pH 8 and a temperature of 5°C is found in an appropriate table to be 198 mg/L-min.

Section 2 CT_{calc} = 0.2 mg/L × 225 min = 45 mg/L min

$$CT_{calc} / CT_{99.9} = \frac{45}{198} = 0.23$$

Section 3 CT_{calc} = 0.4 mg/L × 45 min = 18 mg/L-min

$$CT_{calc} / CT_{99.9} = \frac{18}{198} = 0.09$$

total inactivation ratio = the sum of the inactivation ratios for the three sections

$$0.79 + 0.23 + 0.09 = 1.11$$

Since the sum is greater than 1, the system meets the requirements of providing a 3-log inactivation of *Giardia* cysts.

The log inactivation that is actually being provided can be calculated as follows:

$$\begin{aligned} \text{log inactivation} &= 3 \times \text{sum of inactivation ratios} \\ &= 3 \times 1.11 \\ &= 3.33 \end{aligned}$$

The percent inactivation being provided can be calculated as follows:

$$\text{percent inactivation} = 100 - \frac{100}{100_{3.33}} =$$

$$100 - \frac{100}{2{,}138} = 100 - 0.05 = 99.95\%$$

Table 11.42. CT Values ($CT_{99.9}$) for 99.9% Inactivation of *Giardia* Cysts by Free Chlorine[a].[140,141] Water Temperature 15.0°C (59°F).

Free Residual (mg/L)	pH ≤6.0	≤6.5	≤7.0	≤7.5	≤8.0	≤8.5	≤9.0
0.4	49	59	70	83	99	118	140
0.6	50	60	72	86	102	122	146
0.8	52	61	73	88	105	126	151
1.0	53	63	75	90	108	130	156
1.2	54	64	76	92	111	134	160
1.4	55	65	78	94	114	137	165
1.6	58	66	79	96	116	141	169
1.8	57	68	81	98	119	144	173
2.0	58	69	83	100	122	147	177
2.2	59	70	85	102	124	150	181
2.4	60	72	86	105	127	153	184
2.6	61	73	88	107	129	156	188
2.8	62	74	89	109	132	159	191
3.0	63	76	91	111	134	162	195

[a] *Note:* These CT values achieve greater than a 99.99% inactivation of viruses. CT values between the indicated pH values may be determined by linear interpolation. CT values between the indicated temperatures of different tables may be determined by linear interpolation. If no interpolation is used, use the $CT_{99.9}$ value at the lower temperature and at the higher pH.

Profiling Inactivation With Multiple Disinfected Sources

Systems that combine individually disinfected surface sources at a single point or at different points before the water reaches the first customer have a more complex calculation in order to determine daily compliance with the CT requirements. Detailed examples of these situations are provided in Chapter 3 of Reference 141.

CT Tables

Inactivation of Giardia Cysts

CT values are given in Tables 11.42 to 11.49 for the inactivation of *Giardia* cysts and viruses by free chlorine, chloramine, chlorine dioxide, and ozone at various temperatures and pH values. These values emanate from the USEPA via References 140, 141, and 142. As such, these are the mandated CT values for 99.9% removal of *Giardia* cysts and 99.99% removal of viruses under the SWTR by chemical disinfection and filtration. CT values are not given for the removal of *Cryptosporidium* oocysts. Eventually, this will be addressed by the ESWTR.[143]

Table 11.42 shows the CT values for 99.9% inactivation of *Giardia* cysts by free chlorine at 15°C. These values are available also at other temperatures (0.5°, 5°, 10°, 20°, and 25°C).[140,141] The CT values for free chlorine are based on a statistical analysis.[141] of animal infectivity studies[80] and excystation studies.[144] These two studies were combined to form a best-fit model for predicting CT values at different levels of inactivation. First-order disinfection kinetics were utilized in this model, which incorporated safety factors. CT values for temperatures above 5°C were estimated by assuming a twofold decrease for every 10°C. CT values at 0.5°C were estimated by assuming a 1.5 times increase to CT values at 5°C.

Table 11.44 gives the CT values for several logs of inactivation of *Giardia* cysts by ClO_2 within the pH range of 6 to 9. These values are based on disinfection studies using *in vitro* excystation of *G. muris* CT_{99} values at pH 7 and at 1°, 5°, 15°, and 25°.[145,146] The average CT_{99} value at each temperature was extrapolated using first-order kinetics and multiplied by a safety factor of 1.5 to obtain the CT_{99} values. For example, the CT_{99} value at 1°C was $27.9 \times 1.5 = 42 \times 1.5 = 63$ for $CT_{99.9}$. Since most of the disinfection data was obtained for a pH 7.0, the same CT values were specified for all pH values in Table 11.44.

The CT values for chloramines in Table 11.46 are based on the disinfection and *in vitro* excystation of *Giardia muris*.[147] Here again, the highest CT_{99} values at 1°C (2500) and 5°C (1430) were each multiplied by 1.5 to estimate the $CT_{99.9}$ value. First-order kinetics of disinfection were assumed also (Equation 66). It should be noted that *Giardia muris* appears to be more resistant than *Giardia lamblia* to chloramines.[146]

The CT values for ozone in Table 11.48 are based on disinfection studies using *in vitro* excystation of *Giardia lamblia*.[106] CT_{99} values at 5°C and pH 7 ranged from 0.46 to 0.64 for disinfectant concentrations in the 0.11 to 0.48 mg/L range (Figures 11.35a and b). Since no CT values were available at other pH values, the highest CT_{99} value of 0.64

Table 11.43. CT Values for Inactivation of Viruses by Free Chlorine[a,b].[140,141]

Temperature	Log Inactivation					
	2.0-log		3.0-log		4.0-log	
°C	pH 6–9	pH 10	pH 6–9	pH 10	pH 6–9	pH 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

[a] *Note:* These CT values achieve greater than a 99.99% inactivation of viruses. CT values between the indicated pH values may be determined by linear interpolation. CT values between the indicated temperatures of different tables may be determined by linear interpolation. If no interpolation is used, use the $CT_{99.9}$ value at the lower temperature and at the higher pH.

[b] *Note:* CT values can be adjusted to other temperatures by doubling the CT for each 10°C drop in temperature.

Table 11.44. CT Values for Inactivation of *Giardia* Cysts by Chlorine Dioxide Within the pH Range 6 to 9[a].[140,141]

Inactivation	Temperature (°C)					
	≤1	5	10	15	20	25
0.5-log	10.0	4.3	4.0	3.2	2.5	2.0
1.0-log	21.0	8.7	7.7	6.3	5.0	3.7
1.5-log	32.0	13.0	12.0	10.0	7.5	5.5
2.0-log	42.0	17.0	15.0	13.0	10.0	7.3
2.5-log	52.0	22.0	19.0	16.0	13.0	9.0
3.0-log	63.0	26.0	23.0	19.0	15.0	11.0

[a] *Note:* These CT values achieve greater than a 99.99% inactivation of viruses. CT values between the indicated pH values may be determined by linear interpolation. CT values between the indicated temperatures of different tables may be determined by linear interpolation. If no interpolation is used, use the $CT_{99.9}$ value at the lower temperature and at the higher pH.

Table 11.45. CT Values for Inactivation of Viruses by Chlorine Dioxide Within the pH Range 6 to 9[a].[140,141]

Inactivation	Temperature (°C)					
	≤1	5	10	15	20	25
2.0-log	8.4	5.6	4.2	2.8	2.1	1.4
3.0-log	25.6	17.1	12.8	8.6	6.4	4.3
4.0-log	50.1	33.4	25.1	16.7	12.5	8.4

[a] *Note:* These CT values achieve greater than a 99.99% inactivation of viruses. CT values between the indicated pH values may be determined by linear interpolation. CT values between the indicated temperatures of different tables may be determined by linear interpolation. If no interpolation is used, use the $CT_{99.9}$ value at the lower temperature and at the higher pH.

was employed as a basis for extrapolation to obtain $CT_{99.9}$ values at 5°C by assuming first-order kinetics (Equation 68)[125] and a safety factor of 2; e.g., $0.64 \times 1.5 \times 2.0 = 1.9$. $CT_{99.9}$ values for temperatures above 5°C were estimated by assuming a twofold decrease for every 10°C. The 0.5°C $CT_{99.9}$ values were estimated by assuming a 1.5 times increase over the 5°C values.

The CT values given in Tables 11.42, 11.44, 11.46, and 11.48 should be viewed with caution. First, there is the extrapolation of data from 2 logs to 3 logs of disinfection that

Table 11.46. CT Values for Inactivation of *Giardia* Cysts by Chloramine Within the pH Range 6 to 9[a].[140,141]

	Temperature (°C)					
Inactivation	≤1	5	10	15	20	25
2.0-log	635	365	310	250	185	125
1.0-log	1270	735	615	500	370	250
1.5-log	1900	1100	930	750	550	375
2.0-log	2535	1470	1230	1000	735	500
2.5-log	3170	1830	1540	1250	915	625
3.0-log	3800	2200	1850	1500	1100	750

[a] *Note:* These CT values achieve greater than a 99.99% inactivation of viruses. CT values between the indicated pH values may be determined by linear interpolation. CT values between the indicated temperatures of different tables may be determined by linear interpolation. If no interpolation is used, use the $CT_{99.9}$ value at the lower temperature and at the higher pH.

Table 11.47. CT Values for Inactivation of Viruses by Chloramine[a,b].[140,141]

	Temperature (°C)					
Inactivation	≤1	5	10	15	20	25
2.0-log	1243	857	643	428	321	214
3.0-log	2063	1423	1067	712	534	356
4.0-log	2883	1988	1491	994	746	497

[a] *Note:* These CT values achieve greater than a 99.99% inactivation of viruses. CT values between the indicated pH values may be determined by linear interpolation. CT values between the indicated temperatures of different tables may be determined by linear interpolation. If no interpolation is used, use the $CT_{99.9}$ value at the lower temperature and at the higher pH.

[b] This table applies for systems using combined chlorine where chlorine is added prior to ammonia in the treatment sequence.

Table 11.48. CT Values for Inactivation of *Giardia* Cysts by Ozone Within the pH Range 6 to 9[a].[140,141]

	Temperature (°C)					
Inactivation	≤1	5	10	15	20	25
0.5-log	0.48	0.32	0.23	0.16	0.12	0.08
1.0-log	0.97	0.63	0.48	0.32	0.24	0.16
1.5-log	1.5	0.95	0.72	0.48	0.36	0.24
2.0-log	1.9	1.3	0.95	0.63	0.48	0.32
2.5-log	2.4	1.6	1.2	0.79	0.60	0.40
3.0-log	2.9	1.9	1.43	0.95	0.72	0.48

[a] *Note:* These CT values achieve greater than a 99.99% inactivation of viruses. CT values between the indicated pH values may be determined by linear interpolation. CT values between the indicated temperatures of different tables may be determined by linear interpolation. If no interpolation is used, use the $CT_{99.9}$ value at the lower temperature and at the higher pH.

assumed first-order kinetics from either the Chick model (Equation 66) or the Chick-Watson model (Equation 68). There is considerable evidence from other ozonation studies of *Giardia* cysts that the Chick-Watson-Hom model (Equation 72) is a more appropriate description of the disinfection process.[148] For example, the published value for 3 logs of inactivation was 0.52 mg/L-min at 22°C, which included a safety factor of 2.[141] The above-cited study yielded a CT value about 2.4 times greater. The higher O_3 requirements from this study for 3 logs of disinfection may have

Table 11.49. CT Values for Inactivation of Viruses by Ozone[a].[140,141]

	Temperature (°C)					
Inactivation	**≤1**	**5**	**10**	**15**	**20**	**25**
2.0-log	0.9	0.6	0.5	0.3	0.25	0.15
3.0-log	1.4	0.9	0.8	0.5	0.4	0.25
4.0-log	1.8	1.2	1.0	0.6	0.5	0.3

[a] *Note:* These CT values achieve greater than a 99.99% inactivation of viruses. CT values between the indicated pH values may be determined by linear interpolation. CT values between the indicated temperatures of different tables may be determined by linear interpolation. If no interpolation is used, use the $CT_{99.9}$ value at the lower temperature and at the higher pH.

been caused from a different ozonation protocol, a different viability assay procedure, and differences in the experimental strains of *G. lamblia.*[148] These results also suggest that the human-derived strain of *G. lamblia* used in this study is more resistant to ozone than is *G. muris*, the commonly used surrogate for *G. lamblia* in mice. These points are discussed below also (Table 11.52).

Inactivation of Viruses

The CT values for inactivation of viruses by free chlorine in Table 11.43 are based on data from hepatitis A virus (HAV) strain HM175 at pH values 6 to 10, $[Cl_2]$ of 0.2 to 0.5 mg/L, and a temperature of 5°C.[149] The highest CT values for these conditions that achieved 2, 3, and 4 logs of inactivation of HAV were multiplied by a safety factor of 3 to obtain the values in Table 11.43. For example, the CT value for achieving 4 logs of inactivation at pH values 6–9 was determined by: $2.55 \times 3 = 7.6 = 8$. The CT values at pH 10 (an unlikely value for disinfection) were significantly higher than the others and were calculated using a safety factor of 3. CT values at temperatures other than 5°C were calculated assuming a twofold decrease for every 10°C increase.

The CT values in Table 11.45 for inactivation of viruses are based on the data from HAV disinfection by a $[ClO_2]$ of 0.5 mg/L at pH 6 and 5°C.[149] A safety factor of 2 was applied to the CT values for pH values 6–9 and 5°C.

Since ClO_2 is apparently more effective than Cl_2 at the higher pH values, the safety factor was lowered from 3 to 2. ClO_2 is more effective for inactivating rotavirus and poliovirus than for the inactivation of HAV.[150] This was observed also for Cl_2.

Table 11.47 shows the CT values that are based on data from the inactivation of HAV with preformed chloramines at a pH value of 8.0.[149] No safety factor was applied to the laboratory data since chloramination in the field "is assumed more effective than preformed chloramines"[141] because there may be some transient presence of free chlorine. Also, HAV is less resistant to preformed chloramines than are other viruses. For example, CT values of 3800 to 6500 were needed for 2-log inactivation of simian rotavirus at pH 8.0 and 5°C.[151] The CT values in Table 11.47 are applicable to PWSs that add Cl_2 prior to NH_3 in the treatment sequence. This provides sufficient contact time with free Cl_2 to assure inactivation of rotavirus.[141] Preformed chloramines may not be adequate for disinfection of rotaviruses.

At the time of publication of the Guidance Manual in 1989,[141] no CT data were available on the inactivation of HAV with O_3. The CT values in Table 11.49 are based on the inactivation of poliovirus 1 at 5°C and a pH value of 7.2.[152] In this study, a mean CT value of 0.2 achieved a 2-log inactivation of the poliovirus. The 2-log CT values in Table 11.49 at 5°C were calculated using a safety factor of 3. CT values for the 3- and 4-logs of inactivation were determined by assuming first-order kinetics and a safety factor of 3. The usual twofold decrease of CT values for every 10°C increase was applied to temperatures other than 5°C.

Miscellaneous CT Values

There are several significant CT values for PWSs that have not been cited above where the efficacy of disinfection was not discussed. These values are important for such waterborne diseases as the *Hepatitis A* virus and the oocysts of *Cryptosporidium.* At this writing, CT data were rather sparse for these organisms. Table 11.50 gives a few CT numbers for the HOCl and OCl^- disinfection of *Hepatitis A* at 99% inactivation. Lines 2 and 3 of Table 11.50 indicate a much greater sensitivity of this virus to free chlorine disinfection than the CT of 60 in line 1.

Table 11.51 is a summary of ozonation requirements for the 99% inactivation of *Cryptosporidium* oocysts and their CT values. Conventional CT values of about 3.5 and 7 mg/L-min were required for 99% inactivation at 22° and 7°C, respectively.[126] For 99.9% inactivation, conventional CT values of about 5 and 10 mg/L-min were needed at 22° and 7°C, respectively.[126] Similar results were obtained by Peeters et al.[155] using room temperature in their experimental protocol, which was close to that of Finch et al.[126] A constant O_3 residual of 1.0 mg/L was reported to effect a 99% inactivation after 5 min of contact for a conventional CT of 5.[81] A

Table 11.50. The Inactivation of Hepatitis A With Chlorine Disinfectants.

Test Microorganism	Disinfectant	pH	Temperature (°C)	CT	Reference
Hepatitis A	HOCl	7.0	5	60.0[b]	153
	HOCl	6.0	[a]	<0.32[c]	154
	OCl^-	10.0	[a]	<1.04[c]	154
	NH_2Cl			[a]	

[a] Not reported.

[b] CT estimated from animal infectivity data.

[c] CT estimated from disinfection curves. Chlorine residual data suggested that the test mixtures contained significant demand. Concentration used for calculation was the dose reported.

CT value of 2.6 mg/L-min was reported for a constant O_3 residual of 0.44 mg/L for 6 min.[156] It should be noted that a continuous stream of O_3 to maintain the residual underestimates the actual O_3 dosage in these disinfection studies.[126] The *C. baileyi* oocyst required a conventional CT value of 3.2 mg/L-min for an inactivation between 99.9 and 99.99%, respectively.[157] This CT value was increased to 4.4 mg/L-min for an inactivation between 4 and 5 log units of oocysts (99.99 and 99.999%, respectively).

Table 11.52 shows a comparison of experimental CT values for the inactivation of *G. muris* cysts by O_3[158] and regulatory CT values for *G. lamblia* cysts also inactivated by O_3.[141] These comparisons were generated over the issue of disinfection kinetics. The experimental inactivation of *G. muris* is not pseudo first-order, and does not follow Chick-Watson kinetics.[158] However, the authors of this study assumed that this model was adequate. Consequently, kinetic data were selected from laboratory water and natural water observations to obtain 99.9 and 99.99% Watson plots (not shown here). The b values (Equation 72) were less than one, suggesting that contact time was more important than concentration. The Guidance Manual values were not adjusted for Watson kinetics and assumed pseudo first-order kinetics.[141] The CT values in Table 11.52[158] are given, as well as the recommended CT values for 3 and 4 logs of inactivation at 5° and 22°C with the safety factor of 2 removed. There is some agreement for the CT required for 99.9% inactivation in laboratory water—0.3 at 22°C. However, the recommended CT value of 0.95 at 5°C is approximately three times greater than the Watson-derived value.[158] Under natural water conditions, there are wide discrepancies in CT values 1.9/0.95 at 5°C and 1.9/0.31 at 22°C. The latter value (1.9) was explained by dissipation of O_3 at the higher temperatures. Even greater differences in CT values were observed between the laboratory and the extrapolated Guidance Manual numbers for 99.99% inactivation. Also, natural waters will vary greatly in their organic matter content, which in turn affects the O_3 demand.

An interesting treatment concept was developed from the O_3 inactivation of *Giardia muris* in Reference 158. A design envelope was constructed within which assurance can be achieved for the inactivation required by the SWTR.[158] Such an envelope is seen in Figure 11.41 that uses O_3 residual, O_3 dose to DOC ratio, and a minimum contact time of 5 minutes as the design criteria. Also, this envelope was constructed around the worst-case limits for 99.9% inactivation of *Giardia muris*. It appears that the SWTR requirement for *Giardia* removal by O_3 alone would be met. However, the 4 log inactivation requirement for the MS2 coliphage virus would not be met in this system.

The authors of the above study[158] apparently had some reservations about their experimental results and recommendation therefrom. In a subsequent publication,[148] the authors state: "It is evident that although *Giardia* species have been studied extensively, much remains uncertain regarding their inactivation by chemical disinfectants. Therefore, the use of a chemical disinfectant as the only barrier to the transmission of *Giardia* cysts in potable water supplies cannot be recommended." Essentially, the authors feel that *G. muris* is a reasonable surrogate for *G. lamblia*, but more data are needed on the inactivation of the latter at different water temperatures, in waters of different qualities, and with different strains. All of this is needed to make an adequate judgment on the reliability of chemical oxidation alone as a barrier to the transmission of giardiasis via water.

REMOVAL BY CHEMICAL COAGULATION

Bacteria and Viruses

Since the SWTR and the ESWTR include filtration as part of the disinfection protocol, it is imperative to examine the efficacy of chemical coagulation for the removal of bacteria and viruses. Several studies have reported coagulation and subsequent removal of bacteria and viruses by polyelectrolytes, alum, etc. It is questionable whether or not a coagulation process alone would be effective enough for the required 100% removal of bacteria and viruses. On the other hand, these studies provide an insight into their incidental removal by coagulation as a pretreatment for filtration.

Table 11.51. Summary of Reported Ozonation Requirements for Inactivation of *Cryptosporidium* spp. Oocysts by Using Conventional Linear CT Products.

Species	Ozone Protocol	Water Type	Ozone Residual (mg/L)	Contact Time (min)	Temp (°C)	Conventional Linear CT for 99% Inactivation (mg • min/L)[a]	Reference
C. parvum	Batch liquid, batch ozone	0.05 *M* Phosphate buffer	0.16–1.3	5, 10, 15	7	7.0	126
	Batch liquid, batch ozone	0.05 *M* Phosphate buffer	0.17–1.9	5, 10, 15	22	3.5	126
	Batch liquid, batch ozone	Deionized water	0.77	6	Room	4.6	155
	Batch liquid, batch ozone	Deionized water	0.51	8	Room	4.0	155
	Batch liquid, continuous gas	0.01 *M* Phosphate buffer	1.0	5, 10	25	5.0–10.0	81
	Batch liquid, continuous gas	Distilled water	0.44	6	20	2.6	156
C. baileyi	Batch liquid, modified batch gas	Distilled water	0.6, 0.8	4	25	2.4–3.2	157

[a] Interpretation depends on protocol and method for reduction of ozone data used by authors.

Table 11.52. Experimental CT Values for Inactivation of *Giardia muris* Cysts by Ozone (pH 5.7 to 8.3) and Regulatory CT Values for *Giardia lamblia* Cyst Inactivation by Ozone (pH 6.0 to 9.0).[158]

		Estimated CT Values			
Water Type	***G. muris* Inactivation (log N/N_0)**	**This Study**	**USEPA[a] 5°C**	**This Study**	**USEPA[a] 22°C**
Laboratory	3	0.30	0.95	0.30	0.31
	4	3.1	1.3[b]	3.1	0.61[b]
Natural	3	1.9	0.95	1.9	0.31
	4	3.4	1.3[b]	3.4	0.61[b]

Note: This study has pooled all temperature data into the CT values.

[a] EPA Guidance Manual values divided by 2.[141]

[b] Extrapolated from EPA Guidance Manual.[141]

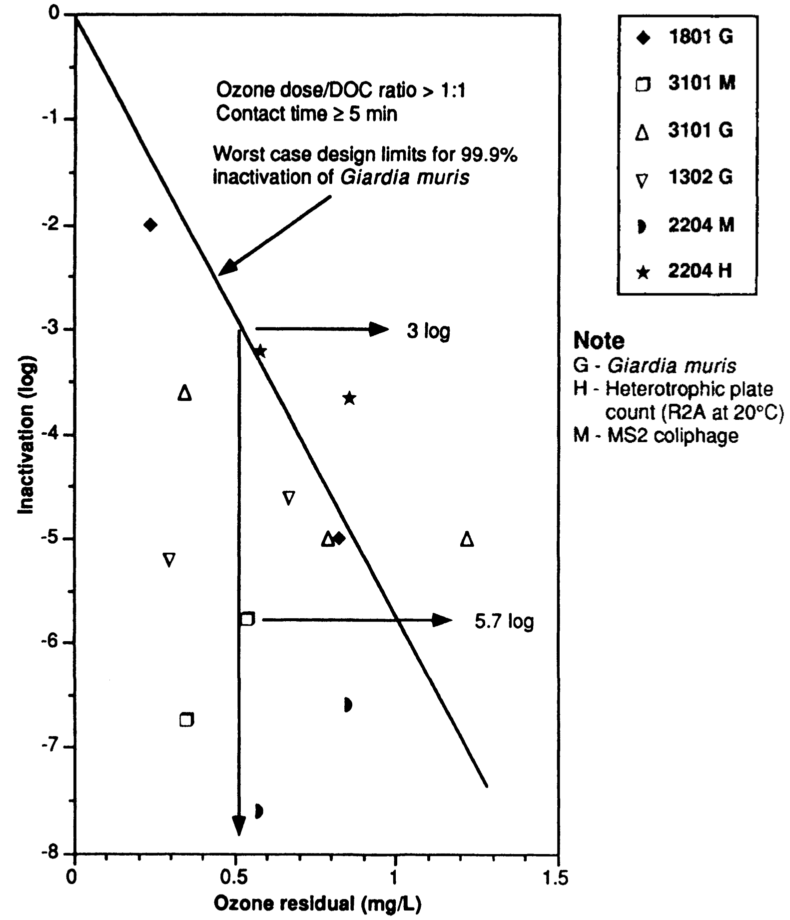

Figure 11.41. Summary of *Giardia* inactivations for conditions that meet the design protocol.[158]

A cationic polyelectrolyte was utilized as a primary coagulant and as a coagulant aid in the removal of a bacterial (bacteriophage T2 of *E. coli*) and an animal (Type 1 poliovirus) virus from artificially seeded water.[159] A summary of this laboratory study appears in Table 11.53, where the polyelectrolyte alone was extremely ineffective for virus reduction. The clay mineral, montmorillonite, was added to simulate the effect of turbidity. It is significant to note that up to 82% virus removal was effected by the clay itself. When either alum or ferric sulfate was utilized as the primary coagulant, the virus removals were poor. However, when the clay was present and coagulated, virus removal as high as

Table 11.53. Removal of Poliovirus and Turbidity by Unaided Coagulation, and Cationic Polyelectrolyte–Aided Coagulation With Aluminum and Ferric Sulfates in Water with Varying Ionic Concentrations.[a]

	CaCl$_2$ Concentration (*M*)									
	0.1		0.01		0.001		0.0001		0	
Substance	Virus Removal (%)	Turbidity Removal (%)	Virus Removal (%)	Turbidity Removal (%)	Virus Removal (%)	Turbidity Removal (%)	Virus Removal (%)	Turbidity Removal (%)	Virus Removal (%)	Turbidity Removal (%)
Aluminum Sulfate										
Polyelectrolyte only	6		36		25		10		0	
Clay only	79	91	82	91	13	26	0	2	0	0
$Al_2(SO_4)_3$ only	12		9		27		33		36	
$Al_2(SO_4)_3$ + clay	79	94	86	96	83	93	26	18	11	0
$Al_2(SO_4)_3$ + clay + + polyelectrolyte[b]	69	95	81	95	75	94	19	93	24	92
Ferric Sulfate										
Polyelectrolyte only	6		36		25		10		0	
Clay only	79	91	82	94	13	26	0	2	0	0
$Fe_2(SO_4)_3$ only	20		20		20		0		0	
$Fe_2(SO_4)_3$ + clay	85	93	83	93	4	0	0	0	0	0
$Fe_2(SO_4)_3$ + clay + polyectrolyte	76	95	75	93	60	83	62	0	35	0

[a] Reproduced from Thorup et al.,[159] courtesy of the American Water Works Association.

[b] pH—6.8, adjusted with 1.25–4.0 mL of 0.1 *N* NaOH. Dosages: polyelectrolyte (Purifloc C32) 1 mg/L; clay 50 mg/L; $Al_2(SO_4)_3$ 10 mg/L (0.29 m*M*); $Fe_2(SO_4)_3$ 11.6 mg/L (0.29 m*M*).

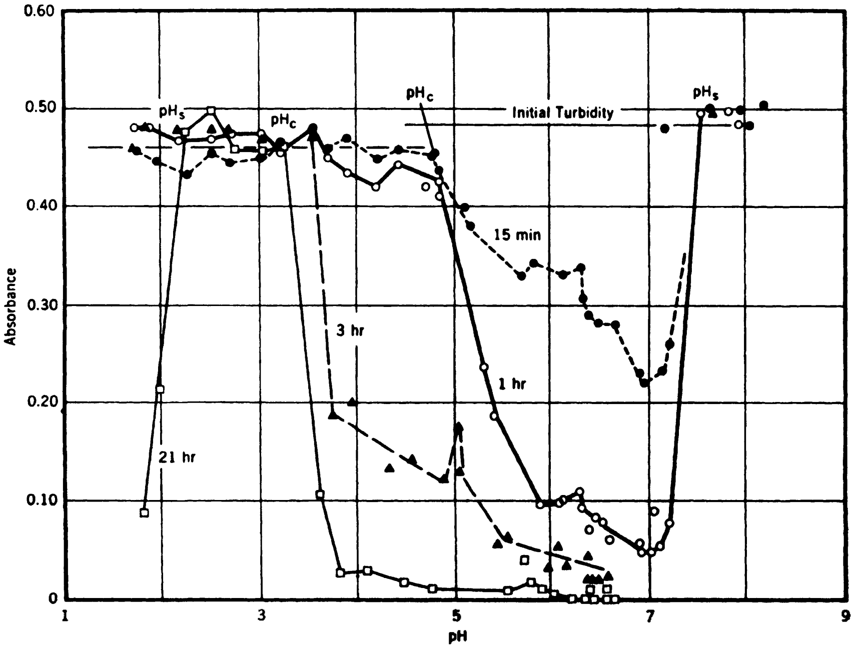

Figure 11.42. Coagulation with 4.5 × 10^{-5} *M* $Al_2(SO_4)_3$. Clarification of *E. coli* suspensions at different times as a function of pH. Reproduced from Hanna and Rubin,[160] courtesy of the American Water Works Association.

86% was recorded. Presence of the polyelectrolyte did not improve this form of virus disinfection.

The alum coagulation of suspensions of *E. coli* was approached in a manner similar to removal of abiotic turbidity from water.[160] In this case, bacterial removal was measured by turbidity reduction. A typical result is seen in Figure 11.42. The initial turbidity represented by the 0.5 absorbance apparently is the initial concentration of *E. coli* (2.5 × 10^8 cells/mL).

In Figure 11.42, two distinct pH ranges of aggregation and settling are observed. Very slow coagulation—essentially complete within 21 hr—occurred in the lower pH range (<3.3). In the higher pH range (>4.75), clarification was essentially complete within 1 hr (sweep zone), and apparently was due to flocculation by hydrolyzed aluminum oxides. This "slow" and "rapid" coagulation was distinguished by the sedimentation data at 1 and 21 hr. The "critical" pH values, pH_c and pH_s, were obtained by extrapolating the steep portions of the sedimentation curves back to the turbidity of the control. Thus, pH_c is that pH value above which coagulation occurs, and pH_s is that pH value above which stabilization (no coagulation or restabilization due to charge reversal) is complete. These critical values at a given $[Al]_t$ are boundary points defining regions within the alum-pH stability domain (Figure 11.43). The authors did not indicate the bacterial contents represented by turbidities by less than 0.1 absorbance. It is nonetheless apparent that signifi-

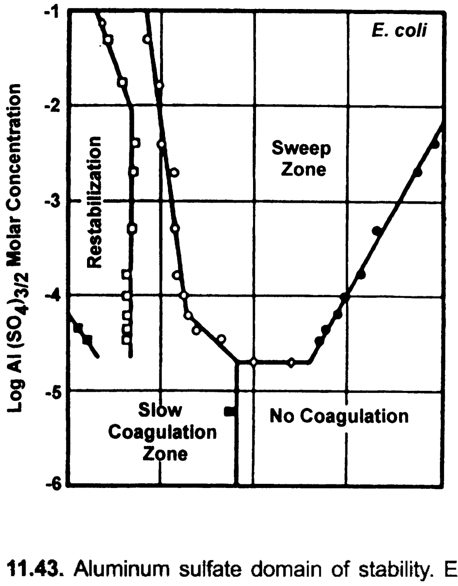

Figure 11.43. Aluminum sulfate domain of stability. Effect of any dose of alum on the stability and coagulation of *E. coli* at any pH. Circles (1 hr) and squares (21 hr) for turbidity-pH settling data, and diamonds (12 hr) for turbidity-concentration data; open symbols are coagulation values and solid symbols are stabilization values. Reproduced from Hanna and Rubin,[160] courtesy of the American Water Works Association.

cant reductions of *E. coli* are accomplished in the coagulation process.

In another study, Manwaring et al.[161] employed ferric chloride for coagulating the bacterial virus, bacteriophage MS2 (against *E. coli*). Figure 11.44 shows the virus and clay turbidity removals at pH values ranging from 5.0 to 8.0, and coagulant contents up to 100 mg/L. Based on these removals, the optimum ferric chloride dosage was 50–60 mg/L with the optimum virus and turbidity removals occurring at a pH value of 5.0. Using an average input of 3.9×10^5 PFU/mL in each experimental system, the highest virus removal was 99.5%. These results with ferric chloride are as effective as with alum (Figure 11.45).[162]

A rather comprehensive study of virus removal from spiked raw surface water and wastewater was published by Shelton and Drewry,[163] who utilized alum, ferric chloride, ferric sulfate, cationic, anionic and nonionic polyelectrolytes, and sodium aluminate ($Na_2OAl_2O_3$). The experimental virus was the bacteriophage f2 (host-specific to *E. coli*). Table 11.54 shows the effectiveness of the various coagulants and combinations thereof on removal of this virus from raw surface water (Little Tennessee River, Tennessee). It appears that greater than 99% removals were obtained in all systems with alum, considered to be the most effective coagulant by the authors. This consideration included turbidity and COD removals as well as the virus. A similar study for removal of the same virus as above[163] from Fort Loudoun Lake, Knoxville, Tennessee water was reported for the same coagulants listed in Table 11.54.[164] Alum and ferric chloride achieved >99% virus removal, and the turbidity was reduced by 90%.

That the removal of the bacterial virus (MS2 against *E. coli*) from distilled, deionized water by a laboratory bench-scale diatomaceous earth filter is feasible was demonstrated by Anurhor and Engelbrecht.[165] Filtration was aided through the addition of a cationic polyelectrolyte, Puriflor C-31, to the diatomaceous earth. The essential results are seen in Figure 11.46 at three concentrations of the polyelectrolyte where breakthrough curves describe the virus removal. Here C_e represents the virus content in the filtrate and C_i is the initial content (1.4×10^8 PFU/mL). It is interesting to note from Figure 11.46 that 0.5 and 2.0 mg/L of the polyelectrolyte caused rapid breakthrough of the virus, whereas there was "significant removal of the virus with 0.25 mg/L of the polyelectrolyte." The higher quantities of the Purifloc C-31 apparently completely coated the virus particles, thereby preventing their removal.

There was successful removal of a virus (bacteriophage MS2 for *E. coli*) from tap water and simulated surface water (by addition of topsoil to tap water) by alum and four cationic polyelectrolytes.[166] Table 11.55 shows the results of this study. Alum was not effective in removing the bacteriophage MS2 within the range of 5–10 mg/L. A removal of 99.7% was achieved with 50 mg/L alum when 14 ntu of turbidity were present. Nalco 8101 was able to reduce the virus content (initially 5.4×10^3 PFU/mL) by 96% at a dosage of 2 mg/L. Better removals of the virus were recorded when turbidity was present in the water.

Sproul[167] has critically reviewed the literature of virus removal by coagulation processes. Enteric virus removal should be in the 90 to 99.999% range by coagulation of water and wastewater containing poliovirus and coxsackievirus A2.

In a study of synthetic polymers for flocculation of *E. coli* in water, filtration rates, electrophoretic mobility, and light transmission were measured to evaluate the effectiveness of removal.[168] *E. coli* concentrations of 50–2700 mg/L and pH values of 4–9 were flocculated with nonionic, anionic and cationic polymers. Molecular weights from 7000 to 3,000,000 for the nonionic and anionic polyacrylamides were not effective flocculants at concentrations of 0.1 to 50 mg/L. On the other hand, cationic polyethyleneimines with molecular weights from 300 to 112,000 were effective at contents of 0.1 to 80 mg/L. These molecular weights, per se, were not factors in the process. Redispersal of the bacteria was experienced with 10 mg/L of the higher-molecular-weight polymers.

The removal of hepatitis A virus (HAV) and rotavirus (RV) from source water was explained by laboratory- and pilot-scale treatment, which included coagulation, filtration, and softening.[169] Poliovirus (PV) was included as a frame of reference, because considerable data are available on its removal during treatment (see above). Typical removals of the viruses are seen in Table 11.56, where the major variable was the initial turbidity concentration. These data indicate an efficient virus removal in all coagulation systems, except perhaps the $FeCl_3$ turbidities (4 to 8.6). Several significant conclusions were drawn from the coagulation portion of this study: (a) alum and iron were as efficient in the removal of HAV and RV as they were in removing PV, (b) turbidity and alkalinity concentration did not influence virus removal, (c) the addition of a nonionic coagulant and aid did not improve the coagulation process, which, in turn, did not significantly enhance virus removal, and (d) coagulation, settling, and filtration in a pilot plant lowered the density of all three viruses by 98.4 to 99.7%. This last conclusion has profound implications in meeting the disinfection requirements for viruses in the SWTR.

Coagulation, sedimentation, and filtration are significant factors in the removal of bacteria and viruses from raw water supplies. As such, most of their disinfection is accomplished prior to the addition of a chemical disinfectant. This should be a consideration in the CT calculation, as it may result in a lower value. The role of pretreatment for chemical disinfection should be examined very carefully in each treatment system with respect to its physical disinfection capabilities.

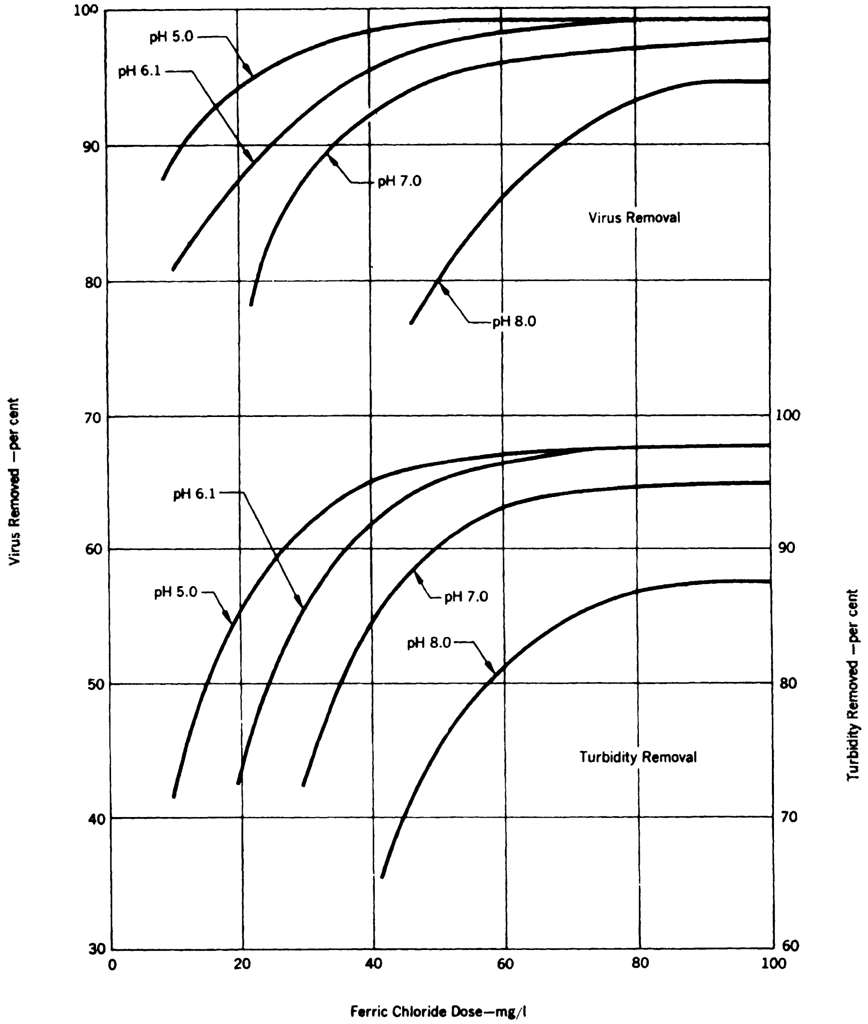

Figure 11.44. Removal of bacteriophage MS2 and clay turbidity by coagulation and flocculation. Average input virus concentration = 3.9 × 10^5 mL. Reproduced from Manwaring et al.,[161] courtesy of the American Water Works Association.

CASE STUDIES

Operational Issues

As cited above, the modern practice of chemical disinfection began with chlorination of waters from the Boonton Reservoir of the Jersey City Water Works in 1908.[1] During these 90 years of disinfection of public and other water supplies, several operational issues have arisen. Also, this span of disinfection practice could be divided into pre- and post-TTHM years. Certainly, the concern over eliminating or minimizing TTHMs in distribution systems has had a profound influence on disinfection practices. Here is a short list of operational issues (not in any order of priority):

a. efficacy of the disinfectant toward various pathogens and indicator organisms
b. chlorine versus chloramine treatment
c. optimization of chloramine treatment
d. minimization of TTHMs
e. regrowth in the distribution system; i.e., repeat samples for compliance
f. maintenance of a disinfectant residual throughout the distribution system
g. conversion from one disinfectant to another; e.g., from chlorine to chloramines

Case studies are cited below that attempt to address these issues.

Regrowth

The relationship between chlorine residual and the bacteriological quality in the distribution system was reported

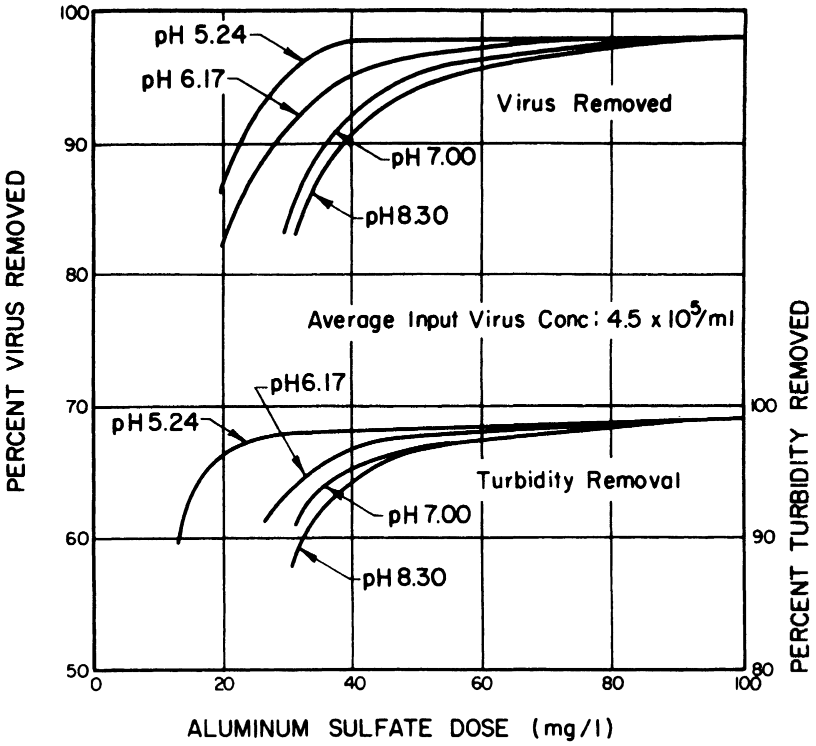

Figure 11.45. Removal of bacteriophage T_4 and clay turbidity by coagulation and flocculation. Reproduced from Chaudhui and Engelbrecht,[162] courtesy of the American Water Works Association.

by Buelow and Walton.[170] Their study attempted to address two issues:

1. How much and what kind of chlorine residual should be carried throughout the distribution system?
2. Where and how many samples should be collected to maintain adequate surveillance to protect consumers?

The authors obtained their data from the Cincinnati Water Works and the National Community Water Supply Survey (CWSS) (969 water supply systems) conducted in 1969 by the Bureau of Water Hygiene, U.S. Public Health Service (PHS).[171] The first issue was discussed by a consideration of the number of "repeat samples." At that time, the PHS standard required that daily samples be taken from the same location and be examined until two successive samples are free from coliform bacteria whenever a sample exceeds 4/100 mL. Table 11.57 shows the number of repeat samples for the Cincinnati Water Works during 1966 and 1967 when combined chlorination was practiced, and during 1969–1970 when free chlorination was practiced. It appears, according to the authors, that free residual chlorine maintained in the distribution system has accomplished its purpose of providing control of local contamination. From the CWSS, it was observed that in chlorinated water supplies, a chlorine residual must be maintained throughout the distribution system in order to have the confidence that disinfection has been accomplished. Figure 11.47 is an example of the data to support this observation. It is interesting to note the percentage of unchlorinated drinking waters that existed in 1969.

Concern for the control of regrowth in distribution systems continues in the 1990s. The Greater Vancouver (B.C.) Water District compared chlorine and chloramines as secondary disinfectants and their effects on bacterial regrowth in a distribution system supplied with disinfected, unfiltered surface water.[172] A section of the distribution system was divided into three areas: control (no disinfectant), free chlorine only, and chloramine only. Water samples were analyzed for Cl_2 residual, coliform bacteria, heterotrophic plant count (HPC) bacteria, and turbidity. Although chlorine and chloramines were both effective in reducing bacterial growth in the distribution system, chloraminated water had a lower HPC, less taste and odor, fewer positive coliforms, and a more stable residual. All of this is summarized in Table 11.58.

Table 11.54. Comparison of the Effectiveness of the Coagulants on Raw Surface Water.[a]

Coagulant and Coagulant Aids	Coagulant Concentration (mg/L)	Maximum Virus Removal (%)	pH[b]	Coagulant Concentration (mg/L)	Maximum Turbidity Removal (%)	Coagulant Concentration (mg/L)	Maximum COD Removal (%)	Optimum Dosage[c]	
								A	B
$Al_2(SO_4)_3$	15.0	99.45	6.8	15.0	96.50	20.0	43.0	12.0	14.0
$FeCl_3$	40.0	99.10	6.8	34.0	94.80	48.0	73.0	37.0	32.0
$Fe_2(SO_4)_3 \cdot nH_2O$	63.0	99.91	7.2	35.0	90.50	38.0	88.50	65.0	42.0
Cationic Flocculant	2.2	92.10	7.5	0.56	46.0	0.51	26.0	[d]	1.5
$Al_2(SO_4)_3$ +	8.0+			8.0+		8.0+		9.2	7.2
Cationic Flocculant	0.25	99.75	6.8	0.25	97.4	2.25	49.5	0.25	0.25
$Al_2(SO_4)_3$ +	10.0+			10.0+		10.0+		9.0	9.0
Nonionic Aid 1	0.25	99.50	6.8	0.25	97.4	0.5	59.3	0.4	0.16
$Al_2(SO_4)_3$ +	10.0			10.0+		10.0+		8.2	[e]
Anionic Aid 1	0.40	99.50	6.7	0.2	99.65	0.4	97.5	0.4	[e]
$Al_2(SO_4)_3$ +	9.1			9.0+		10.0+		7.1	[e]
Anionic Aid 2	0.2	99.93	6.8	0.2	98.6	0.2	79.5	0.2	[e]
$Al_2(SO_4)_3$ +	10.0+			10.0+		7.0+		6.4	5.4
Nonionic Aid 2	0.4	98.60	6.8	0.2	97.20	0.4	85.00	0.4	0.4
$Al_2(SO_4)_3$ +	10.0+			10.0+		10.0+		10.0	[e]
$Na_2OAl_2O_3$	3.0	99.89	6.9	12.0	98.70	9.0	86.00	9.0	[e]

[a] Reproduced from Shelton and Drewry,[163] courtesy of the American Water Works Association.

[b] pH of supernatant immediately after sedimentation.

[c] Isoelectric point as indicated by (A) zeta potential; (B) colloidal titration.

[d] Isoelectric point was not reached with test dosage.

[e] More than one isoelectric point was indicated.

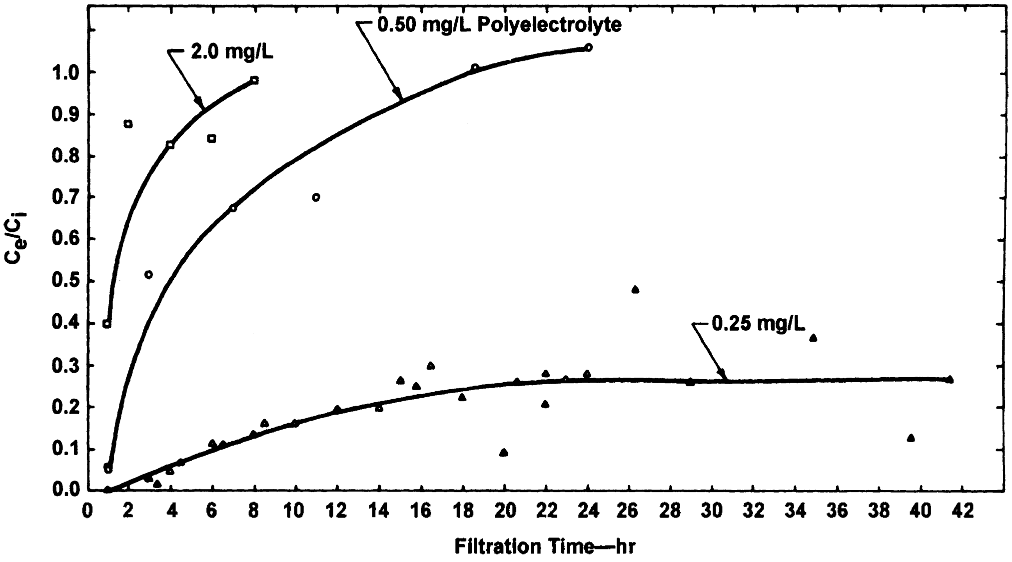

Figure 11.46. Removal of bacteriophage MS2 by uncoated diatomaceous earth with various levels of polyelectrolyte added to the suspending medium. pH 6.0, average virus input concentration = 1.40 x 10^8 PFU/mL; flow rate = 1 gpm/ft^2. Reproduced from Anurhor and Engelbrecht,[165] courtesy of the American Water Works Association.

Minimization of TTHMs

Concern about the appearance of TTHMs in distribution systems appeared in the 1970s (see Chapter 2). Various disinfection strategies were considered to prevent their formation. Alternative disinfectants to chlorine were considered. Alternative points of chlorine addition within the treatment plant were considered. This strategy required the removal of TTHM precursors before the addition of Cl_2. Considerable treatment plant practice has been obtained in the 20 or more years in implementing these strategies. Much of the experience and information is found in George et al.[173] where 20 case studies are presented. A summary of these case studies is presented here, with the participants listed in Table 11.59.

Chloramination is the first TTHM control strategy presented here. For the six utilities that participated in this case study survey, this disinfection practice resulted from a conversion to chloramines from free chlorine. Mean values of finished water quality parameters before and after conversion to chloramines are presented in Table 11.60. Perusal of these data suggests that there is effective disinfection of the total coliforms and HPC and reduction of the TTHMs. Operational details of these six PWSs are found in George et al.,[173] where advantages and disadvantages of chloramination are discussed.

Chlorine dioxide is the second TTHM control strategy presented here. In four of the five PWSs that were surveyed and reported in George et al.,[173] ClO_2 was added as a pretreatment replacement for chlorine. Posttreatment disinfection with chlorine continued in these four plants. Only the Kentucky River Station employed ClO_2 as its primary disinfectant. Satisfactory coliform and HPC counts were achieved starting in December, 1983. Table 11.61 gives the appropriate water quality parameters before and after conversion to ClO_2. Effective reduction of the TTHMs is evident. Advantages and disadvantages of ClO_2 utilization are discussed by George et al.[173] After a few years of experience with ClO_2, its use was limited only to those quarters of the year with the highest THMP. This became necessary due to operational problems, consumer complaints of tastes and odors, and an increase in background, noncoliform bacterial counts from filter effluents after ClO_2 usage was reduced. All of this led to the decision to change from ClO_2 to postchloramination (Kirmeyer et al.[174]). The conversion to chloramines occurred in December, 1988 after a year of reconstruction and an intensive public education program. Bacteriological quality was excellent in the distribution system, with the TCC averaging 0.01, 0.005, and 0.001 cfu/100 mL for 1989, 1990, and 1991, respectively. Average HPCs were less than 10 cfu/mL in this time frame. Customer reception to chloramine treatment was excellent. Many persons reported an improved taste, and none of the taste and odor problems associated with ClO_2 was experienced.

Ozone is the third strategy presented here for control of TTHMs. The three PWSs cited in Table 11.62 employed O_3 as a pretreatment for taste and odor control, oxidation of NOM, etc.[173] Data are rather sparse on the effectiveness of O_3 for reduction of TTHMs (Belle Glade), and in one case (monroe) the TTHMs were higher with the O_3 on than off. This may have been due to an outlier value of 325 mg/L

Table 11.55. Bacteriophage MS2 Removal from Water by Various Coagulants Without Sedimentation.[a]

		MS2 Removal (%)	
Coagulant	Dosage (mg/L)	In Water Without Turbidity	In Water With 14 ntu Turbidity
A	5	33.0	Insignificant
	6	27.5	Insignificant
	7	Insignificant	Insignificant
	8	Insignificant	Insignificant
	9	Insignificant	Insignificant
	10	Insignificant	Insignificant
	20		94.0
	30		99.0
	40		99.5
	50		99.7
B	2	Insignificant	75.0
	4	Insignificant	71.5
	6	Insignificant	64.0
	8	Insignificant	65.5
	10	Insignificant	45.0
C	2	96.0	96.0
	4	93.5	97.0
	6	93.0	95.5
	8	92.0	97.0
	10	90.0	96.0
D	2	48.5	63.0
	4	44.5	58.0
	6	30.0	28.0
	8	38.0	41.0
	10	39.0	38.0
E	2	56.5	57.5
	4	57.0	55.5
	6	39.0	23.5
	8	49.5	41.0
	10	54.5	43.5

[a] Reproduced from Malek et al.,[166] courtesy of the American Water Works Association.

Table 11.56. Turbidity and Virus Removal by Coagulation and Settling of Raw Water Containing Different Turbidities[a].[169]

Initial Turbidity (ntu)	Coagulant	Coagulant Dosage (mg as metal/L)	Turbidity Reduction (%)	Virus Removal (%)[b]		
				PV	RV	HAV
120–146	$FeCl_3$	32	98.9	>99.0	>99	>94.5
			99.3[c]	>99.0	>99	>94.5
	Alum	20	99.1	95.7	>99	93.6
			99.5	97.2	>99	>96.8
20–26	$FeCl_3$	16	92.9	91.0	>99	96.0
			94.0	94.0	>99	>99.2
	Alum	8	90.0	87.6	>99	96.7
			90.7	92.0	99	98.5
4–8.6	$FeCl_3$	16	81.4	52.7	>99	>96.5
			82.6	52.7	>99	>96.5
	Alum	8	71.4	90.7	>99	91.1
			77.9	90.7	>99	92.9

[a] The initial alkalinity of Lake Houston water varied for 35 to 40 mg as $CaCO_3$/L (pH 6.51; 50 mg as $CaCO_3$/L [in the form of $NaHCO_3$]) was added to raise the pH to 7.8–8.0.

[b] The initial numbers of viruses in 1,500 mL of water were PV—2.2 x 10^4 PFU, RV—4.5 x 10^5 PFU, and HAV—36–250 x 10^7 physical particles.

[c] Duplicate experiment.

Table 11.57. Results of Repeat Samples for Cincinnati Waterworks.[a]

	1966 Combined Cl_2 Residual	1967 Combined Cl_2 Residual	1669–70 Free Cl_2 Residual
No. of regular samples containing more than 4 coliform bacteria in 100 mL of water	19	20	8
No. of repeat samples required to obtain 2 successive 1/100 mL coliform counts	49	48	17
No. of repeat samples found to contain coliform bacteria	10	6	1

[a] Reproduced from Buelow and Walton,[170] courtesy of the American Water Works Association.

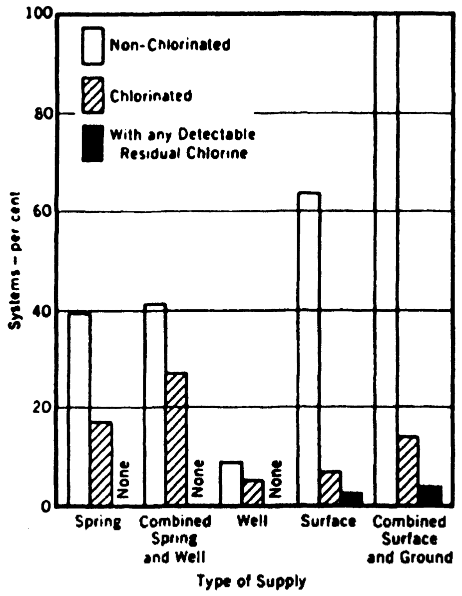

Figure 11.47. Percentage of water supply distribution systems found to have average total coliforms greater than 1/100 mL in various types of supplies. Reproduced from Buelow and Walton,[170] courtesy of the American Water Works Association.

during the study period when most of the TTHM concentrations were less than 100 mg/L. These plants used chlorine as their primary disinfectant in posttreatment.

Four PWSs were surveyed for TTHM reduction where $KMn0_4$ replaced Cl_2 as a pretreatment for taste and odor control.[173] Chlorine was used as the primary posttreatment disinfectant. Table 11.63 gives the relevant water quality data and the TTHM mean concentrations before and after the conversion to $KMn0_4$. It appears that there was a sufficient and statistically significant reduction of TTHMs to justify the conversion. One of the major disadvantages with $KMn0_4$ is the postprecipitation of $Mn0_{2(s)}$ in distribution systems that creates a "black" water. This is a difficult problem to remedy because of the slow kinetics of the precipitation reaction.

Some PWSs installed a combination of several processes to achieve lower TTHM contents (Table 11.59).[173] These combined processes were: chlorine dioxide plus chlorination, followed by air stripping plus ammoniation (Chesapeake) and potassium permanganate plus $Cl0_2$ and Cl_2 (Medina), and were employed as pretreatment for precursor removal. TTHMs were reduced to 24.5 mg/L from 62 mg/L (average values) in the Chesapeake PWS and from 110 mg/L to 44 mg/L in the Medina PWS. No disinfection data were given for these two systems.

The report cited by George et al.[173] lists several recommendations for each of the strategies presented above. The reader should review these recommendations as well as the supporting data carefully if they are considering a conversion in their TTHM/disinfection removal strategies.

Optimizing Chloramine Treatment

Chloramination was one of the TTHM control strategies discussed above. Several major PWSs in the United States and elsewhere employ chloramines in this manner as well to meet their disinfection requirements.[174] Certainly, chloramination is not a recent innovation in the public/preventive water treatment industry. Its history can be traced back to 1916, when the concept of ammonia-chlorine disinfection was developed.[1] Its effectiveness as a disinfectant has been controversial on occasion. In any event, we shall explore the viability of this water treatment process for the 1990s and beyond.

Chloramines are considered, generally, to be suitable secondary disinfectants because they are effective in maintaining an effective disinfectant residual in the distribution

Table 11.58. Comparison of Chlorine and Chloramine for Secondary Disinfection.[172]

Criterion	Chlorine	Chloramine
Biocidal effectiveness	Generally effective in controlling coliforms Effective in controlling HPC levels only if sufficient residual can be maintained	More effective in controlling coliforms Very effective in controlling HPC levels
Residual attainability	Limited geographical range Relatively unstable residual	Large geographical range Relatively stable residual
Taste and odor	Detectable chlorinous taste, stronger than chloramine Slightly detectable odor	Detectable chlorinous taste, less than chlorine Almost no detectable odor
Environmental effect	Toxic to fish but more easily removed from water than chloramine Accidental discharge to fish-bearing streams is a concern and requires spill containment	Toxic to fish and may also require removal of ammonia to protect fish in ponds and aquariums Accidental discharge to fish-bearing streams is a concern and requires spill containment
Cost	Estimated capital cost of Can$45 to Can$55 million Additional capital costs would be incurred to provide adequate contact time for primary disinfection, in GVWD system Estimated annual operating costs of Can$5 to Can$6 million	Estimated capital cost of Can$7.5 million Estimated annual operating costs of Can$1.2 million
Treatment jurisdiction	Would require wide distribution of facilities with plant operation responsibilities placed on GVWD and member municipalities	Would permit centralized treatment by GVWD
Compatibility with other treatments	Compatibility with recommended treatments for primary disinfection and corrosion control THM levels within present Canadian standards	Compatible with recommended treatments for primary disinfection and corrosion control THM levels with present Canadian standards, lower than those associated with chlorination

system. Since the kinetics of disinfection with chloramines is slower, generally, than Cl_2 and other oxidants, their role as a primary disinfectant is somewhat limited.

The major advantages of chloramines are: (a) their persistence and ability to reach remote areas in the distribution system, (b) their effectiveness as a secondary disinfectant and ability to penetrate biofilms in the distribution system, (c) their tendency not to form TTHMs and other DBPs, and (d) their ability to minimize chlorinous or other objectionable tastes and odors.[174]

There are some major disadvantages with chloramine treatment: (a) there are potential adverse effects on such special water uses as kidney dialysis, fish rearing, etc., (b) potential deleterious effects on elastomeric materials sometimes used in distribution system equipment and plumbing fixtures, and (c) potential vulnerability to the microbiological nitrification process, i.e., the conversion of NH_4^+ to NO_2^- and NO_3^- by nitrifying bacteria.[174]

In any event, the balance of advantages and disadvantages has persuaded many PWSs to adopt chloramination as a disinfection control strategy. Some of the most important design and operational parameters are:[174]

a. Chemical application points—where they are added in the treatment process, the order in which they are injected, and control of the chemical feed rates.
b. pH and temperature—pH 7.5 to 9.0 and 10° to 15°C.
c. Chloramine residual—depends on local conditions, but a range of residuals, 0.6 to 5.0 mg/L, is usually cited. Some 75% of U.S. utilities have had 1.0 and 3.0 mg/L in their distribution systems.
d. Chlorine to ammonia-nitrogen ratio—should be maintained between 3:1 and 5:1 to enhance formation of NH_2Cl and to reduce the [NH_3-N].
e. Mixing and reaction time—requires a thorough mixing and reaction time, with a velocity gradient of 300 to 100 sec^{-1}.
f. Periodic switch to free chlorine—application of free Cl_2 periodically for short periods of time is recommended to purge the system of chloramine-resistant bacteria and to reduce the potential for nitrification.

Plant Surveys of Chloramine Disinfection

The Philadelphia Suburban Water Co. (PSWC) produced an early report on their 50 years of experience with chloram-

Table 11.59. Case Study Participants.[173]

Alternative Treatment	Utility	Flow[a] (MGD)	State	Years of Use[b]	Water Source	Treatment Type
Chloramines	Ann Arbor	40.0	Michigan	6	River/GW[c]	Softening
	Contra Costa Co. (Ralph D. Bollman, Concord)	90.0	California	9	River	Conventional
	Miami-Dade (John E. Preston, Hialeah)	165.0	Florida	5	GW	Softening
	New Orleans (Carrollton)	124.0	Louisiana	5	River	Conventional
	San Diego County (Otay)	15.0	California	6	Reservoir	Conventional
	Terrell	3.6	Texas	3	Reservoir	Conventional
Chlorine dioxide	Bristol County (Bristol)	4.0	Rhode Island	4	Reservoir	Conventional
	Centralia	3.0	Illinois	2	Reservoir	Conventional
	Las Vegas (Alfred Merritt Smith)	175.0	Nevada	5	Reservoir	Direct filtration
	KY-American Water Co. (Lexington)	40.0	Kentucky	3	River	Conventional
	Mobile Water Service Center	40.0	Alabama	4	Reservoir	Conventional
Ozone	Bay City	40.0	Michigan	6	Lake	Softening
	Belle Glade	5.5	Florida	2	Lake	Softening
	Monroe	18.0	Michigan	5	Lake	Conventional
Potassium permanganate	Columbia	10.0	Tennessee	4	River	Conventional
	Illinois-American Water Works Co. (Peoria)	20.0	Illinois	1	River	Conventional
	Shelbyville	8.0	Tennessee	4	River	Conventional
	City of Wilmington (Sweeney)	9.0	North Carolina	3	Reservoir	Conventional
Combined THM control processes	Chesapeake	10.0	Virginia	3	River	Conventional
	Medina Water	2.0	Ohio	2	Reservoir/GW	Softening

[a] m^3/min = 2.628 x MGD.
[b] Number of years alternative treatment used.
[c] GW = groundwater.

ine disinfection.[175] The principal sources of supply for this company are four rural streams that are tributaries to the Schuylkill and Delaware Rivers. Pre- and postchloramine treatment has been used for over 50 years with considerable success. Table 11.64 shows the average (total) bacteria and coliform counts for a 50-yr period at PSWC. There were obvious excellent results. The prechlorine to ammonia ratio averaged 3.3, the prechlorine dosage was 1.34 mg/L, and the average residual chlorine was 0.58 mg/L. It is significant to note that the residual chlorine concentration increased steadily from an average of 0.28 mg/L in the 1930s to greater than 1.0 mg/L in 1979.

The East Bay Municipal Utility District (EBMUD) is located in northern California immediately east of San Francisco Bay, and provides water to approximately 1.2 million people.[174] Water for EBMUD's system comes primarily from Pardee Reservoir on the Mokelumme River. Three treatment plants utilize aeration, coagulation, flocculation, sedimentation, filtration, and disinfection with free chlorine. Two of EBMUD's pressure zones have had a history of noncoliform bacterial regrowth since 1967. The source of the contamination was identified, whereupon corrective measurements were taken that reduced, but did not eliminate the regrowth. Subsequently a decision was made to evaluate the performance of chloramines as a postdisinfectant. After a year of baseline monitoring, chloramine treatment was initiated in 1982 at one of their treatment plants. Four indicators were employed to evaluate the efficacy of chloramines to control regrowth: total coliforms, total colony count (TCC) of coliform and noncoliform bacteria, HPCs, and frequency of reservoir treatment with free chlorine. A typical result is illustrated by mean TCC values, which averaged 18.3/100

Table 11.60. Mean Values of Finished Water Quality Parameters Before and After Conversion to Chloramines.[173]

	Ann Arbor		Contra Cost Water District Ralph D. Bollman		Miami-Dade Water and Sewer Authority		New Orleans Carrollton		San Diego Lower Otay		Terrell	
	Before[a] 12/75–9/81	After 9/81–11/86	Before 1/77–9/81	After 9/81–5/87	Before 11/75–11/81	After 11/81–4/87	Before 7/76–10/81	After 10/81–12/86	Before 7/77–8/81	After 8/81–1/87	Before 11/81–11/83	After 11/83–12/86
Total chlorine residual (mg/L)	1.3	3.7	—	0.8	2.5[c]	3.5	1.3	2.0	2.2[c]	1.7	2.7[c]	2.9
pH	9.9	9.3[b]	8.4	8.5[b]	8.6	9.0[b]	9.9	10.1[b]	8.2	8.0[b]	7.9	8.4[b]
TTHM (μg/L)	105	25[b]	67	47[b]	228	27[b]	100	9[b]	175	80[b]	146	35[b]
Turbidity (ntu)	0.52	0.28	0.06	0.06	0.40	0.27[b]	0.19	0.17	0.32	0.18[b]	0.66	0.59
Total coliform count (tap) (cfu/100mL)	<1.0	<1.0	<2.2	<2.2	<1.0	<1.0	<1.0	<1.0	<2.2	<2.2	<1	<1.0
Heterotrophic plate count (cfu/mL) distribution	—	43	39	21	7	4	32	5[d]	—	7	—	—

[a] Time period for finished water quality database.

[b] A significant difference at 95% confidence level.

[c] Free chlorine residual.

[d] Instances of positive coliform bacteria counts did occur in the distribution lines after flashing during the first year of chloramine use.

— = No data reported.

Table 11.61. Mean Values of Finished Water Quality Parameters Before and After Conversion to Chlorine Dioxide.[173]

	Bristol County Child Street Plant		Centralia		Las Vegas Valley Water District Alfred Merritt Smith		Kentucky-American Water Company Kentucky River Station		Mobile	
	Before 1/80–2/83	After 2/83–12/85[a]	Before 1/83–12/84	After 12/84–6/87	Before 3/75–10/84	After 10/8–9/86	Before 2/81–1/84	After 1/84–1/87	Before 7/79–1/83	After 1/83–3/87
Residual chlorine (mg/L)	1.1	0.8[b]	—	2.0–2.2[c]	1.2	1.2	2.6	2.5	2.8	2.4[b]
pH	7.3	7.3	—	8.0–8.3[c]	7.8	8.0	8.0	8.1	9.2	8.1[b]
TTHM (μg/L)	112	53[b]	180	50	62	45	103	70	124	72[b]
TTHM running average (mg/L)	—	—	—	—	—	—	103	74	—	—

[a] Time period for finished water quality database.

[b] Significant difference at 95% confidence level.

[c] Value range is given due to insufficient data.

— = No data reported.

Table 11.62. Mean Values of Finished Water Quality Parameters Before and After Conversion to Ozone.[173]

	Bay City		Belle Glade		Monroe	
	Before[a] 6/74–9/79	After 9/79–5/86	Before 8/82–9/84	After 9/84–8/86	Ozone Off[b] 5/79–2/87	Ozone On[c] 5/79–2/87
pH	8.5	8.4	9.7	7.8[d]	7.1	7.1
TOC (mg/L)	—	—	11.1	12.0	—	—
TTHM (µg/L)	—	67	643	60[d]	44	70
MTP (mg/L)	—	—	808	236[d]	—	—

[a] Time period for water quality database.
[b] Period after ozone online when generating system was off (normally March through May).
[c] Period after ozone online when generating system was on (normally June through February).
[d] Significant difference at 95% confidence level.
— = No data reported.

mL with free chlorine vs. 2.2/100 mL during chloramine treatment. Mean values for HPCs were not significantly different as the result of chloramination. Frequency of distribution reservoir treatments were significantly reduced as a result of chloramination. The study concluded that chloramines were more effective than free chlorine in improving bacteriological quality and reducing TTHMs in the distribution system. Presumably, EBMUD converted to chloramination on a system-wide basis after this study was completed.

The Greater Vancouver Water District (GVWD) is a wholesale supplier of drinking water for 1.6 million people in the Lower Mainland of British Columbia.[174] Surface water impoundments are located in three uninhabited, mountainous waterbeds to the north of the general service area. Since raw water quality is excellent, treatment for most of the water system consisted of screening at source inlets and disinfection with free chlorine. In 1988, GVWD initiated a comprehensive water quality study to address problems associated with bacterial regrowth, corrosion, turbidity events, tastes, and odors that had been identified in its system. A portion of this study was an evaluation of chloramination for secondary disinfection of the regrowth problem (seasonal occurrence of coliform bacteria and high HPCs). Subsequently, service areas were selected and a secondary disinfection plant was designed to simultaneously chlorinate and chloraminate the water supply. This demonstration plant commenced operation in early September 1988. Water quality monitoring during 1989–1991 found chloramines to be more effective than Cl_2 for reducing HPC and coliform levels in the test area. For example, no more than 3% of the samples collected from the chloramine test area during any one month were found to have HPCs greater than 500 cfu/mL in 1989 and 1990. Biofilms collected from the chloramine test area had a much lower incidence of coliforms and somewhat lower concentration of heterotrophic bacteria than biofilms in the chlorine test area. The reader is directed to Reference 175. Residuals in the chloramine test area were much more stable than in the chlorine area. Chloraminated water was found to be more acceptable from a taste-and-odor standpoint than chlorinated water based on a flavor profile analysis. However, there is a negative aspect of chloramination treatment. Based on public response; i.e., consumer complaints, chloramine produced more negative reaction at the beginning of the treatment program chlorine. It is imperative for a PWS to conduct an extensive public education program prior to a conversion to chloramine treatment.

Kirmeyer et al.[174] also report the experiences of the Metropolitan Water District (MWD) of Southern California and the Tampa Water Department (Florida) with chloramination as the secondary disinfectant. Their results are essentially the same as those described above. The MWD experience is described also in Kreft et al.[176] and Barrett et al.[177]

Miscellaneous

Pilot plant experiments, using O_3 for disinfection of the waters of Lake Winnipesaukee, the supply for Laconia, New Hampshire, were reported by Keller et al.[178] This was an unusual case, where the lake water quality was such that complete treatment was not necessary. Instead, this study was conducted to determine the effectiveness of O_3 as a viricide following carbon adsorption. Two types of viruses were employed: type II poliovirus and coxsackievirus B-3 (Nancy strain). The essential results are seen in Table 11.65 for viruses. Sufficient disinfection was achieved at initial $[O_3]$ of 0.33 to 2.9 mg/L and with contact times of 5 min and less. Coliform counts during this test period were, for the most part, less than 2 to 2.2/100 mL. One of the disadvantages of O_3 is its inability to carry a residual concentration into the distribution system. This is usually corrected by the addition of chlorine or chloramines as secondary disinfectants (see above).

An unique disinfection problem occurs with bacteria associated with particles released from GAC filter-adsorbers[179] (see also Chapter 4). These beds may release particles of carbon with attached bacteria that are protected from disin-

Table 11.63. Mean Values of Finished Water Quality Parameters Before and After Conversion to Potassium Permanganate.[173]

	Columbia		Illinois-American Water Company Peoria		Wilmington Shelbyville		Sweeny	
	Before[a] 4/81–5/84	After 5/84–8/87	Before 8/84–8/86	After 8/86–7/87	Before 5/81–5/84	After 5/84–2/87	Before 1/80–5/84	After 5/84–6/87
Manganese (mg/L)	—	—	0.01	0.01	0.043	0.032	—	0.03
Manganese (distribution system) (mg/L)	—	—	—	—	0.042	0.048	—	—
pH	7.6	7.6	7.6	7.6	6.9	6.7[b]	7.2	7.2
TTHM (μg/L)	99	68	79	48	90	53[b]	98	88
TTHM (mg/L) running 4 quarter average	103	61	—	—	—	—	104	85

[a] Time period for water quality database.

[b] Significant difference at 95% confidence interval.

— = No data reported.

Table 11.64. Bacteria and Coliform Counts for a 50-year Period at PSWC.[a,b]

	Average Bacteria (count/mL)				Coliforms (count/100 mL)			
Years	Raw Water	Water at Top of Filter	Plant Filtered Water	Effluent Water	Raw Water	Water at Top of Filter	Filtered Water	Water
1930–1939	379	12.0	1.0	1.1	1,749	5.1	0.02	0.14
1940–1949	426	12.5	2.6	1.1	2,124	1.9	0.08	0.012
1950–1959	2,559	27.7	5.3	3.3	7,869	0.7	0.22	0.26
1960–1969	2,709	86.0	8.2	5.6	10,289	4.0	0.42	0.15
1970–1979	7,661	106.0	40.0	13.2	31,420	5.3	0.12	0.16
1979	10,265	51.0	13.9	4.5	45,000	0.6	0.01	0.00

[a] Reproduced from Shull,[175] courtesy of the American Water Works Association.

[b] Each result based on approximately 2000 samples.

Table 11.65. Pilot Plant Studies Results of Seeding Coxsackievirus B-3, Laconia Water Works.[a]

Run	Date	Ozone Generated (ppm)	Ozone Dosage (ppm)	Ozone Residual (ppm)	Virus Application (PFU)	Virus Survival (PFU)	Inact. (%)	Sample Coll. (gal)
1	8–2–74	4.03	2.9	1.2 after 1 min 0.47 after 4 min	1×10^5	0	>99.99	300
2	8–2–74	4.03	2.9	1.04 after 1 min 0.74 after 15 min	1×10^8	0	>99.999	150
3	9–12–74	2.0	1.53	0.59 after 1 min	7.6×10^7	0	>99.999	150
4	9–12–74	1.45	1.13	0.28 after 1 min	7.6×10^7	0	>99.999	150

[a] Reproduced from Keller et al. (178), courtesy of the American Water Works Association.

fection. A pilot plant study was conducted to evaluate chlorination as a means of inactivating heterotrophic bacteria adsorbed on the carbon particles. Particle size and concentration were the major factors influencing the efficacy of chlorination. If particle concentrations were "low," <20 mg/L, and particle size <20 μm, the bacteria associated with the GAC were disinfected with 2.0 mg/L Cl_2 within 5 min. Particle concentration is especially a significant factor in this situation. Most experiments were conducted with 0.014 mg/L of particles where no culturable bacteria were found after 1 min with 0.5 mg/L Cl_2. However, when the particle concentration was increased to 4 and 40 mg/L, less than one log reduction in HPC was observed with this chlorine dosage. Evidence was presented whereby 2.0 mg/L Cl_2, 3 min, was able to effect a 4-log reduction in HPC.

DECHLORINATION

There are occasions when it is necessary to reduce chlorine from the finished water prior to entry into the distribution system. This is usually the case following superchlorination to breakpoint. Dechlorination is accomplished by sulfur dioxide or other types of reduced sulfur compounds. There are occasions when activated carbon is employed. The following chemical reactions are applicable:

$$SO_2 + Cl_2 + 2H_2O = 2HCl + H_2SO_4 \qquad (80)$$

$$NaHSO_3 + Cl_2 + H_2O = NaHSO_4 + 2HCl \qquad (81)$$

$$Na_2SO_3 + Cl_2 + H_2O = Na_2SO_4 + 2HCl \qquad (82)$$

$$C + Cl_2 + 2H_2O = 4HCl + CO_2 \qquad (83)$$

Since all four of these reactions produce acidic substances, the alkalinity of the water will be reduced. The stoichiometries of these reactions are:

Dechlorinating Agent	Parts Required part Parts Chlorine Removed (theoretical)	Alkalinity Consumed (as $CaCO_3$) (presumed to be mg/L)
Sulfur Dioxide	0.90	2.8
Sodium Bisulfite	1.46	1.38
Sodium Sulfite	1.77	1.38
Activated Carbon	0.085	2.1

ADDENDUM

An important and significant issue of the *Journal of the American Water Works Association* was published in 1995. It was devoted to *Giardia* and *Cryptosporidium* in raw and finished water. Summaries of the papers in this issue are given below.

Results from an extensive monitoring of its operations since 1988 by the American Water System were reported.[180] Analysis of 347 surface water samples collected between 1988 and 1993 showed that the prevalence rate of *Giardia* and *Cryptosporidium* was 53.9% and 60.2%, respectively. But because the parasite assay does not indicate viability or virulence, these results do not necessarily indicate that these water systems were at risk from waterborne pathogens. To supplement coagulation and filtration, the average system will have to apply sufficient disinfection to reduce viable *Giardia* levels by 3.1 $\log_{10}$. An analysis of existing disinfection practices shows that most systems are already applying disinfectant at a level sufficient to reduce *Giardia* levels. However, the proposed Disinfectants/Disinfection By-Products (D/DBP) Rule may hamper the ability of water utilities to apply sufficient disinfection under current operating conditions. Careful integration of the D/DBP and the Enhanced Surface Water Treatment Rule is encouraged. Several technical, treatment, and regulatory issues are discussed herein that concern the supplies. The questions of cyst and oocyst viability and the subsequent health risk are discussed.

Cryptosporidiosis and public health were the subjects of a workshop held in 1994.[182] Representatives from 40 states and from regulatory and public health agencies, water utilities, and advocacy groups met to discuss prevention and control of waterborne cryptosporidiosis. Workgroups addressed surveillance systems and epidemiologic study designs, public health responses when oocysts are detected in drinking water, cryptosporidiosis in immunocompromised individuals, and water sampling methods and interpretation of results. The groups defined problems associated with these issues and developed strategies that could be used initially to manage these problems. An outgrowth of the workshop has been the formation of the Working Group on Waterborne Cryptosporidiosis, which holds regular teleconferences.

An action level of 10–30 oocysts/100 L was proposed for *Cryptosporidium* oocysts in finished water.[182] This came from a consideration of prior monitoring studies on finished water, *Cryptosporidium* and measurements made during and after detected outbreaks, and action level for *Cryptosporidium* oocysts is defined. At concentrations within and above 10–30 oocysts/100 L in finished water, the possibility of an outbreak would appear to exist. In the lower range of this region and below, outbreaks may occur but may not be detectable. If a single sample exhibits counts at or above this level, further sampling on an expedited basis or consideration of supplemental performance data to support a decision should be undertaken.

Bench-scale studies were used to investigate the effectiveness of dissolved-air flotation (DAF) for the removal of *Cryptosporidium parvum* oocysts from a drinking water supply.[183] Oocysts were spiked into a natural water at a concentration of $3–4 \times 10^5$ oocysts/L. Results indicate that DAF achieved a >2-log removal of oocysts under a variety of conditions. In addition, flotation was a superior clarification process to sedimentation for the conditions tested. Coagulation and DAF conditions that minimize residual turbidity and maximize the removals of organic matter are conditions that produce high log removals of *Cryptosporidium*. The >2-log removal of *C. parvum* from a natural water source was achieved under a variety of conditions: a coagulant dosage of 3 to 5 mg/L ferric chloride as Fe, pH values from 4.3 to 6.2, flocculation times as low as 5 min, and recycle ratios of 6 to 10%. Under "good" coagulation conditions with 5 mg/L ferric chloride, log removals of 3.7 were achieved by DAF. Sedimentation was less effective than DAF for all experimental conditions with a maximum log removal of 0.81 for the oocysts given a 20 min flocculation time and coagulant dosage of 40 mg/L.

A two-year evaluation of *Giardia* cyst and *Cryptosporidium* oocyst removal was conducted at a full-scale 900 gpm water treatment plant and at a 0.5 gpm pilot plant, both operated under conventional treatment and direct filtration regimes.[184] The full-scale plant is located at Bluffdale, Utah and treats Provo River Water downstream from Deer Creek Reservoir. The watershed is known as a beaver habitat and has many cattle ranches in the runoff area. Raw water quality (turbidity and algal content)—as well as treatment effectiveness in removing turbidity—controlled the removal of seeded cysts more than the mode of treatment. A high correlation was found between cyst removal rates and removal of the respective size particles; poorer correlation was found between the cysts and turbidity removal, whereas no correlation was established between the removals of cysts and heterotrophic bacteria. Several significant conclusions were drawn from this study: (a) a properly operated treatment plant that produces a finished water turbidity of 0.1 to 0.2 ntu can achieve a 3-log removal of *Giardia* cysts with either conventional treatment or direct filtration, (b) *Cryptosporidium* oocysts are more difficult to remove than *Giardia* cysts with a 0.4-log difference in a conventional plant and through direct filtration, and (c) removal of cyst-size particles and turbidity can be used as indicators of cyst and oocyst reduction.

Mechanisms of *Cryptosporidium, Giardia,* and MS2 virus removal by microfiltration (MF) and ultrafiltration (UF) were investigated on these natural source waters.[185] All of the hollow-fiber membranes evaluated removed *Giardia muris* cysts and *Cryptosporidium parvum* oocysts to below detection limits. No cysts or oocysts were detected in the permeate as long as the membrane remained intact. Physical straining of these organisms from the feed water appeared to be a primary mechanism of action. The extent of virus removal was membrane-specific, with removals ranging from <0.5 log to >6 logs. Three phenomena appeared to contribute to virus removal: physical sieving or adsorption, cake layer formation, and fouling state of the membrane. The relative contribution of each of these was a function of water quality, time of operation or filtration, and membrane characteristics.

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Index