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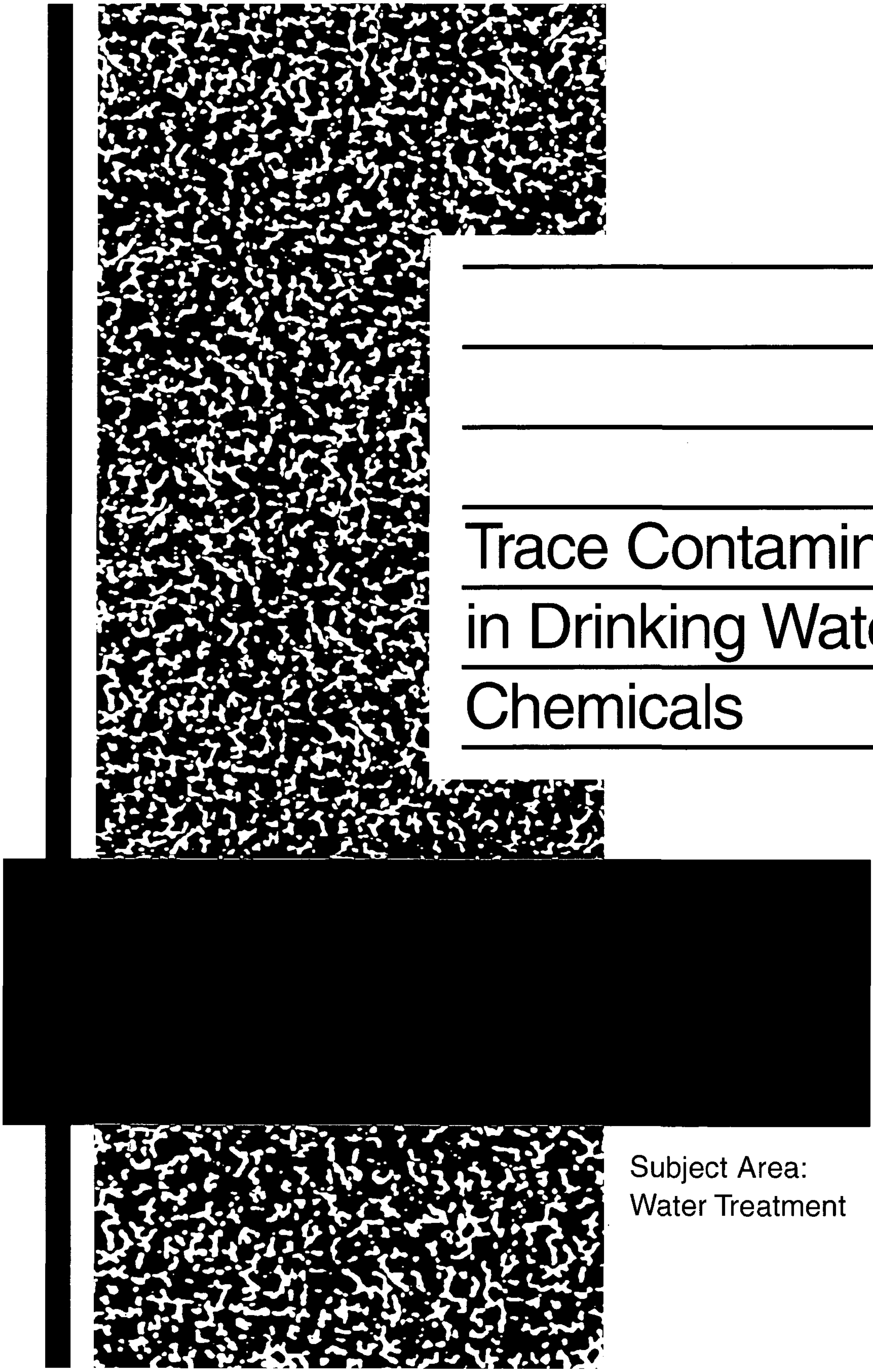

Trace Contaminants in Drinking Water Chemicals

Subject Area:
Water Treatment

Trace Contaminants in Drinking Water Chemicals

The mission of the Awwa Research Foundation is to advance the science of water to improve the quality of life. Funded primarily through annual subscription payments from over 1,000 utilities, consulting firms, and manufacturers in North America and abroad, AwwaRF sponsors research on all aspects of drinking water, including supply and resources, treatment, monitoring and analysis, distribution, management, and health effects.

From its headquarters in Denver, Colorado, the AwwaRF staff directs and supports the efforts of over 500 volunteers, who are the heart of the research program. These volunteers, serving on various boards and committees, use their expertise to select and monitor research studies to benefit the entire drinking water community.

Research findings are disseminated through a number of technology transfer activities, including research reports, conferences, videotape summaries, and periodicals.

Trace Contaminants in Drinking Water Chemicals

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Sponsored by:
Awwa Research Foundation
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Published by the
Awwa Research Foundation and
American Water Works Association

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Library of Congress Cataloging-in-Publication Data has been applied for.

Printed in the U.S.A.

ISBN 1-58321-247-7

Printed on recycled paper

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FOREWORD

The Awwa Research Foundation is a nonprofit corporation that is dedicated to the implementation of a research effort to help utilities respond to regulatory requirements and traditional high-priority concerns of the industry. The research agenda is developed through a process of consultation with subscribers and drinking water professionals. Under the umbrella of the Strategic Research Plan, the Research Advisory Council prioritizes the suggested projects based upon current and future needs, applicability, and past work; the recommendations are forwarded to the Board of Trustees for final selection. The foundation also sponsors research projects through the unsolicited proposal process; the Collaborative Research, Research Application, and Tailored Collaboration programs; and various joint research efforts with organizations such as the U.S. Environmental Protection Agency, the U.S. Bureau of Reclamation, and the Association of California Water Agencies.

This publication is a result of one of these sponsored studies, and it is hoped that its findings will be applied in communities throughout the world. The following report serves not only as a means of communicating the results of the water industry's centralized research program but also as a tool to enlist the further support of the nonmember utilities and individuals.

Projects are managed closely from their inception to the final report by the foundation's staff and large cadre of volunteers who willingly contribute their time and expertise. The foundation serves a planning and management function and awards contracts to other institutions such as water utilities, universities, and engineering firms. The funding for this research effort comes primarily from the Subscription Program, through which water utilities subscribe to the research program and make an annual payment proportionate to the volume of water they deliver and consultants and manufacturers subscribe based on their annual billings. The program offers a cost-effective and fair method for funding research in the public interest.

A broad spectrum of water supply issues is addressed by the foundation's research agenda: resources, treatment and operation, distribution and storage, water quality and analysis, toxicology, economics, and management. The ultimate purpose of the coordinated effort is to assist water suppliers to provide the highest possible quality of water economically and reliably. The true benefits are realized when the results are implemented at the utility level. The foundation trustees are pleased to offer this publication as a contribution toward that end.

Ever-tightening drinking water standards for regulated constituents in drinking water and continuing concern regarding emerging contaminants mandate the ongoing investigation of potential sources of these substances in finished drinking water. While monitoring of raw water sources is important, treatment chemicals should not be overlooked as possible contamination sources. This report characterizes potential sources of impurities in water treatment chemicals, quantifies levels of major and minor constituents in products commonly used at water treatment facilities, and provides practical guidance for selection and application of the highest quality treatment chemical additives necessary to meet site-specific and industry-wide goals.

Edmund G. Archaleta, P.E.	James F. Manwaring, P.E.
Chair, Board of Trustees	Executive Director
Awwa Research Foundation	Awwa Research Foundation

ACKNOWLEDGMENTS

Environmental Engineering & Technology, Inc. (EE&T) would like to thank all of the utilities and chemical manufacturers who participated in this research effort. Several utilities put forth considerable effort in collecting water samples and providing treatment chemical samples for analysis, including Philadelphia Water Department, Denver Water, Cincinnati Water Works, Southern Nevada Water Authority, Richmond Department of Public Utilities, South Central Connecticut Regional Water Authority and the American Water Works Service Company. Also, detailed surveys were answered by numerous utilities and manufacturers. General Chemical Corporation contributed technical expertise on various aspects of treatment chemical manufacturing and analysis, including the contribution of staff time and analytical costs associated with analyzing the treatment chemical samples collected by participating utilities. A special thanks is extended to PAC members Mr. Bruce Bartley and Mr. Peter Greiner (NSF International), Mr. Phil Vella (Carus Chemical), Mr. John Wierenga (City of Grand Rapids, Michigan), and AwwaRF Project Manager Ms. Traci Case for their assistance during this project.

EXECUTIVE SUMMARY

PURPOSE AND OBJECTIVES

There have been growing concerns in recent years about the quality and reliability of water treatment chemicals. Concerns have been perpetuated by contamination incidents that received significant public attention (such as the problems with carbon tetrachloride in chlorine) and continue as emerging contamination issues arise, including concerns associated with bromate in sodium hypochlorite. Unfortunately, the industry does not know whether there are widespread problems associated with contaminants in water treatment chemicals, or if concerns are limited to isolated events. This project was intended to answer this basic question using the best available information across the U.S. and beyond. It endeavored to quantify contamination levels in typical water treatment chemicals and focus on the likely sources of the problems. Finally, the project provides practical recommendations for utilities and the industry as a whole on how to identify, limit, and prevent contamination of treatment chemicals to improve water plant operations, lower treatment costs, and above all, protect public health.

Seven AwwaRF member drinking water utilities and one large chemical manufacturer helped assess the character, frequency of occurrence, and approaches to reduce or eliminate trace contaminants in chemicals used for drinking water treatment. In addition, the composition of trace constituents in commonly used drinking water treatment chemicals was evaluated and their potential significance on finished water and residuals quality was assessed. The objectives of this project included the following:

- Assess the extent of problems with trace contaminants in drinking water chemicals using the literature, utility and manufacturer surveys, and interviews
- Evaluate and describe sources of contamination associated with manufacture or refinement of water treatment chemicals
- Conduct pilot- and full-scale studies to characterize the composition and partitioning of chemical contaminants between finished water and residuals

- Relate differences in composition of treatment chemicals to differences in raw materials and manufacturing processes
- Bring awareness of issues associated with trace contaminants in water treatment chemicals to the attention of drinking water utilities and provide practical tools for utilities to assess and reduce impacts on finished water or residuals quality

Fundamental questions addressed in this research included: Are contaminant levels added by chemicals important? Do the contaminants remain in the water phase or are they partitioned to residuals? Can this behavior be predicted? What tools are available to utilities that could be used to estimate how trace contaminants in chemicals could affect finished water quality or residuals quality? Can contaminants in chemicals impact compliance with drinking water MCLs or ability to meet residuals quality goals or disposal options?

BACKGROUND

With ever-tightening drinking water standards for regulated contaminants and with identification of potential future constituents of concern through such means as the Unregulated Contaminant Monitoring Rule (UCMR), it is important to investigate sources of contaminants in finished drinking water and residuals. Control and monitoring of raw water is always important; however, treatment chemicals should not be overlooked as possible sources of contamination.

Recognizing the importance of controlling the presence of contaminants in drinking water treatment chemicals or additives, the United States Environmental Protection Agency (USEPA) and the American National Standards Institute (ANSI) adopted standards and a certification program developed by the National Sanitation Foundation-International (NSF) for treatment chemicals and other direct additives used to treat drinking water [ANSI/NSF Standard 60 (NSF 1999)]. However, the ANSI/NSF certification program outlined in Standard 60 has certain limitations. One of these is that certification testing is based upon a few periodic sampling events intended to provide a general evaluation of the typical quality of products produced by a given manufacturing facility. Although the testing results are used to establish the maximum allowable dose of a given chemical so that it will not have an impact on finished water quality, the procedures do not incorporate any provision to estimate impacts on the quality of water plant residuals. NSF Standard 60 certification only deals with the quality of the product up to the point the material leaves the production facility, so contamination that might occur during transport or on-site storage is missed.

The requirement for Standard 60 certified products is an important first step in reducing the chances of contamination, but experience suggests that utilities should consider stricter limitations on treatment chemical quality. Each water treatment facility should also incorporate some type of inspection and evaluation program to validate that the materials delivered meet the utility's specifications, and establish that the material leaving the production facility was not contaminated during shipment. Some utilities may have the capability and resources to perform more detailed testing inspections than other utilities. This report includes a description of routine activities that all facilities should conduct to evaluate each incoming chemical shipment, including inspection of paperwork, visual inspection of products and delivery vehicles during unloading, checking for unusual odors and simple physical or chemical tests.

OCCURRENCE SURVEY

In order to establish the types and frequency of problems associated with contaminants in chemicals used at U.S. drinking water facilities, a survey was sent to about 10 percent of AwwaRF member utilities, including at least one utility in each state (South Dakota was the only state without an AwwaRF subscriber utility). In all, about 150 utilities survey forms were distributed and the response rate was approximately 30 percent (quite good for a survey of this type). Those who returned completed survey forms generally dedicated a significant amount of effort to the task and often attached exhibits with example chemical specifications and other details. Responses were received from utilities in 38 U.S. states, representing the collective experiences of 266 water treatment plants across the U.S. (see Figure ES.1).

Although there were a few reported concerns about specific trace contaminants, by far the most frequent complaints reported by water utilities were associated with the presence of gross contaminants in drinking water treatment chemicals. Many utilities continue to report incidents of foreign materials, primarily sediment or floating debris in liquid chemicals, even though they are using NSF certified products. In some instances, utilities were not able to determine the source or cause of the contamination in the products delivered to their facilities. In other cases, the source of the contamination was traced to a deficiency in the chemical manufacturing or refining process. However, the most frequently reported contamination incidents occurred during transport, primarily associated with improperly cleaned or maintained delivery containers or transfer hoses.

Another category of problems identified during the utility survey was comprised of blunders associated with attempted delivery or unloading of the wrong chemical. These were not the same as contamination issues associated with manufacture or shipment of treatment chemicals, but are problems that continue to plague U.S. water utilities and were cited frequently during the utility survey. Common examples of these kinds of incidents include:

- Attempted delivery of a chemical intended for delivery at a nearby wastewater plant
- Attempted delivery to a water plant in a city with the same or similar sounding name as a city in another region of the country
- Delivery or attempted delivery of wrong chemical, wrong strength, or wrong formulation
- Off-loading of chemicals into the wrong storage area
- Off-loading of more chemical than was ordered and exceedance of available on-site storage capacity

Many of these incidents could have been avoided through the use of inspection programs including routine activities such as careful checking of paperwork, comparison of amount of material ordered to amount of on-site storage space available, and supervision by water plant personnel of all activities associated with delivery of chemical products (connection, off-loading, disconnection and clean-up). More stringent specifications could also have helped, but an inspection and evaluation program would still have been needed in order to verify that the more rigorous specifications were achieved.

COMPOSITION OF COMMONLY USED WATER TREATMENT CHEMICALS

Using data from published literature, coupled with new information provided by water treatment chemical manufacturers and suppliers, sources of contamination associated with raw materials and specific chemical manufacturing processes were identified. Compositional data were gathered from the manufacturer and water utility surveys, and through a large number of samples analyzed during this project for up to 28 metals in a variety of treatment chemicals, plus total organic carbon (TOC) and disinfection by-product precursor (DBP) content for iron- and aluminum-based coagulants. Chemicals analyzed included aluminum- and iron-based coagulants, sodium hypochlorite, chlorine, caustic soda, lime, organic polymers, corrosion inhibitors, potassium permanganate, and hydrofluorosilicic acid.

Compositional data presented in this report indicate that products generated by certain manufacturing processes or using better quality raw materials can result in products with improved characteristics. A good example of this was the difference in characteristics of various aluminum-based coagulants. As indicated in Figure ES.2, standard alum is produced by direct sulfuric acid leaching of aluminum-containing ore, while low-iron alum is produced by leaching a processed, higher quality aluminum source with sulfuric acid. Polyaluminum chloride products are produced by reacting a similar processed aluminum material with hydrochloric acid. Compositional data for these three general classes of aluminum-based coagulants showed that standard alum contained much higher levels of most metals (except sodium and zinc) than low-iron alum or polyaluminum chloride due to the higher quality of the aluminum source. These differences are represented graphically in Figure ES.3. Details on the trace metal content of other types of chemicals are presented in detail within the report.

Analysis of TOC and DBP precursor content in iron- and aluminum-based coagulants indicated that coagulant doses typically used during water treatment are not likely to contribute appreciable amounts of these organic constituents. Calculations presented in this report indicate that the four coagulants tested would result in TOC increases of less than 0.06 mg/L at typical water treatment doses (50 mg/L as alum and 33 mg/L as ferric sulfate, or about 0.17 mM as Fe or Al). At these same doses, the potential DBP contribution from aluminum- and iron-based coagulants was estimated to be less than 1 µg/L.

SOURCE AND FATE OF TRACE CONTAMINANTS ADDED BY TREATMENT CHEMICALS

Pilot-scale studies were conducted during this project using three coagulants (alum, polyaluminum chloride, and ferric chloride). Full-scale studies were conducted at two participating utilities, one using alum and polymer as coagulants and the other using ferric chloride. The studies were performed to assess the significance of trace contaminants in water treatment chemicals and how those contaminants partition between finished water and residuals. Observations arising from that work included:

- More trace metals were contributed by coagulants than by other treatment chemicals due to higher dose, higher metal content, or both.
- Arsenic, antimony, lead, selenium and silver were typically below detection limits in treatment chemicals and raw water during pilot- and full-scale studies. Although these metals were also below detection limits in the finished water, they were often detected in residuals. Therefore, these metals may have originated in the treatment chemicals and then concentrated in the residuals streams.
- Higher levels of major cations (calcium, magnesium, sodium, potassium), barium, and copper were contributed by the incoming raw water than were added by treatment chemicals (except calcium added by lime addition). This occurred even in pilot studies using a purified water source with minimal metallic content.
- Metals contributed by both aluminum- and iron-based coagulants included: aluminum, chromium, cobalt, mercury, nickel, titanium, and vanadium. Additionally, iron coagulants contributed iron, cadmium, manganese, and molybdenum while aluminum-based coagulants contributed zinc.
- Metals contributed by coagulants typically partitioned into the residuals streams rather than into the finished water during both full- and pilot-scale studies.

Table ES.1 provides an overview of the findings from the pilot- and full-scale work. The table indicates whether the source of a given constituent was predominantly from a treatment chemical or raw water, and whether this metal primarily partitioned into the finished water or residuals streams after treatment. The pilot- and full-scale findings were quite consistent with one another and suggest that the results would be generally applicable to water utilities across the U.S. and beyond that employ coagulation.

Table ES.1

Comparison of source and fate of contaminants during pilot- and full-scale studies

	Source	Fate
Coagulant metals		
Aluminum	C	R
Iron	W* / C†	R
Major cations		
Calcium	W	W
Magnesium	W	W
Sodium	W	W
Potassium	W	W
Trace metals		
Antimony	ND	ND
Arsenic	ND	R
Barium	W	W
Cadmium	ND* / C†	ND or R
Chromium	C	R
Cobalt	C	ND or R
Copper	W	R
Lead	ND	R
Manganese	W* / C†	R
Mercury	C	ND
Molybdenum	ND or W* / C†	ND* / R†
Nickel	C	R
Selenium	ND	ND or R
Silver	ND	ND
Titanium	C	R
Vanadium	C	R
Zinc	C* / W†	R

*Aluminum-based coagulants
†Iron-based coagulants

W	mostly from water
C	mostly from chemical
R	mostly in residuals/sludge
ND	not detected

ESTIMATING IMPACT OF CONTAMINANTS IN TREATMENT CHEMICALS ON FINISHED WATER QUALITY

The maximum allowable dose for a treatment chemical additive of known composition can be estimated using a methodology based on ANSI/NSF Standard 60. This approach establishes the maximum allowable dose as the amount of a treatment chemical that will contribute less than 10 percent of any MCL, except that sodium hypochlorite is allowed to contribute up to 50 percent of the bromate MCL. A key assumption in this approach is that all constituents added by the chemical partition into the finished water. For treatment chemicals that are added prior to filtration or clarification, this research shows that this approach is conservative because many of the contaminants in the treatment chemical will partition into the residuals streams.

Using this approach for data generated during this research project, the limiting dose for standard alum was calculated as 156 mg/L as alum with chromium as the limiting constituent. The mercury content of low-iron alum and standard alum were about the same, but chromium and other metals are removed during production of low-iron alum, as described in this report. Consequently, for low-iron alum the limiting constituent was mercury and the limiting dose was 189 mg/L as alum. Limiting constituents for other treatment chemicals analyzed during this project are summarized in Table ES.2. Key findings from this table include the following:

- Even though the NSF Standard 60 approach is conservative with respect to predicting impact of treatment chemicals on finished water quality, limiting doses calculated by this method were typically far higher than those required at most U.S. treatment facilities.
- Mercury and chromium were the limiting trace constituents for many products, including aluminum- and iron-containing coagulants, potassium permanganate, and corrosion inhibitors.
- The relative trace metals content in sodium hypochlorite, caustic soda, and lime were much lower than for other chemicals, thereby resulting in markedly higher limiting doses determined using the NSF Standard 60 approach.

- The maximum allowable dose for sodium hypochlorite was typically driven by bromate composition.

Table ES.2

Maximum allowable doses and limiting constituents for typical water treatment chemicals

Treatment chemical	Maximum allowable dose	Limiting constituent
Standard alum	14 mg/L as Al 156 mg/L as alum	Cr
Low-iron alum	17 mg/L as Al 189 mg/L as alum	Hg
Polyaluminum chloride	18 mg/L as Al	Hg
Hydrofluorosilicic acid	4.3 mg/L as F	As
Steel pickle liquor- derived ferric chloride	28 mg/L as Fe 81 mg/L as $FeCl_3$	Cr
Titanium dioxide-derived ferric chloride	13 mg/L as Fe 37 mg/L as $FeCl_3$	Hg
Ferric sulfate	8 mg/L as Fe 29 mg/L as $Fe_2(SO_4)_3$	Pb
Zinc phosphate	103 mg/L as P	Cr
Potassium permanganate	0.8 mg/L as Mn 2.3 mg/L as $KMnO_4$	Hg
Sodium hypochlorite*	3.8 mg/L as Cl_2	BrO_3^-
Sodium hydroxide	> 2,000 mg/L as Na > 3,500 mg/L as NaOH	Cu
Lime	1,320 mg/L as Ca 2,400 mg/L as $Ca(OH)_2$	Ba

*Metals from this study, bromate (BrO_3^-) from Delcomyn 2000, 50 percent of bromate MCL allowed for sodium hypochlorite.

Bromate in sodium hypochlorite was not analyzed in this research project since that is the specific focus of other ongoing research. Using mean data reported by Delcomyn (2000), the limiting dose for sodium hypochlorite was 19 mg/L as Cl_2. After this time, careful selection of raw materials and monitoring and control of the production process have reduced bromate levels to the point where typical limiting doses for sodium hypochlorite are closer to 80 mg/L as Cl_2. Before the NSF Standard 60 was modified to allow sodium hypochlorite to contribute 50 percent of bromate MCL rather than 10 percent, the Delcomyn data would have resulted in a calculated limiting dose of 3.8 mg/L as Cl_2. This would have severely limited the use of sodium hypochlorite products in most U.S. drinking water applications.

Based on this research, and using the NSF Standard 60 approach, arsenic was the limiting constituent in hydrofluorosilicic acid. Using the highest arsenic result from this research, a maximum allowable dose of 4.3 mg/L as F was calculated. If the arsenic MCL had been reduced to 3 µg/L instead of the current 10 µg/L, the limiting dose would have been 1.3 mg/L as F. This example and the example of bromate in sodium hypochlorite show that very low MCLs for certain contaminants could impact selection of chemical products and/or force manufacturers to lower levels of particular trace contaminants.

Although the bromate in sodium hypochlorite and arsenic in hydrofluorosilicic acid examples show how trace contaminant levels in water treatment chemicals can be a significant problem with respect to meeting drinking water MCLs, this research showed that these are unusual cases. These two problems were related to a contaminant that remains in the water phase through treatment (bromate) and a contaminant present in a chemical added after coagulation and filtration (hydrofluorosilicic acid). Most other contaminants are contributed by chemicals added early in the treatment process, especially coagulants, and these contaminants mostly partition to the residuals streams rather than the finished water.

ESTIMATING IMPACT OF CONTAMINANTS IN TREATMENT CHEMICALS ON RESIDUALS QUALITY

Although the ANSI/NSF Standard 60 approach addresses the potential impact of treatment chemicals on finished water quality, this method does not address the potential impact on residuals streams. Partitioning study results from this research indicate that residuals quality may be an important consideration since most of the contaminants added by treatment chemicals partition to residuals streams. This report provides a simple, straightforward procedure to calculate the maximum allowable composition in a treatment chemical needed to meet a utility's residuals quality goals. The method presented can be used to evaluate any treatment chemical, although results from this project indicate that coagulants contribute much more trace metals than other treatment chemicals. A utility could select its specific residuals quality goal based on local disposal or beneficial use requirements.

The maximum allowable concentration of a trace metal in a coagulant can be calculated using the following input factors: a) the residuals quality goal, b) amount of trace metal contributed by raw water, and c) dose of coagulant needed. The relationship is defined as:

$$X = \frac{L - R}{\text{Dose}} = \frac{(M * \text{limit}) - R}{\text{Dose}}$$

where X = Allowable metal concentration in coagulant so that land application limits or other residuals quality goals are not exceeded (mg/kg dry)

L = Allowable metal level in sludge per million gallons (MG) of finished water produced

R = Metal concentration in raw water (mg/L)

Dose = Chemical dose (mg/L)

limit = Trace metal limit or residuals quality goals (mg contaminant per kg dry sludge)

M = Dry sludge production per volume of finished water produced (e.g., lb/MG)

The key assumption in this expression is that the ultimate fate of trace metals is residuals. This could be regarded as a "worst-case" scenario from the perspective of residuals quality, but was consistent with the actual findings of the metals partitioning studies from this project.

For example, this expression would predict that the maximum allowable molybdenum content in ferric chloride would be approximately 100 mg Mo/kg of $FeCl_3$ for a raw water turbidity of 6 ntu, a ferric chloride dose of 33 mg/L, a land application limit for molybdenum of 75 mg/kg, and no detectable molybdenum in the raw water. The highest molybdenum content in ferric chloride samples analyzed during this project was about 18 mg Mo/kg of $FeCl_3$. In this example, the land application limit for molybdenum would theoretically not be exceeded under these conditions. Water utilities that wish to perform similar calculations for their facilities will need to modify some of the assumptions, especially land application limits and sludge production estimates, for their facilities.

HOW CAN UTILITIES LIMIT TRACE CONTAMINANTS IN TREATMENT CHEMICALS?

Figure ES.4 summarizes contamination sources and general control measures evalauted during this project. Recommended activities for utilities to implement in order to limit the potential for trace constituents in water treatment chemicals to impact finished water and/or residuals quality include the following:

- Specify ANSI/NSF Standard 60-certified products
- Employ additional and/or tighter specifications in order to address utility concerns. Figure ES.5 graphically illustrates the results attained by one utility that tightened its specification for ferric chloride
- Develop and implement procedures for inspection and evaluation of each incoming shipment of treatment chemicals. These procedures are detailed in the text
- Require or give preference to vendors who use dedicated delivery vehicles
- Contact NSF if visual inspection indicates potential contamination of products delivered to a water treatment plant

Utilities can perform additional compositional analyses on delivered treatment chemicals, as time and resources permit. Also, many utilities interviewed during this project reported success using cooperative regional purchasing agreements with nearby water plants. An obvious benefit of cooperative chemical purchase agreements would be economy-of-scale cost savings, but another consequence can be better quality products because of more clout (especially for smaller utilities) to enforce tighter specifications.

RESEARCH NEEDS AND FUTURE ACTIVITIES

Research questions and future activities identified from this project include:

- Development of a plan for regional chemical purchasing consortiums to enhance treatment chemical quality and lower chemical and shipping costs to utilities
- How should general water plant security issues dovetail with treatment chemical integrity protection?
- Identification of N-nitrosodimethylamine (NDMA) precursors in both natural waters and water treatment chemicals
- How utility responses to changing regulatory requirements affect treatment chemical specifications?
- How can chemical specifications provide incentives for suppliers of superior products?
- Are changes to the NSF Standard 60 protocol for establishing limiting chemical doses required?
- Should exceptions be made for certain chemicals or contaminants, such as was done for bromate in sodium hypochlorite?
- Should the AWWA Standards Council develop standards for trace contaminants in all drinking water treatment chemicals?

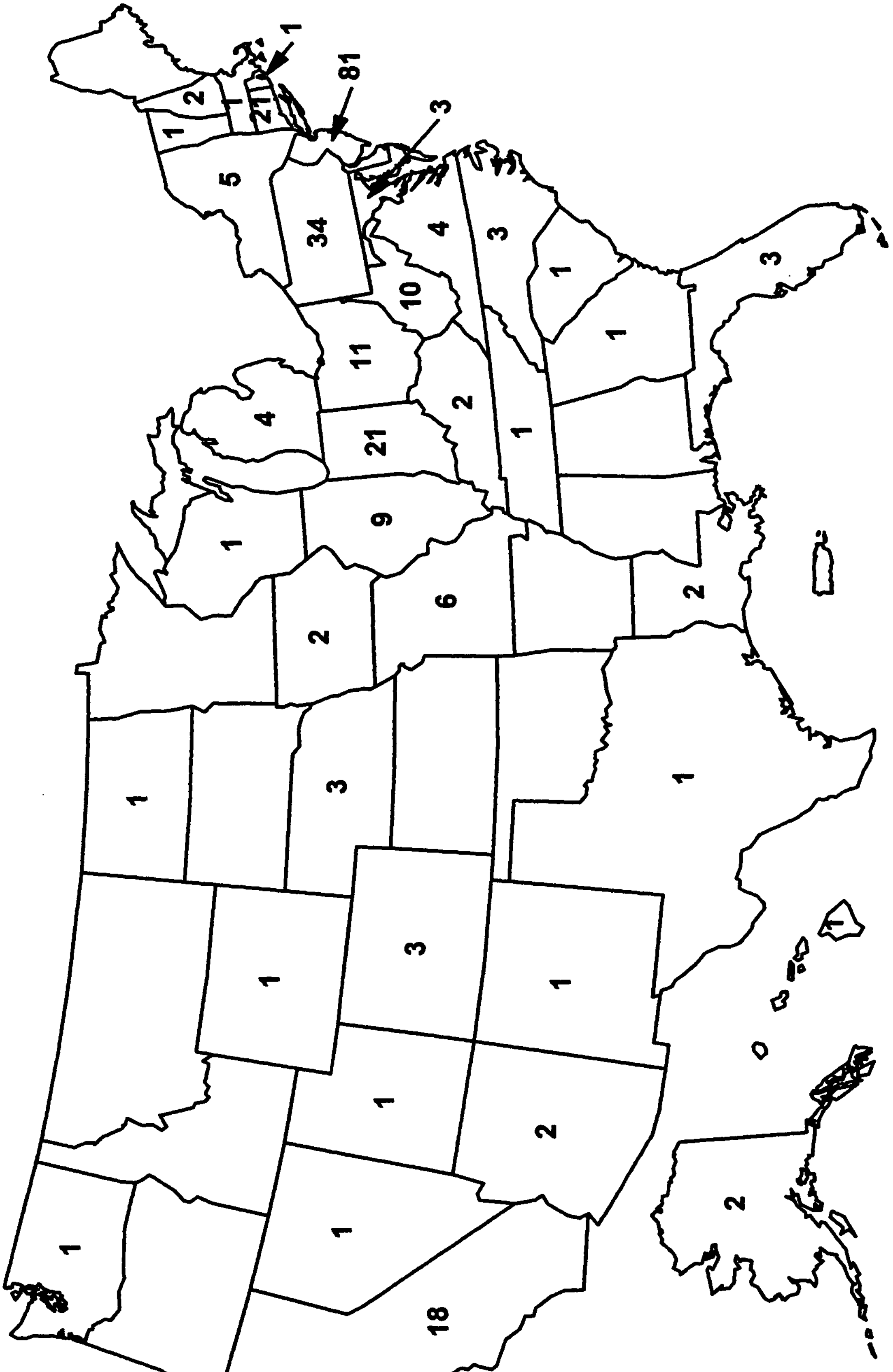


Figure ES.1 Utility survey responses

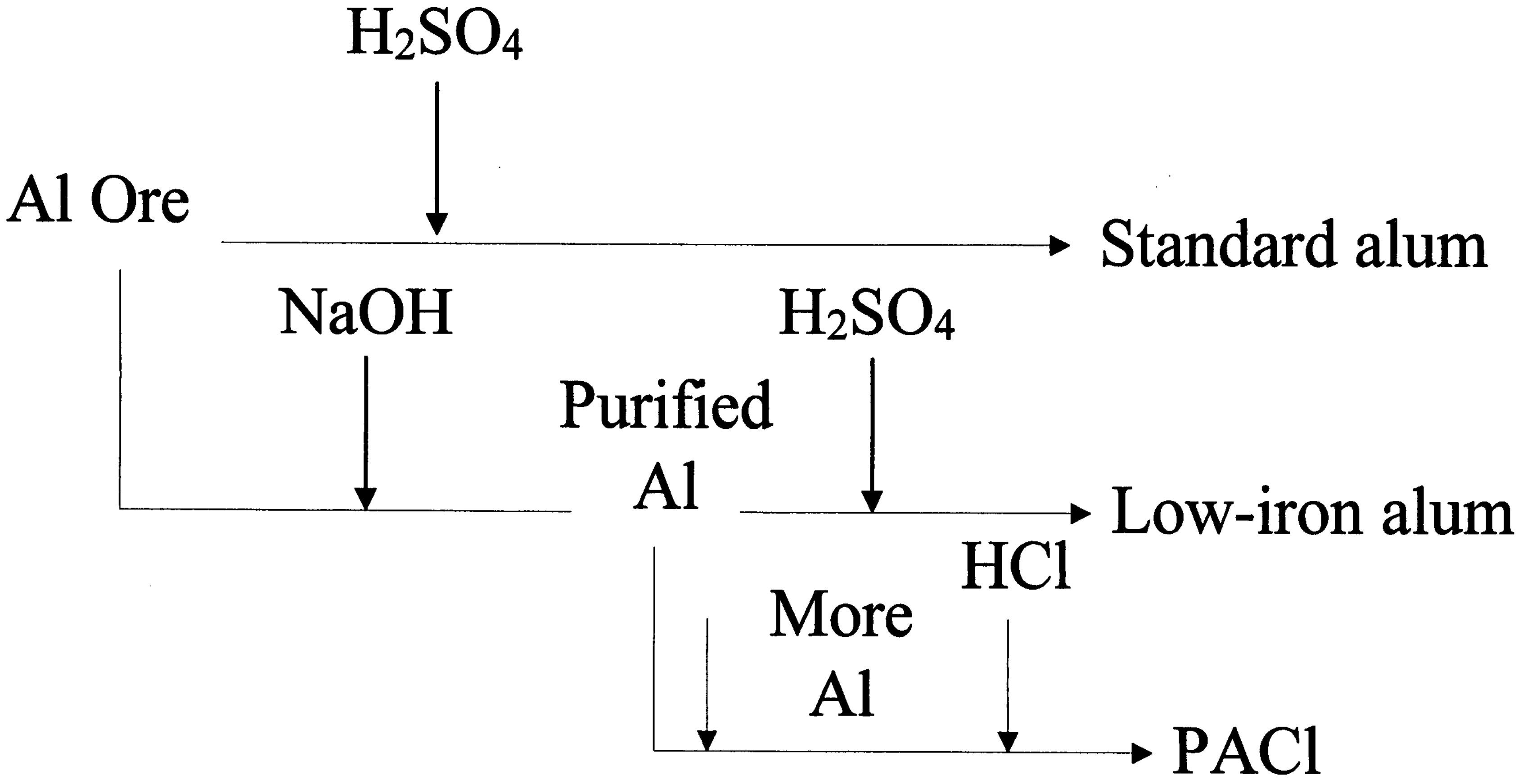


Figure ES.2 Sources and manufacture of aluminum-based coagulants

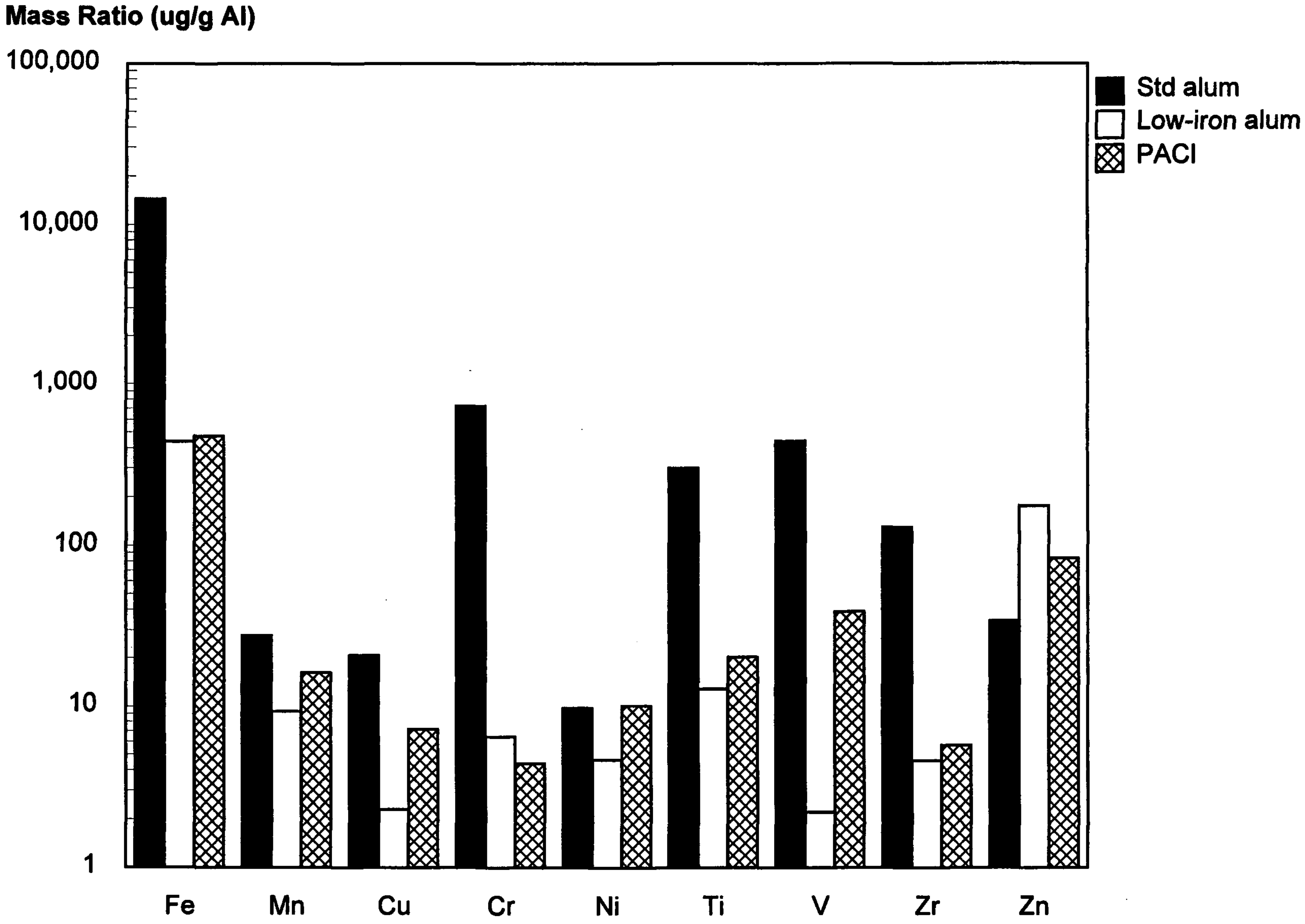


Figure ES.3 Trace contaminants in aluminum-based coagulants

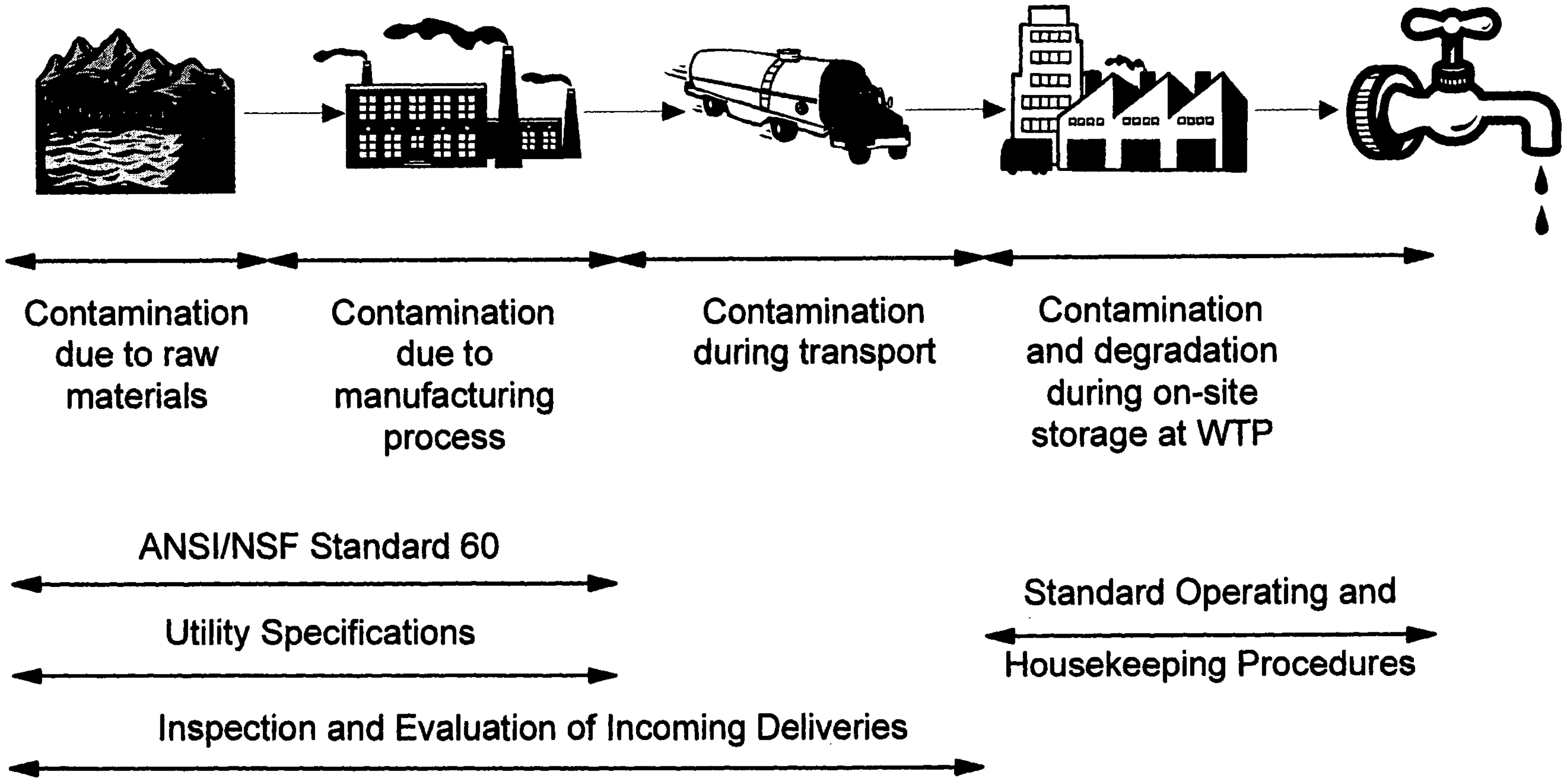


Figure ES.4 Sources of treatment chemical contamination and control options

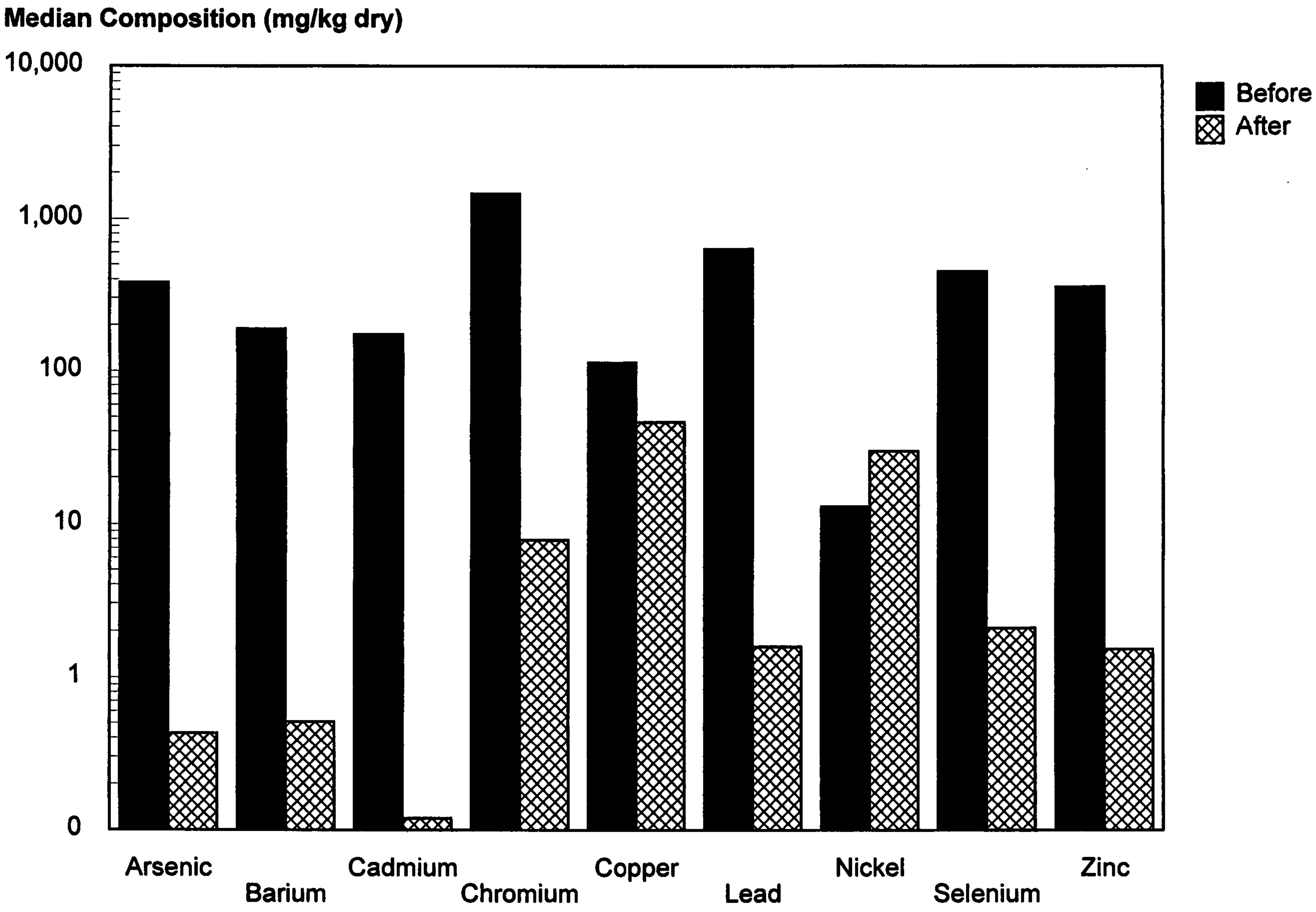


Figure ES.5 Impact of implementing tighter specifications for ferric chloride

CHAPTER 1
OVERVIEW

OBJECTIVES

Seven AwwaRF member drinking water utilities and one large chemical manufacturer helped assess the character, frequency of occurrence, and approaches to reduce or eliminate trace contaminants in chemicals used for drinking water treatment. In addition, the composition of trace constituents in commonly used drinking water treatment chemicals was evaluated and their potential significance on finished water and residuals quality was assessed. The objectives of this project included the following:

- Assess the extent of problems with trace contaminants in drinking water chemicals using the literature, utility and manufacturer surveys, and interviews
- Evaluate and describe sources of contamination associated with manufacture or refinement of water treatment chemicals
- Conduct experimental studies to characterize the composition and partitioning of chemical contaminants between finished water and residuals
- Relate differences in composition of treatment chemicals to differences in raw materials and manufacturing processes
- Bring awareness of issues associated with trace contaminants in water treatment chemicals to the attention of drinking water utilities and provide practical tools for utilities to assess and reduce impacts on finished water or residuals quality

SIGNIFICANCE OF PROJECT

With ever-tightening drinking water standards for regulated contaminants and with continuing investigation of potential future constituents of concern through such efforts as the unregulated contaminant monitoring rule (UCMR), it is important to study potential sources of contaminants in finished drinking water. Along with control and monitoring of raw water sources, treatment chemicals should be considered as potential sources of contaminants of concern. The issue is also important because utilities continue to report instances of drinking water contamination due to water treatment chemicals, and experience gross contamination with chemicals themselves. However, until this project was conducted, the industry did not know whether widespread problems with trace contaminants existed, or whether contaminant levels in chemicals impacted finished water and residuals quality, beyond isolated incidents.

SCOPE

The discussion in this report deals only with water treatment chemical additives. This includes consumable products added directly to water in liquid or solid form, or products delivered to a treatment facility in solid or powder form, then mixed into a solution or slurry prior to use in the water plant. Most of these chemicals are added to the water stream, but some can be added to residuals streams, such as clarifier sludge or spent filter backwash water. More durable, non-consumable materials (such as filter media) or equipment are not the subject of this report.

PROJECT PARTICIPANTS

EE&T is the principal investigator for this project. The effort was supported by seven water utilities and one manufacturer of water treatment chemicals, as outlined in Table 1.1.

Table 1.1

Participating utilities and organizations

Name of organization		Location
Principal Investigator		
EE&T	Environmental Engineering & Technology, Inc.	Newport News, VA
Water Utilities		
AWWSC	American Water Works Service Company	Vorhees, NJ
CWW	Cincinnati Water Works	Cincinnati, OH

(continued)

Table 1.1 (continued)

Name of organization		Location
DW	Denver Water	Denver, CO
PWD	Philadelphia Water Department	Philadelphia, PA
RDPU	Richmond Department of Public Utilities	Richmond, VA
SCCRWA	South Central Connecticut Regional Water Authority	New Haven, CT
SNWA	Southern Nevada Water Authority	Boulder City, NV
Chemical Manufacturer/Supplier		
GCC	General Chemical Company	Syracuse, NY

The water utilities provided extensive background information including:

- Specifications for ordering and delivery of water treatment chemicals
- Standard operating procedures for delivery of treatment chemicals at water treatment facilities
- Summary of experiences and anecdotal evidence of difficulties with delivery or use of treatment chemicals
- Compositional data on different treatment chemicals

These project participants also supplied samples of treatment chemicals used at their facilities for analysis of trace metals and other constituents. These samples were analyzed by GCC and the results are presented in Chapter 4. Two of these participants also collected and analyzed water, sludge, and backwash samples from various points in the water treatment process (on the dates that treatment chemicals were sampled) so that partitioning of trace constituents in the treatment chemicals could be evaluated at the full-scale treatment plant. Those results are presented in Chapter 5.

As part of its "in-kind" contribution for this project, GCC provided analytical services for all of the treatment chemical samples provided by participating utilities. More than 40 treatment chemical samples were analyzed, including liquid alum, ferric chloride, polyaluminum chloride, ferric sulfate, sodium hypochlorite, potassium permanganate, hydrated lime, caustic soda, organic polymers, and a variety of phosphate-based corrosion inhibitors. These results are described in Chapter 4. In addition, GCC analyzed sludge from the field studies.

The Philadelphia Water Department analyzed trace metal content of sludge and water-phase samples generated during laboratory bench-scale partitioning studies investigating three commonly used coagulants (see Chapter 5). The City of Grand Rapids, MI, provided samples and contributed analytical costs for analysis of trace constituents in three samples of fluorosilic acid. These samples were analyzed by Short Environmental Laboratories (Sebring, FL). Other contributors to this project included about 40 drinking water utilities that responded to the survey of AwwaRF subscribers, and five manufacturers and suppliers of water treatment chemicals that responded to a manufacturer's survey.

CHAPTER 2

IDENTIFICATION OF PROBLEMS ENCOUNTERED DURING DELIVERY, STORAGE, OR APPLICATION OF DRINKING WATER TREATMENT CHEMICALS

FINDINGS FROM OCCURRENCE SURVEY

This chapter identifies and enumerates the magnitude and frequency of problems encountered during delivery and use of treatment chemicals at drinking water treatment facilities. General problems identified included:

- Evidence of gross contamination in delivered products such as sediment or floating debris in liquid chemicals
- Trace contaminants in specific products
- Contamination introduced during manufacturing or refinement of treatment chemicals
- Contamination introduced during chemical shipment, mostly due to improperly cleaned or maintained delivery containers or transfer hoses
- Delivery of incorrect product
- Delivery of product that did not meet specifications ordered

Some of these instances were detected before or during unloading of delivered product, while others were uncovered after the fact. In a few rare instances, contaminated products were identified after disruptions in operations of key equipment in the treatment process, including chemical feed equipment. Occasionally, this resulted in poor to unacceptable finished water or residuals quality. Efforts to reduce the occurrence of these incidents through implementation of stricter specifications or inspection procedures are addressed in Chapter 6.

AWWSC INTERNAL SURVEY OF TREATMENT FACILITIES

Much of the information provided by the American Water Works Service Company (AWWSC) for this project was later published by Casale (2001). This information included:

1. Listing of chemicals currently used at their 185 facilities throughout the U.S.
2. Summary of the types of evaluations performed by AWWSC upon delivery of individual chemicals (specific gravity, odor, visual appearance, pH, etc.)
3. Summary of types of problems encountered in the past with chemical deliveries, mostly involving presence of sediment or other contamination, delivery of wrong chemical, or damaged containers
4. Description of instances where contamination of treatment chemicals resulted in contamination of finished water or treatment residuals
5. Summary of available historical constituent analyses performed by the utility or reported by manufacturers/suppliers for individual treatment chemicals

Items 1, 3, and 4 are described in more detail in this section of the report, while items 2 and 5 are specifically discussed in Chapters 6 and 4, respectively.

SURVEY OF AwwaRF SUBSCRIBER UTILITIES

AwwaRF supplied a list of subscriber utilities that included >1,100 contact names and addresses in the U.S., Canada, and from international locations. About 10 percent of the utilities from this list were selected, with representation from all of the states with AwwaRF subscriber utilities. Other utilities were recommended by the AwwaRF PAC or others. The resulting distribution list included about 150 utilities. These included at least one utility from each U.S. state except South Dakota (no AwwaRF subscribers) and New Mexico (already included in AWWSC survey), plus appropriate numbers of additional surveys sent to states with proportionately more AwwaRF subscribers. Five surveys were sent to Canadian AwwaRF subscribers in four provinces.

The utility survey form shown in Figure 2.1 was reviewed and approved by the AwwaRF PAC, then transmitted to this distribution list at the end of March 2001. EE&T received responses from 46 utilities in 30 states, representing 81 water treatment plants (WTPs). This is a response rate of about 30 percent, which is a good return rate given the complexity of survey. These 81 responses, coupled with the AWWSC internal survey, represent responses from 266 WTPs in 38 states, as demonstrated in Figure 2.2. Respondents mostly included surface water treatment facilities, but also included a few groundwater facilities. Facility sizes ranged from less than 1 mgd to greater than 100 mgd.

In general, utilities dedicated a significant amount of effort to their survey responses and included a high level of detail in many cases. Numerous utilities described frustrating experiences encountered due to contaminants and other foreign material in treatment chemicals delivered to their facilities. Many utilities reported that they have either implemented or are contemplating the use of stricter specifications or testing of chemical deliveries. Utilities mentioned that they are seeking guidance on how to set up these procedures, and are interested in sharing information about common experiences with other utilities.

Additional information requested in the survey questionnaire included items such as specifications, bid lists (lists of chemical suppliers), and written procedures for assessing whether to accept or reject chemical deliveries. About 80 percent of the survey responses included electronic or hard copies of one or more of these requested documents. Many respondents appended copies of analytical data (about half), and most described some of the typical and the unusual problems encountered with delivery and use of water treatment chemicals.

COMBINED SURVEY RESULTS: AWWSC AND AwwaRF MEMBER SURVEYS

Results from both the AWWSC internal survey and from the AwwaRF member survey are described in this section of the report. In most instances, the findings from both sets of surveys were similar, and therefore, results from each survey have been combined.

Treatment Chemical Usage by Survey Respondents

Approximately 30 different treatment chemicals, and about 80 different products from about 90 different manufacturers or suppliers, were identified during the AWWSC and AwwaRF surveys. The greatest number of chemicals (up to 14 different treatment chemicals at one plant) are used at surface water treatment plants.

The most commonly used treatment chemicals according to the AWWSC and AwwaRF surveys include:

- Chlorination agents (roughly 60 percent chlorine gas and 40 percent hypochlorite)
- Fluoridation chemicals (almost exclusively hydrofluorosilicic acid)
- Aluminum sulfate (alum)
- Organic polymers
- Phosphate-based corrosion inhibitors
- Lime
- Caustic soda
- Iron-based coagulants
- Polyaluminum chloride
- Potassium permanganate
- Other miscellaneous (copper sulfate, sodium aluminate, sodium chloride, etc.)

Alum was the most commonly used metal-salt coagulant cited in the surveys, reported about three times more often then iron-based coagulants, and about four times more frequently than other aluminum-based coagulants. Organic polymers were reportedly used about as often as alum, except that facilities often used more than one type of polymer and applied these polymers at multiple points in the treatment process.

Problems Identified by Utilities During Chemical Delivery and Application

Although some of the information included in this section is based on a review of plant records, most is based on personal recollections of individual personnel at a given facility. This means that a few of the problems are associated with events that occurred a number of years ago. However, it is important to note that most of the incidents reported in this chapter have occurred in the past few years, and many of these incidents continue to re-occur periodically. Some of the products involved in these incidents have been identified as NSF certified products, though most utility responses were not specific as to whether they involved NSF certified products or not.

Although the presence of specific contaminants is important, especially those with regulatory consequences like arsenic, contamination from dirt, dust, debris, and sediment was the most frequently occurring problem for most utilities. These problems not only make the quality of the treatment chemical questionable, but also can potentially interrupt the proper functioning of the chemical feed equipment by clogging storage facilities, piping, valves, and feed pumps. Operational problems due to gross chemical contamination have been experienced at various treatment plants. Typical origins of these foreign materials were identified as: 1) the manufacturing process, 2) delivery truck or tank (improper cleaning between deliveries), or 3) the hose used to transfer chemical from the delivery truck to the storage facilities (improper or incomplete cleaning between uses).

Although there were a few recurring concerns associated with particular manufacturing processes, and isolated incidents associated with manufacture of other specific water treatment chemicals, the most frequently documented problems occurred after the chemical left the manufacturing facility. These transport-related incidents occurred frequently enough to concern water utility personnel across the country. Most of the transport-related incidents occurred in non-dedicated vehicles. This term refers to the fact that a particular chemical delivery vehicle could carry a number of different types of chemicals over a short period of time.

The most frequently reported survey problems, are summarized in Table 2.1.

Table 2.1

Problems encountered during delivery or use of water treatment chemicals

		Foreign material						Contaminants					
Treatment chemical	Damaged containers	Sediment/solid only	Floating only	Unspecified	Wrong chemical delivered	Crystallization	Moisture	Organic only	Inorganic only	Unspecified	Unspecified load rejection	Transfer hose	Improper cleaning of transport container
Dry alum		X					X	X					
Liquid alum		X	X	X		X		X	X	X		X	X
Polyaluminum chloride			X			X							
Sodium aluminate		X											X
Iron-based coagulants	X	X	X		X				X				X
Polymers		X	X	X	X	X		X		X			X
Chlorine gas	X			X				X		X			X
Hypochlorite		X	X	X					X	X			
Sodium hydroxide		X	X		X	X		X	X	X			X
Lime products		X			X			X	X			X	X
Soda ash		X						X	X				
Corrosion inhibitors		X	X	X				X		X	X		X
Fluoridation chemicals	X	X	X					X	X	X	X	X	X
Potassium permanganate							X						
Sodium silicate					X								

“X” indicates at least one reported incident in utility survey.

The following list summarizes some of the survey responses describing problems or incidents associated with a broad spectrum of treatment chemical products. These include:

- Sediment or contamination in delivered chemicals due to residue from material previously transported in delivery vehicle. Incidents appeared to be the result of improperly or incompletely cleaned delivery vehicles
- Contaminated, improperly cleaned, or improperly maintained transfer hoses. Reported incidents included contamination from residue remaining in hoses from previous use plus breakdown and release of materials from the hose itself
- Attempted delivery of damaged containers of all types
- Improperly or inadequately equipped and trained delivery personnel
- Lack of accountability by third-party transport companies
- Delivery of wrong material or delivery to wrong address
- Attempted delivery of solid treatment chemicals with damaged or torn containers or lumpy (caked) material
- Delivery personnel delivering, or attempting to deliver, chemicals into the wrong storage area
- Rushed delivery of bulk dry materials (i.e., pressure too high). This resulted in abrasion damage, blown pressure relief valves, and release of dust plumes
- "Blow out" of plugged chemical discharge hoses into the atmosphere, discharging debris onto driveways and neighboring buildings
- Problems with use of non-standard totes, especially those that are too big and difficult to maneuver due to their weight
- Dirt, dust, and debris encountered in a variety of liquid and solid chemicals including sediment, tar-like lumps, newspaper, plastic, and rocks
- Other common delivery problems such as deliveries received outside of normal operating hours, or attempted deliveries by vendors that do not comply with specified unloading requirements

The above difficulties occurred with many different kinds of chemicals. Survey responses dealing with problems associated with specific treatment chemical products are listed separately below. The problems listed above referring to general problems with all types of chemical products were based on responses from multiple utilities. Most of the problems identified below associated with individual treatment chemical products are also based upon similar responses received from multiple utilities, though some responses refer to isolated incidents that occurred at one specific treatment plant.

Alum

- One incident where delivered alum that did not meet AWWA specifications resulted in high finished water turbidity and high residual aluminum levels. To rectify this situation, the utility implemented stricter specifications and periodic analysis of delivered product.
- One incident of an oily substance in delivered liquid alum that coated the storage tank. This material was not detected in the finished water. Analysis revealed that composition of the material was similar to gear oil. The source of the problem was traced to a bad seal in the mixer at the manufacturing facility.
- Crystallization of liquid alum caused upset and disruptions of coagulant feed rate at one utility, which consequently impacted finished water quality. The problem was traced by the manufacturer to the quality of ore used to make alum (this respondent did not indicate whether alum was standard or iron-free alum — see discussion in Chapter 3). Other utilities have also reported feed rate problems due to crystallization of alum that occurs two to three times per year.
- One incident where discolored material was first accepted, then later rejected, with the supplier required to clean out storage tank.
- One alum delivery was rejected when odor was detected prior to unloading. The cause of the odor was later determined to be the result of improper cleaning of a pesticide product transported previously in the delivery vehicle.

- Organic material was found in delivered liquid alum products during two separate incidents, presumably from residual material left in delivery vehicle from previous shipments.
- Reports of sediment in liquid alum deliveries, including residuals from improperly cleaned transfer vehicles and transfer hoses, or breakdown/release of transfer hoses.
- One utility reported deliveries of dry bagged alum with grease contamination. In other instances, crushed plastic debris in dry alum have caused dry chemical feed system to clog.
- One reported incident of iron bacteria in alum, resulting in clogged transfer line. Response did not indicate whether iron bacteria growth occurred before or after delivery.

Ferric Chloride and Ferric Sulfate

- Frequent reports of clogged ferric chloride storage tanks and feed pumps due to sediment in delivered ferric chloride solutions. Multiple plants have indicated multiple problems with ferric chloride from various vendors. Several plants have successfully identified ferric problems prior to unloading. Inspection of a sample has indicated suspended solids, discoloration, and tar-like material. Other facilities have found problems only after excessive buildup of solids in storage tanks and feed systems have clogged piping and caused an interruption in coagulant feed.
- One incident where a shipment of ferric chloride contained plastic liners from soda pop bottle caps and large volumes of dirt. The manufacturer's iron source for the ferric chloride was old metal soda pop bottle caps. The caps were stored outside on the ground and dirt was scooped up with bottle caps when loaded into the ferric chloride production process. The plastic liners of the bottle caps were not dissolved by the hydrochloric acid during the ferric chloride manufacturing process, and the particular production process did not include a filtration step prior to delivery. The plastic bottle cap liners plugged chemical feed pumps and the dirt in the chemical created even more problems.

- Discolored ferric chloride with large amounts of sediment was rejected after partial unloading of shipment. The manufacturer investigated the matter and reported that the manufacturing process had "not been complete".
- One utility switched from alum to ferric chloride for a brief period. After receiving too many complaints of discoloration and staining in the distribution system, the utility switched back to an aluminum-based coagulant. Another utility reported a similar situation where it switched from alum to ferric chloride and had customer complaints due to staining problems in residential plumbing fixtures. However, the main reason this utility switched back to alum was not due to customer complaints, but because of chemical feed problems experienced as a result of settleable solids present in the ferric chloride.
- One utility reported "rare" incidents where sediment in ferric sulfate created "pumping reliability" problems.
- In two instances, contaminants in treatment plant residuals were traced to contamination of ferric coagulants with arsenic and cadmium.

Sodium Aluminate

- Sediment in sodium aluminate delivery due to improperly cleaned delivery containers.

Chlorine Gas

- Carbon tetrachloride was detected in 1-ton chlorine cylinders, resulting from a chlorine manufacturing processes that includes a processing step using liquid carbon tetrachloride to recover chlorine. This was reported by at least six utilities in the AwwaRF survey alone. One utility reported that carbon tetrachloride was always detected in finished water during these incidents, occasionally at concentrations above the MCL. This includes incidents that have occurred since 1998.
- Many utilities report occasionally receiving damaged 1-ton chlorine cylinders.

- One utility reported problems with chlorine cylinder valves inserted too deep to allow proper attachment of chlorine supply lines.
- One large utility had problems with contaminated deliveries of liquid chlorine. This utility now uses rail cars dedicated to transporting liquid chlorine to and from their treatment plant.

Sodium and Calcium Hypochlorite

- One utility reported occasionally finding twigs, sticks, and other debris in sodium hypochlorite.
- Some problems were reported when utilities did not specify filtration of sodium hypochlorite prior to shipment (sediment and discoloration). Survey respondents reported that altering specifications to require filtration prior to shipment has eliminated these problems.
- Concern about bromide, bromate, chlorite, and chlorate in sodium hypochlorite and calcium hypochlorite (see Chapters 3 and 4).
- One instance of sodium hypochlorite delivery rejected because of detected odor.
- One utility had data demonstrating that incremental increases in bromate levels found after ozonation, versus levels in its finished water reservoir, may have been due to use of sodium hypochlorite for residual disinfection.
- One discolored sodium hypochlorite shipment traced to "problem" with manufacturing process. "Problem" later identified as a wrench that had accidentally dropped into manufacturer's storage tank.
- Trace metal contamination of sodium hypochlorite has been identified at some facilities.

Sodium Chlorite and Other Chlorite Salts

- One incident where sodium chlorite crystals were dropped into a container of alum resulting in release of chlorine gas.

Potassium Permanganate

- Product from sources outside the U.S. have contained lumped or caked product. (see Chapter 3 for a discussion of manufacturing processes for U.S. versus non-U.S. products).

Corrosion Inhibitors

- One utility reported problems with feeding zinc orthophosphate due to solids clogging feed equipment. The source of solids was traced to manufacturer QA/QC problems.
- Phosphate arrived with hydrogen sulfide (rotten egg) odor and residual material (apparently polymer) remaining from a previous shipment.
- Multiple facilities have experienced buildup of particulates and foreign materials in corrosion inhibitor feed systems.

Hydrofluorosilicic Acid and Sodium Fluorosilicate

- Frequent low levels of black particles in hydrofluorosilicic acid deliveries attributed to breakdown of tank liner in delivery vehicle. One respondent characterized frequency of occurrence as "always".
- Bird's nest and dead bird in solid sodium fluorosilicate jammed and broke feed equipment. Fluoride feed was disrupted for several days during repairs. No microbial contamination of finished water was detected, though utility was concerned since this organic material was fed to the system after chlorine addition.
- One incident where plastic bags clogged feed lines during delivery of sodium fluorosilicate. Bagged material was used to supplement delivery because vendor did not have enough bulk material on hand.
- One incident of hydrofluorosilicic acid delivery with layer of waxy material of indeterminate composition.

- One facility traced the occurrence of 1,2-dichlorobenzene in the finished water to contaminated hydrofluorosilicic acid.
- Iodine contamination was identified in some fluoridation chemicals.

Organic Polymers

- One utility reported an incident where delivery of the wrong strength polymer upset the coagulation process and resulted in elevated finished water turbidity.
- Another utility lost control of the treatment process because their polymer supplier could not provide the type of polymer normally used and sent a substitute that was a completely different type of polymer.
- Chemical loads rejected at one utility when delivered product contained particulate matter or pH outside of the specified range.
- "Gooey" material in polymer shipment formed a separate phase in the storage tank and required difficult clean-up.
- Two loads of polymer were rejected when large chunks of material were found in samples that were later identified by the supplier as undissolved reactants.
- Major incident described by one respondent involved contamination from residual styrene in improperly cleaned mechanical transfer pump used to offload polymer. This polymer was used as the primary coagulant at this drinking water facility. Corrections implemented after this incident included requiring use of pneumatic (i.e., pressurized air) devices instead of mechanical pumps to off-load chemicals.
- One utility noted problems with polymer deliveries in winter. It needed to reject one load because it was frozen and could not be unloaded.

Caustic Soda

- Deliveries at one utility contained particulate matter in their caustic soda. The material was assumed to be residue from corrosion of metal storage tanks and piping during manufacturer storage and transport of the caustic soda (the particulate matter had a high iron content). A replacement shipment was received in time to avoid an interruption in service.

- One utility noted that occurrences of delivery of the wrong strength product were more frequent with drum deliveries than bulk deliveries. There were several reported situations with drum deliveries where the correct strength material was provided, but was mislabeled as the incorrect strength.
- One sodium hydroxide delivery was rejected because of discoloration. Another load was rejected at another utility because black, tar-like solids were found floating in the caustic delivery.
- Temperature of sodium hydroxide was sometimes a problem when the temperature exceeds 115°F (45°C) because it melted plastic delivery piping.
- In one instance, an unknown "cleaning solution" was inadvertently dumped into a caustic storage tank resulting in need to flush out and clean the feed system and tanks before the facilities could be returned to service.

Lime and Hydrated Lime

- One incident where lime delivery was contaminated with urea fertilizer (apparently residue from previous delivery in delivery vehicle). The incident created problems in finished water with maintenance of free chlorine residual.
- Several shipments of hydrated lime from one vendor contained large volumes of sand.
- Problems with pebble lime delivery a couple of times where delivery hose burst, spraying lime on buildings and surrounding area. Heat from lime generated localized fires in several cases.
- In two instances, contamination in treatment plant residuals was traced to contamination of lime with arsenic and zinc.
- One respondent reported finding pieces of screen about three times per year in lime shipments.

- Excessive grit, dust, and metallic debris in lime shipments caused one utility to implement random testing to try to get supplier to exercise better quality control. Presence of these materials damaged slaking equipment.
- Corn discovered in a lime storage silo several weeks after delivery. The material was traced to improper cleaning of the delivery vehicle. The vendor paid removal and disposal costs and the utility now requires dedicated trucks for all deliveries.
- One utility reported recurring problems controlling dust release during lime deliveries. This utility is considering a switch from lime to caustic soda because of these difficulties.

Soda Ash

- One utility reported periodically finding chunks of asphalt or stone in soda ash.

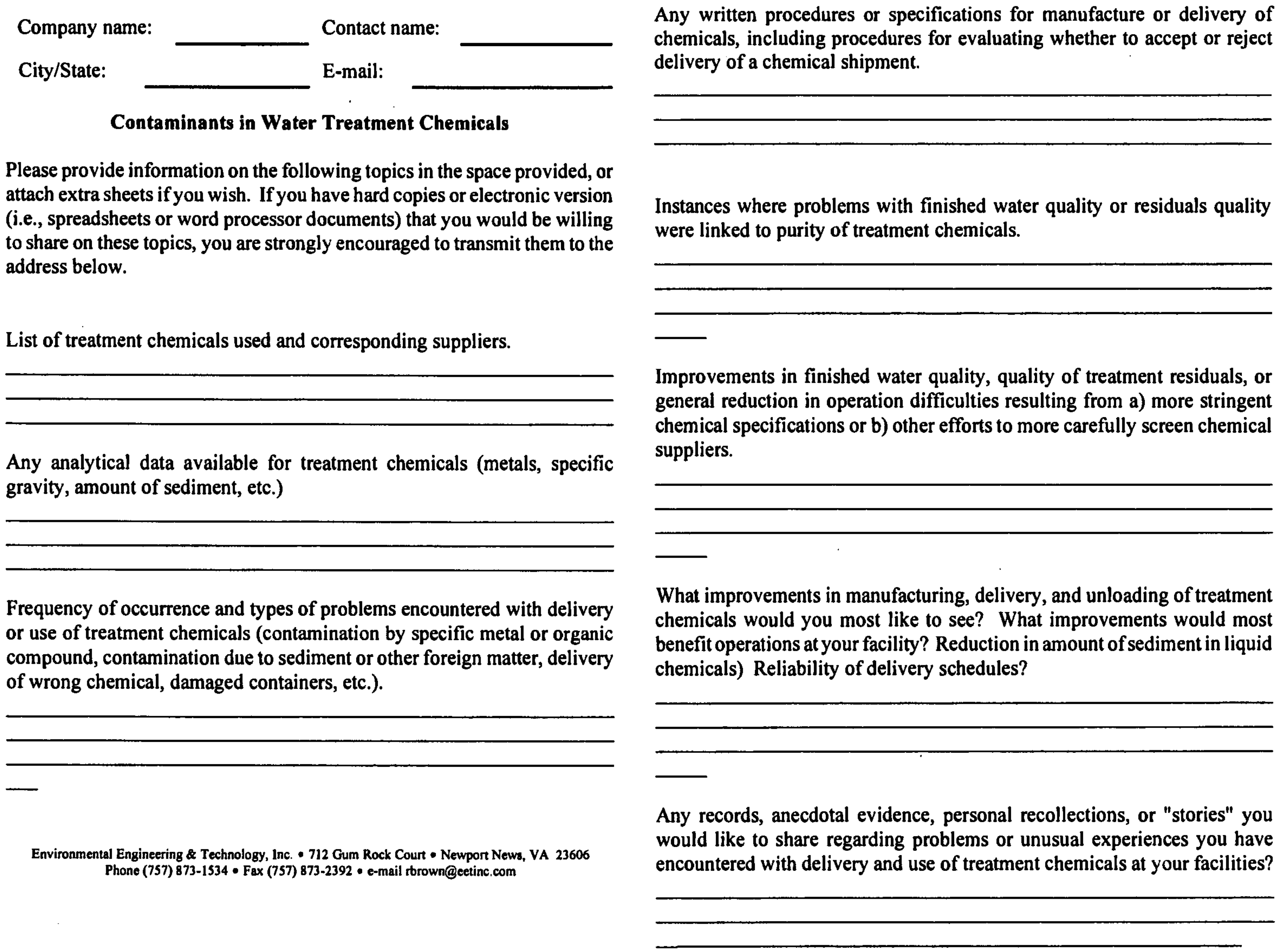
Polyaluminum Chloride

- One utility reported having difficulties with high basicity polyaluminum chloride that always precipitated in storage tanks. It switched to a lower basicity product and reduced the frequency of this problem to once or twice a year.

SUMMARY OF FINDINGS FROM SURVEYS

Results from the utility surveys suggest that most utilities generally do not have major, recurring problems with treatment chemicals. However, when contamination or other deficiencies in delivered treatment chemicals did occur, operations and water quality were sometimes impacted. However, utilities with some form of an inspection and evaluation program, including simple activities like checking paperwork, visual inspections, and basic simple physical/chemical tests, did frequently identify these deficiencies before plant operations were impacted.

When contamination or other deficiencies in treatment chemical quality were detected, the source was sometimes traced to a deficiency in the manufacturing process. However, the overwhelming majority of these contamination incidents were transport-related. Often the source of the problem was residue remaining in the delivery vehicle from a previous delivery.



Company name: ____________ Contact name: ____________

City/State: ____________ E-mail: ____________

Contaminants in Water Treatment Chemicals

Please provide information on the following topics in the space provided, or attach extra sheets if you wish. If you have hard copies or electronic version (i.e., spreadsheets or word processor documents) that you would be willing to share on these topics, you are strongly encouraged to transmit them to the address below.

List of treatment chemicals used and corresponding suppliers.

Any analytical data available for treatment chemicals (metals, specific gravity, amount of sediment, etc.)

Frequency of occurrence and types of problems encountered with delivery or use of treatment chemicals (contamination by specific metal or organic compound, contamination due to sediment or other foreign matter, delivery of wrong chemical, damaged containers, etc.).

Environmental Engineering & Technology, Inc. • 712 Gum Rock Court • Newport News, VA 23606
Phone (757) 873-1534 • Fax (757) 873-2392 • e-mail rbrown@eetinc.com

Any written procedures or specifications for manufacture or delivery of chemicals, including procedures for evaluating whether to accept or reject delivery of a chemical shipment.

Instances where problems with finished water quality or residuals quality were linked to purity of treatment chemicals.

Improvements in finished water quality, quality of treatment residuals, or general reduction in operation difficulties resulting from a) more stringent chemical specifications or b) other efforts to more carefully screen chemical suppliers.

What improvements in manufacturing, delivery, and unloading of treatment chemicals would you most like to see? What improvements would most benefit operations at your facility? Reduction in amount of sediment in liquid chemicals) Reliability of delivery schedules?

Any records, anecdotal evidence, personal recollections, or "stories" you would like to share regarding problems or unusual experiences you have encountered with delivery and use of treatment chemicals at your facilities?

Figure 2.1 Example utility survey

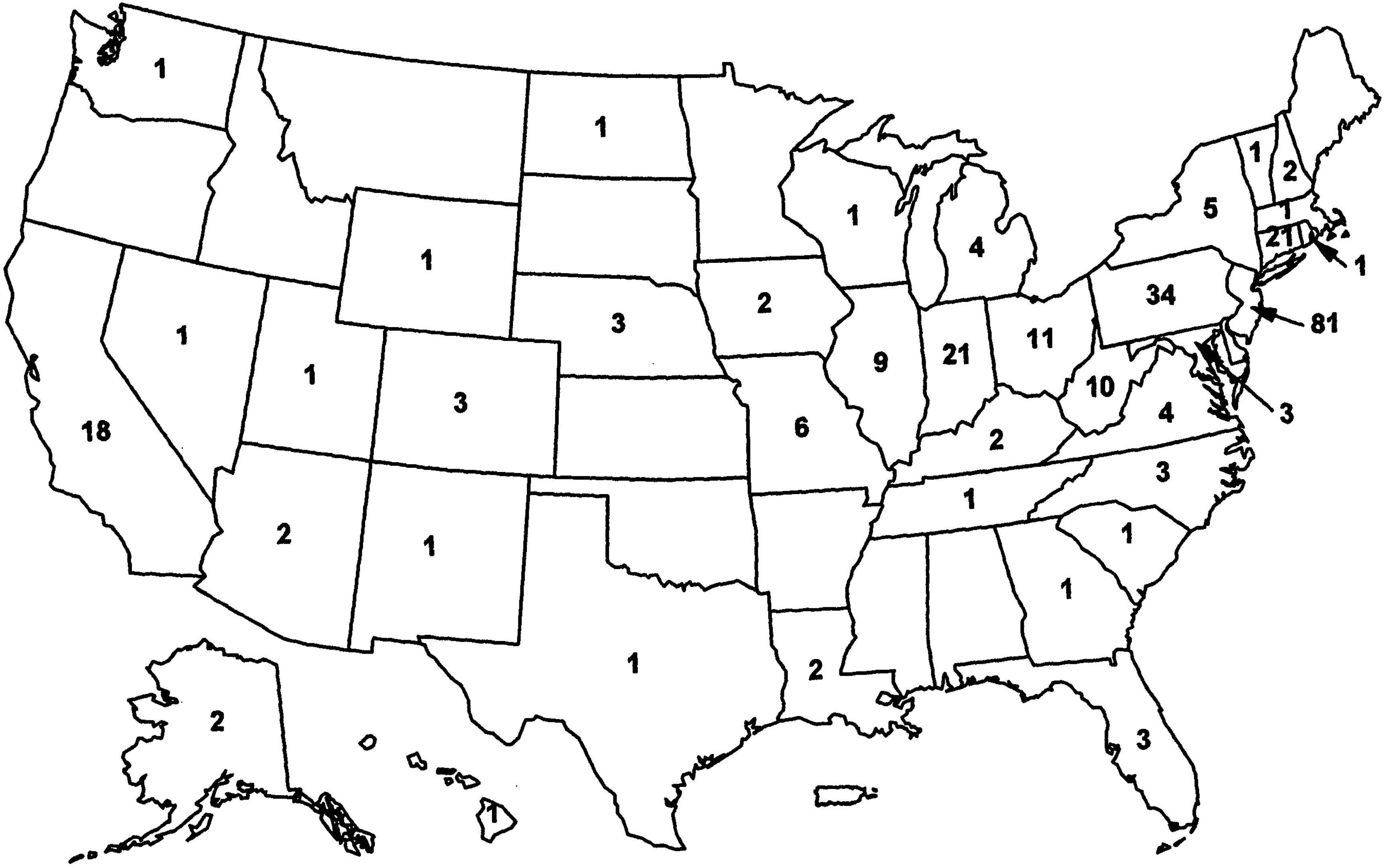


Figure 2.2 Utility survey responses (266 facilities in 38 states)

CHAPTER 3

MANUFACTURING PROCESSES FOR PRODUCTION OF WATER TREATMENT CHEMICALS

INTRODUCTION

This chapter contains descriptions of raw materials and manufacturing/refining processes used to produce drinking water treatment chemicals. The goal of this chapter is to outline the potential sources of contamination during the manufacturing process, how manufacturers control these sources, and what characteristics are indicators that the production process has not gone to completion, or that something else has gone wrong during production. One anticipated use of this information is as a consolidated reference source outlining production processes associated with commonly used treatment chemicals.

This chapter also forms an integral part of the plan to describe potential contamination sources in commonly used water treatment chemicals, and ways that water utilities can limit the occurrence of contamination events. Chapter 2 dealt mostly with transport-related contamination sources, while this chapter describes sources associated with manufacture of these chemicals. Manufacturing process descriptions presented in Chapter 3 can aid in the understanding and evaluation of data presented in Chapters 4 and 5 on composition and fate of trace contaminants. This chapter is intended as a resource guide for readers. Some will want to focus on learning more detailed information about several specific chemical manufacturing processes, while others will be interested in only one.

INFORMATION SOURCES

Information included in this chapter was derived from input by manufacturers of different water treatment products, and from review of pertinent literature. Various manufacturers and suppliers provided information about aspects production processes and raw materials associated with their products, but did not share proprietary information. A general survey of chemical manufacturers was also conducted, providing an opportunity for them to directly participate in this project. The manufacturer's survey was conducted after the utility survey and some of those responses were provided to specific manufacturer's thereby giving them an opportunity to provide their perspective.

Survey forms were sent to at least one contact at 30 manufacturers or suppliers, some of which manufacture a few specialized water treatment chemicals and others who handle a wide variety of products. The number of responses was disappointing with five manufacturers and two trade organizations returning their forms. However, these sources were able to provide information about iron and aluminum-based coagulants, caustic soda, chlorine and hypochlorite, potassium permanganate, sulfuric acid, phosphate-based corrosion inhibitors, and fluoridation chemicals.

DESCRIPTION OF MANUFACTURING PROCESSES

Production or refining processes for the following treatment chemicals are described in the following discussion:

- Hydrochloric and sulfuric acids
- Aluminum-based coagulants
- Iron-based coagulants
- Fluoridation chemicals
- Phosphate-based corrosion inhibitors
- Chlor-alkali related products (chlorine, caustic soda, sodium hypochlorite)
- Lime
- Soda ash
- Potassium permanganate

Generally, higher quality raw materials result in higher quality finished products. Conversely, none of the manufacturing processes for treatment chemicals can compensate for poor quality raw materials to reliably produce finished products of suitable quality.

Production of organic polymers is not discussed in this report. A more detailed discussion of polymer manufacture is provided in another AwwaRF project entitled "Reaction of

Polyelectrolytes with Other Water Treatment Chemicals and Subsequent Effects on Water Quality and Operational Efficiencies".

Hydrochloric and Sulfuric Acids

Sulfuric acid (H_2SO_4) is used occasionally to depress pH during coagulation, but hydrochloric acid (HCl) is not normally used as a water treatment chemical. However, certain hydrochloric acid products are NSF certified for drinking water use, primarily for pH adjustment and corrosion/scale control. However, since these acids are used during the manufacture of other chemicals used in water treatment, their quality indirectly impacts the presence of contaminants in certain water treatment chemicals. For example, aluminum- or iron-based coagulants contain either chloride or sulfate, depending upon which acid was involved in the manufacturing process. These acids can induce contamination in water treatment chemical agents due to either contaminants in the acids themselves, or their ability to leach contaminants from other raw materials involved in the process.

Hydrochloric acid can be produced from salt and sulfuric acid, from direct reaction of hydrogen and chlorine gases, and as a byproduct from various processes (including production of chlorinated hydrocarbons). Sulfuric acid, on the other hand, is typically produced from sulfur oxide gases. Sulfur oxide gases can be produced intentionally from iron-sulfide (pyrite) or other sulfur containing materials. These gases can also be recovered as off-gases from processes where air pollution or other waste generation control concerns mandate their removal prior to discharge into the environment (see Figure 3.1). In this report, the term "regen acid" refers to sulfuric acid recovered from sulfur oxide off-gases, while the term "virgin acid" refers to products resulting from burning of sulfur, hydrogen sulfide, or metal sulfides. Most virgin and regen acids are high quality products. Poorer quality sources of hydrochloric and sulfuric acids result when they are recovered or reclaimed after one or more previous uses in other processes.

Hydrochloric and sulfuric acid can potentially contain trace metal or other contaminants depending upon the source of the material, especially if the acids are recovered or reclaimed from other processes. Hydrochloric acid is also a much stronger leaching agent than sulfuric acid. Consequently, hydrochloric acid can potentially leach more trace metals and contaminants from the same starting material. For this reason, coagulants formed from hydrochloric acid have greater potential for contamination, and consequently, greater care should be exercised when selecting raw materials to react with this acid to form coagulants. For example, high quality aluminum hydroxide should be used to produce polyaluminum chloride. Arsenic, mercury, and lead are potential contaminants in sulfuric acid, depending upon the source. Potential contaminants in hydrochloric acid include residual chlorine or sulfuric acid, and certain organic contaminants (e.g. monochloroacetic acid).

Aluminum-Based Coagulants

The most commonly used aluminum-containing coagulant is aluminum sulfate, also called alum. Some utilities use sodium aluminate ($NaAlO_2$). Numerous different polyaluminum chloride (PACl) products are also used, including occasional use of a specific product called ACH (aluminum chlorohydrate). Polymeric aluminum sulfate compounds are analogous to PACl, but are rarely used. Figure 3.2 outlines the manufacturing processes and raw materials for each of these coagulants. Other related aluminum containing coagulants include polymeric aluminum silica sulfate, sodium aluminum sulfate, and polymeric aluminum hydroxychlolosulfate.

Most aluminum sulfate or alum is produced either directly or indirectly from bauxite. Some alum is produced directly from bauxitic clay (kaolin). It can be packaged as either a solid (i.e., dehydrated) or liquid (i.e., solution) form. The liquid form has 18 waters of hydration and typically comes in solutions that are about 50 percent water and have an active strength of about 7.5 to 8.5 percent as Al_2O_3 (40,000 to 45,000 ppm as aluminum on a wet weight basis). Dry alum has 13 to14 waters of hydration and has an active strength of 17.0 to 17.5 percent as Al_2O_3 (90,000 to 93,000 ppm as aluminum on a dry weight basis). Dry alum is typically packaged as either a ground or lump solid. However, both liquid and granular alum have similar aluminum content when both are expressed on a dry weight basis.

Standard alum, in either solid or liquid form, is produced by leaching bauxite or bauxitic clay with sulfuric acid (see Figure 3.3). Metallurgical grade bauxite could be used to make standard alum, except that too many trace metals, particularly iron, can be leached by the sulfuric acid. Standard alum is typically made from either bauxitic clay or from chemical grade bauxite.

Iron-free or low-iron alum is made by first reacting metallurgical grade bauxite with caustic (the bayer process) to form liquid aluminum hydroxide, liquid sodium aluminate, and a solid residue (see Figure 3.2). Hydrochloric and sulfuric acids can leach trace metals, especially iron, during direct acid leaching of bauxite as described for standard alum. However, these trace metals are not leached by caustic, and thus are concentrated in the solid residue rather than in the liquid aluminum hydroxide product. The aluminum hydroxide and sodium aluminate generated from this process are both relatively high quality products, though high sodium levels in sodium aluminate can limit some of its applications. Aluminum hydroxide is used to make a variety of aluminum metal products, but can be further processed to produce water treatment coagulants such as low-iron alum, polyaluminum chloride, or aluminum chlorohydrate. Low-iron alum is produced by reacting aluminum hydroxide with sulfuric acid, with some manufacturers incorporating minor quantities of recycled aluminum hydroxide or acid. Another use of aluminum hydroxide is to react it with caustic to produce additional sodium aluminate.

Polyaluminum chloride products are formed by reacting aluminum hydroxide with hydrochloric acid to form aluminum trichloride, which in turn is reacted with either aluminum metal or aluminum hydroxide to form PACl. Some manufacturers supplement the PACl production process with recycled materials. Polyaluminum chloride products are polymeric compounds with the general chemical formula $Al_n(OH)_mCl_{3n-m}$. The actual formulation of a given product tends to be a closely guarded trade secret, and involves a complex series of reactions that are incompletely understood, even by the manufacturers. Due to the diversity of polyaluminum chloride products, they are often described by citing their "basicity" as defined below:

$$\text{Basicity} = \frac{100 \text{ percent} \bullet m}{3n}$$

For example, typical polyaluminum chloride products are usually about 50 percent or about 83 percent basicity (i.e., $Al_2(OH)_3Cl_3$ for 50 percent basicity and $Al_2(OH)_5Cl$ for 83 percent basicity). Lower basicity products are produced by reacting aluminum hydroxide with hydrochloric acid, plus an additional aluminum source. Higher basicity polyaluminum chloride products are formed by adding greater and greater amounts of aluminum metal. The highest basicity products are also called aluminum chlorohydrate (ACH). ACH is not only used for water treatment, but is also produced in large quantities for anti-perspirant manufacture.

Direct reaction of sulfuric acid with aluminum metal is possible, but is not suitable for commercial production of alum. Hydrochloric acid is a much stronger leaching agent than sulfuric and can be used to leach aluminum from aluminum metal. Thus, although aluminum metal is not used in alum manufacturing, hydrochloric acid plus aluminum metal and aluminum hydroxide are used to manufacture PACl and ACH.

For standard alum, sources of contamination are the aluminum source (bauxite or bauxitic clay) or sulfuric acid. Arsenic, mercury, and lead are possible contaminants in the acid, depending upon the source. However, if virgin or other high quality sulfuric acid sources are used, the main source of contamination for standard alum is the aluminum source. Characteristics of standard alum from bauxite include: greater than 500 mg/kg iron, greater than 20 mg/kg chromium, higher titanium, and potential for high insoluble matter content. Characteristics of alum produced from bauxitic clay are similar, except that there is generally higher potassium, higher sodium, and more waste generated (the rule of thumb is a 1:1 ratio of waste versus alum production using bauxitic clay, versus a 1:3 ratio of waste versus alum production using bauxite).

Low-iron alum has much lower potential for contamination than standard alum, especially when high quality (i.e., non-reclaimed) source materials are used. In such instances, low-iron alum is characterized by higher sodium, high zinc, ten times less iron, and lower trace metal concentrations than from standard alum. Since polyaluminum chloride is produced by a reaction pathway that is similar to low-iron alum, as indicated in Figure 3.2, its trace metal content is similar to low-iron alum. Polyaluminum chloride does have higher aluminum content than most low-iron alum products, and the aluminum content increases as PACl basicity increases. Potential contaminants from recycled aluminum raw materials are limited only by the source of the recycled material. These could include trace metals, radionuclides, or dioxin.

Iron-Based Coagulants

Iron-based coagulants used in drinking water include ferric chloride ($FeCl_3$) and ferric sulfate, ($Fe_2(SO_4)_3$), with ferrous forms ($FeCl_2$ and $FeSO_4$) occasionally used for wastewater and other applications. Sources of iron-based coagulants are summarized in Figure 3.4 and include:

- Ferric chloride and ferric sulfate by-products produced during titanium dioxide manufacture
- Ferric chloride and ferric sulfate produced by oxidation of ferrous salts contained in steel pickle liquor
- Direct hydrochloric and sulfuric acid leaching of iron ore and scrap iron.

The direct acid-leaching approach closely resembles leaching of bauxite with sulfuric acid to produce standard alum. Approximately 80 to 95 percent of the ferric sulfate material suitable for potable water use is produced by direct acid leaching of iron ore and scrap. By contrast, only minor amounts of ferric chloride are produced by the direct acid leaching of iron ore and scrap. Most ferric chloride is produced either as a by-product from the titanium dioxide manufacturing process (about 25 to 33 percent of ferric chloride produced in the U.S. and Canada) or by oxidation of ferrous iron in steel pickle liquor (about 67 to 75 percent of U.S. and Canadian ferric chloride production).

Details regarding the manufacture or recovery of iron salts from these three process approaches are described separately below. The bulk of this discussion focuses on issues related to quality of the iron source. However, the quality of the acids and oxidants involved can also impact the quality of the finished iron coagulant product and should not be overlooked as a potential source of contaminants.

Iron Coagulants Produced as By-Products from Titanium Dioxide Manufacture

Titanium dioxide (TiO_2) is principally produced for use as a white pigment in paint, plastics, paper, and inks. It can also be used as catalyst, sunblock, or in ceramic manufacturing applications. The titanium dioxide production process can proceed along one of two pathways, one involving oxidation with chlorine, and the other involving acid leaching with sulfuric acid. These pathways both involve multi-step processes in which titanium and iron-containing ores are either leached with acid or oxidized with chlorine, then processed and separated to produce the desired titanium dioxide final product. Along these pathways, ferric salts are produced as by-products; ferric sulfate in the sulfuric acid process and ferric chloride in the chlorine process. Historically, the acid leaching process has been most common, but production by oxidation with chlorine has become more prevalent because of environmental and regulatory difficulties in disposing of wastes from the acid leaching process. However, improvement in handling of the acid leaching process wastes has progressed so that there is no longer any inherent difference in the environmental acceptability of the chlorine oxidation versus acid leaching process wastes (Kroschwitz 1994, 1999).

Potential contaminants in TiO_2-derived ferric coagulants, in addition to trace metals leached from the source minerals, include hexachlorobenzene, dioxin, and radionuclides. In fact, TiO_2-derived ferric products have been discontinued for use in poultry feed supplements because of risk for bioconcentration of these organic contaminants.

Another unresolved question related to ferric coagulants produced by this process is how factors that optimize the quality of the quality of the desired final titanium dioxide product impact the quantity and quality of ferric by-products. For example, according to the literature, the titanium containing minerals used in the chlorine oxidation process have a lower iron content than do the titanium minerals used in acid process.

Iron Coagulants Produced from Steel Pickle Liquor

Pickling agents can be alkaline, but most are acidic. These acids are used to remove surface oxides, also called rust, scale, and smut, that form at the surface of steel products. Sulfuric acid has been used in the past, but hydrochloric acid is the preferred pickling agent because it is a much more aggressive. The pickling agent must be aggressive enough to remove the rust, but must be controlled by temperature, concentration, degree of agitation, use of inhibitors, or other measures to limit or prohibit leaching of the base metal.

The acidic steel pickle liquor contains dissolved ferrous salts and other dissolved metals. This pickle liquor contains roughly 10 to 12 percent iron in the form of ferrous chloride when hydrochloric acid is used as the pickling agent. When this pickle liquor source is used for ferric chloride production, material is shipped to a ferric coagulant production facility where it is supplemented by iron ore/scrap sources, concentrated using a proprietary method, filtered, oxidized with chlorine, and then returned to the same vehicles that delivered the original pickle liquor.

According to a manufacturer of ferric salts using oxidation of steel pickle liquor, customer complaints due to delivery of ferric coagulants with large amounts of sediment led to the inclusion of the filtration step in the early 1990's. This filtration step has significantly reduced the number of complaints. Most sediment in current deliveries of finished product are believed to be residue remaining in delivery vehicles from preceding deliveries of unoxidized steel pickle liquor. The industry tends to use the same vehicles both to transport unoxidized steel pickle liquor to the ferric chloride manufacturing facility, and to transport the finished oxidized products. Some installations pass the finished product through a bag filter or strainer while loading the delivery vehicle, if requested by the client.

As with other water treatment products, the quality of iron coagulants is only as good as the starting raw materials. In general, none of the manufacturing and refining process for water treatment chemicals can make up for a contaminated or otherwise poor quality starting material. However, although nominally a by-product of the steel making process, high quality ferric chloride products produced from steel pickle liquor are used successfully by numerous drinking water utilities throughout the U.S. The mechanisms by which ferric chloride produced from steel pickle liquor can produce a higher quality product than could be produced by direct acid leaching of iron ore and steel products are summarized below:

- Different iron ores can contain many other metals in the lattice. These metals can end up in the ferric coagulant following direct acid leaching of the ore. The quality of iron salts produced by direct acid leaching can be improved by starting with a higher quality ore.
- Steelmaking involves purifying the ore to create a product with elemental carbon added to iron to make steel. Many of the metallic impurities from the ore are removed and discarded during the steelmaking process. Therefore, processed steel

contains fewer impurities than the original ore, assuming that the steel is not supplemented with molybdenum, chromium, nickel or other metals.

- "Pickling" of steel involves using hydrochloric or sulfuric acid to remove oxides that form at surface of steel. Iron oxides and a few other metallic oxides formed at the steel surface are likely to contain less trace metal constituents than the parent steel itself because many of the trace constituents deep inside the steel matrix will not be able to migrate to the steel surface.
- Therefore, by this argument, ferric chloride from steel pickle liquor is of higher quality than ferric chloride from the parent steel or from the original ore. The reason for this is that the proportion of iron to trace constituents gets progressively greater in moving from ore to steel to surface oxides.

Pickle liquor from surface treatment of most steel products can be suitable for further processing to produce ferric salts for drinking water treatment, especially if the coagulants meet NSF criteria. One exception is iron coagulants produced from steel pickle liquor resulting from acid leaching of steel wire. Since lead is used as a "drawing" agent to produce steel wire, iron-based coagulants produced from pickle liquor resulting from surface treatment of wire products will contain too much lead to pass NSF certification for use at drinking water plants, though these products are sometimes suitable for wastewater applications.

Iron Coagulants Produced from Direct Acid Leaching of Iron Ore and Scrap

Two U.S. patents that describe similar methods for production of ferric sulfate from iron ore/scrap and sulfuric acid are available in Everill (1989) and Hjersted (1987). The process summarized by Everill involves a pressurized batch process in which prescribed amounts of reactants are processed under specific temperature and pressure conditions for a specified period of time. In this case, the reactants include a proprietary processed ore with a large fraction of the iron already in the ferric state. Additional reactants include water and acid.

The process described by Hjersted includes a sequence of batch reactions in which iron ore and scrap are leached with acid, then processed through two oxidation steps, followed by filtration, and finally dilution to required strength. The preliminary oxidation step uses air or molecular oxygen for about a half day, followed by a second stage oxidation with hydrogen peroxide for about three hours. A critical method to control the correct proportion of reactants, specifically in order to avoid adding excess acid, is to assay the iron ore and scrap sources for iron content so that stoichiometric amounts of acid can be added (1.5 moles of sulfuric acid per mole of iron in iron source). This not only optimizes the amount of acid reactant used, but also limits potential for over dosing with acid, which can create problems with pH control when the iron product is used to coagulate water.

Both of these manufacturing processes depend upon using high quality iron ores of known iron content, coupled with strict control of temperature, pH and reaction time. Proper temperature control is critical for all methods of producing iron-based coagulants (including those from steel pickle liquor) because this influences conversion of ferrous to ferric iron. That conversion not only impacts the ability of the product to act as coagulant, but also impacts subsequent production of sediment. In general, more ferrous iron content results in more sediment generation during storage.

Fluoridation Chemicals

Chemical forms of the three commonly used fluoridation chemicals include hydrofluorosilicic acid (H_2SiF_6), sodium fluorosilicate (Na_2SiF_6), and sodium fluoride (NaF).

Of the three major potential fluoridation chemicals, sodium fluoride is the least used in the U.S. Sodium fluoride is produced by reacting hydrofluoric acid with either soda ash or caustic soda. The hydrofluoric acid is produced by reacting sulfuric acid with fluorospar (CaF_2). Some sodium fluoride products are NSF certified, including materials imported from China, Japan and Europe. However, these sodium fluoride sources are much more expensive than the fluoride available as a by-product from the phosphate production process. Therefore, there is little current use of sodium fluoride in U.S. for drinking water treatment.

Sodium fluorosilicate and hydrofluorosilicic acid used in drinking water are produced almost exclusively as by-products from phosphate manufacture by the "wet process". This process is outlined in Figure 3.5 and in EFMA (2001). The fluoride source used to make hydrofluorosilicic acid and sodium fluorosilicate originally comes from minerals called apatites, otherwise know as phosphate rock. Apatites contain calcium, phosphate, and iron, plus variable amounts of silicon, magnesium, potassium and chloride. The bony structure of human teeth are composed of apatite.

Apatite is not used with the goal of producing hydrofluorosilicic acid or sodium fluorosilicate. Apatite is used to produce phosphoric acid, which in turn is used to make fertilizer or animal feed supplements. It could also be further purified for direct use as phosphoric acid, or for production of other phosphate-containing products, such as food and beverage additives. Unfortunately, one of the processing steps typically used in phosphoric acid production involves acidification of a silicon- and fluoride-containing waste stream. This leads to liberation of acutely toxic hydrofluoric and silicon tetrafluoride gases (see Figure 3.5). Consequently, part of the cost of phosphoric acid production using this method is the need to clean the silicon tetrafluoride- and hydrofluoric-containing gas with a wet scrubber. The liquid product from the wet scrubber contains a large amount of hydrofluorosilicic acid. The liquid product can be processed for direct use a hydrofluorosilicic acid product for drinking water use, or the liquid recovered from the scrubber can be reacted with soda ash to form solid sodium fluorosilicate. Although other processes can produce either hydrofluorosilicic acid or sodium fluorosilicate, products from these other pathways cannot be produced as cheaply as the fluoride products derived as by-products from phosphoric acid production.

Hydrofluorosilicic acid is one of the products that is routinely delivered in dedicated vehicles, principally because the product is so corrosive that it must be delivered in special lined tanker trucks. One supplier notes that about 80 percent of their deliveries to water utilities, or to intermediate distributors/resellers, are made in dedicated vehicles. The manufacturers and suppliers are aware of the problems utilities have noted with delivery of black particulates in hydrofluorosilicic acid. A suggested inspection and preventative maintenance program to reduce these incidents would include periodic replacement of lining material in delivery vehicles, periodic inspection of interior, filtration at the point of origin, and filtration of the product as it is off-loaded at the water treatment plant.

Phosphate-Based Corrosion Inhibitors

Phosphoric acid is the second largest volume mineral acid produced, after sulfuric acid (Kroschwitz 1999). Figure 3.6 briefly summarizes the two major processes for phosphoric acid production. The first is a high cost, energy-intensive, and high purity "thermal" process, while the second is the much more widely used "wet" process. The wet process phosphoric acid or WPA is produced by leaching phosphate-containing minerals called apatites with dilute sulfuric acid, as illustrated previously in Figure 3.5. Unpurified WPA can be used to make fertilizer or animal feed supplements. Wet process phosphoric acid can be purified to roughly the same quality as acid from the much more expensive and energy intensive thermal process, and then used for manufacture of products requiring higher purity, including food and beverage additives. One family of phosphate products of interest to water industry are phosphate-containing corrosion inhibitors, including zinc orthophosphate produced by reacting zinc sulfate ($ZnSO_4$) with trisodium phosphate (Na_3PO_4).

The wet process is less expensive but does create some waste products that must be properly managed. To minimize quantities of these wastes, some manufacturers recycle a portion of the processing water and use it to dilute the sulfuric acid rather than using tap water or other water sources. Recycling these waste streams not only reduces consumption of water, but also leads to recovery of residual phosphorus in these waste streams. Unfortunately, these waste streams also contain silicon and fluoride, which evolve as acutely toxic silicon tetrafluoride and hydrofluoric acid gases when acidified. These gases need to be passed through a scrubber before the gas can be discharged. Fortunately, the fluoride collected in wet scrubber can be recovered as hydrofluorosilicic acid or sodium fluorosilicate and can be used for drinking water fluoridation.

Chlor-Alkali and Related Products

The chlor-alkali processes involve the electrolytic conversion of chloride salt brines into chlorine gas, hydrogen gas, and either caustic soda or caustic potash, depending upon whether sodium chloride or potassium chloride salt brines is used. Synonyms for caustic soda and caustic potash are sodium hydroxide and potassium hydroxide, respectively. Other chlor-alkali products include hydrochloric acid, soda ash, sodium hypochlorite, and calcium hypochlorite.

Since sodium chloride salt brines are the most commonly used, this discussion focuses on sodium-containing products, rather than potassium-containing products. Potassium would replace sodium if potassium chloride salt brine was used instead of sodium chloride. Figure 3.7 illustrates the products produced from chlor-alkali processes using sodium chloride.

There are three alternative chlor-alkali processes, including mercury cell, diaphragm cell, and membrane cell. The main similarity between these processes is that chloride ion is oxidized to chlorine gas at the anode in each system. The principal difference between the three processes is the method by which chlorine gas produced at the anode is separated from sodium hydroxide products at the cathode. A fourth type of electrolytic cell will also be described that does not have any means of separating chlorine gas and sodium hydroxide so that they are free to react to form sodium hypochlorite.

Manufacture and Separation of Sodium Hydroxide and Chlorine Gas

Information sources presented here on chlor-alkali processes were derived from Kroschwitz (1994) and White (1986). The three chlor-alkali processes are described first, followed by a separate section describing production of hypochlorite.

The membrane and diaphragm processes both involve a single electrolytic cell with a barrier placed so that chlorine gas production at the anode can be isolated from the cathode. Figure 3.8 includes a schematic representation of these two processes.

In each process, sodium chloride brine is fed to the process and chlorine gas electrolytically produced at the anode ("+" electrode) as described by the following reaction:

$$2Cl^- \rightarrow Cl_2 + e^-$$

The chlorine gas is saturated with water vapor, and therefore, is processed by a cooling step followed by a "drying" step (acidification with concentrated sulfuric). The dry chlorine gas is then liquified (compressed) so that it can be stored and shipped as liquid chlorine. Off-gas from liquefaction, i.e., chlorine gas that is not liquified, plus other mixed gas streams that contain chlorine gas can be processed using a carbon tetrachloride (CCl_4) adsorption process as outlined in Figure 3.9.

For example, residual chlorine gas in nominally "empty" tank cars and chlorine cylinders can be recovered along with other chlorine-containing gas streams. Chlorine in a mixed gas stream is dissolved in liquid carbon tetrachloride, while the remaining gases can be vented to the atmosphere (Kroschwitz 1994). Chlorine gas is then separated from carbon tetrachloride and returned to the liquefaction process while carbon tetrachloride is recovered and recirculated back to the chlorine gas recovery process.

The reaction at the cathode in either the diaphragm or membrane electrolytic cell is as follows:

$$2H_2O \rightarrow H_2 + 2\,OH^-$$

The hydrogen (H_2) gas is recovered at the cathode. The solution on the cathode side of the membrane cell is about 30 percent sodium hydroxide, which is typically cooled and concentrated to about 50 percent strength. The solution on the cathode side of the diaphragm cell is a mixture of about 10 percent sodium hydroxide and 15 percent sodium chloride. Sodium chloride is separated and returned to the electrolytic process as salt brine, while the remaining sodium hydroxide is chilled and concentrated to about 50 percent strength.

The mercury cell involves two sequential electrolytic processes as outlined in Figure 3.10. The first electrolytic cell is commonly designated as the "electrolyzer" while the second cell is referred to as the "decomposer". Chlorine gas is produced in the electrolyzer, and sodium hydroxide plus hydrogen gas produced at the decomposer.

Historically, the mercury process was used more frequently in Europe and Japan, whereas the diaphragm process was predominant in North America, principally due to the availability of asbestos sources in U.S. In 1988, U.S. capacity for chlorine was 13 x 10^6 tons/yr, with 80 percent produced west of the Mississippi River. Mercury and diaphragm processes predominate east of the Mississippi River, while west of the Mississippi River >85 percent of chlorine production is from diaphragm process. In the future, additional capacity or replacement of existing capacity is expected to be produced by new membrane units (Kroschwitz 1994).

Manufacture of Sodium or Calcium Hypochlorite

Sodium hypochlorite ($NaOCl$) can be produced directly in an electrolytic cell similar to the membrane or diaphragm cell, except that products at the anode and cathode are not isolated so that sodium hypochlorite can be produced instead of separately producing hydrogen gas, chlorine gas, and sodium hydroxide solution. Alternately, sodium hypochlorite can be produced by reacting chlorine gas produced from any process with sodium hydroxide produced separately by any process.

The production of sodium hypochlorite can take place at a centralized location, with solutions up to 15 percent available as shipped from the production facility to the customer. The difficulty with this is that sodium hypochlorite solutions are unstable and can quickly decay, thereby lowering effective strength and leading to production of undesirable decay products (chlorite [ClO_2^-] and chlorate [ClO_3^-]). The stability of sodium hypochlorite deteriorates at higher concentrations, higher temperatures, longer storage times, lower pH, or when trace amounts of iron, copper, nickel, or cobalt are present.

Therefore, an alternative to shipping sodium hypochlorite from a centralized manufacturing plant is to generate sodium hypochlorite on-site, at the drinking water treatment plant. On-site sodium hypochlorite generators can be either direct electrolytic cells, i.e., similar to a diaphragm cell without a diaphragm, or the on-site process can actually be a composite process where a membrane electrolytic cell, for example, produces chlorine gas and sodium hydroxide separately, and then chlorine gas and sodium hydroxide products are reacted in a separate part of the process to produce sodium hypochlorite (White 1986). In either situation, raw materials needed are salt and water, or naturally occurring saltwater if a suitable source is available.

Calcium hypochlorite [$Ca(OCl)_2$] is produced by reacting slaked lime [$Ca(OH)_2$] with chlorine gas, produced almost exclusively on-site. Raw materials are chlorine gas and lime. Support facilities needed on-site include lime slaking equipment.

Impurities in chlorine, and sources of these impurities, are listed in Table 3.1 (table derived from White 1986). Moisture causes the most potential problems in chlorination equipment (corrosion). Other constituents of concern to drinking water operations are carbon tetrachloride (Cairo et al. 1979), chloroform and other halogenated hydrocarbons, and nitrogen chloride (NCl_3 (nuisance taste and odors, explosive hazard). Also of interest is bromine (Br_2), bromine chloride (BrC1), and other brominated contaminants in chlorine gas, including potential bromate (BrO_3^-) formation in sodium hypochlorite.

Table 3.1

Impurities and major sources of contamination in chlorine (derived from White1986)

Impurities

Gases = CO_2, H_2, 0_2, N_2, NCl_3

Volatile liquids and solids = Br_2, CCl_4, $CHCl_3$, HCl, H_2O, CH_2Cl_2, C_6Cl_6, C_2Cl_6

Solids = $FeCl_3$, $Fe_2(SO_4)_3$, H_2SO_4

Sources

- Moisture entrapment during packaging
- Ammonia in brine
- Organic impurities in salt
- Graphite from carbon anodes in all processes, or from packed beds in the mercury process
- Hydrocarbons from lubricants, pump seals and packing, etc.
- Chlorine gas recovery system (CCl_4) - See Figure 3.9
- Chlorine used for drinking water needs to be segregated from Cl_2 gas recovery process (because of potential CCl_4 contact), though AWWA Standard B301 allows use of chlorine gas from these sources if CCl_4 is measured and found below 100 ppm (otherwise, CCl_4 in Cl_2 does not have to be measured)

Impurities in sodium hypochlorite that are of particular concern in drinking water applications include chlorite, chlorate, and bromate. Chlorite and chlorate are decay products of hypochlorite ion (OCl^-) as described by Gordon et al (1995). Bromate is produced from bromide impurities in the salt used to generate chlorine gas, sodium hydroxide, and sodium hypochlorite (Chlorine Institute 1999). Chlorite and bromate levels in drinking water have primary MCLs of 1.0 mg/L as ClO_2^- and 0.010 mg/L as BrO_3^-, respectively. These MCLs are currently included in the Stage 1 DBPR, and are scheduled to be retained at these levels in the Stage 2 DBPR.

Lime

Lime (CaO), also called quicklime, is produced in a heated kiln using crushed limestone ($CaCO_3$) minerals as illustrated in Figure 3.11. Quicklime can be sold as pebble lime, or crushed to produce ground or pulverized lime. Hydrated lime, also called slaked lime, is produced by hydrating quicklime.

Trace impurities in solid CaO products can end up in $Ca(OH)_2$ products derived from these products, and these can end up in the finished water or treatment plant residuals. One utility survey respondent (Chapter 2), for example, noted an incident where arsenic and zinc contamination in residuals was traced to impurities in lime products. However, lime processing does not incorporate any steps to limit or remove these trace impurities if they are present in the raw materials. Consequently, selecting high quality raw materials is the only real defense against trace impurities for lime products.

Mechanical processing is of greater importance for lime products because of the need to limit presence of materials that can damage or inhibit slaking equipment or chemical feed equipment. However, processing steps also need to be monitored so that they do not produce unintended consequences (e.g., broken pieces of screening material in lime, as noted in the survey). However, the greatest potential source of contamination in lime products probably occurs after processing, i.e., foreign debris added during storage and transport.

Soda Ash

The two major soda ash (Na_2CO_3) sources include mined material and synthetically produced material. Most soda ash used in areas outside the U.S. have been produced synthetically using the Solvay process as outlined in Figure 3.12. However, synthetic production in the U.S. is declining due to high energy costs and environmental concerns about disposal of calcium chloride ($CaCl_2$) wastes from Solvay process. Consequently, most of the soda ash available in the U.S. is derived from mining in the western U.S. (Kroschwitz 1999, McCoy 2000, and Cunningham 2000).

As with lime, trace impurities in mined soda ash are probably mostly a function of the quality of the source, and the greatest contamination threat is foreign debris added during storage and/or transport.

Potassium Permanganate

Potassium permanganate ($KMnO_4$) is produced in the U.S., China, the former USSR (Crimea), India, Spain, and the Czech Republic. Potassium permanganate production methods include (a) liquid-phase oxidation, (b) a process called "roasting", and (c) single-stage, anodic oxidation of ferromanganese materials. The roasting process is the most common method used outside the U.S. In the U.S., potassium permanganate is manufactured using a large scale, continuous liquid-phase oxidation process. Some locations outside the U.S. also use a similar, smaller scale, liquid-phase oxidation process that involves a sequence of batch operations rather than the continuous process used in U.S. Single-stage electrolytic production of potassium permanganate is only available at one facility in the former USSR.

The liquid-phase oxidation process is outlined in Figure 3.13 from information provided by AwwaRF PAC member Mr. Phil Vella (Vella 2000), complimented by information available in the literature (Kroschwitz 1994). This process starts with oxidation of manganese oxide (MnO_2) ore and caustic potash (KOH) in the presence of air, producing K_2MnO_4 as an intermediate product. This intermediate product is later oxidized in an electrolytic cell, converting K_2MnO_4 into potassium permanganate ($KMnO_4$). This material is later separated and dried to produce a dry powder shipped to the customer.

The roasting process used to manufacture most products outside the U.S. involves high temperatures and high caustic potash (KOH) concentrations to produce potassium permanganate ($KMnO_4$) from manganese oxide (MnO_2) as illustrated in Figure 3.14. The process uses two sequential roasting kilns in place of the "liquid-phase oxidizer" and "K_2MnO_4 separator" steps in the liquid-phase oxidation process described in Figure 3.13. One difference between the two processes is that the roasting process includes two intermediate products (K_2MnO_4 and K_3MnO_4) instead of just one (K_2MnO_4) in the liquid-phase oxidation process. The rate-determining step for the roasting process is typically the rate at which water is removed from the K_3MnO_4 intermediate product. Larger diameter roasting kilns are being used in new installations to more finely distribute the KOH-H_2O-MnO_2 spray in order to reduce the amount of undesirable agglomeration of the roasted material.

The water utility survey responses frequently referenced problems feeding potassium permanganate in the past due to caked or lumped products. However, all of these incidents were described as occurring with materials manufactured outside the U.S. Furthermore, all utilities reporting problems with caking and lumped products mentioned that the problem has not occurred since they switched to suppliers of the U.S. produced product (continuous, liquid-phase oxidation process). The preceding paragraph describes some solutions that manufacturers of potassium permanganate outside the U.S., who mostly use the roasting process, are investigating to reduce the amount of lumping and caking in these other products.

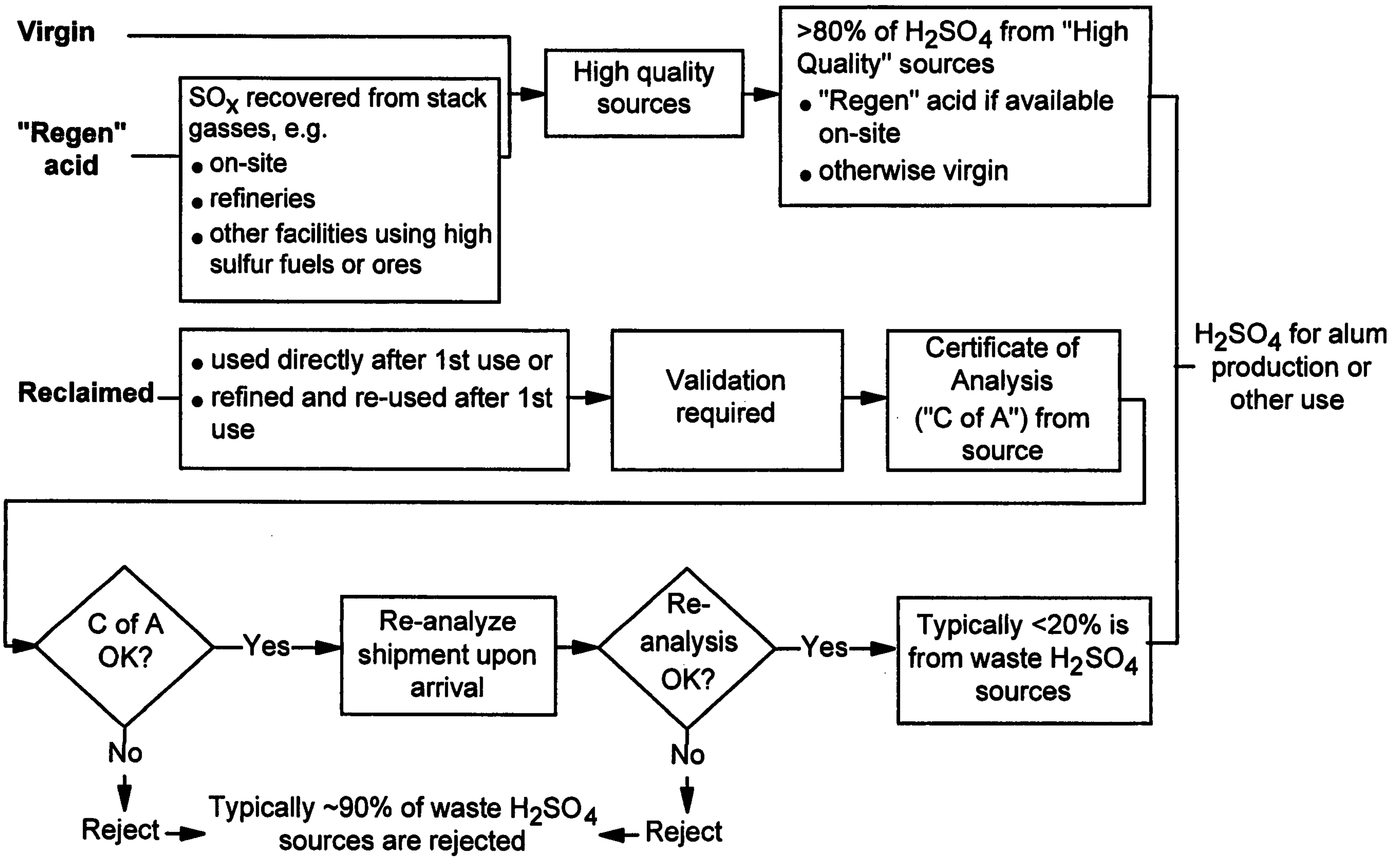


Figure 3.1 Sources of sulfuric acid used for aluminum or ferric sulfate production

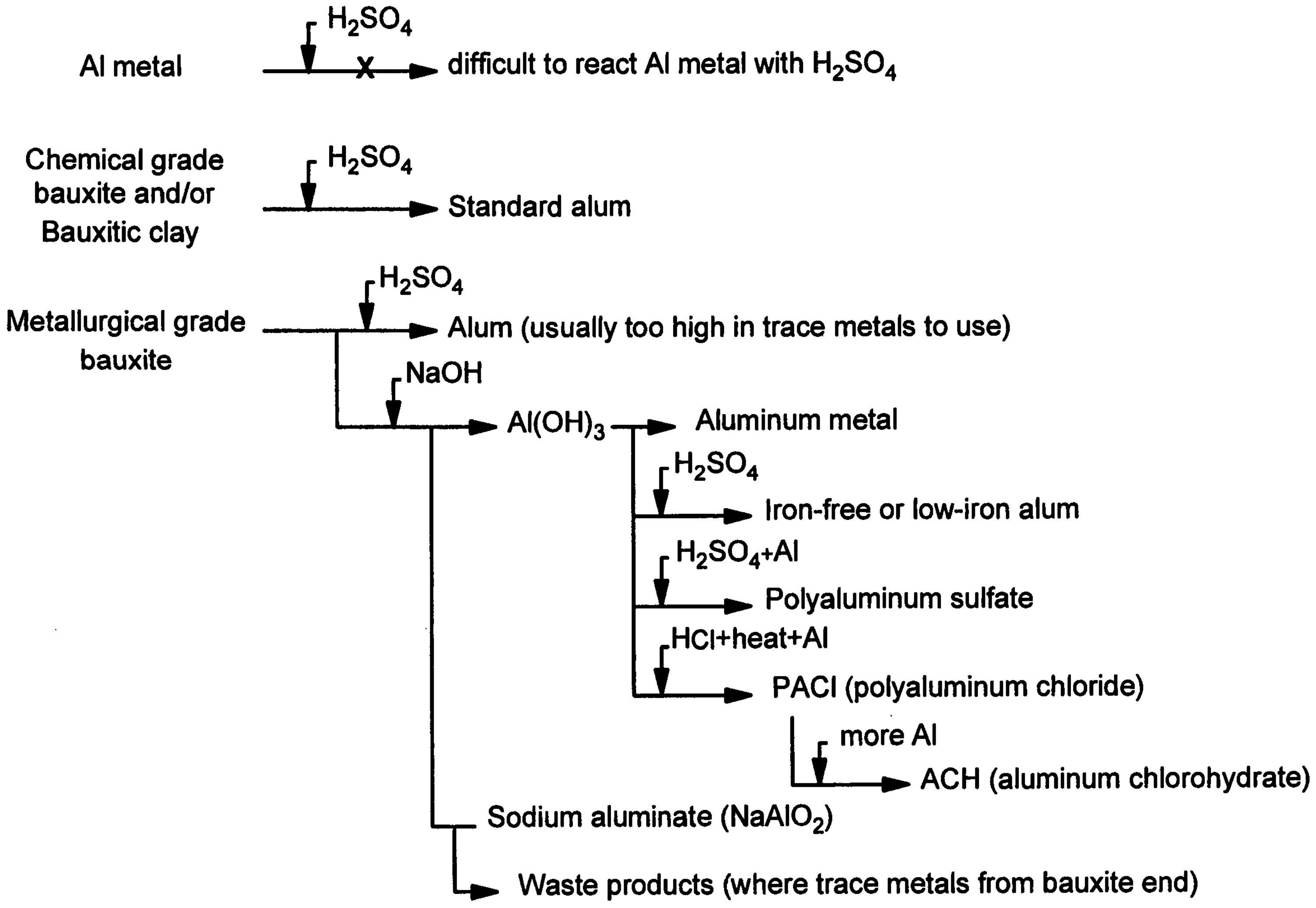


Figure 3.2 Sources and manufacture of aluminum-based coagulants

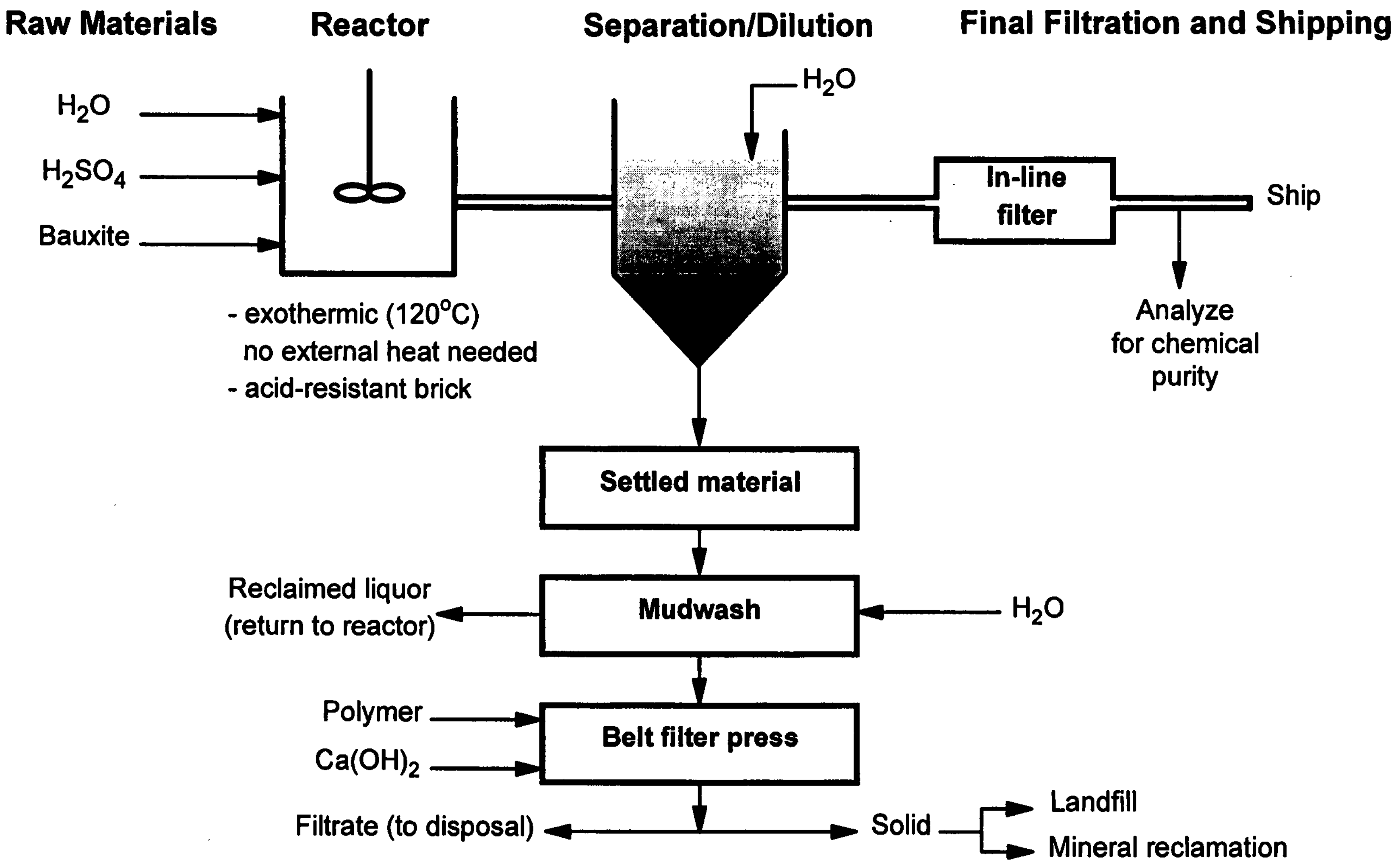


Figure 3.3 Standard alum production process

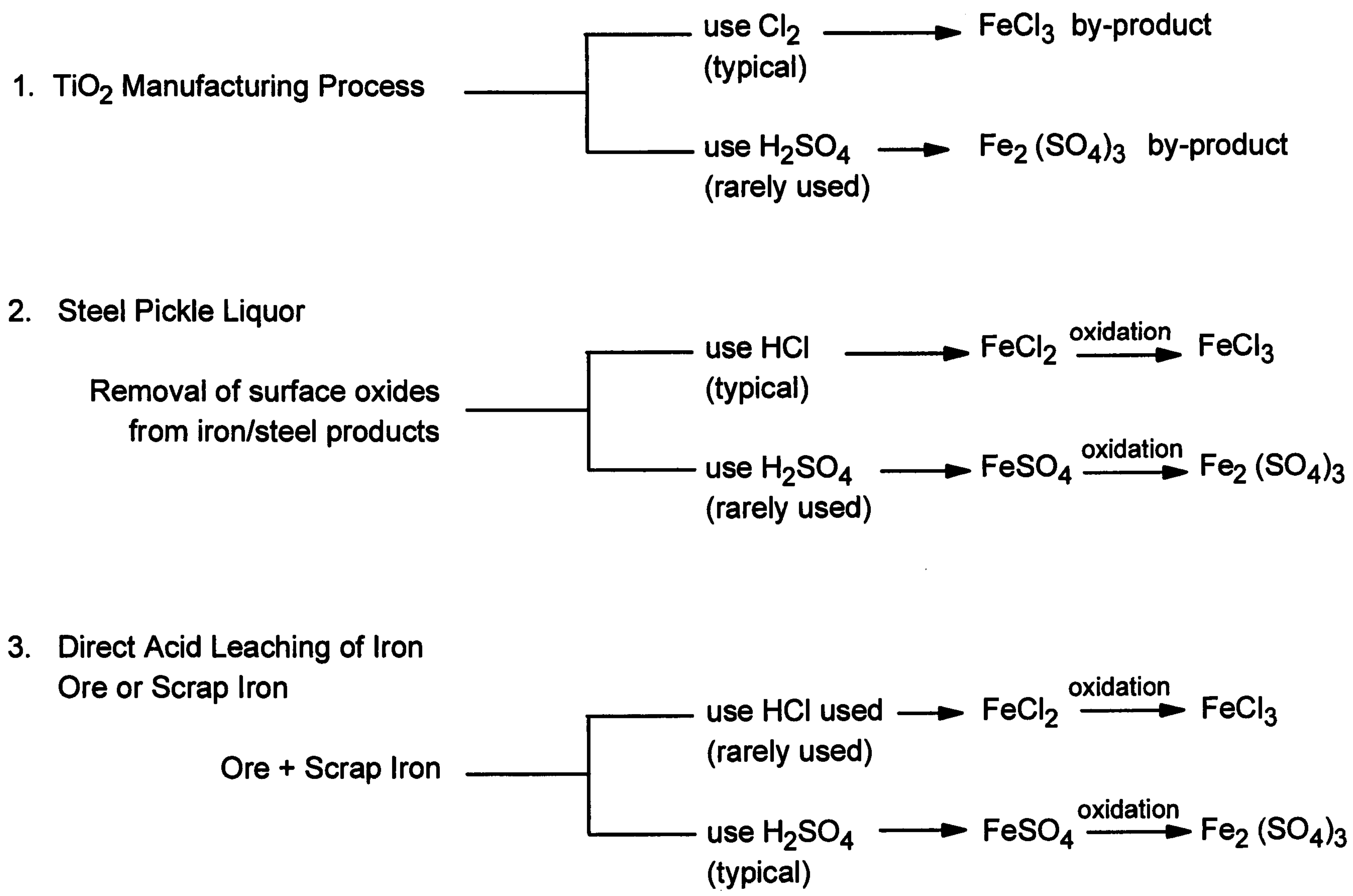
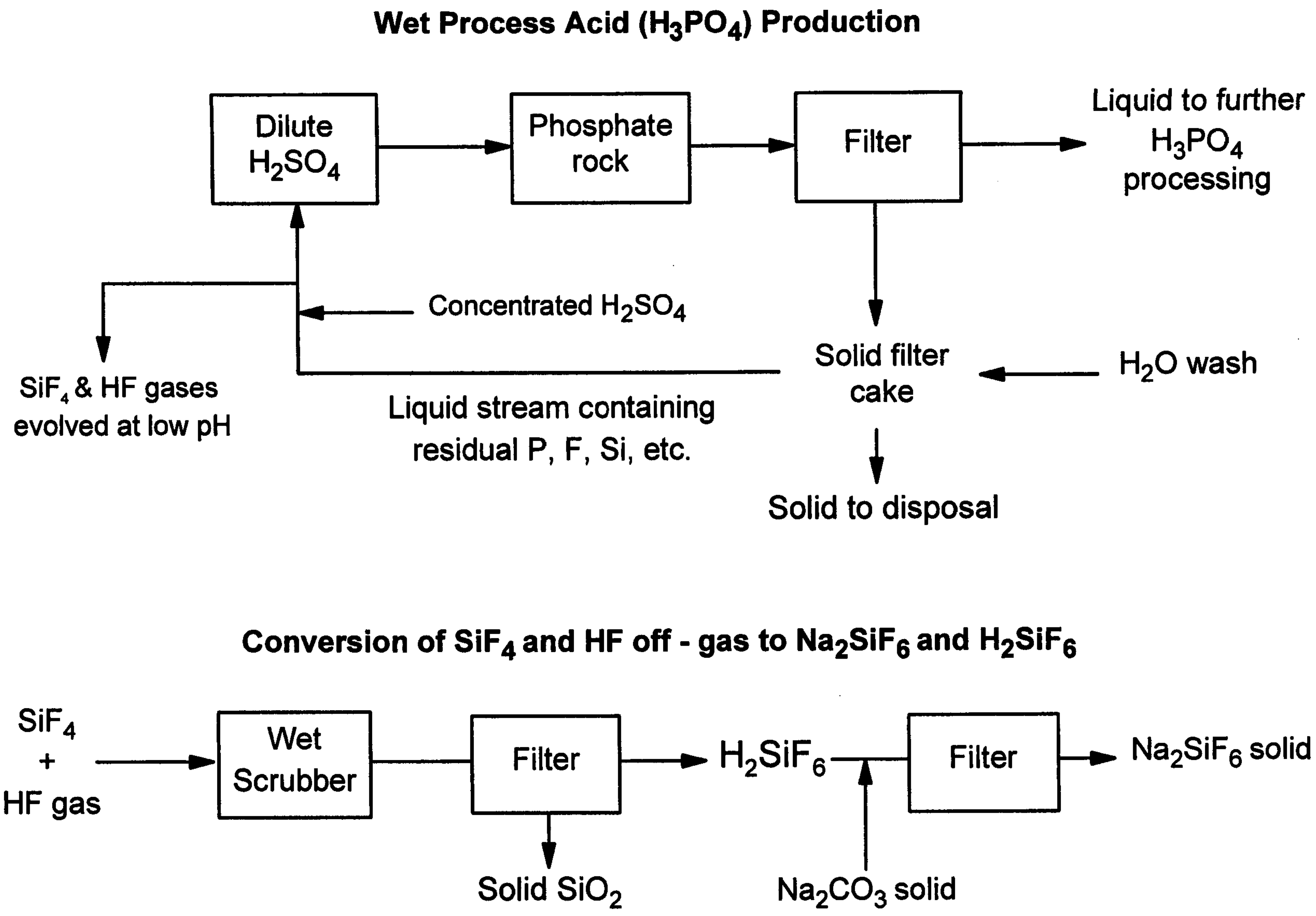


Figure 3.4 Source and manufacture of iron-based coagulants


Wet Process Acid (H_3PO_4) Production

Conversion of SiF_4 and HF off - gas to Na_2SiF_6 and H_2SiF_6

Figure 3.5 Manufacture of phosphoric acid and recovery of fluoride (derived from Walker 1979)

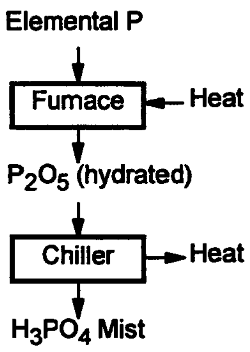
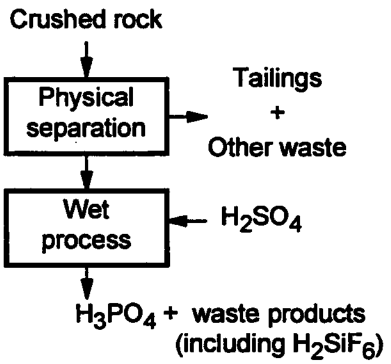
Process name	**Thermal (furnace)**	**Wet**
Source of "P"	White or Yellow elemental P	"phosphate" rock or apatites [$Ca_5(PO_4)_3F$ = fluorapatite, for example]
Percent of H_3PO_4 production (US and Worldwide)	10 Percent	90 Percent
Process description		
Comments	• called "thermal acid" • high purity • high cost • cost dependent upon electrical cost (heat)	• called "WPA" or wet-process acid • Fluoride in source rock recovered in products suitable for use in drinking water fluoridation
Purification	None required	Purified WPA is cheaper than "thermal acid" and has about the same quality
Product uses	Unpurified WPA = • Fertilizer and animal supplements Purified WPA and thermal acid = • Phosphate salts • Food + beverage additives • Other products, including corrosion inhibitors	

Figure 3.6 Phosphate and phosphoric acid manufacture

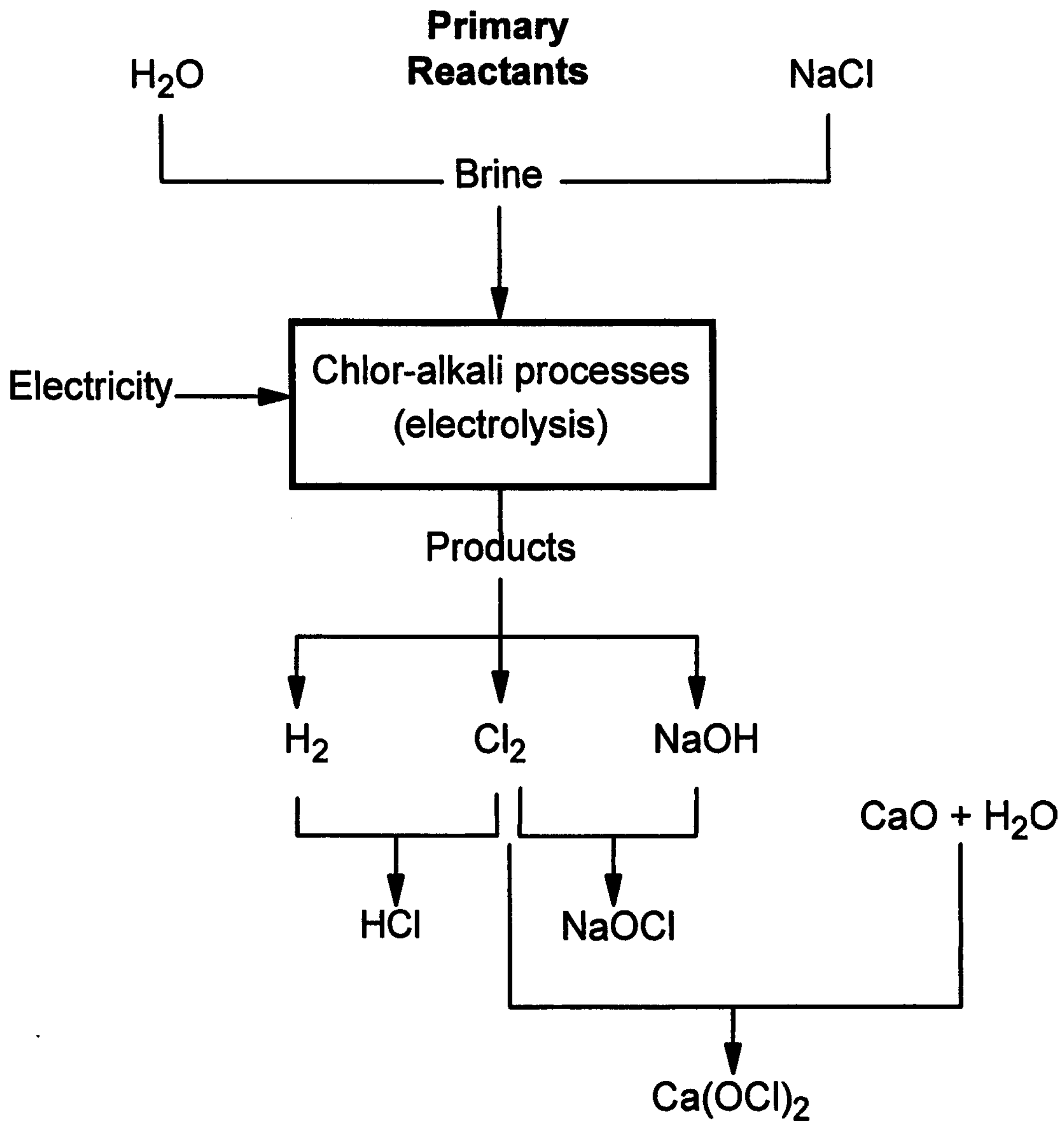


Figure 3.7 Chlor-alkali manufacturing processes

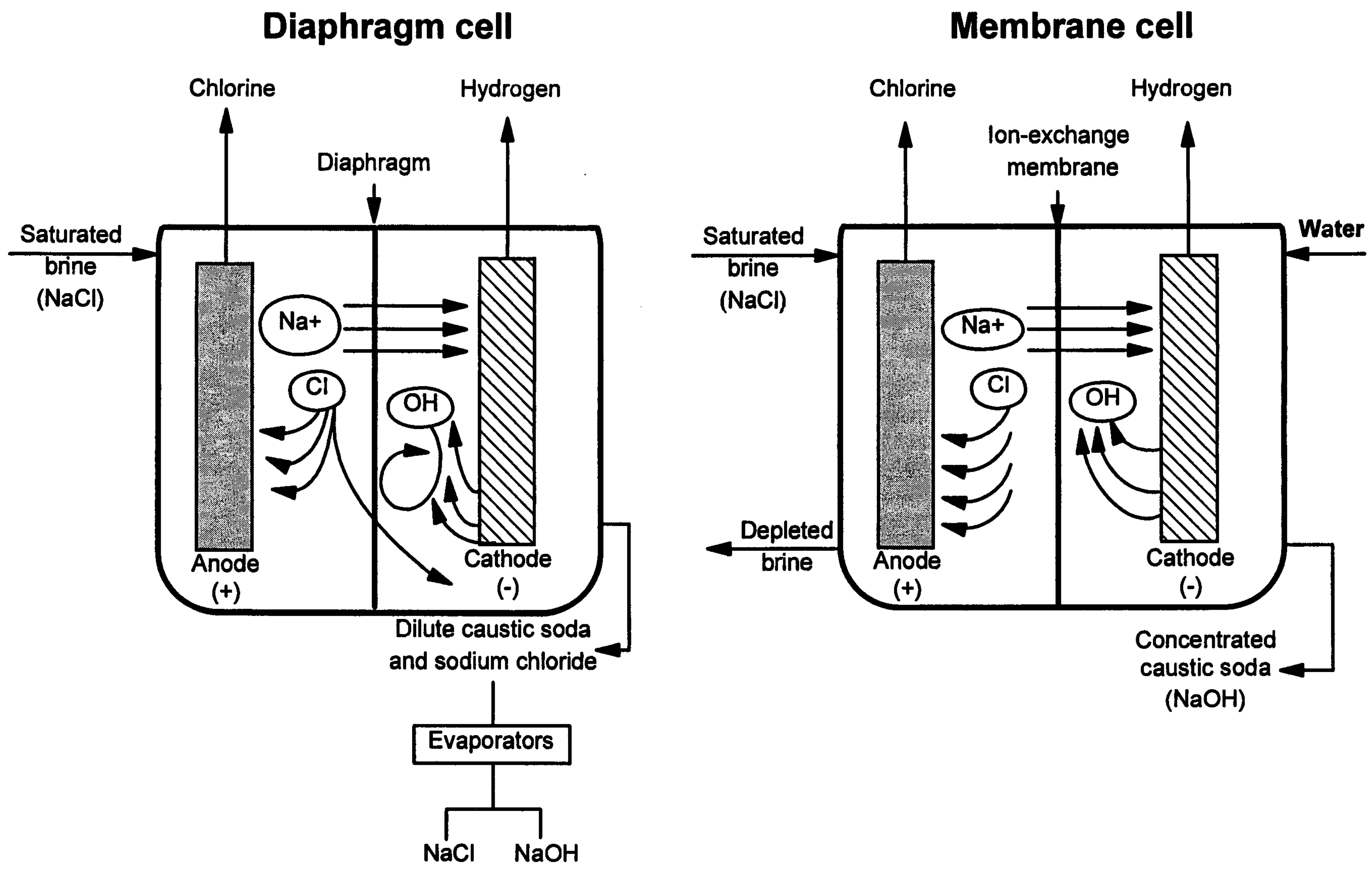


Figure 3.8 Diaphragm versus membrane electrolytic cell for chlor-alkali production (adapted from Kroschwitz 1994 and White 1986)

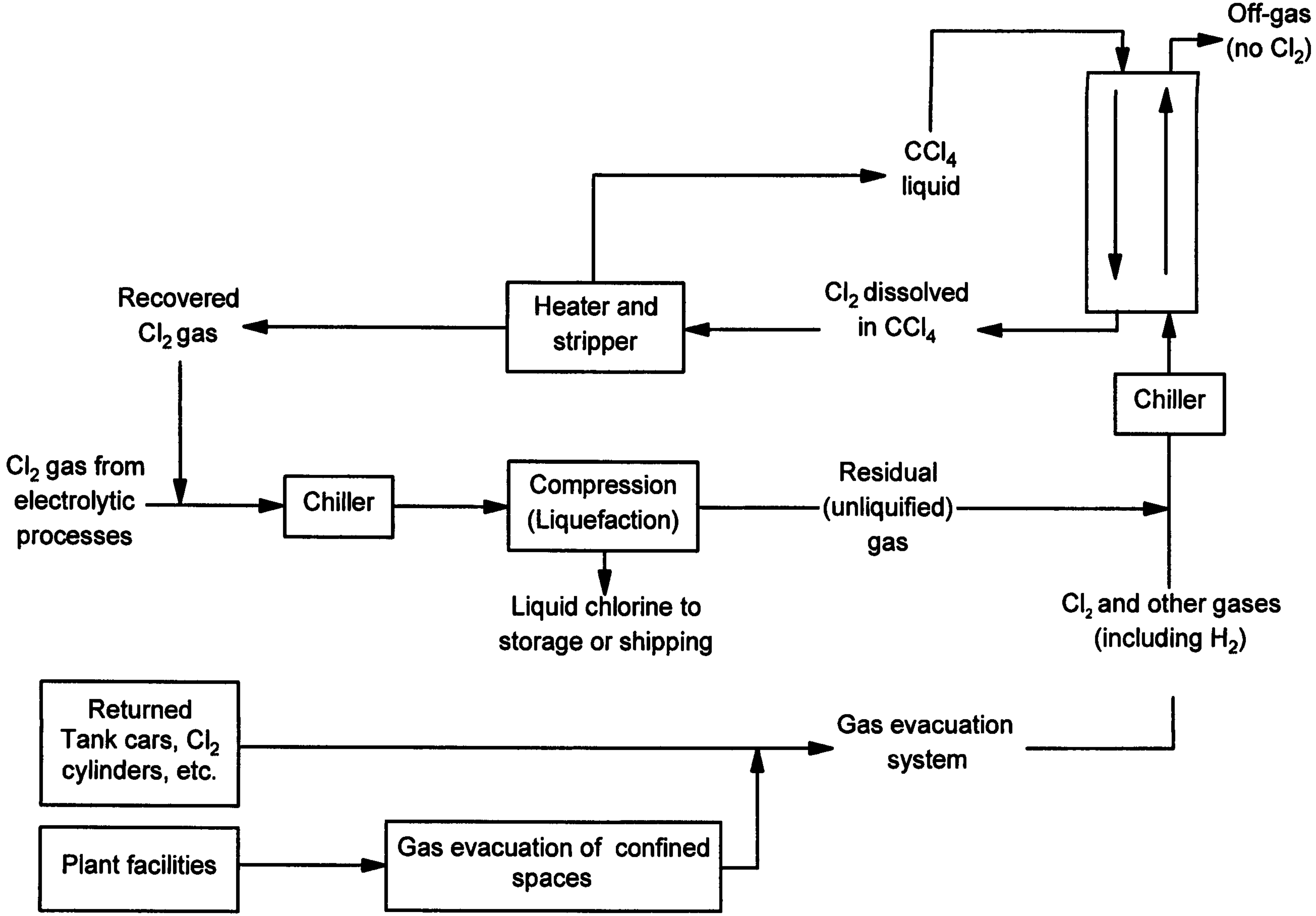
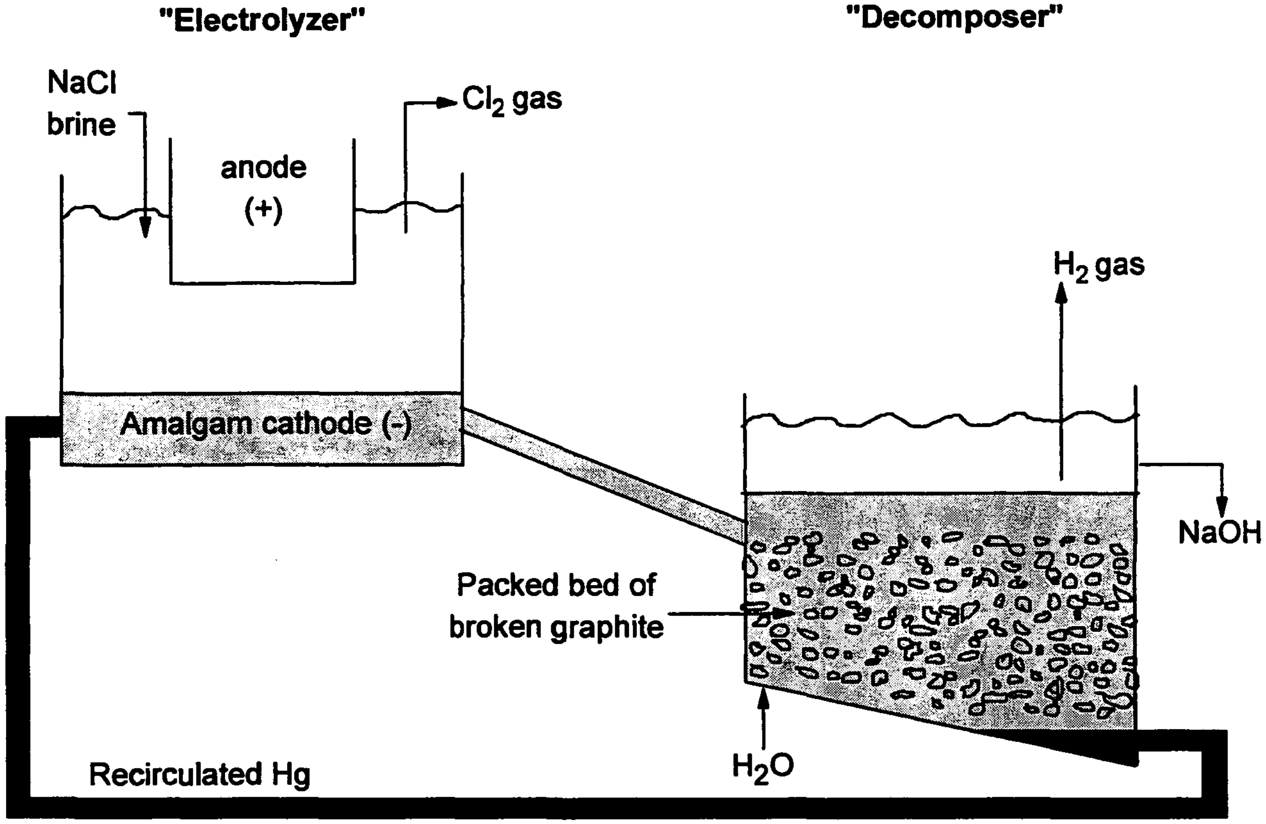


Figure 3.9 Carbon tetrachloride recovery of chlorine at chlor-alkali plants



1st Electrolytic Cell

- Cl_2 gas produced at anode

  $(2Cl^- \longrightarrow Cl_2 + e^-)$

- Na^+ ions in solution reduced and combine with liquid Hg cathode to produce liquid Na-Hg amalgam

  $(Na^+ + e^- + Hg \longrightarrow Na\text{-}Hg)$

- Na-Hg amalgam continuously withdrawn into 2nd cell

2nd Electrolytic Cell

- Na-Hg acts as anode, releasing Na^+ into solution and converting Na-Hg amalgam back into liquid Hg

  $(Na\text{-}Hg \longrightarrow Na^+ + Hg + e^-)$

- Graphite acts as cathode producing H_2 gas and OH^-

  $(2H_2O + e^- \longrightarrow H_2 + 2OH^-)$

- NaOH drawn off for further processing

- Hg recirculated back to 1st cell

Figure 3.10 Mercury cell chlor-alkali process [derived from White (1986) and Kroschwitz (1994)]

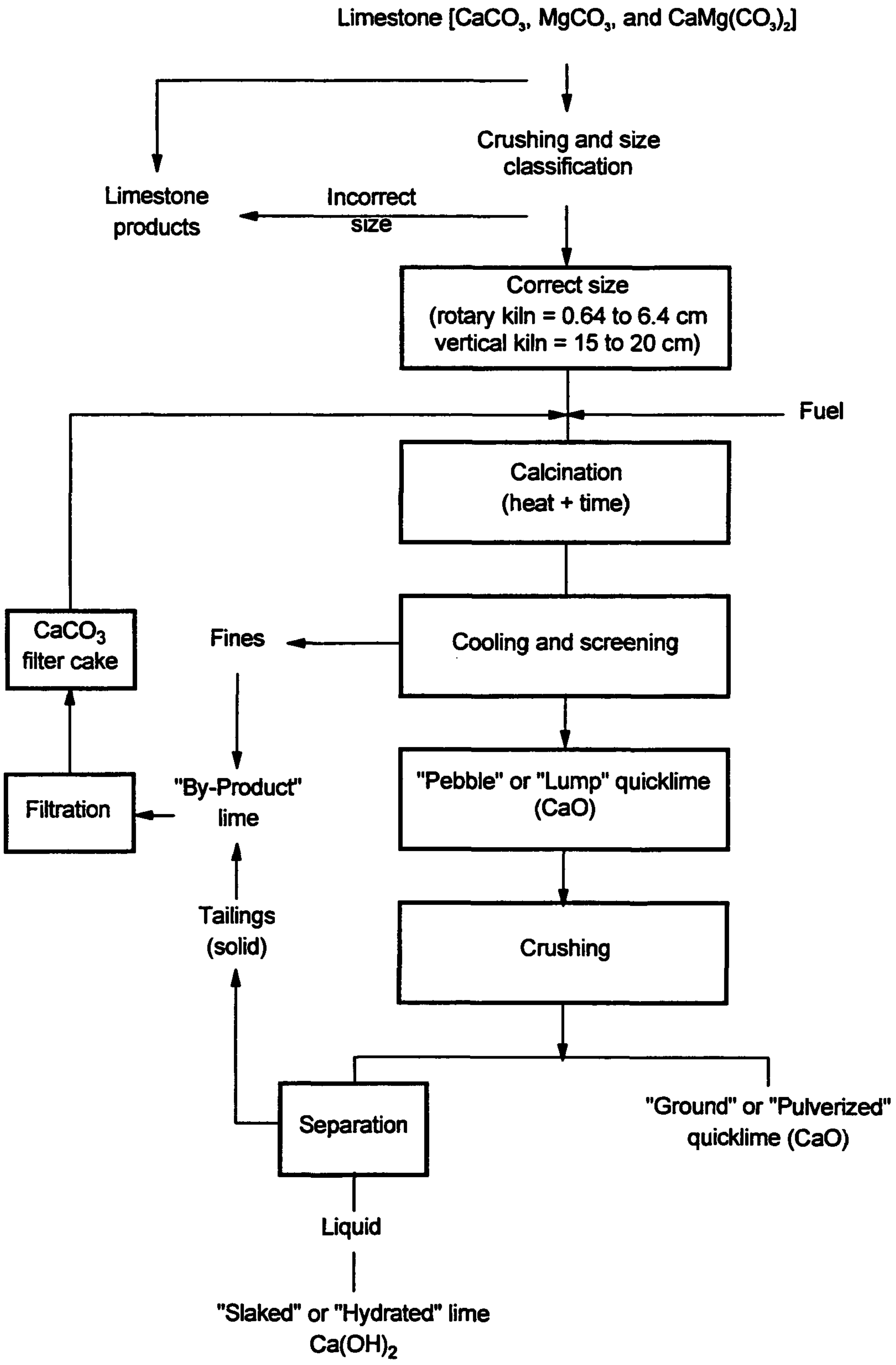


Figure 3.11 Lime production from crushed limestone (derived from Kroschwitz 1999)

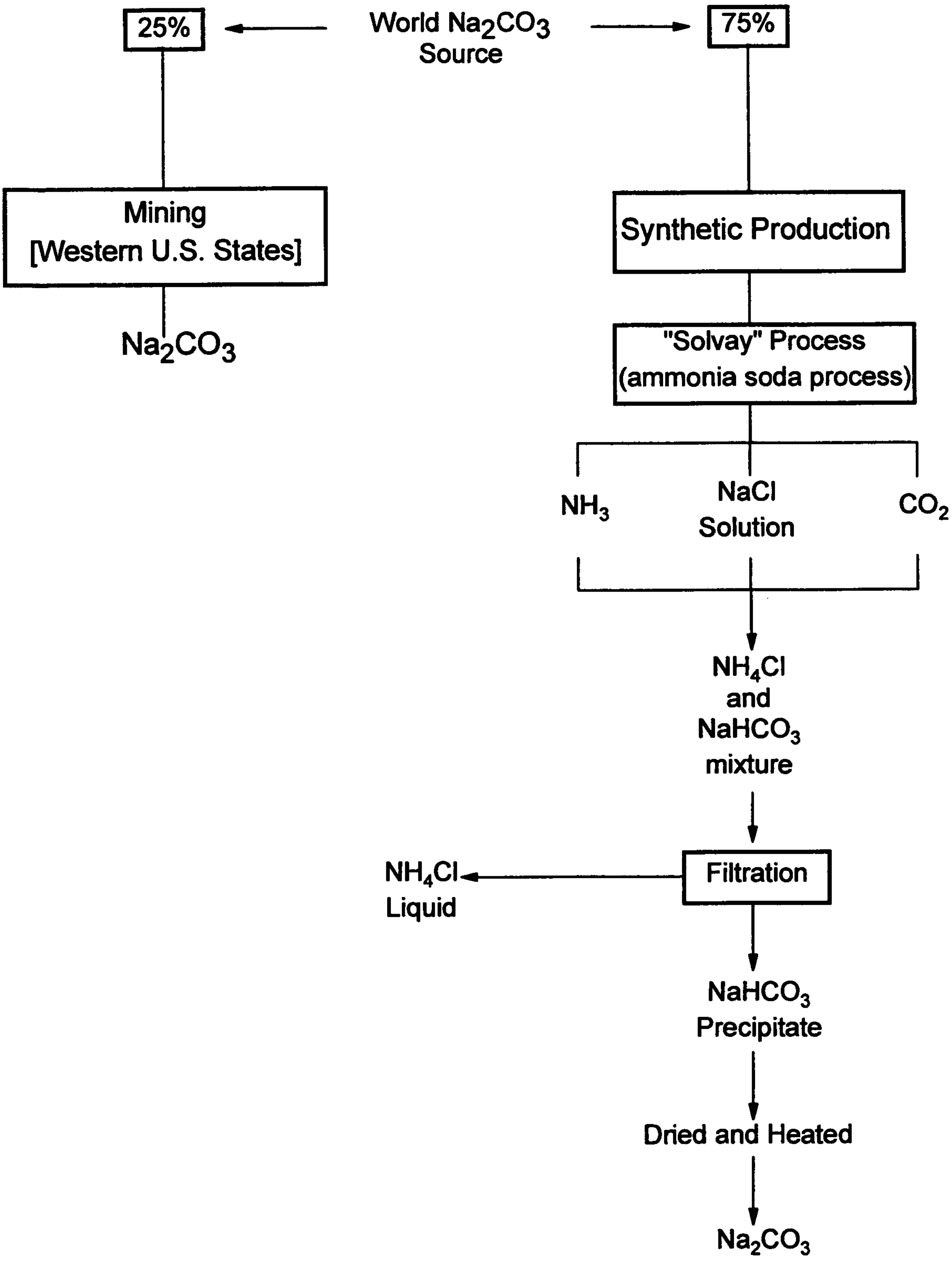


Figure 3.12 Mining and manufacture of soda ash (derived from Kroschwitz 1999)

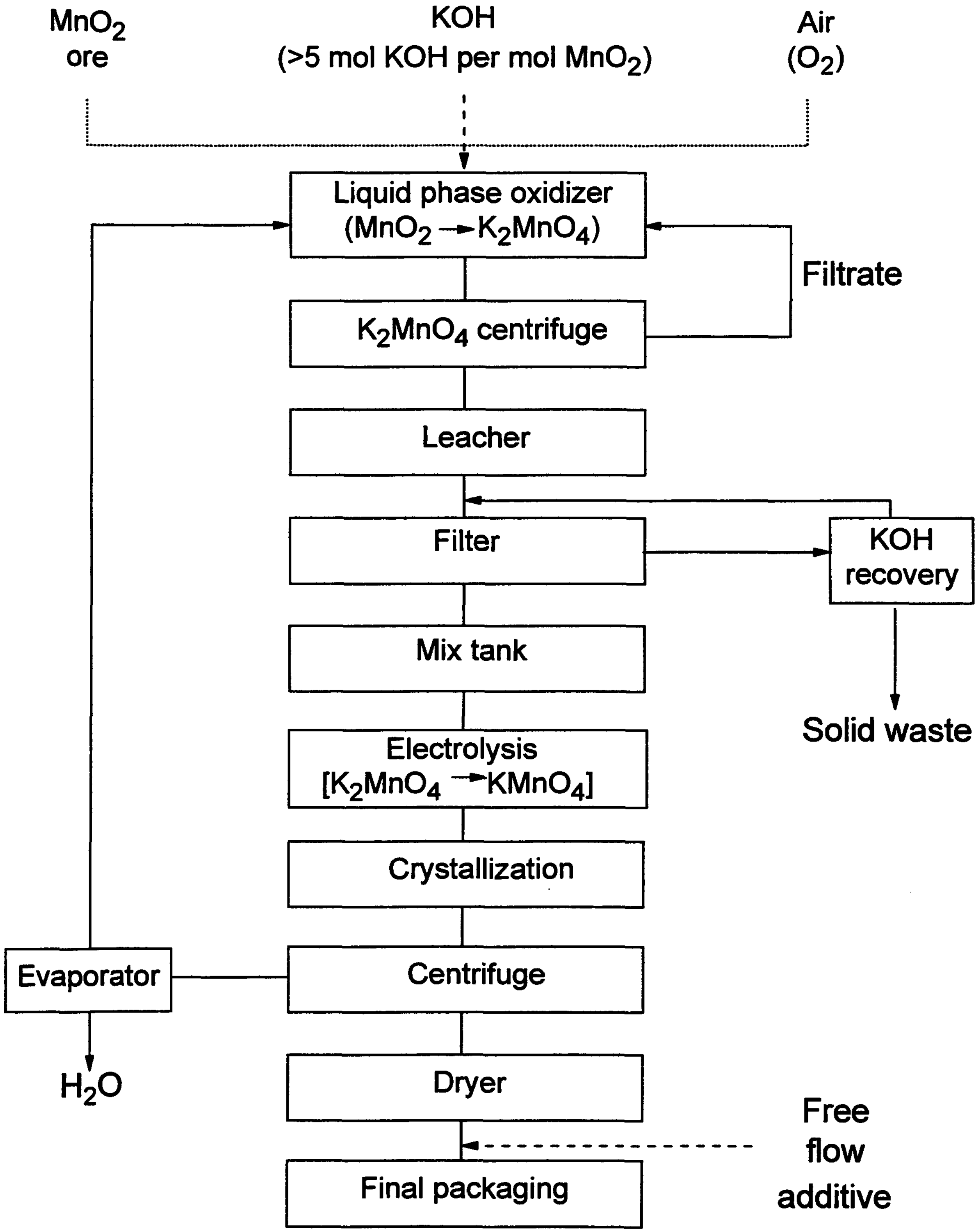


Figure 3.13 Production of potassium permanganate using liquid phase oxidation (derived from Vella 2000 and Kroschwitz 1994)

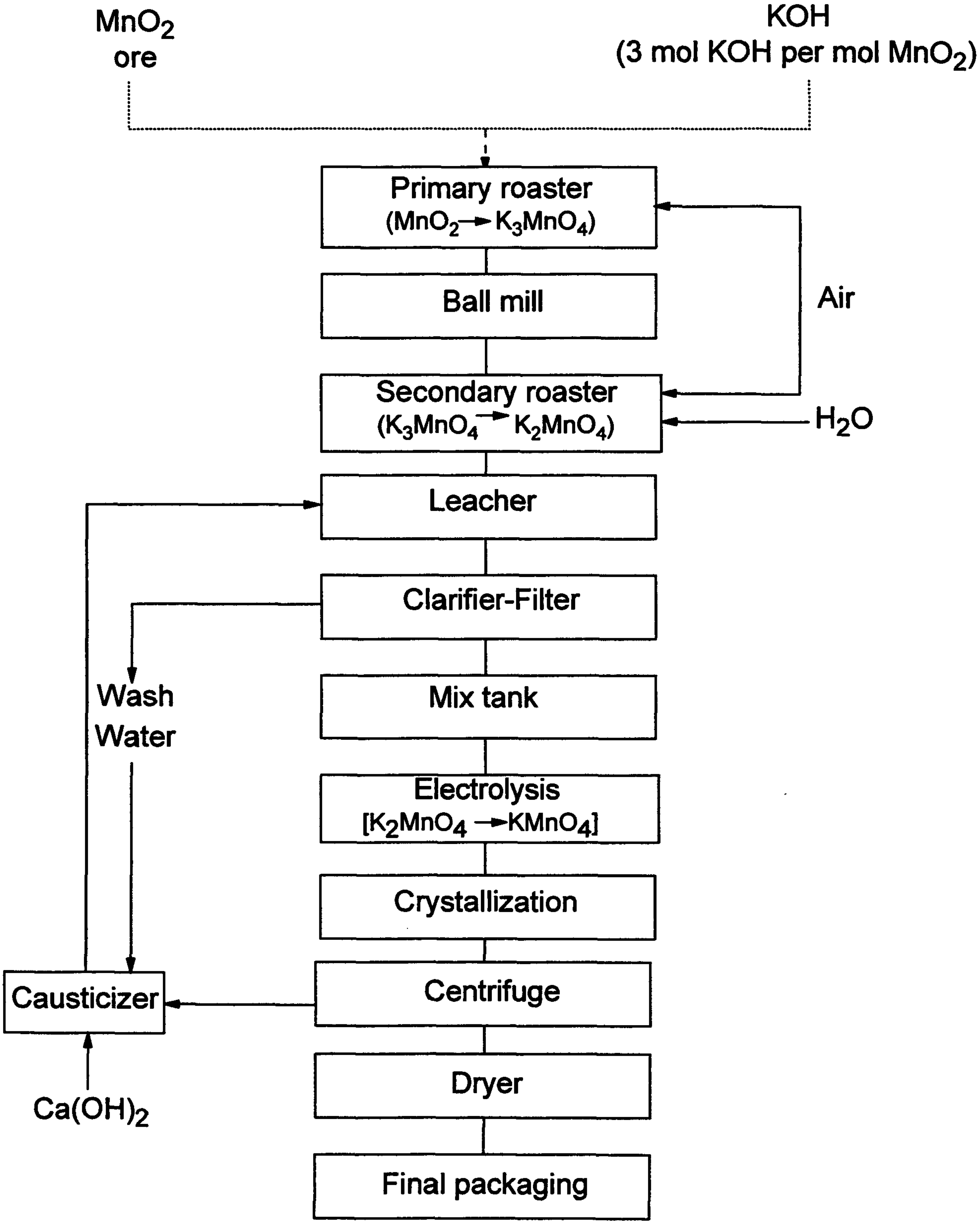


Figure 3.14 Production of potassium permanganate using roasting process (derived from Kroschwitz 1994)

CHAPTER 4

COMPOSITION OF COMMONLY USED WATER TREATMENT CHEMICALS

This chapter presents compositional analyses for commonly used water treatment chemicals. The bulk of the results are based on samples collected and analyzed during this study. Other data from the utility survey (Chapter 2), the manufacturer/supplier survey (Chapter 3), and the literature were included for comparison purposes. Compositional data from each of these sources are presented for:

- Aluminum-based coagulants (alum and polyaluminum chloride (PAC1))
- Iron-based coagulants (ferric chloride or ferric sulfate)
- Chlor-alkali related products (Chlorine, caustic soda, sodium hypochlorite)
- Lime products
- Corrosion inhibitors (zinc and phosphate based)
- Fluoridation chemicals
- Potassium permanganate
- Organic polymers
- Other treatment chemicals

Within each of these sections, the typical composition of these products and the range of available data are presented. Comparisons are shown for certain products made by different manufacturer processes, or by different manufacturers using similar manufacturing processes. At the end of this chapter is a description of results from this study investigating the total organic carbon and disinfection by-product (DBP) precursor content, specifically precursors of trihalomethanes and haloacetic acids, for commonly used aluminum- or iron-based coagulants.

Composition of solid chemicals are expressed on a mg/kg dry weight basis. Liquid concentration (mg/L) and mass concentrations (mg/kg) based on either a dry or wet weight basis are typically used to represent the composition of liquid chemicals. However, expressing mass concentration on a dry weight basis is recommended for liquid products in order to limit confusion when comparing different products. For example, two ferric chloride products may have the same composition on a dry weight basis, but if one is diluted and shipped as a 38 percent solution and the other is shipped as a 40 percent solution, the two products will have an apparent compositional difference if evaluated on a wet weight basis or on a mg/L basis.

Liquid concentration and mass concentration (dry or wet) are only suitable to evaluate and compare similar formulations of the same product (e.g., comparison of different ferric chloride types). They are not suitable for comparison of products with different formulations, such as alum versus polyaluminum chloride. In order to make comparisons for the wide variety of products listed in this report, the terms "mass ratio" and "molar ratio" are defined as follows:

- Mass ratio: The ratio of trace constituent relative to the major constituent in a given treatment chemical on a mass per mass basis. For example, mass ratio for alum and PACl would be relative to Al.
- Molar ratio: The molar ratio is analogous to mass ratio, except the ratio is expressed on a molar basis. For example, just as for mass ratio, molar ratio for aluminum-based products would be relative to Al.

Mass ratio is used to compare composition of trace constituents in products that have a common principal element, whereas molar ratio will be limited to comparison of treatment chemicals that are not based upon a common element. For example, mass ratio is used to compare an alum product to a PACl product, whereas molar ratio will be used to compare alum to ferric chloride. Chapter 5 demonstrates how the mass ratio can be useful to calculate the contribution of trace constituents added at a given treatment chemical dose. Appendix A demonstrates how to calculate and convert between mass ratio, molar ratio, liquid concentration, and/or mass concentration on dry or wet weight basis.

ANALYTICAL METHODS

Complicated matrix effects involving large dilution factors (1,000 x or greater) are required in order to analyze trace metals in treatment chemicals, unless advanced techniques are used. Chemical manufacturers analyze these types of samples every day and have refined sample preparation and analytical techniques for these types of samples. Utilities analyze these samples infrequently, if at all. Consequently, data from manufacturers are generally more reliable. One of the largest manufactures of a broad range of chemicals analyzed samples during this project.

The analytical technique used in this study was inductively coupled plasma-optical emission spectroscopy (ICP-OES). The instrument used in this study was a Thermo Jarrell Ash (Franklin, MA) AtomScan 16. One important advantage or using this technique is that dilution factors of four are suitable, thus sensitivity was greater. A second major advantage of ICP-OES over other methods is that multiple metals (up to 27 in this study) can be analyzed in a single run. Sample preparation for treatment chemical samples prior to aspiration into the ICP-OES included dilution with deionized or distilled water and acidification with reagent grade hydrochloric acid. For sludges, samples were prepared by addition of lithium metaborate and melting the mixture at greater than 1,000°C in order to form a homogenous solid product. This material was acidified and then aspirated into the ICP like other samples. A blank was analyzed each time this method was used in order to correct for background metals in the lithium metaborate.

Samples of treatment chemicals were collected between September 2000 and February 2001 by seven utility participants during this project. Samples were collected and shipped in high density polyethylene (HDPE) or polypropylene (PP) sample containers. (i.e., Nalgene 2104 or equivalent). Sample sizes were about 100 mL for liquids and 100 grams for solids.

ALUMINUM-BASED COAGULANTS

Table B.1 in Appendix B is a combined summary of compositional data for aluminum-based coagulants from the manufacturer survey and from utility participants in units of mg/kg on dry weight basis. Table B.2 contains similar data, except units are on mass ratio basis (µg/g Al). These tables include data for seven standard alum products, 13 low-iron alum products, and eight polyaluminum chloride products. The breakdown of these aluminum-containing products is shown in Table 4.1. These samples represent results from 12 different manufacturers.

Table 4.1

Summary of aluminum-based coagulant samples evaluated

	AwwaRF study participants	Manufacturer survey	Total
Standard alum	1	6	7
Low-iron alum	4	9	13
Polyaluminum chloride low basicity	0	3	3
High basicity polyaluminum chloride	0	3	3
Polyaluminum hydroxychlorosulfate	1	1	2
Total	6	22	28

Table 4.2 is a summary of the data in Tables B.1 and B.2 for three classes of aluminum-based coagulants (standard alum, low-iron alum and PACl). Figure 4.1 is a graphical representation of key data from Table 4.2, including data for eleven trace metals. As described in Chapter 3, many trace metal levels are higher in standard alum than in PACl or low-iron alum because the latter two products are produced by acid leaching of a purified aluminum source, versus standard alum that is produced from bauxite ore. Figure 4.1 and Table 4.2 illustrate that this is the case for metals such as iron, manganese, copper, titanium, vanadium, zirconium, and chromium. However, Figure 4.1 and Table 4.2 also indicate that the production process (leaching of bauxite with caustic) produces higher sodium and zinc in low-iron alum or polyaluminum chloride than in standard alum.

Available data for aluminum-based coagulants indicates that mercury was generally found at concentrations in the range of 8 to 12 µg Hg/g Al, with a mean of about 11.6 µg Hg/g Al when it was detected. This includes standard alum as well as low-iron alum and PACl. Consequently, unlike chromium, iron, and other metals, mercury is not removed during production of PACl or low-iron alum.

Table 4.2

Median composition of aluminum-based coagulants

	Standard alum	Low-iron alum	PACl	Standard alum	Low-iron alum	PACl
Constituent	(mg/kg dry weight basis)			(µg metal/g Al)		
No. of samples	7	13	8	7	13	8
Al	90,000	89,400	153,911	1,000,000	1,000,000	1,000,000
Ca	62	62	149	691	697	792
Fe	1,300	39	91	14,444	438	472
K	7.5	7.7	10.7	81.5	84.6	78.6
Mg	33	14	41	369	157	233
Mn	2.5	0.8	3.2	27.9	9.3	16.2
Na	247	577	546	2,764	6,434	4,611
Sb	<0.8	<0.8	<1.2	<9.3	<9.2	<10
As	<2.06	<2.00	<2.6	<23	<22	<13
Ba	<0.10	<0.10	0.21	<1.2	<1.2	0.97
Cd	<0.1	<0.1	<0.2	<1	<1	<1
Cr	66	0.6	0.6	729	6	4
Co	<0.20	<0.15	<0.41	<2.2	1.7	<2.0
Cu	1.86	0.21	1.34	21	2	7
Pb	<4.1	<4.1	<4.1	<45	<46	<34
Hg	<0.82	1.03	1.44	<9	11	11
Mo	<1.7	<1.7	<1.4	<18	<18	<12
Ni	0.90	0.41	1.65	9.8	4.7	10.1
Y	<0.41	<0.30	<0.52	<4.6	<3.3	<2.85
Se	<4.1	<5.1	<2.1	<4.7	<49	<17
Ag	<0.82	<0.82	<1.65	<9	<9	<8
Sr	1.03	0.41	0.41	11.6	4.6	3.5
Ti	27	1.2	3.0	299	13	20
V	39	0.20	6	442	2	39
Zn	3	16	14	34	176	83
Zr	12	0.4	0.9	130	5	6
Si	52	14	56	581	161	335
Sn	<2.1	<2.1	<2.7	<24	<23	<13
P	89	<4	<9	991	<46	<38
S	not analyzed	not analyzed	not analyzed			

As demonstrated in Table 4.2 and Figure 4.1, vanadium, nickel, and manganese are higher in polyaluminum chloride than in low-iron alum. However, it is also important to re-emphasize that levels of these metals in both polyaluminum chloride and low-iron alum are still lower than in standard alum.

Some trace metals were rarely found above detection limits in the 28 aluminum-based coagulant samples. This includes arsenic (not detected in any sample), lead (detected in 7 of 28 samples), silver (only detected in 1 of 28 samples), and cadmium (only detected in 2 of 28 samples). Table B.1 in the appendix summarizes these results.

Although it is possible to make generalizations about the typical composition of standard alum products versus composition of low-iron alum or polyaluminum chloride products, it is also important to note that there is variability in trace metal composition within each of these three groups depending upon the manufacturer. Figures 4.2 through 4.4 illustrate the median and range of data for trace contaminants in standard alum (Figure 4.2), low-iron alum (Figure 4.3), and polyaluminum chloride (Figure 4.4).

There are data in the literature on trace metals composition for alum, but not for PACl. The most recent data were reported by Eyring (1997) and these are summarized in Table 4.3 for nine alum products from three different manufacturers. These alum products were not specifically identified as either standard or low-iron alum, though the characteristics are consistent with results for low-iron alum. One difference in the data from Eyring (1997) versus data from this research is that the minimum detection limit for arsenic in this case was 9 μg As/g Al, versus a median detection in the Eyring study of 2 μg As/g Al. An important similarity between results reported in both studies was that silver, cadmium, cobalt, and lead were only found above detection limit in a couple of samples. Figure 4.5 compares the ranges of data from this research versus the Eyring data. Results were generally similar, although products in this research represent a broader diversity of chemicals. Another difference between the two studies is the fact that twelve metals were analyzed using five separate sets of sample preparation and analytical techniques in the Eyring study, versus 27 metals from a single ICP-OES run in this study.

Cornwell et al. (1987) reported data for a commercial standard alum. These data are compared to data from this study in Table 4.4. Reported results in this study for some metals are slightly higher than reported by Cornwell et al. (1987), especially for chromium, magnesium, calcium, sodium, and zinc. By contrast, the arsenic result was higher in the Cornwell et al. study. The only other alum compositional data reported in the literature is from Altree-Williams and Lewis (1997). They reported results for standard alum products as follows: iron at 90 to 1,100 mg/kg, calcium at 60 to 180 mg/kg, and zinc at about 30 mg/kg.

Table 4.3

Analysis of trace metals in commercial alum products (adapted from Eyring 1997)

		Median	
Constituent	Analytical method*	Concentration (mg/L)	Mass ratio (μg/g Al)
Al	IC	60,200	–
Ag	AA	<0.02	<0.3
As	HGAF	0.10	2
Cd	CAA	<0.4	<7
Co	CIC	<0.4	<7
Cu	AA	1.1	18
Cr	CIC, CAA	3.7	61
Fe	IC	32.0	532
Mn	CIC, CAA	2.6	43
Ni	CIC, CAA	7.0	116
Pb	CAA	<3.0	<50
Zn	CIC	10.5	174

* Methods include:
IC = direct ion chromatography
CIC = ion chromatography preceded by chelation
AA = direct atomic adsorption spectroscopy
CAA = atomic adsorption spectroscopy preceded by chelation extraction
HGAF = hydride generation atomic fluorescence

Table 4.4

Comparison of standard alum content with literature data

	Cornwell et al. (1987)		This study
Constituent	(mg/L)	(µg metal/g Al)	(µg metal/g Al)
Al	63,000	--	--
Fe	1,160	18,400	14,000
Mn	1.7	27	28
Cd	ND	--	<1
Cr	9.5	151	729
Cu	0.1	1.6	21
Ni	0.1	1.6	10
Pb	1.5	24	<45
Zn	1.1	17.5	34
Ag	0.4	6.3	<9
As	3.0	48	<23
Se	ND	--	<4.7
Hg	0.001	0.016	<9
Si	14.2	225	580
Ba	0.5	8	<1.2
Mg	12.5	198	370
Ca	6.3	100	690
Na	57	905	2,700
K	5.6	89	80

ND = not detected

Table C.1 in Appendix C includes a summary of data reported in the utility survey for PACl and for alum products. The analytical methods used to generate these results were not reported. Results from the utility survey, in general, agreed with new data developed in this project. However, a few of the metals results (e.g., arsenic) were markedly different than reported elsewhere and may be the result of analytical methods that do not properly correct for large aluminum peak.

IRON-BASED COAGULANTS

Table 4.5 is a summary of data collected by project participants for iron-based coagulants. Units include both mg/kg of product on dry weight basis and µg/g Fe. Reported results include two ferric chloride products derived from the steel pickle liquor process, one ferric chloride derived from titanium dioxide manufacture, and one ferric sulfate product derived from direct acid leaching of iron ore. Figure 4.6 summarizes data from this table, except that only one of the two ferric chloride products from the steel pickle process is included. Important observations regarding this data include:

- Ferric chloride derived from titanium dioxide has higher trace metal content than ferric chloride derived from steel pickle liquor
- Steel pickle liquor derived ferric chloride is generally higher in trace metals than ferric sulfate
- Lead was found above detection limits in one steel pickle liquor derived ferric chloride product and in the ferric sulfate product, but not in the other two ferric coagulant samples
- Chromium was found in all three ferric chloride samples at about the same ratio relative to Fe, but chromium was not detected in the ferric sulfate sample
- No arsenic was detected in any of the four samples
- Copper and nickel were highest in steel pickle liquor derived ferric chloride
- Mercury was detected in titanium dioxide-derived ferric chloride, but was not detected in either of the other two ferric chloride samples

- Titanium, vanadium, zirconium, manganese, and sodium were appreciably higher in the titanium dioxide-derived ferric chloride than in the other ferric products tested
- All four products, especially the ferric chloride products, had appreciable aluminum levels.

Table 4.5

Composition of iron-based coagulants from samples

	Ferric chloride			Ferric	Ferric chloride			Ferric
	SPL #1	SPL #2	TiO_2 #1	Sulfate	SPL #1	SPL #2	TiO_2 #1	Sulfate
Constituent		(mg/kg dry)				(μg/g Fe)		
Al	1,289	19,737	3,158	82	3,630	64,655	10,000	360
Ca	158	974	153	371	444	3,190	483	1,622
Fe	355,263	305,263	315,789	228,866	1,000,000	1,000,000	1,000,000	1,000,000
K	26	23	50	56	74	75	158	243
Mg	55	316	316	173	156	1,034	1,000	757
Mn	1,868	1,079	2,553	169	5,259	3,534	8,083	739
Na	211	395	895	47	593	1,293	2,833	207
Sb	9	6	7	<4	27	21	22	<18
As	<5	<3	<3	<4	<15	<9	<8	<18
Ba	0.3	1	18	1	1	3	56	4
Cd	1.0	1.0	1.0	1.4	3.0	2.6	2.5	6.3
Cr	124	111	100	<1	348	362	317	<4
Co	17	8	22	8	49	26	69	35
Cu	95	82	6	<0.4	267	267	19	<2
Pb	53	<5	<13	41	148	<17	<42	180
Hg	<5	<3	5		<5	<9	15	
Mo	<1	3	18	<0.8	3	11	56	<4
Ni	58	39	11	23	163	129	35	99
Y	<1	<0.5	<0.5	<0.8	<3.0	<1.7	<1.7	<3.6
Se		<3	<3			<8.6	<8.3	
Ag	<5	<2	<2	<4	<15	<7	<7	<18

(continued)

Table 4.5 (continued)

	Ferric chloride			Ferric	Ferric chloride			Ferric
	SPL #1	SPL #2	TiO_2 #1	Sulfate	SPL #1	SPL #2	TiO_2 #1	Sulfate
Constituent	(mg/kg dry)				(µg/g Fe)			
Sr	2	4	9	2	5	13	29	7
Ti	2	24	10,789	13	4	78	34,167	59
V	95	79	1,553	227	267	259	4,917	991
Zn	45	53	258	37	126	172	817	162
Zr	10	8	4,474	6	28	27	14,167	26
Si	12	<1	15	8	33	<4	4	34
Sn	<5	<3	14	<4	<15	<9	44	18
P	29	263	42	163	82	862	133	712
S	158	2,579	63	206,186	444	8,448	200	900,901
Sg	1.4	1.4	1.4					

Notes: SPL = Steel pickle liquor derived, TiO_2 = Derived during manufacture of titanium oxide

As a result of the manufacturer survey, one supplier provided data from two of their production facilities located in different regions of the U.S. Table 4.6 shows variability of steel pickle liquor derived ferric chloride produced at these two facilities (mean and standard deviation of daily samples for one month at each facility). The results from the two locations are comparable for many constituents, but there are a few constituents like copper (239 versus mg/kg at one facility and 118 mg/kg at the other) that are different even though the production processes at the two facilities are similar. Differences in quality of products from each facility could be due to slight differences in ferric chloride production processes, steel making practices, steel pickling processes, and/or composition of iron source materials feeding the steel making process. However, in general, products from these two processes are fairly similar. Both arsenic and mercury were found above detection limits at these two locations. These findings are consistent with results reported earlier for steel pickle liquor-derived ferric chloride analyzed during this AwwaRF study, except that the detection limit in this study was higher than the arsenic and mercury levels detected in the manufacturer's data reported in Table 4.6.

Table 4.6

Composition of ferric chloride produced from steel pickle liquor at two U.S. production facilities

	Manufacturer 1		Manufacturer 2	
	Mean	Standard deviation	Mean	Standard deviation
Constituent	(mg/kg dry)		(mg/kg dry)	
Cd	0.8	0.7	0.5	0.6
Cr	168	17	186	12
Cu	239	34	118	20
Ni	97	7	67	7
Pb	2.5	3.3	2.1	1.9
Zn	33	43	32	2
Ag	0.4	0.5	0.3	0.6
As	2.0	1.8	1.9	1.7
Ba	1.5	0.2	0.9	0.1
Be	ND	ND	ND	ND
Hg	0.2	0.4	0.1	0.3
Mg	96	30	87	27
Mn	1,270	256	1,519	395
Mo	34	10	27	7
P	182	164	58	25
S	33	11	406	69
Se	5	6	5	4
Ti	34	9	22	8
V	20	3	14	2

ND = not detected

Data from the utility survey reported are in Table C.1. In general, data from the utility survey were consistent with the ferric chloride or ferric sulfate data reported in this study, though some of the reported results in the utility survey are suspect. For example, maximum arsenic and zinc in ferric chloride were reported in the survey at 410 and 26,900 mg/kg, respectively, and these are at least two orders of magnitude higher than reported in this study for other samples. Table 4.7 and Figure 4.7 include data reported by one utility during the utility survey. These results reflect the impact of tighter specifications on the quality of ferric chloride used by the utility. The improvement was not necessarily the result of improvements by the ferric chloride manufacturers, either individually or as a group, to produce higher quality products. The utility was also not forced to reject any bids that did not meet the new specification. The impact of tighter specifications in this instance was that providers of the poorer quality products saw that they could not meet the new tighter specifications and voluntarily stopped submitting bids. The improved quality after implementation of the tighter specifications is reflected in the markedly lower levels for all nine trace metals. Even in the case of nickel, which had a median of 14 mg/kg before the switch and 30 mg/kg after, the maximum reported values decreased from 385 to 34 mg/kg after the switch.

Table 4.7

Impact of tighter specifications for ferric chloride

	Before (mg/kg dry)					After (mg/kg dry)				
Constituent	obs	min	max	median	mean	obs	min	max	median	mean
As	8	335	410	380	378	5	0.2	1.7	0.4	0.6
Ba	6	13	250	189	146	4	0.3	0.6	0.5	0.5
Cd	4	150	198	174	174	4	0.1	0.2	0.1	0.1
Cr	8	500	1,913	1,459	1,271	4	68	93	78	79
Cu	7	1	2,830	113	677	4	41	60	46	48
Pd	8	1	1,118	635	590	4	0.6	2.5	1.6	1.6
Ni	5	5	385	13	141	4	27	34	30	30
Se	7	5	505	450	402	4	1.7	3.3	2.1	2.3
Zn	7	1	26,900	355	4,162	4	8	15	12	11

CHLOR-ALKALI PRODUCTS

Sodium Hypochlorite and Sodium Chlorite

Table 4.8 summarizes data for wet weight composition of one sodium chlorite sample and three sodium hypochlorite samples collected and analyzed during this project. Trace metals levels in all four of these samples are below or near the detection limit. Potassium (K), probably due to presence of trace amounts of potassium chloride in the sodium chloride salt solutions used in the chlor-alkali process (Chapter 3) is the only metal other than sodium that was found in appreciable quantities. Nickel, copper, and iron are important metals to limit because of their ability to catalyze or enhance the degradation of hypochlorite to chlorite and then to chlorate as discussed previously in Chapter 3 (Gordon et al. 1995). However, except for one occurrence of iron barely above the detection limit, these metals were not found above detection limits in the three sodium hypochlorite products tested.

Table 4.8

Composition of sodium hypochlorite and sodium chlorite ($Ca(OCl)_2$)

	$Na(OC1)_2$	Sodium hypochlorite		
	25 percent solution	13 percent solution	5.25 percent solution	10 percent solution
Constituent	mg/kg dry	mg/kg dry	mg/kg dry	mg/kg dry
Al	<0.5	<1	<1	<1
Ca	2.4	1	3	25
Fe	0.3	0.4	<0.2	0.2
K	21	63	14	25
Mg	<0.0	<0.0	0.2	0.2
Mn	0.7	<0.2	<0.2	<0.02
Na	74,000	87,000	35,000	66,000
Sb	<1.0	<1	<1	<1

(continued)

Table 4.8 (continued)

	$Na(OC1)_2$	Sodium hypochlorite		
	25 percent solution	13 percent solution	5.25 percent solution	10 percent solution
Constituent	mg/kg dry	mg/kg dry	mg/kg dry	mg/kg dry
As	<1.0	<1	<1	<1
Ba	0.0	<0.01	0.0	<0.01
Cd	<0.1	<0.1	0.2	<0.1
Cr	<0.2	<0.2	<0.2	<0.2
Co	<0.2	<0.2	<0.2	<0.2
Cu	<0.1	<0.1	<0.1	<0.1
Pb	<2.0	<2	<1	<2
Hg	<1.0	<1	<1	<1
Mo	<0.2	<0.2	<0.2	<0.2
Ni	<0.2	<0.2	<0.2	<0.2
Y	<0.2	<0.2	<0.2	<0.2
Se	<0.1	<1	<1	<1
Ag	<0.8	<1	<1	<1
Sr	<0.01	0.1	0.2	0.2
Ti	<0.2	<0.1	0.2	<0.2
V	<0.2	<0.2	<0.2	<0.2
Zn	3.0	<0.1	1	1
Zr	<0.2	<0.2	<0.2	<0.2
Si	22	7	4	43
Sn	<1.0	<1	<1	<1
P	12.0	<1	14	18
S	<3.0	9	7	15
Specific gravity	1.21	1.19	1.08	1.06
pH	12.2	11.8	12.6	12.00

Studies by Bolyard and Fair (1992) and Delcomyn (2000) provide data on bromate (BrO_3^-), chlorite (ClO_2^-), and chlorate (ClO_3^-) concentration in sodium hypochlorite products used for drinking water treatment purposes as summarized in Tables 4.9 and 4.10. Results in these tables are expressed in units of µg of constituent per g of free chlorine. Even though the later study by Delcomyn is able to incorporate some analytical improvements over what was reported in the study eight years earlier by Bolyard and Fair, the results are comparable for bromate and chlorite. However, the Bolyard and Fair data indicate about three times higher chlorate than reported by Delcomyn. Gordon et al. (1997) indicates that a factor of three is consistent with chlorate decay during storage of sodium hypochlorite. Consequently, this could explain the difference in chlorate results for Delcomyn versus Bolyard and Fair.

Table 4.9

Bromate, chlorate, and chlorite in sodium hypochlorite

(adapted from Bolyard and Fair 1992)

Description	Bromate (µg BrO_3^- per g Cl_2)	Chlorite (µg ClO_2^- per g Cl_2)	Chlorate (µg ClO_3^- per g Cl_2)
1991 Data			
No. above DL	none	6	14
Mean		2,992	247,854
Median		2,667	110,000
1992 Data			
No. above DL	9	8	14
Mean	844	1,133	300,000
Median	30	1,115	109,091

Table 4.10

Bromate, chlorate, and chlorite in 10 to 13 percent solutions of sodium hypochlorite (adapted from Delcomyn 2000)

Manufacture	Bromate ($\mu g\ BrO_3^-$ per g Cl_2)	Chlorite ($\mu g\ ClO_2^-$ per g Cl_2)	Chlorate ($\mu g\ ClO_3^-$ per g Cl_2)
A	157	4,150	30,769
B	233	1,175	5,084
C	280	1,009	9,551
D	678	3,779	34,612
E	255	824	46,098
F	121	1,442	8,595
G	85	547	63,205
H	305	1,161	35,346
Mean	264	1,761	29,157
Median	244	1,168	32,690

Gordon et al. (1995) describes factors impacting decay of sodium hypochlorite to produce chlorite and chlorate. The studies describe how various factors such as storage time, temperature, initial hypochlorite ion (OCl^-) concentration, concentration of metal catalysts (copper, nickel, iron, and cobalt), and other factors impact decomposition of hypochlorite ion to chlorite and chlorate. However, the Gordon et al. study does not include measurements or assessments of occurrence of trace metals, in commercial sodium hypochlorite products. The study investigated what happened over time when temperature, initial hypochlorite ion concentration, or concentration of trace metals were manipulated during laboratory spiking studies.

These results for sodium hypochlorite are consistent with data provided during the water utility survey, as summarized in Table C.1 of Appendix C. No data for sodium chlorite were included in responses from the utility survey.

Caustic soda

Four samples of caustic soda were analyzed during this project, as summarized in Table 4.11. These data indicate only minor amounts of potassium, strontium, silicon, magnesium, calcium, iron, phosphorus, sulfur, and aluminum were found above detection limits. This is consistent with data from a number of samples reported in the utility survey, as summarized in Table C.1 of Appendix C. Some of the extreme values reported in the utility survey for certain metals (aluminum, iron, and strontium) were higher than results from this study, but these could have been due to inappropriate analytical techniques.

Table 4.11

Composition of caustic soda

	Dry weight (mg/kg)			
Constituent	50 percent	50 percent	25 percent	50 percent
Al	8	5	<2	<1
Ca	<1	1.0	24	6
Fe	1	2.0	6	36
K	320	1,180	560	980
Mg	0.2	0.4	4	2
Mn	<0.04	<0.04	<0.08	0.6
Na	508,000	510,000	444,000	508,000
Sb	<2	<2.0	<4	<2
As	<2	<2.0	<4	<2
Ba	<0.02	<0.02	0.2	0.6
Cd	<0.2	<0.2	<0.4	<0.2
Cr	<0.4	<0.4	<0.8	1
Co	<0.4	<0.4	<0.8	<0.4
Cu	0.2	<0.2	<0.4	<0.2
Pb	<2	<2.0	<20	<20
Hg	<2	<2.0	<4	<2
Mo	<0.4	<0.4	<0.8	0.6
Ni	<0.4	<0.4	<0.8	1
Y	<0.4	<0.4	<0.8	<0.4

(continued)

Table 4.11 (continued)

	Dry weight (mg/kg)			
Constituent	50 percent	50 percent	25 percent	50 percent
Se	<2.0	<2.0	<4	<2
Ag	<2	<1.6	<3	<2
Sr	0.4	0.2	4	2.4
Ti	<0.2	<0.4	0.8	<0.2
V	<0.4	<0.4	<0.8	<0.4
Zn	0.4	<0.2	1.2	0.4
Zr	<0.4	<0.4	<0.8	<0.4
Si	340	480	44	166
Sn	<2	<2	<4	<2
P	112	<8	<4	7
S	18	36	60	168
Specific gravity	1.53	1.53	1.22	1.52
pH	9.94	11.10	12.80	10.70

LIME PRODUCTS

Table 4.12 includes results from four lime samples collected and analyzed by participants in this study. Composition of the four samples is fairly consistent, with respect to major cations such as aluminum, iron, manganese, magnesium, sodium, potassium, and silicon, as well as other metals like zinc, strontium, and titanium. Most other metals were not found above detection limits. Other observations from this data included the following:

- The fourth sample in Table 4.12 labeled as "pebble lime" had lower levels of all metals listed than the other three samples.
- Other alkaline earth metals like strontium, barium, and magnesium were detected as expected, as were alkali metals like sodium and potassium, and other metals like aluminum, iron, manganese.

- Significant levels of titanium and zinc were detected in these four samples. Titanium was found at higher levels (on a molar basis) than zinc, barium, and manganese in all samples, and even higher than sodium in two samples.
- Most of the trace metals of regulatory concern (antimony, arsenic, cadmium, chromium, copper, lead, mercury, nickel, selenium, and silver) are near or below detection limits in these four samples.
- As opposed to many other water treatment chemicals, lime is not processed by any purification steps prior to use at the water plant. Since it is a mined product, the only protection for the water plant is to find high quality raw materials, which this data demonstrates is achievable.

Table 4.12

Composition of lime products

	Dry weight [mg/kg as $Ca(OH)_2$]			
Constituent	Hydrated lime #1	Hydrated lime #2	Hydrated lime #3	Pebble lime
Al	2,154	2,700	2,267	1,135
Ca	507,692	495,000	493,733	495,676
Fe	846	1,600	1,067	560
K	785	860	1,067	832
Mg	7,231	7,700	16,667	4,465
Mn	35	23	73	16
Na	1,277	49	3,000	22
Sb	<15	<2	<67	<2
As	<15	<2	<67	<2
Ba	77	13	27	5
Cd	<1.5	0.2	<6.7	<0.2
Cr	<3.1	2	<13.3	1

(continued)

Table 4.12 (continued)

	Dry weight [mg/kg as $Ca(OH)_2$]			
Constituent	Hydrated lime #1	Hydrated lime #2	Hydrated lime #3	Pebble lime
Co	<3.1	0.4	<13.3	<0.3
Cu	1.5	2	<6.7	0.5
Pb	<15	<4	<333	<3
Hg	<15	<2	<6.7	<2
Mo	4.6	<0.4	<13.3	<0.3
Ni	<3.1	1	<13.3	0.5
Y	<3.1	1	<13.3	1
Se	<15	<2	<67	<2
Ag	<12	<2	<53	<2
Sr	338	240	307	212
Ti	74	66	87	26
V	3.1	3	<13.3	2
Zn	9	4	6.7	2
Zr	3.1	3	<13.3	2
Si	4,154	4,600	6,467	1,665
Sn	<15	<2	<67	<2

Data obtained from the utility survey for both quicklime (CaO) and hydrated lime [$Ca(OH)_2$] are summarized in Table C.1 in the Appendix. The units for lime in Table 4.12 and Table C.1 are mg/kg as $Ca(OH)_2$ on a dry weight basis (i.e., pebble lime has been converted to mg/kg as $Ca(OH)_2$). In general, the results of the utility survey are comparable to the results of the rest of this study. Differences between the utility survey results in Table C.1 versus results from the remainder of the study in Table 4.12 include: higher potassium in samples from this study versus the utility survey, and higher utility survey results for arsenic, barium, chromium, manganese, and selenium. No data were reported in the utility survey for titanium in lime products.

PHOSPHATE-BASED CORROSION INHIBITORS

Phosphate-based corrosion inhibitors can include a variety of different formulations, many of which are proprietary. Five phosphate-based corrosion inhibitors were sampled and analyzed by project participants, as summarized in Table 4.13. However, since the products are different formulations, the data are presented in a different set of units in Table 4.14 with all results normalized with respect to phosphorus content. Observations to note regarding data in these tables and this figure include the following items:

- Major components in Product #1 are zinc and phosphate
- Major components in Products #2 and 3 are hydrogen, zinc, phosphorus, and sulfur
- Major components of Product #4 are hydrogen, zinc, and phosphorus
- Major components of Product #5 are sodium, zinc, and phosphorus
- Products #2, 3, and 4 have high hydrogen ion content (i.e., pH <1)
- All five products tested contained chromium detected at greater than 50 µg Cr/g P
- All five products have about the same levels of most trace metals
- The only exception to the previous statement is that Product #5 contained more than twice as much aluminum, copper, manganese, nickel, titanium and zirconium per g of phosphorus than any of the other products
- Six metals of regulatory concern were not found above detection limits in any of the five products, including arsenic, antimony, lead, mercury, selenium, and silver
- For cadmium, the quantified levels in three products was below or near the detection limits of the other two products. Therefore, for these five products, cadmium was found at or below the minimum quantifiable level of about 7 µg Cd per g of P

Table 4.13

Composition of phosphate-based corrosion inhibitors

		Dry weight composition (mg/kg)				
Constituent	Symbol	Product #1	Product #2	Product #3	Product #4	Product #5
Aluminum	Al	9	38	48	<1	17
Calcium	Ca	92	169	132	31	42
Iron	Fe	8	12	10	4	5
Potassium	K	<12	477	385	22	112
Magnesium	Mg	37	92	80	7	34
Manganese	Mn	0.5	6	2	4	1
Sodium	Na	508	846	523	477	27,692
Antimony	Sb	<3	<2	<2	<2	<2
Arsenic	As	<3	<2	<2	<2	<2
Barium	Ba	0.3	0.2	0.6	0.3	0.1
Cadmium	Cd	<0.3	0.5	0.5	1	<0.2
Chromium	Cr	5	11	13	12	2
Cobalt	Co	<0.6	<0.3	<0.3	<0.3	<0.3
Copper	Cu	<0.3	0.2	0.5	<0.2	2
Lead	Pb	<2	<2	<8	<8	<2
Mercury	Hg	<3	<2	<2	<2	<2
Molybdenum	Mo	3	<1	2	1	0.5
Nickel	Ni	2	3	2	0.3	2
Yttrium	Y	<0.6	<0.3	<0.3	<0.3	<0.3
Selenium	Se		<2	<2	<2	<2
Silver	Ag	<3	<1.2	<1	<1	<1
Strontium	Sr	1	0.1	0.1	0.2	0.1
Titanium	Ti	1	1	4	<2	2
Vanadium	V	<0.6	<0.3	<0.3	<0.3	<0.3
Zinc	Zn	152,308	67,692	60,000	189,231	8,615
Zirconium	Zr	<1	1	3	<0.3	4
Silicon	Si	200	43	31	42	51
Tin	Sn	<3	<2	<2	<2	<2
Phosphorus	P	47,692	201,538	181,538	167,692	29,231
Sulfur	S	98	29,231	27,692	20	7,846
pH			0.42	0.04	0.81	2.67
Percent Phosphoric acid				28.5	29.3	
Specific gravity		1.29	1.43	1.40	1.54	1.08

Table 4.14

Normalized composition of phosphate-based corrosion inhibitors relative to phosphorus (P) content

		Mass ratio (µg/g P)				
Constituent	Symbol	Product #1	Product #2	Product #3	Product #4	Product #5
Aluminum	Al	197	191	263	<5	579
Calcium	Ca	1,935	840	729	183	1,421
Iron	Fe	161	59	58	24	158
Potassium	K	<258	2,366	2,119	128	3,842
Magnesium	Mg	774	458	441	42	1,158
Manganese	Mn	9.7	31	10	22	47
Sodium	Na	10,645	4,198	2,881	2,844	947,368
Antimony	Sb	<65	<8	<8	<9	<53
Arsenic	As	<65	<8	<8	<9	<53
Barium	Ba	6.5	0.8	3.4	1.8	2.6
Cadmium	Cd	<6.5	2.3	2.5	7	<5.3
Chromium	Cr	97	56	71	71	58
Cobalt	Co	<12.9	<1.5	<1.7	<1.8	<10.5
Copper	Cu	<6.5	0.8	2.5	<0.9	68
Lead	Pb	<32	<8	<42	<46	<53
Mercury	Hg	<65	<8	<8	<9	<53
Molybdenum	Mo	58	<6	13	8	15.8
Nickel	Ni	32	13	9	1.8	63
Yttrium	Y	<12.9	<1.5	<1.7	<1.8	<10.5
Selenium	Se		<3	<3	<4	<21
Silver	Ag	<65	<6.1	<7	<7	<42
Strontium	Sr	23	0.7	0.6	0.9	4.2
Titanium	Ti	26	6	22	<9	63
Vanadium	V	<12.9	<1.5	<1.7	<1.8	<10.5
Zinc	Zn	3,193,548	335,878	330,508	1,128,440	294,737
Zirconium	Zr	<13	5	18	<1.8	126
Silicon	Si	4,194	214	169	248	1,737
Tin	Sn	<65	<8	<8	<9	<53
Phosphorus	P	1,000,000	1,000,000	1,000,000	1,000,000	1,000,000
Sulfur	S	2,065	145,038	152,542	119	268,421

Implications of the data presented in Chapter 4 for corrosion inhibitors and other treatment chemicals will be discussed in more detail in Chapter 5. However, it is important to note that unlike coagulants and many other treatment chemicals, corrosion inhibitors are normally added at points in the treatment process after all solids/liquid separation processes, such as clarification or filtration. Therefore, unlike other treatment chemicals added earlier in the treatment process, there are often no physical/chemical processes located after corrosion inhibitor addition, and consequently no physical barrier prior to the consumer to remove contaminants. This means that elevated levels of chromium, aluminum, copper, manganese, nickel, titanium and zirconium noted above for one or more the above corrosion inhibitor samples may be more problematic than elevated levels of the same constituents in treatment chemicals added earlier in the treatment process.

Table C.1 in the Appendix lists results for a few constituents in some phosphate-based corrosion inhibitors reported during the utility survey. Unless stated otherwise, a 33 percent solution was assumed for concentrations reported on a wet weight basis in the utility survey. Comparing this data in the appendix with data in Table 4.13, the utility survey data report higher levels of arsenic, chromium, lead, and selenium. Arsenic, lead, and selenium were not found above detection limits in the five samples in Table 4.14, even though the detection limits were at least an order of magnitude lower than the quantified levels reported in the utility survey. Chromium was quantified in both the utility survey and this study, but the levels reported in the utility survey were a factor of two or more higher. These higher levels in the utility survey may have been due to inappropriate analytical methods for the sample matrix involved.

FLUORIDATION CHEMICALS

Four commercially available hydrofluorosilicic acid products were analyzed during this study. One product contained 3.3 percent hydrofluoric acid (HF), well in excess of the AWWA Standard of one percent. Therefore, this product would not be suitable for drinking water use. The other three products were suitable for use in drinking water treatment. Arsenic was the only trace metal found above detection limit in all three products. Reported values were 9, 20 and 47 mg/kg on a wet weight basis, or 35, 85, and 231 μg As per kg F. Titanium, vanadium, zinc, and cadmium were found in one product, but these were either not measured or not found above detection limits in other samples.

Weng et al. (2000) reported arsenic data from several different treatment chemicals, including hydrofluorosilicic acid. Reported results averaged 28 mg/L as As, with a maximum of 60 mg/L as As, for a 24.5 percent solution of hydrofluorosilicic acid. This translates to an average mass ratio of 144 μg As/g F, or 309 μg As/g F at maximum. This is consistent with data reported in this study, through the maximum value reported by Weng et al. is higher than the largest value reported in this study.

There are no data reported in this study from any source for sodium fluoride or sodium fluorosilicate. Some data were reported during the utility survey for hydrofluorosilicic acid, as summarized in Table C.1 in Appendix C. The arsenic data in the utility survey includes data reported by Weng et al. (2000). Results from the utility survey are consistent with results reported in this study except the maximum values of some metals in the utility survey are higher than those reported in this study.

POTASSIUM PERMANGANATE

Most potassium permanganate manufactured and used in the U.S. is produced by the liquid-phase oxidation process described in Chapter 3. Two samples of this material were collected and analyzed for this project, as summarized in Table 4.15. Product #2 has slightly higher levels of aluminum, iron, nickel, chromium, titanium, and silicon. It also has about ten times higher levels of sodium, barium, and strontium. Product #1 has higher levels of mercury and molybdenum. Both products have equal amounts of nickel (~30 mg/kg), selenium (~80 mg/kg), and silver (mg/kg). With regard to metals of regulatory concern, the two potassium permanganate samples contained the following:

- Arsenic, cadmium, and copper at or below detection limits
- Appreciable amounts of aluminum, iron, molybdenum, chromium, nickel, selenium, silver, and titanium, and
- Some mercury was detected in one product

Data from the utility survey for potassium permanganate are listed in Table C.1 in Appendix C. It is assumed that all of the reported data is for similar material as summarized in Table 4.15 (i.e., liquid-phase oxidation process). Mercury, aluminum, and silver are lower in the utility survey data and copper and silicon are higher in the utility data than in products summarized in Table 4.15. The other results are consistent between the two sets of data, including chromium, barium, lead, selenium, molybdenum, and nickel.

Table 4.15

Composition of potassium permanganate in samples from this study

		Dry weight (mg/kg)		Mass ratio (µg/g Mn)	
Constituent	Symbol	Product #1	Product #2	Product #1	Product #2
Aluminum	Al	560	610	1,682	1,815
Calcium	Ca	39	230	117	685
Iron	Fe	320	520	961	1,548
Potassium	K	238,000	234,000	714,715	696,429
Magnesium	Mg	<0.3	<0.3	<0.9	<0.9
Manganese	Mn	333,000	336,000	1,000,000	1,000,000
Sodium	Na	370	3,300	1,111	9,821
Antimony	Sb	<10	<10	<30	<30
Arsenic	As	<10	<10	<30	<30
Barium	Ba	11	100	33	298
Cadmium	Cd	<1	<1	<3	<3
Chromium	Cr	44	72	132	214
Cobalt	Co	<2	<2	<6	<6
Copper	Cu	<1	<1	<3	<3
Lead	Pb	<49	<400	<147	<1,190
Mercury	Hg	79	<10	237	<30
Molybdenum	Mo	24	12	72	36
Nickel	Ni	26	31	78	92
Yttrium	Y	2	<2	6	<6
Selenium	Se	73	80	219	238
Silver	Ag	82	79	246	235
Strontium	Sr	1	7	2	20

(continued)

Table 4.15 (continued)

		Dry weight (mg/kg)		Mass ratio (µg/g Mn)	
Constituent	Symbol	Product #1	Product #2	Product #1	Product #2
Titanium	Ti	4	9	13	27
Vanadium	V	<2	<2	<6	<6
Zinc	Zn	2	3	5	10
Zirconium	Zr	3	<2	8	<6
Silicon	Si	750	1,000	2,252	2,976
Tin	Sn	<10	<10	<30	<30

No data have been identified for potassium permanganate produced from facilities outside the U.S. or produced by methods other than the liquid-phase oxidation process. Utility responses have indicated some operational difficulties due to clumping of dry chemical feeders when using potassium permanganate products that were not produced by the liquid-phase oxidation process. However, there is no indication that these utilities switched due to any actual or perceived "contamination" issues.

ORGANIC POLYMERS

Approximately twelve different organic polymers were collected and analyzed from project participants as summarized in Table 4.16. Table B.3 in the Appendix includes the actual data (mg/kg wet basis) for each of the twelve samples, with minimum, maximum, and median reported in Table 4.16. The samples included polymers added to rapid mix as a coagulation aid, prior to the filter as a filter aid, or prior to clarification of recycled spent filter backwash water. Only one sample, "Polymer #10", had appreciable trace metals levels (aluminum, iron, titanium, zinc, zirconium, and silicon). All other samples had minor or below detection levels of metals, except for some of the major cations like calcium, magnesium, or sodium.

Table 4.16

Compositional data for water treatment plant organic polymers

Constituent	Symbol	Summary statistics for polymers (mg/kg wet weight)			
		Count	Min	Max	Median
Aluminum	Al	12	<0.50	2,200	<40
Calcium	Ca	12	0.50	120	73
Iron	Fe	12	<0.20	<340	<17
Potassium	K	12	<4.00	<970	<324
Magnesium	Mg	12	<0.30	54	7
Manganese	Mn	12	<0.02	8	3
Sodium	Na	12	85	27,000	940
Antimony	Sb	12	<1	<240	<76
Arsenic	As	12	<1	<240	<76
Barium	Ba	12	<0.01	<3	<1
Cadmium	Cd	12	<0.10	<25	<8
Chromium	Cr	12	<0.20	<49	<16
Cobalt	Co	12	<0.20	<49	<16
Copper	Cu	12	<0.10	<25	<8
Lead	Pb	12	<1	<460	<78
Mercury	Hg	12	<1	<240	<76
Molybdenum	Mo	12	<0.20	<49	<16
Nickel	Ni	12	<0.04	<49	<16
Yttrium	Y	12	<0.20	<49	<16
Selenium	Se	11	<1	<240	<160
Silver	Ag	12	<0.80	<190	<61
Strontium	Sr	12	<0.02	<3	<1
Titanium	Ti	12	<0.10	490	<8

(continued)

Table 4.16 (continued)

		Summary statistics for polymers (mg/kg wet weight)			
Constituent	Symbol	Count	Min	Max	Median
Vanadium	V	12	<0.20	<49	<16
Zinc	Zn	12	<0.10	230	<12
Zirconium	Zr	12	<0.20	140	<17
Silicon	Si	12	<1	130	<52
Tin	Sn	12	<1	<240	<76
Sulfur	S	12	13	4,100	695
TOC		1	4,178		
		Summary statistics for polymers (units as indicated)			
pH	unitless	9	4.2	6.8	5.7
Specific gravity	unitless	11	0.99	1.14	1.04
Percent polymer					
as dadmac	percent	1	1.76		
as epi	percent	1	1.60		

Two groups of organic polymer data collected from the utility survey are summarized in Table C.1 in Appendix C. One includes results from a few polymers identified as "organic polymers". Also listed separately are results from a couple of aluminum and polymer blends identified as "polymer + Al blend". The organic polymer data are comparable to the data reported in Table 4.16. The polymer blend data include only a few metals, i.e., aluminum, iron, sodium, and zinc all of which are higher due to inclusion of alum into the blend.

The Ontario Ministry of the Environment, in the Province of Ontario, Canada, has identified one alum-polymer blend as a potential N-nitrosodimethylamine (NDMA) precursor. This is the only reported instance where a treatment chemical has been identified as the precursor for NDMA. The solution to the problem of NDMA formation associated with this particular alum-polymer blend is to add the alum and polymer portions to the water separately, with alum added first and allowed to be well-mixed before adding the polymer. The NDMA formation problem occurs when the polymer is exposed to localized packets of low pH water immediately after alum addition, before alum is well mixed in reactor (Edmonds 2001). There is no evidence to indicate that residual dimethylamine polymer can be oxidized by free chlorine to form NDMA (Najm and Trussel 2000; Siddiqui and Atasi 2001). In laboratory experiments dosed with dimethylamine, an NDMA precursor, no NDMA was formed after reaction with free chlorine, but 13 µg/L of NDMA was formed after 24 hours reaction with monochloramine (Choi and Valentine 2001).

OTHER TREATMENT CHEMICALS

No other treatment chemicals were analyzed by participants in this study. However, respondents to the utility survey provided data for one or two samples each of soda ash (Na_2CO_3), ammonia, sulfuric acid and powdered activated carbon. These results are summarized in Table C.1 in Appendix C.

TOC AND DBP PRECURSOR CONTENT OF COMMONLY USED COAGULANTS

The objective of this portion of the study was to determine the organic content, particularly precursor material for total trihalomethanes (TTHM), haloacetic acids (HAA), and other regulated disinfection byproducts (DBPs) in metal-based coagulants. Analyses included TOC and a procedure to determine TTHM and HAA formation potential. The procedure for TTHM and HAA formation potential included the following steps for the coagulants tested (one ferric chloride, one ferric sulfate, two PACl products, and one alum product):

- Add prescribed amount of full strength coagulant to each of two 500-mL amber glass vials as needed to produce 1.5 mM solution (as Al or Fe) after dilution
- Dilute with deionized water
- Measure and record pH
- Add phosphate buffer to each vial
- Measure and record pH

- Add sodium hypochlorite dose to each vial, one vial at nominal chlorine dose of 1 mg/L as Cl_2 and the other at 2 mg/L as Cl_2
- Measure and record pH and free chlorine residual immediately after sodium hypochlorite addition
- Store samples headspace free for seven days at room temperature
- Measure free chlorine residual and pH at the end of seven days at each chlorine dose
- Quench and analyze both vials for TTHM and HAA

The dose of coagulant used in the formation potential tests was approximately 1.5 mM of coagulant metal per liter (i.e., 1.5 mM as Fe or Al). Appendix D lists sample calculations for preparation of samples for all five coagulants analyzed.

Results of DBP precursor evaluation procedure are summarized in Tables 4.17 and 4.18. These results show that at a coagulant dose equivalent to 50 mg/L as alum (0.167 mmol/L of coagulant metal), the DBP levels did not exceed the 1 µg/L detection limit for either TTHM or HAA5.

Table 4.17

Seven-day DBP formation potential for commonly used aluminum containing coagulants

Coagulant	Standard alum		PACl (50 percent basicity)		ACH (84 percent basicity PACl)	
Chlorine (mg/L as Cl_2)						
Dose	1.1	2.2	1.1	2.2	1.1	2.2
7-day residual	0.3	0.2	0.2	1.1	0.1	1.0
pH						
7-day	6.6	6.7	7.0	7.0	7.1	7.1
THM and HAA (µg/L)						
HAA5	4.6	11.3	7.8	5.8	8.7	6.7
TTHM	4.2	10.3	6.2	6.9	4.3	6.3
Coagulant dose						
mmol/L of Al	1.5		1.5		1.5	
mg/L as Al	41		40		41	

(continued)

Table 4.17 (continued)

Coagulant	Standard alum		PACl (50 percent basicity)		ACH (84 percent basicity PACl)	
DBP precursor content						
µg THM/mg of Al	0.10	0.25	0.16	0.17	0.11	0.15
µg HAA/mg of Al	0.12	0.28	0.20	0.15	0.21	0.16
Potential DBP contribution from coagulant (assume coagulant dose of 0.167 mmol of metal/L, i.e., equivalent to alum dose of 50 mg/L as alum)						
THM (µg/L)	0.5	1.1	0.7	0.8	0.5	0.7
HAA (µg/L)	0.5	1.3	0.9	0.7	1.0	0.7

Table 4.18

Seven-day DBP formation potential for commonly used iron containing coagulants

Coagulant	Ferric sulfate		Ferric chloride	
Chlorine (mg/L as Cl_2)				
Dose	1.1	2.2	1.1	2.2
7-day residual	0.3	0.6	<0.05	<0.05
pH				
7-day	6.49	6.48	6.52	6.60
THM and HAA (µg/L)				
HAA5	0.0	0.0	0.0	3.4
TTHM	1.0	1.9	0.0	0.0
Coagulant dose				
mmol/L of Fe		1.5		1.5
mg/L as Fe		84		84
DBP precursor content				
µg THM/mg of Fe	0.012	0.023	none	0.012
µg HAA/mg of Fe	none	none	none	0.040
Potential DBP contribution from coagulant (assume coagulant dose of 0.167 mmol of metal/L, i.e., equivalent to 27 mg/L as ferric chloride or 67 mg/L as sulfate)				
THM (µg/L)	0.11	0.21	none	0.11
HAA (µg/L)	none	none	none	0.38

TOC content was determined by diluting each full-strength product by 1:20 or 1:100, and analyzing for TOC. The TOC methodology used was UV persulfate oxidation. Results are listed in Table 4.19. The results reported for standard alum and ferric sulfate are median values from multiple replicates. Data for the other coagulants represent only one result. UV persulfate oxidation, also called "wet oxidation", could not be used to analyze TOC levels in ferric chloride.

Based on results reported in Table 4.19, typical water treatment doses of polyaluminum chloride (PACl), aluminum chlorohydrate (ACH), or ferric sulfate would result in a TOC contribution from coagulant addition of less than 0.06 mg/L. These calculations and similar calculations regarding the DBP precursor content of coagulants described in Tables 4.17 and 4.18 indicate that these coagulants are not significant sources of TOC or DBP precursors at doses typically used for water treatment.

Table 4.19

TOC composition in coagulants

	Source concentration	Dilution	TOC	TOC/Al ratio	TOC added to water*
Al-based coagulant	mg/L as Al		mg/L as C	µg C/ mg Al	mg/L as C
PACl	74,320	1:20	20.4	12.35	0.056
ACH	163,120	1:20	26.6	7.34	0.033
Standard alum	58,400	1:100	0.58	2.25	0.010
	Source concentration	Dilution	TOC	TOC/Al ratio	TOC added to water†
Fe-based coagulant	mg/L as Fe		mg/L as C	µg C/ mg Fe	mg/L
Ferric sulfate	192,000	1:100	0.21	0.51	0.005
Ferric chloride			Unable to analyze		

*Dose of 4.5 mg/L as Al (50 mg/L as alum)
†dose of 9.3 mg/L as Fe (33 mg/L as ferric sulfate)

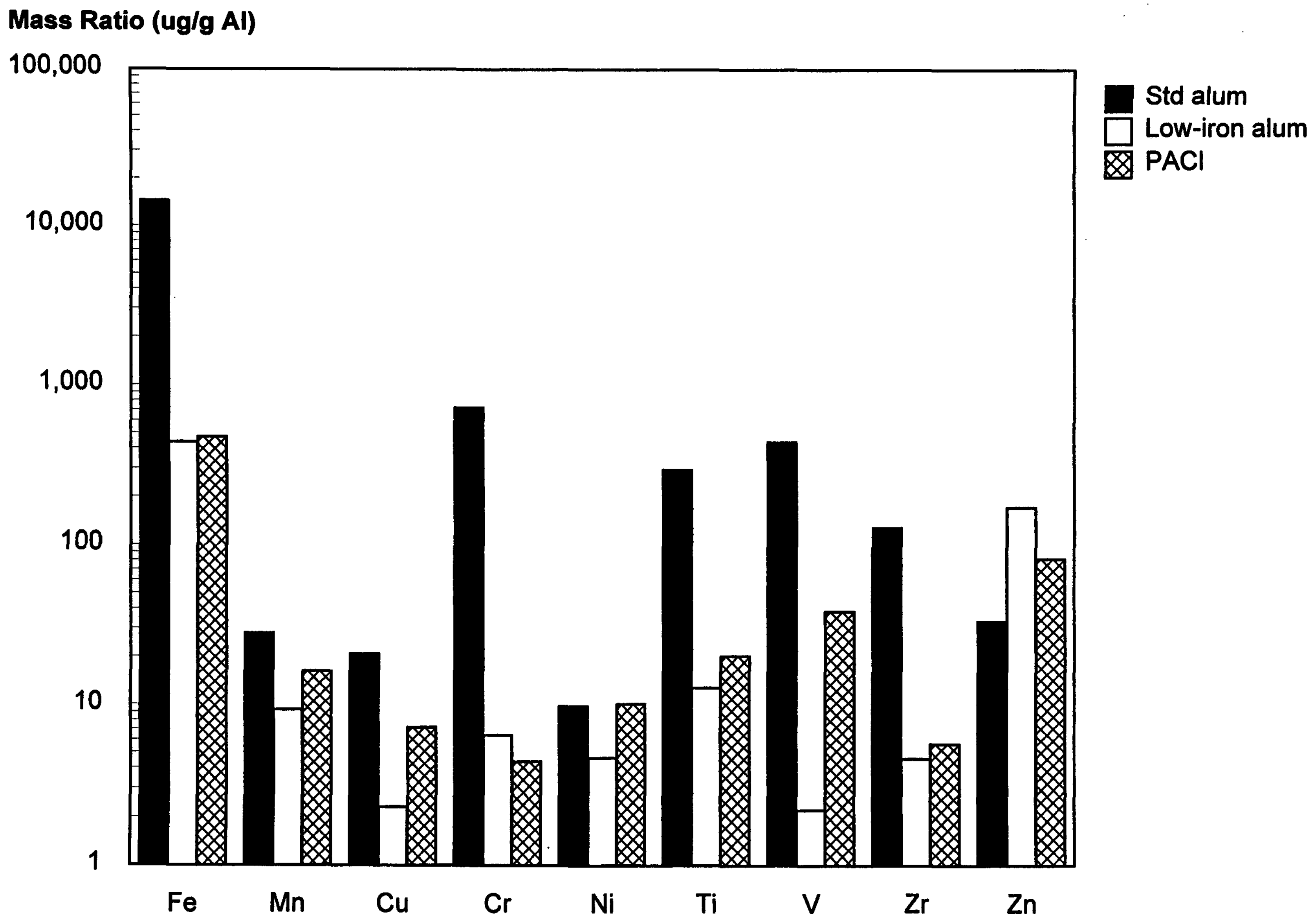


Figure 4.1 Trace contaminants in aluminum-based coagulants

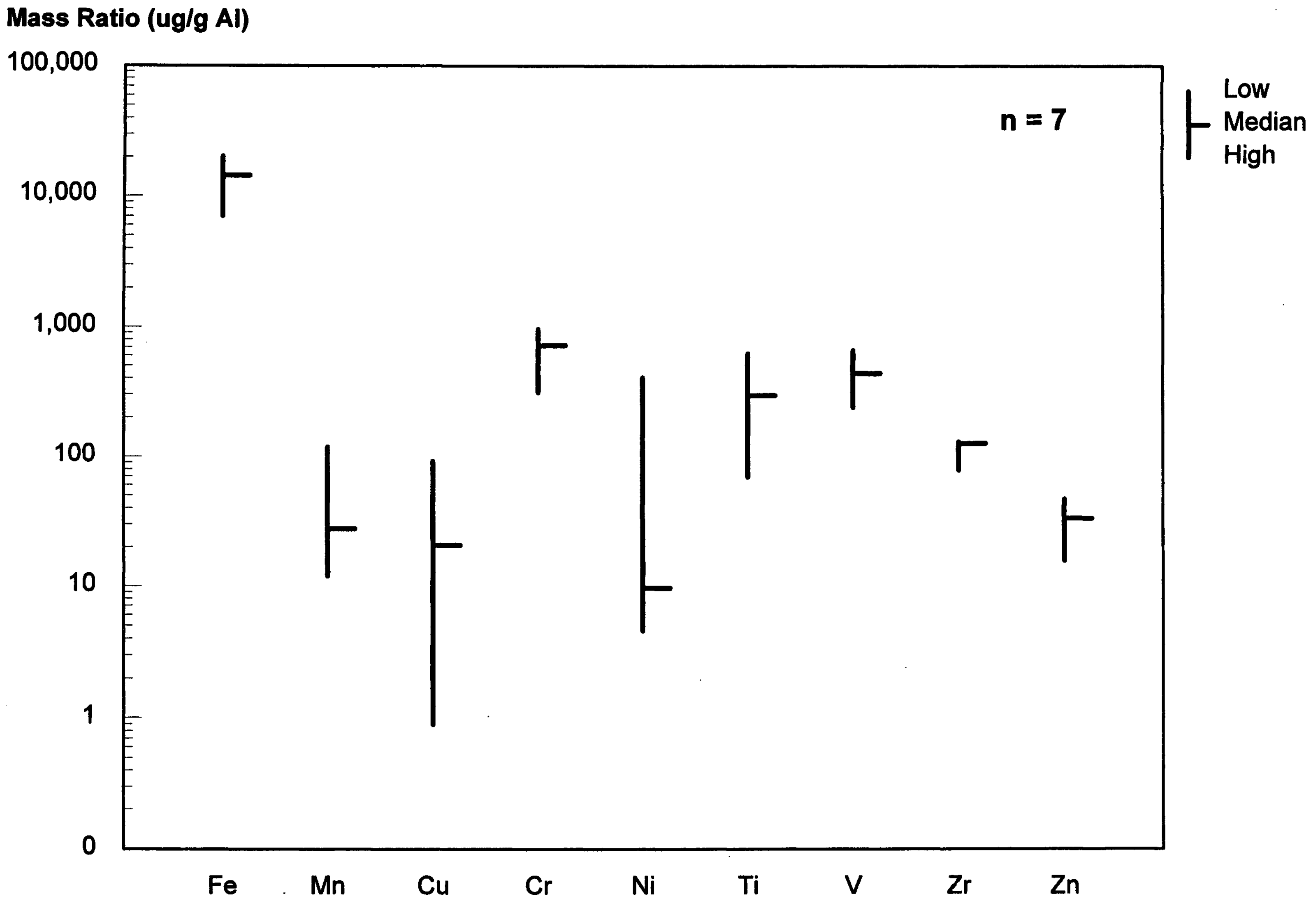


Figure 4.2 Range and median of trace metals in standard alum

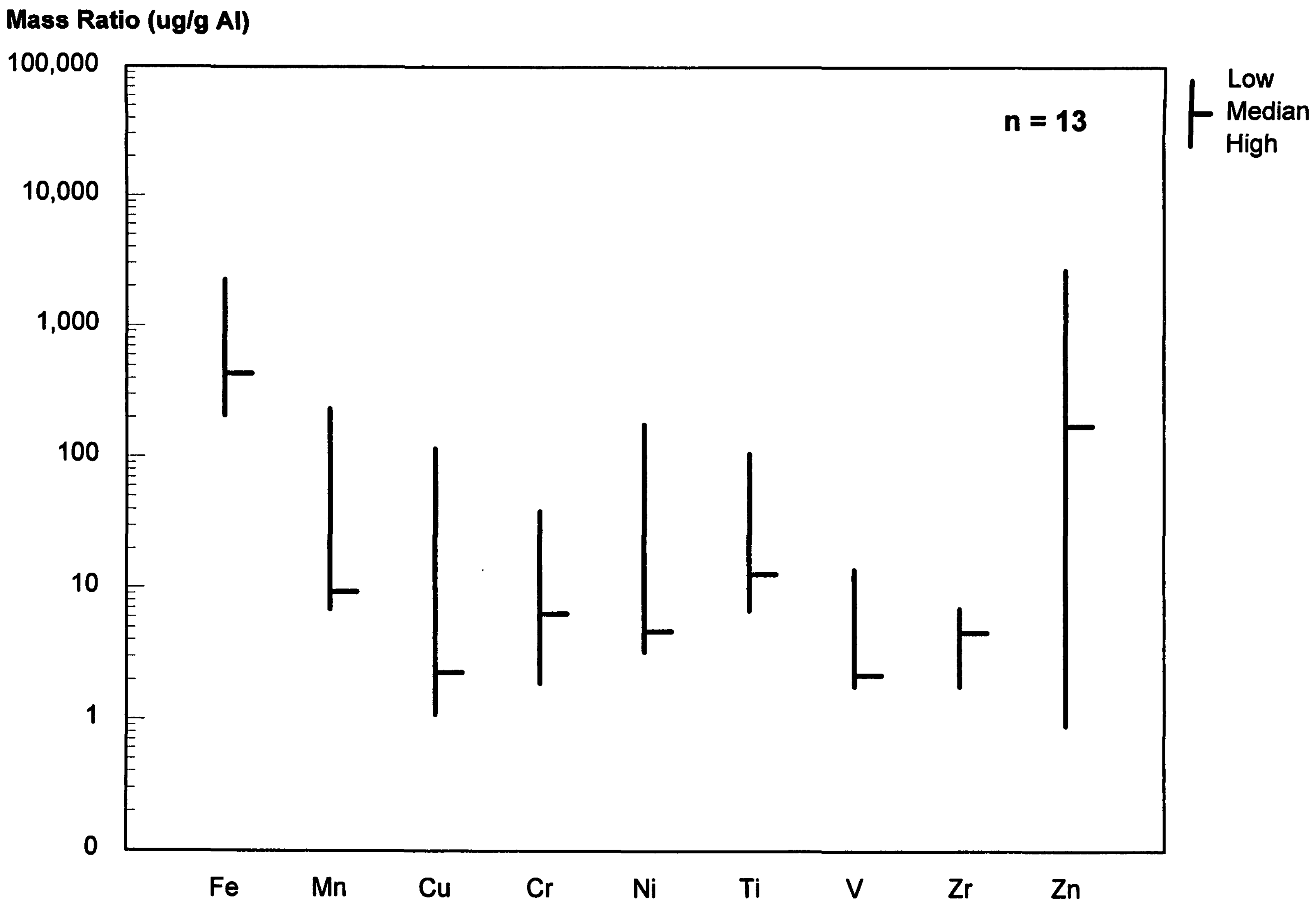


Figure 4.3 Range and median of trace metals in low-iron alum

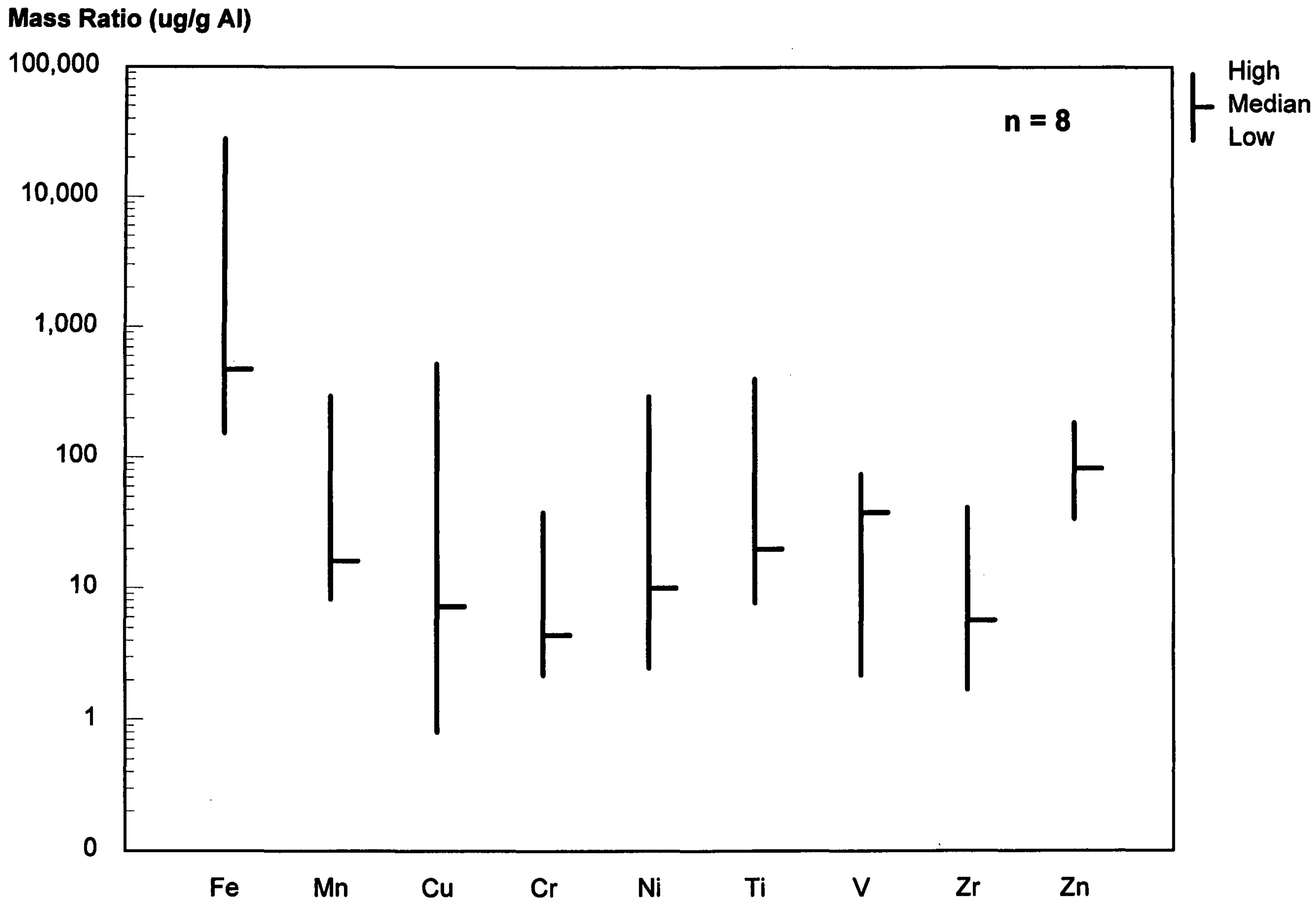


Figure 4.4 Range and median of trace metals in polyaluminum chloride

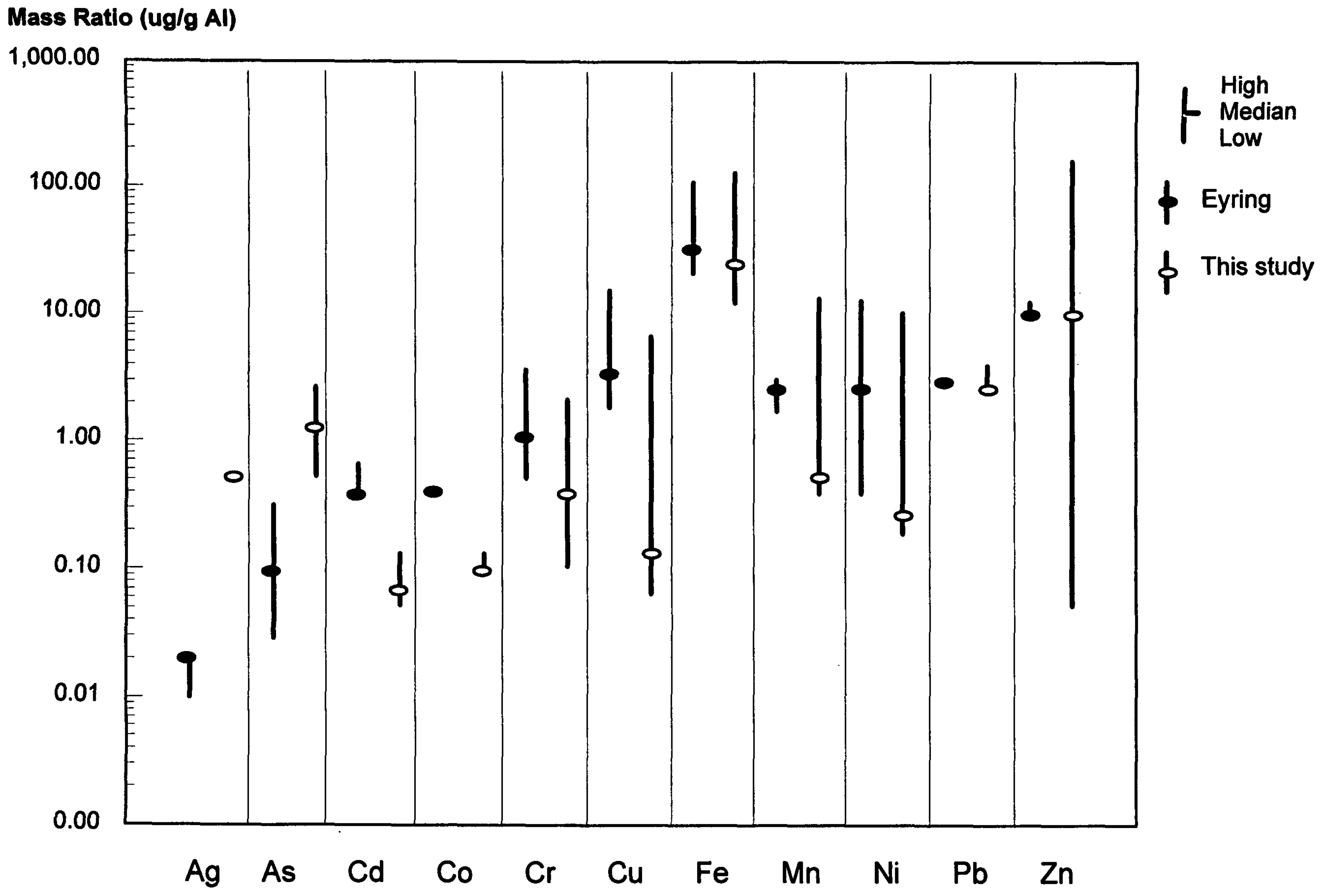


Figure 4.5 Comparison of trace contaminant levels in low-iron alum versus published literature

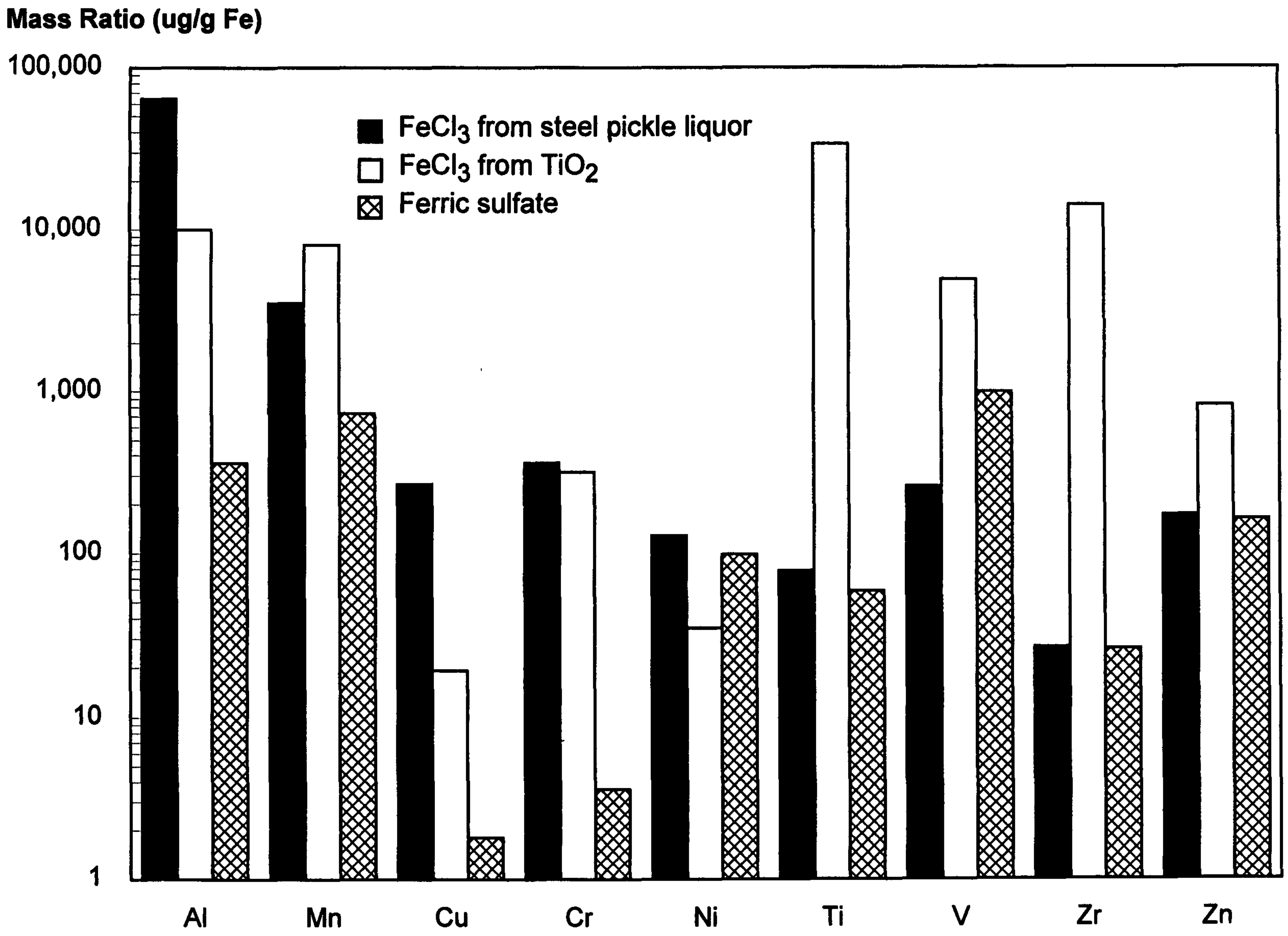


Figure 4.6 Trace contaminants in iron-based coagulants

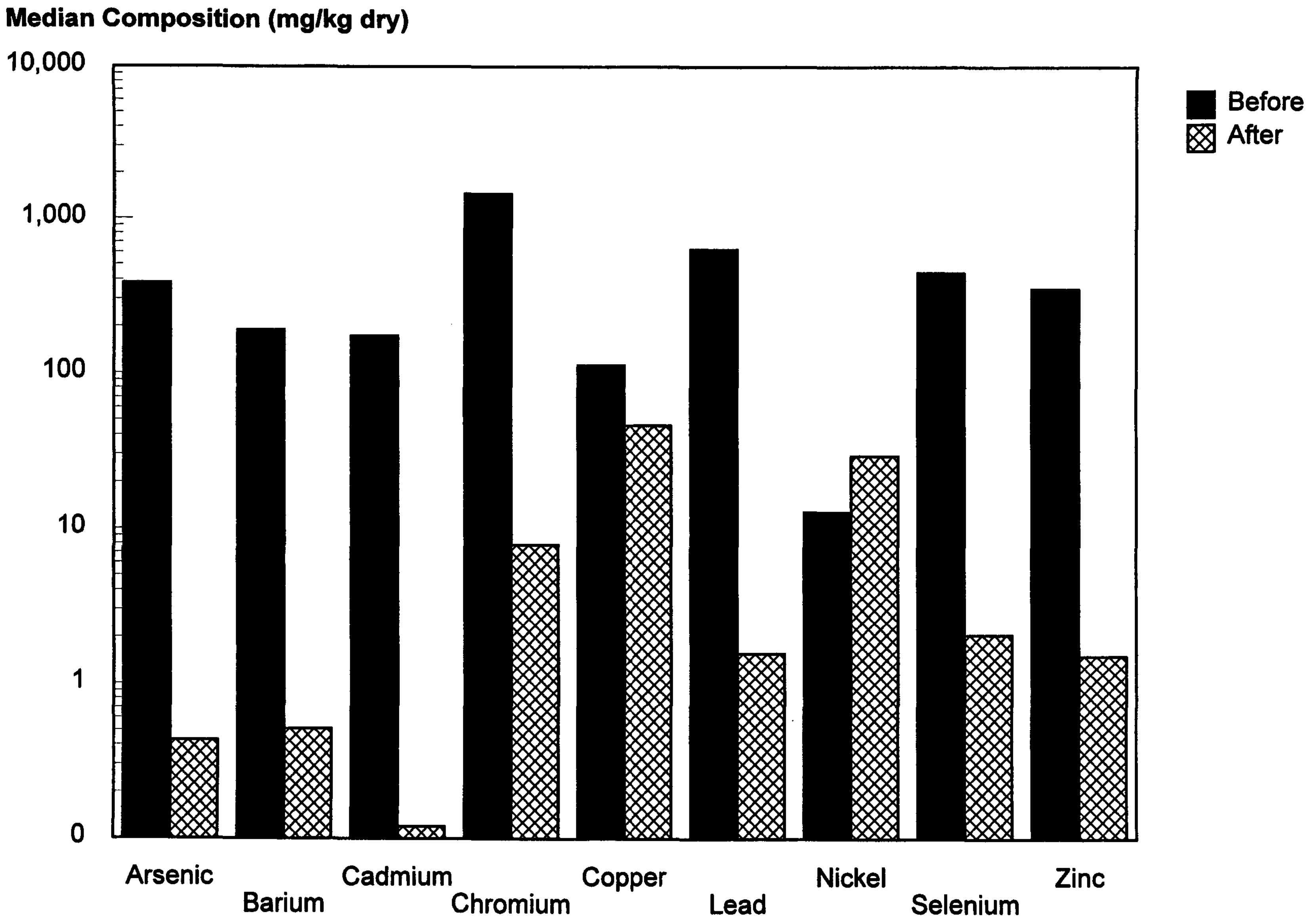


Figure 4.7 Impact of implementing tighter specifications for ferric chloride

CHAPTER 5

PARTITIONING AND FATE OF TRACE CONTAMINANTS ADDED BY DRINKING WATER TREATMENT CHEMICALS

APPROACH

One of the fundamental issues addressed in this research was to gain a better understanding of the fate of trace contaminants in treatment chemicals after they are added in a water treatment plant. Key questions included: Are contaminant levels added by chemicals important? Do the contaminants remain in the water phase or are they partitioned to residuals? Can this behavior be predicted? What tools are available to utilities that could be used to estimate how trace contaminant in chemicals could affect finished water quality or residuals quality? Can contaminants in chemicals impact compliance with drinking water MCLs or ability to meet residuals quality goals or disposal options? This chapter sheds light on these fundamental questions and provides the practical link to utilities on the issue of trace contaminants in drinking water chemicals.

Partitioning behavior of aluminum- and iron-containing coagulants was investigated in pilot-scale and full-scale studies described in this report. These studies included measurement of trace metal content of raw and finished water, spent filter backwash water (SFBW), clarifier sludge, and treatment chemicals in order to compare the treatment chemicals versus raw water as sources of these trace metals, as well as an assessment of whether these metals end up in finished water or one of the residuals streams (clarifier sludge versus SFBW). Findings from these studies were then compared to the assessment of treatment chemical composition using the approach outlined in ANSI/NSF Standard 60 guidelines (NSF 1999). Furthermore, this report includes some simple, straightforward calculations that utilities can use to evaluate treatment chemical impacts on residuals quality at their facilities. These calculations are based upon information and insights derived from this study, and from the research team's experience and understanding of the quality and quantity of residuals produced during water treatment.

PILOT PARTITIONING STUDIES

Methods

Pilot-scale studies were conducted at EE&T's process facility over a period of three months. This work was done to investigate contaminant partitioning under controlled conditions that could later be compared to full-scale results. Control over the test conditions included limiting the contaminant source to the coagulant only, and thereby generating a coagulant sludge without contaminants contributed by raw water. Pilot-scale partitioning studies were conducted using three metal coagulants including a standard alum, a titanium dioxide-derived ferric chloride, and a high basicity polyaluminum chloride product (aluminum chlorohydrate or ACH). The coagulants were tested using at least three different sets of conditions, as outlined in Table 5.1. One test condition included a repeat of the highest dosage for a given coagulant into which arsenic, lead, and copper were spiked, as listed in Table 5.1.

Table 5.1

Summary of coagulant and spike doses used for pilot partitioning studies

Coagulant dose (as Al or Fe)			Test duration	Flow rate	Finished	Metal spike (µg/L)		
(mg/L)*	(mg/L)†	(mM)†	(hours)	(mL/min)	pH	As	Pb	Cu
High-basicity polyaluminum chloride (ACH)								
12	4.6	0.17	76	423	6.9		None	
24	9.9	0.37	35	423	7.0		None	
24	9.7	0.36	32	429	7.0	87	157	1,049
Low-iron alum								
56	5.0	0.19	73	432	6.9		None	
28	2.5	0.09	69	429	6.3		None	
53	4.7	0.18	48	425	5.8	91	163	1,089

(continued)

Table 5.1 (continued)

Coagulant dose (as Al or Fe)			Test duration	Flow rate	Finished	Metal spike (µg/L)		
(mg/L)*	(mg/L)†	(mM)†	(hours)	(mL/min)	pH	As	Pb	Cu
Ferric chloride								
13	4.5	0.08	50	449	6.7		None	
26	9.1	0.16	30	441	6.5		None	
26	9.1	0.16	34	431	5.2	85	152	1,015

*As dry polyaluminum chloride, alum, or ferric chloride
†As Al or Fe

Figure 5.1 includes a schematic diagram of the experimental apparatus used for the pilot studies. The coagulant solution was fed by a peristaltic pump into a stream of finished city water fed by another peristaltic pump. The coagulant and raw water mixture passed through an in-line static mixer, a square flocculation basin with a paddle mixer, and then into a sedimentation basin. Finished city water was used to feed the pilot system so that a mostly chemical sludge could be generated. Flow rate during the pilot studies was approximately 450 mL/min, resulting in a basin overflow rate of about 0.14 gpm/sf.

Characteristics of the pilot influent water include the following:

- pH = 7.6
- Alkalinity = 36 mg/L as $CaCO_3$
- Turbidity = 0.22 ntu
- TDS = 135 mg/L
- Al = 56 µg/L
- Fe = 35 µg/L
- Total combined chlorine residual = 3.4 mg/L as Cl_2

Table 5.2 summarizes the composition of the three coagulants used in the pilot partitioning studies (µg constituent per g of Al or Fe). Table 5.1 indicates the coagulant dose used in each experiment. The concentration of a given trace metal contributed by the coagulant in each study can be determined by multiplying the dose from Table 5.1 by the composition in Table 5.2. For example, in the first experiment with ACH the dose was 4.6 mg/L as Al and the nickel composition was 15 μg Ni per g of Al. Therefore, at this dose the coagulant contributed 6.9 x 10^{-5} mg/L as Ni, or 69 ng/L as Ni.

Table 5.2

Coagulants used for laboratory partitioning studies

[alum, aluminum chlorohydrate (ACH), and ferric chloride]

Constituent	Symbol	Alum (μg/g Al)	ACH (μg/g Al)	Ferric chloride (μg/g Fe)
Aluminum	Al	1,000,000	1,000,000	10,000
Antimony	Sb	<9		22
Arsenic	As	<9	<16	<8
Barium	Ba	1	1	56
Cadmium	Cd	<1	<2	3
Calcium	Ca	391	478	483
Chromium	Cr	7	<2	317
Cobalt	Co	<2	<2	69
Copper	Cu	2	7	19
Iron	Fe	299	396	1,000,000
Potassium	K	67	48	158
Lead	Pb	<46	<16	<42
Magnesium	Mg	122	206	1,000
Manganese	Mn	7	8	8,083
Mercury	Hg	<9	11	15
Molybdenum	Mo	<2	<2	56
Nickel	Ni	5	15	35
Phosphorus	P	<46	<41	133
Selenium	Se	<69		<8
Silver	Ag	<9	<7	<7
Sodium	Na	6,434	1,320	2,833
Sulfur	S		157	200
Titanium	Ti	44	12	34,167
Vanadium	V	<2	31	4,917
Zinc	Zn	<1	35	817
Zirconium	Zr	5	4	14,167

Filtered samples (0.45 μm) were collected at the end of each experiment and analyzed for trace metals content. Sludge retained in the clarifier was decanted and analyzed for trace metals composition and total suspended solids (TSS). The trace metal concentration in the sludge slurry (mg/L) divided by the TSS (mg/L) was used to calculate the solid phase concentration of trace metals (mg of trace metals per kg of sludge on a dry weight basis). The mass of trace metal in the sludge was calculated by multiplying the sludge compositional data by the test duration (see Table 5.1) and the sludge production rate estimated by methods described in Cornwell (1999) and as summarized in Appendix E. Similarly, the mass of trace metals in the influent and effluent water phases was calculated by multiplying the flow rate times the test duration and by the liquid phase concentration. These data are summarized in Appendix F, including sample calculations.

Results

Tables 5.3 and 5.4 summarize data from Appendix F, indicating whether the coagulant or the water was the predominant source of a given constituent into the pilot-scale sedimentation basin, and whether this constituent partitioned into the liquid phase effluent from the basin or into the sludge phase collected in the basin.

Highly soluble major cations like calcium, magnesium, sodium, and potassium originated in the water and remained in the water phase effluent from the basin. Aluminum and iron added by coagulants was partitioned primarily to the clarifier sludge. Titanium, vanadium, and nickel were contributed by all three coagulants and these metals also partitioned to the sludge. Arsenic was not detected in any of the three treatment chemicals, but was detected in sludge, especially in studies where arsenic was spiked into the coagulant. In studies using ferric chloride, the coagulant contributed more manganese, cadmium, cobalt, and molybdenum than did the water, and these metals plus selenium, chromium, copper and lead partitioned into the sludge. By contrast, these metals originated in the raw water and remained in the finished water in studies with ACH or alum.

Table 5.3

Percentage of metals contributed by coagulants and percentage partitioning into residuals during pilot studies

	Source (percent from chemical)			Fate (percent into sludge)		
	ACH	Alum	Ferric chloride	ACH	Alum	Ferric chloride
Major cations						
Calcium	0	0	0	7	1	1
Magnesium	0	0	0	4	1	0
Sodium	0	0	0	4	1	0
Potassium	0	0	0	5	1	0
Aluminum	98	97	38	98	88	39
Iron	17	7	100	83	76	99
Manganese	1	0	81	61	35	3
Trace metals						
Barium	0	0	2	6	3	6
Beryllium				ND	ND	ND
Cadmium	ND	ND	100	ND	ND	ND
Chromium	0	1	33	ND	0	100
Cobalt	ND	ND	100	ND	ND	ND
Molybdenum	ND	ND	100	ND	ND	100
Nickel	100	100	100	100	100	100
Selenium				ND	ND	100
Silver	ND	ND	ND	ND	ND	ND
Thallium				ND	ND	ND
Titanium	100	100	100	100	100	100
Vanadium	100	ND	100	100	100	100
Zinc	0	0	7	93	24	24
Without spike						
Arsenic	ND	ND	ND	100	100	100
Copper	1	0	2	100	75	100
Lead	ND	ND	ND	100	ND	100
With spike						
Arsenic	100	100	100	100	100	100
Copper	100	100	100	52	12	1
Lead	100	100	100	94	53	86

Table 5.4

Comparison of source and fate of metals during full-scale studies

	Source (percent from chemical)			Fate (percent into sludge)		
	ACH	Alum	Ferric chloride	ACH	Alum	Ferric chloride
Major cations						
Calcium	W	W	W	W	W	W
Magnesium	W	W	W	W	W	W
Sodium	W	W	W	W	W	W
Potassium	W	W	W	W	W	W
Aluminum	C	C	W	R	R	W
Iron	W	W	C	R	R	R
Manganese	W	W	C	R	W	W
Trace metals						
Barium	W	W	W	W	W	W
Beryllium				ND	ND	ND
Cadmium	ND	ND	C	ND	ND	ND
Chromium	W	W	W	ND	W	R
Cobalt	ND	ND	C	ND	ND	ND
Molybdenum	ND	ND	C	ND	ND	R
Nickel	C	C	C	R	R	R
Selenium				ND	ND	R
Silver	ND	ND	ND	ND	ND	ND
Thallium				ND	ND	ND
Titanium	C	C	C	R	R	R
Vanadium	C	ND	C	R	R	R
Zinc	W	W	W	R	W	W
Without spike						
Arsenic	ND	ND	ND	R	R	R
Copper	W	W	W	R	R	R
Lead	ND	ND	ND	R	ND	R
With spike						
Arsenic	C	C	C	R	R	R
Copper	C	C	C	R	W	W
Lead	C	C	C	R	R	R

W	mostly in water phase
C	mostly from chemical
ND	not detected
R	mostly in residuals/sludge
blank	not analyzed

Table 5.5 illustrates the impact of spiking copper, lead, and arsenic into the coagulants used during the pilot partitioning studies. Arsenic and lead levels in the sludge increased when the water was spiked with these metals, but the clarifier effluent levels did not increase. However, for copper there was a measurable increase in the water phase copper concentration leaving the clarifier.

Of the trace metals that were found above the detection limit and that partitioned into the liquid phase, only barium and chromium have primary MCLs. Metals levels in water plant residuals are typically not regulated, but some states have restrictions if residuals are land applied for beneficial use purposes. In some cases, water plant residuals are combined with wastewater biosolids for disposal and federal 40 CFR 503 limits for metals apply. Certain states use these same limits as guidelines for establishing water plant sludge beneficial use criteria. Using metals regulated under 40 CFR 503 limits, those metals that partitioned into the residuals streams during the experimental studies included cadmium, copper, nickel, lead, zinc, arsenic, molybdenum, and selenium. Of these ten metals that have either MCLs or Federal 503 biosolids limits, only cadmium, molybdenum, and nickel originated predominantly in the treatment chemicals. The source water contributed more of the other seven metals than did the coagulants, even though the water concentrations were barely above detection limits. Mercury was not analyzed due to analytical limitations.

Table 5.5

Impact of spiking on pilot sludge and effluent water concentrations

		Concentration			
		Residuals (mg/kg dry)		Effluent water (mg/L)	
Coagulant	Spiked metal	unspiked	spiked	unspiked	spiked
Alum	Copper	434	5,200	0.005	0.943
	Lead	<0.52	270	<0.001	0.006
	Arsenic	34	2,590	<0.001	<0.001
ACH	Copper	212	7,000	<0.001	0.304
	Lead	0.88	360	<0.001	<0.001
	Arsenic	5	777	<0.001	<0.001
Ferric chloride	Copper	380	752	<0.001	1.43
	Lead	132	483	<0.001	<0.001
	Arsenic	7	871	<0.001	<0.001

It is important to recognize that the pilot sludge samples are somewhat different than sludge produced at water plants. The sludges produced in the pilot studies were primarily chemical sludges. In a water treatment situation where the raw water has turbidity but almost no trace metals, the mass of sludge produced would be greater due to the turbidity removed, but the mass of trace metals would stay constant. Thus, the trace metal composition of the sludge would be lower than the composition of the pure chemical sludges produced in the pilot studies described in this report. In this way the study results are conservative, unless the raw water has elevated trace metals concentrations.

FULL-SCALE PARTITIONING STUDIES

Methods

Figure 5.2 includes a general process flow schematic for the full-scale treatment plants at the Philadelphia Water Department (PWD) and Denver Water (DW). The study at PWD was conducted at the Baxter Water Treatment Plant (WTP) and the DW portion of the study was conducted at the Foothills WTP. Table 5.6 describes flow rate, residuals generation rates, and chemical addition points throughout the two processes. Both utilities recycle spent filter backwash water, though Denver clarifies the SFBW before recycling the water while Philadelphia returns untreated SFBW. Another major difference between facilities is that DW uses a low-iron alum as coagulant while PWD uses ferric chloride. A final difference is the lower raw water turbidity at Denver (0.80 ntu) relative to Philadelphia (6.0 ntu).

Samples for SFBW and all other water-based samples were analyzed by each individual utility. These samples were collected on the same day the sludge and treatment chemical samples were collected and shipped to a central specialized laboratory for analysis (see Chapter 4).

Table 5.6

Characteristics of full-scale study facilities

Characteristics		Facility	
		Denver	Philadelphia
Flow rate			
Raw + SFBW	mgd	262	175
Filtered water	mgd	256	157
Residuals production rate			
Main process clarifier	lb/day (dry)	7,814	57,429
SFBW recycle	mgd	6.0	2.3
SFBW treatment		polymer addition and clarification prior to recycle return	no treatment prior to recycle return
Chemical addition - Raw water			
Potassium permanganate	mg/L as $KMnO_4$	none	1
Chlorine		yes	none
Chemical addition - Raw + SFBW			
Alum	mg/L as alum	15	none
Ferric chloride	mg/L as Fe	none	11.4
Cationic polymer	mg/L	1.8	none
Chlorine	mg/L as Cl_2	none	3
Chemical addition - Finished water			
Chlorine		yes	none
Sodium hypochlorite	mg/L as Cl_2	none	6
Fluoride	mg/l as F	none	none
Zinc orthophosphate	mg/L as PO_4	none	0.46
Ammonia		yes	yes
Caustic soda	mg/L	3.9	none
Process turbidity			
Raw	ntu	0.80	6.0
Raw + SFBW	ntu	1.63	4.0
Settled	ntu	0.86	0.6
Filtered	ntu	0.04	0.07

Sample Calculations

The data in Appendix G includes the mass flow rate of each constituent, mostly metals, measured at various stages in the process from raw to finished water. Table G.1 and G.2 summarize data for DW and PWD, respectively. The mass flow rate was calculated by multiplying the flow rate by the measured concentration. For example, the filtered water flow rate at DW was 256 mgd and the aluminum concentration was 0.06 mg/L as Al, resulting in a mass flow rate of 58 kg/day as Al at this point in the process. The contribution of trace metals from treatment chemicals was calculated in a similar manner with chemical dose multiplied by flow rate to determine the mass flow rate of treatment chemical added, then this result multiplied by the composition of trace metal in the treatment chemical to determine mass flow rate of a given trace metal. For example, at DW the alum dose was 15 mg/L as alum (1.35 mg/L as Al), the flow rate at this point in the process is 262 mgd, and the composition of iron in the alum was 209 mg Fe per kg Al. The resulting contribution of iron due to alum addition is 0.28 kg/day of iron.

The mass flow rate of untreated SFBW out of the system for each facility was calculated in a manner similar to other points in the process, i.e. recycle flow rate times concentration of constituents in SFBW. The mass flow rate of clarifier sludge out of the process was calculated by multiplying the dry sludge production rate by the measured composition of sludge. The dry sludge production used for DW was the value reported by the utility. The dry sludge production value used for PWD was calculated based upon the method outlined by Cornwell (1999) as discussed in Appendix E. This sludge production value at PWD was calculated as follows:

$$S_{turb} = 6.0 \text{ ntu raw water turbidity} * \frac{1.8 \text{ mg/L TSS}}{\text{ntu removal}} * \frac{8.34 \text{ lb/MG}}{\text{mg/L}} * \frac{157 \text{ MG}}{\text{day}}$$

$$= 14{,}100 \text{ lb/day}$$

$$S_{ferric} = 11.4 \text{ mg/L as Fe} * \frac{2.9 \text{ mg sludge}}{\text{mg Fe}} * \frac{8.34 \text{ lb/MG}}{\text{mg/L}} * \frac{157 \text{ MG}}{\text{day}} = 43{,}300 \text{ lb/day}$$

$$S_{total} = S_{turb} + S_{ferric} = (14{,}100 + 43{,}300) \text{ lb/day} = 57{,}400 \text{ lb/day}$$

where S_{total} = total sludge production

S_{turb} = sludge production resulting from turbidity removal

S_{ferric} = sludge production resulting from ferric coagulant

Results From Mass-Balance

Tables 5.7 and 5.8 present results of a mass-balance from the two full-scale study locations, using data summarized in Appendix G. Table 5.7 summarizes data from Denver and Table 5.8 includes data from Philadelphia. Input in the mass balance calculations includes untreated water and treatment chemicals, while output includes filtered water, solids from the sedimentation basin, and SFBW. The untreated water sample entering the process was collected prior to chemical addition in the rapid mix chamber and represents a mixture of raw water and recycled SFBW. The filtered water sample was collected from the combined filter effluent prior to addition of post-filter treatment chemicals. Chemicals accounted for in mass-balance calculations at DW include alum (rapid mix), cationic polymer (rapid mix), and non-ionic polymer (pre-filter) while at PWD contributions from lime and ferric chloride (both added at rapid mix) were accounted for in calculations. Chlorine was not included in the mass balance.

Findings reported in Tables 5.7 and 5.8 indicate that the source and fate of trace metals at the two facilities are similar even though the raw water quality at the two facilities is vastly different. The two facilities also use a different coagulant. Observations from the information collected from these two facilities are summarized in the following sections.

Major Cations

Calcium, magnesium, sodium, and potassium generally originated in the influent water stream (raw + SFBW), except calcium that was added through lime addition at Philadelphia. Only 1 to 12 percent of these metals was diverted to residuals streams, thus most of the major cations remained in filtered water.

Table 5.7

Mass-balance during full-scale study at Denver Water (DW)

Sample description	Input			Output				Summary statistics		
Constituent	Treatment chemicals* (kg/day)	Raw + SFBW† (kg/day)	Total (kg/day)	Sludge (kg/day)	SFBW (kg/day)	Filtered water (kg/day)	Total (kg/day)	Difference (percent)	Input from chemicals (percent)	Output in residuals (percent)
Calcium	1.1	34,510	34,511	35	729	33,623	34,388	0.4	0.0	2.2
Magnesium	0.2	11,01	11,801	12	252	11,531	11,795	0.1	0.0	2.2
Potassium	0.1	11,84	1,884	13	40	1,841	1,894	0.5	0.0	2.8
Sodium	77.8	27,668	27,745	9	610	26,937	27,557	0.7	0.3	2.2
Aluminum	1,339	218	1,557	642	784	58	1,484	4.8	86.0	96.1
Iron	0.28	69	70	50	46	19	115	48.9	0.4	83.1
Manganese	0.01	43	43	22	40	ND	62	37.6	0.0	100.0
Barium	0.0004	39.7	3.6	0.9	2.1	38.8	41.7	5.1	0.0	7.1
Zinc	3.6	ND		1	1.5	ND	2.3	44.9	100.0	100.0
Antimony	ND	ND		ND	ND	ND				
Arsenic	ND	ND		ND	0.25	ND	0.25			100.0
Cadmium	ND	ND		ND	ND	ND				
Chromium	0.006	ND	0.006	0.05	ND	ND	0.05		100.0	100.0
Cobalt	ND			0.02						
Copper	0.01	ND	0.01	ND	0.21	ND	0.21		100.0	100.0
Lead	ND	ND		0.43	0.15	ND	0.57			100.0
Mercury	0.015	ND	0.015	ND	ND	ND			100.0	
Molybdenum	ND	4.0	4.0	ND	0.1	3.9	4.0	1.4	0.0	96.3
Nickel	0.01	ND	0.01	0.12	0.06	ND	0.18		100.0	100.0
Selenium	0.003	ND	0.003	ND	ND	ND			100.0	
Silver	ND	ND		ND	ND	ND				
Titanium	0.010									
Vanadium	ND									

*15 mg/L as alum, 1.8 mg/L cationic polymer in rapid mix, 0.055 mg/L non-ionic polymer pre-filter.

†Raw water plus SFBW recycle return prior to chemical addition at rapid mix.

Table 5.8

Mass-balance during full-scale study at Philadelphia Water Department (PWD)

	Input			Output				Summary statistics		
Sample description Constituent	Treatment chemicals* (kg/day)	Raw + SFBW† (kg/day)	Total (kg/day)	Sludge (kg/day)	SFBW (kg/day)	Filtered water (kg/day)	Total (kg/day)	Difference (percent)	Input from chemicals (percent)	Output in residuals (percent)
Calcium	13,752	13,645	27,397	1,330	333	21,512	23,175	16.7	50.2	7.2
Magnesium	221	4,717	4,939	216	69	4,400	4,686	5.3	4.5	6.1
Potassium	25	1,788	1,813	214	22	1,705	1,941	6.8	1.4	12.1
Sodium	23	11,790	11,813	26	158	10,696	10,880	8.2	0.2	1.7
Aluminum	151	130	280	287	10	46	342	19.9	53.7	86.6
Iron	7,596	318	7,913	8,109	197	12	8,318	5.0	96.0	99.8
Manganese	62	22	84	86	10	ND	96	14.3	73.8	100
Barium	0.78	19.9	20.7	8.3	0.4	10.7	19.4	6.1	3.8	44.9
Zinc	6	14	20	15	8	7	30	38	31.1	78
Antimony	0.16	ND	0.16	ND	ND	ND	ND		100.0	
Arsenic	ND	ND		ND	0.018	ND	0.018			
Cadmium	0.024	ND	0.024	0.110	0.009	ND	0.118		100.0	92.5
Chromium	2.44	ND	2.44	4.17	ND	ND	4.17	52.3	100.0	100
Cobalt	0.53	ND	0.53	0.89	0.03	ND	0.91		100.0	97.1
Copper	0.19	2.65	2.84	1.12	0.09	2.38	3.59	23.2	6.8	33.7
Lead	ND	ND		ND	0.09	ND	0.088			100
Mercury	0.113			ND						
Molybdenum	0.42	0.66	1.08	1.15	0.03	ND	1.17	7.9	38.9	100
Nickel	0.30	1.32	1.63	0.96	0.04	0.59	1.59	2.1	18.6	62.7
Selenium	ND	ND		ND	0.009	ND	0.009			100
Silver	ND	ND		ND	ND	ND	ND			
Titanium	260	5	265	313	5	ND	318	18.2	98.0	100
Vanadium	37	1	39	42	1	ND	43	10.2	96.6	100

*Ferric chloride dose = 11.4 mg/L as Fe (33 mg/L as $FeCl_3$), lime dose = 38.4 mg/L as $Ca(OH)_2$.

†Raw water plus SFBW recycle return prior to chemical addition at rapid mix.

Iron and Aluminum

Trace amounts of iron are present in alum and trace amounts of aluminum can be found in ferric chloride. Whether added as the primary coagulant or as a contaminant in ferric chloride, aluminum is contributed primarily by treatment chemicals and then is removed in the residuals streams. Similarly, iron added as a coagulant or as a contaminant in alum is partitioned to the residuals streams. However, since the alum used at Denver Water was a low-iron product, the predominant source of iron in that case was raw water, not the coagulant. Even if a standard alum product had been used, which typically contains about 33 times more iron than a low-iron product, the raw water would still contribute about eight times more mass of iron at DW than would addition of a typical standard alum product.

Regulated Metals in Finished Water and Residuals

Arsenic and lead are regulated metals that were not detected in the treatment chemicals or raw water. Selenium was not detected in raw water or in any treatment chemicals, except the cationic polymer used at Denver. Alum and ferric chloride were the major input sources of chromium at both PWD and DW. Alum was the major input source of copper, mercury, and zinc at DW. Ferric chloride was the major input source of cadmium at PWD. Metals with primary drinking water MCLs or biosolids limits (if applicable) were either not detected or they partitioned primarily into the residuals streams, except barium at both facilities, molybdenum at DW, and copper at PWD (though about one-third of copper at PWD was accounted for in residuals streams).

Other Constituents

The major input source of manganese at PWD was ferric chloride, while at DW the raw water contributed more manganese than alum or other treatment chemicals. At both facilities, the manganese partitioned almost completely to the residuals streams. Cobalt, titanium, and vanadium were not measured in water samples at DW so it was not possible to evaluate the sources and fate of these metals at this facility. Titanium and vanadium can be potential contaminants in alum products, though they are usually found at one to two orders of magnitude higher levels in standard alum products than in the low-iron product used at DW. Ferric chloride was the principal source of titanium, vanadium, and cobalt at PWD, and these metals partitioned into the residuals streams during treatment. Silver was not detected in water samples, treatment chemicals, or residuals streams at these two facilities.

Residuals From SFBW Versus Main Sedimentation Basin

Solids removed in the SFBW clarifier at DW are not directly included in the mass-balance calculations in Table 5.7, though they are indirectly incorporated. Table 5.9 compares the solids removed in the SFBW clarifier at DW with the main sedimentation basin in the process. Typically, 50 percent or more of the total removal of many trace metals at this facility occurs in the SFBW clarifier. For example, about equal amounts of aluminum, iron, barium, manganese, and zinc were removed in the SFBW clarifier versus the main sedimentation basin. Measured removal of lead, chromium, and nickel was greater in the main clarifier than in the SFBW clarifier, while arsenic, molybdenum, copper, mercury, antimony, and selenium were not detected in the solids collected from the main sedimentation basin but were removed in the SFBW clarifier. Similarly, removal of zinc in the SFBW clarifier was about 1.5 times the mass removed in the main sedimentation basin.

The arsenic result, for example, is interesting because it demonstrates the importance of SFBW treatment prior to recycle return. At DW, the arsenic concentration in the untreated SFBW was 0.012 mg/L, which is above the current 0.010 mg/L arsenic MCL, but was reduced to <0.001 mg/L after treatment. Similar removal was observed for other constituents during SFBW treatment.

Trace Metal Contribution From Post-Filter Chemical Addition

Treatment chemicals added to finished water did not contribute appreciable metals levels at either facility. The composition of the fluoridation chemical used at DW (sodium fluorosilicate) was not analyzed during this study so it was not possible to calculate the trace metals contributed from this chemical to finished water at DW. However, hydrofluorosilicic acid did not contribute significant trace metals at the dosage used at PWD. The only post-filter chemical that contributed appreciable levels of any trace metal are zinc added from the zinc-based corrosion inhibitor at PWD.

Table 5.9

Comparison of trace metals removed in sedimentation basin versus SFBW clarifier at Denver

			SFBW				
		Main clarifier (kg/day)	Untreated (kg/day)	Treated (kg/day)	Amount removed (kg/day)	Percent removed (percent)	Total removal due to SFBW clarifier (percent)
Aluminum	Al	642	784	64	721	92	52.9
Calcium	Ca	35	729	731	0		0.0
Iron	Fe	50	46	4	42	91	45.5
Potassium	K	13	40	40	0		0.0
Magnesium	Mg	12	252	248	4	2	26.6
Manganese	Mn	22	40	4	36	91	62.0
Sodium	Na	9	610	600	11	2	53.5
Silver	Ag	ND	ND	ND			
Arsenic	As	ND	0.25	0.02	0.23	92	100
Barium	Ba	0.85	2.12	1.06	1.06	50	55.5
Cadmium	Cd	ND	ND	ND			
Chromium	Cr	0.046	ND	ND			
Copper	Cu	ND	0.21	ND	0.21	100	100.0
Mercury	Hg	ND	0.002	ND	0.002	100	100.0
Molybdenum	Mo	ND	0.15	0.11	0.04	29	100.0
Nickel	Ni	0.12	0.06	ND	0.06	100	35.2
Lead	Pb	0.43	0.15	ND	0.15	100	25.8
Antimony	Sb	ND	0.06	ND	0.06	100	100.0
Selenium	Se	ND	0.04	ND	0.04	100	100.0
Zinc	Zn	0.78	1.53	0.23	1.29	85	62.4

ND = not detected

Residuals Quality Versus Federal 40 CFR 503 Residuals Limits

Table 5.10 summarizes the measured residuals concentration in the main sedimentation basins at PWD and DW during the full-scale studies. Because the metals composition in the SFBW solids was not measured in this study, it was calculated using the example methodology presented in Appendix E. A similar technique was used to estimate the trace metals content of the combined residuals stream.

Data from Table 5.10 indicate that residuals from the PWD and DW facilities would meet metals limits outlined in Federal 40 CFR 503. Of course these are only applicable if a utility combines its water plant residuals with wastewater biosolids for disposal, or if a state uses these limits as a guideline for regulating metals levels in water plant residuals that are land applied for beneficial use. This finding confirms the results from the pilot-scale studies.

The arsenic composition for the SFBW clarifier solids at Denver was calculated as 38 mg/kg (dry weight basis), which is close to the 40 CFR 503 limit of 41 mg/kg (dry) from Table 5.10. Arsenic was not detected in the raw water, alum, or other treatment chemicals. If any of these sources of arsenic increased in the future, for example due to arsenic contamination of the alum, then land application or other beneficial use disposal options for the SFBW clarifier solids may not be available.

Table 5.10

Comparison of residuals with Federal 40 CFR 503 biosolids limits

		Measured or calculated residuals composition			
		PWD†	DW‡		
Constituent	Biosolids limit* (mg/kg dry)	Measured main sed basin (mg/kg dry)	Measured main sed basin (mg/kg dry)	Calculated SFBW clarifier (mg/kg dry)	Calculated combined residuals (mg/kg dry)
Arsenic	41	ND	ND	38	24
Cadmium	39	4.2	ND	ND	ND

(continued)

Table 5.10 (continued)

		Measured or calculated residuals composition			
		PWD†	DW‡		
Constituent	Biosolids limit* (mg/kg dry)	Measured main sed basin (mg/kg dry)	Measured main sed basin (mg/kg dry)	Calculated SFBW clarifier (mg/kg dry)	Calculated combined residuals (mg/kg dry)
Chromium	1,200	160	13	ND	5
Copper	1,500	43	ND	34	22
Lead	300	ND	120	24	59
Mercury	17	ND	ND	0.34	0.22
Molybdenum	75	44	ND	7	4
Nickel	420	37	33	10	19
Selenium	100	ND	ND	7	4
Zinc	2,800	34	220	209	213

*40 CFR 503 Federal limits for sewage biosolids
†Iron-based coagulant
‡Aluminum-based coagulant
ND = not detected

COMPARISON OF PILOT- AND FULL-SCALE STUDIES

Findings from the two full-scale studies are similar to those recorded for the pilot-scale studies. Table 5.11 combines findings from both pilot- and full-scale studies using the three coagulants tested.

Table 5.11

Comparison of source and fate of contaminants during pilot- and full-scale studies

	Source	Fate
Coagulant metals		
Aluminum	C	R
Iron	W* / C†	R
Major cations		
Calcium	W	W
Magnesium	W	W
Sodium	W	W
Potassium	W	W
Trace metals		
Antimony	ND	ND
Arsenic	ND	R
Barium	W	W
Cadmium	ND* / C†	ND or R
Chromium	C	R
Cobalt	C	ND or R
Copper	W	R
Lead	ND	R
Manganese	W* / C†	R
Mercury	C	ND
Molybdenum	ND or W* / C†	ND* / R†
Nickel	C	R
Selenium	ND	ND or R
Silver	ND	ND
Titanium	C	R
Vanadium	C	R
Zinc	C* / W†	R

*Aluminum-based coagulants
†Iron-based coagulants

W	mostly from water
C	mostly from chemical
R	mostly in residuals/sludge
ND	not detected

Observations based upon Table 5.11 information include the following:

- More trace metals were contributed by coagulants than by other treatment chemicals due to higher dose, higher metal content, or both. This is consistent with results reported by Croker and Dixon (1989).
- Arsenic, antimony, lead, selenium and silver were typically below detection limits in treatment chemicals and raw water during pilot- and full-scale studies. Although these metals were also below detection limits in finished water, they were often detected in residuals. Therefore, these metals may have originated in the treatment chemicals and then concentrated in the residuals streams.
- Greater levels of major cations (calcium, magnesium, sodium, potassium), barium, and copper were contributed by the incoming raw water than were added by treatment chemicals (except calcium added by lime addition). This occurred even in pilot studies using a water source with minimal metallic content.
- Metals contributed by both aluminum- and iron-based coagulants included: aluminum, chromium, cobalt, mercury, nickel, titanium, and vanadium. Additionally, iron coagulants contributed iron, cadmium, manganese, and molybdenum while aluminum-based coagulants contributed zinc.
- Metals contributed by coagulants partitioned into the residuals streams rather than into the finished water during full- and pilot-scale studies.
- Scale-up from pilot- to full-scale was very good.

ESTIMATING IMPACT OF CONTAMINANTS IN TREATMENT CHEMICALS ON FINISHED WATER QUALITY

Maximum Allowable Dose Using NSF Standard 60

The objective of the maximum allowable dose computation using the ANSI/NSF Standard 60 protocol (NSF 1999) is to limit the contribution of trace contaminants added by treatment chemicals to less than 10 percent of the finished water MCL. Certification of the maximum allowable dose can be performed by NSF or any other laboratory complying with the Standard 60 protocol. A manufacturer requesting certification of a treatment product could estimate the maximum allowable dose in a number of ways, including knowledge of past experiences. A conservative estimate of the maximum allowable dose can be calculated by multiplying the MCL by 0.10 and dividing by the composition of that constituent in the treatment chemical. Data reported in Chapter 4 can be used for this purpose. The calculation is repeated for each constituent with an MCL, and the lowest calculated dose would be a conservative estimate of the limiting dose.

After estimating the maximum allowable dose, a manufacturer would request that the laboratory performing the certification testing evaluate the chemical at this dose. The certification laboratory evaluates the chemical at the dose requested on a pass/fail basis in order to see if it meets the objective of adding less than 10 percent of all MCLs.

In this report, the compositional data reported in Chapter 4 was used to establish the maximum allowable dose. This evaluation process was referred to in this document as the "NSF Standard 60 approach". To avoid confusion, it is important to recognize that the actual Standard 60 certification testing would occur as the next step in the process at an independent certification laboratory that would verify the suitability of the dose calculated in this report.

One modification to the NSF Standard 60 protocol was required recently due to the establishment of an MCL for bromate of 0.010 mg/L in the Stage 1 Disinfectants and Disinfection By-Products Rule (DBPR) that became effective on January 1, 2002. Due to concerns over bromate content of sodium hypochlorite (Chlorine Institute 1999), NSF, USEPA, AWWA, and sodium hypochlorite manufacturers negotiated an agreement whereby the manufacturers agreed to undertake steps to limit bromate composition in sodium hypochlorite products. However, in the interim all parties agreed to allow sodium hypochlorite to contribute up to 50 percent, not just 10 percent of the finished water bromate MCL.

Calculation of Limiting Dose

A key assumption in the ANSI/NSF Standard 60 approach is that all constituents added by the treatment chemical partition into the finished water. For treatment chemicals that are added prior to filtration or clarification, this research shows that this approach is conservative because many of the contaminants in the treatment chemical will partition into the residuals streams.

Using this approach for data generated during this study, the limiting dose for standard alum was calculated as 156 mg/L as alum (14 mg/L as Al) with chromium as the limiting constituent. The mercury content of low-iron alum and standard alum were about the same (see Chapter 4), but chromium and other metals are removed during production of low-iron alum (see Chapter 3). Consequently, for low-iron alum the limiting constituent was mercury and the limiting dose was 189 mg/L as alum (17 mg/L as Al). Similar calculations for other treatment chemicals analyzed during this project are summarized in Table 5.12. Key findings from this table include the following:

- Even though the NSF Standard 60 approach is conservative with respect to predicting impact of treatment chemicals on finished water quality, limiting doses calculated by this method were typically far higher than those required at most U.S. treatment facilities.
- Mercury and chromium were the limiting trace constituents for many products, including aluminum- and iron-containing coagulants, potassium permanganate, and corrosion inhibitors.
- The relative trace metals content in sodium hypochlorite, caustic soda, and lime were much lower than for other chemicals, thereby resulting in markedly higher limiting doses determined using the NSF Standard 60 approach.
- The maximum allowable dose for sodium hypochlorite was typically driven by bromate composition.

The dose calculated in Table 5.12 would theoretically limit the contribution of the treatment chemical product to less than 10 percent of the finished water MCL for all constituents, assuming that all constituents added by the chemical partition to the finished water. While this partitioning assumption is valid for treatment chemicals added after filtration, this research demonstrated that most contaminants partition to the residuals streams if the treatment chemicals are added prior to clarification and filtration. Therefore, the NSF Standard 60 approach provides a very conservative estimate of the potential impact of trace contaminants in treatment chemicals on finished water quality.

Table 5.12

Maximum allowable doses and limiting constituents for typical water treatment chemicals

Treatment chemical	Maximum allowable dose	Limiting constituent
Standard alum	14 mg/L as Al 156 mg/L as alum	Cr
Low-iron alum	17 mg/L as Al 189 mg/L as alum	Hg
Polyaluminum chloride	18 mg/L as Al	Hg
Hydrofluorosilicic acid	4.3 mg/L as F	As
Steel pickle liquor- derived ferric chloride	28 mg/L as Fe 81 mg/L as $FeCl_3$	Cr
Titanium dioxide-derived ferric chloride	13 mg/L as Fe 37 mg/L as $FeCl_3$	Hg
Ferric sulfate	8 mg/L as Fe 29 mg/L as $Fe_2(SO_4)_3$	Pb
Zinc phosphate	103 mg/L as P	Cr
Potassium permanganate	0.8 mg/L as Mn 2.3 mg/L as $KMnO_4$	Hg
Sodium hypochlorite*	19 mg/L as Cl_2	BrO_3^-
Sodium hydroxide	> 2,000 mg/L as Na > 3,500 mg/L as NaOH	Cu
Lime	1,320 mg/L as Ca 2,400 mg/L as $Ca(OH)_2$	Ba

*Metals from this study, bromate (BrO_3^-) from Delcomyn 2000. Fifty percent of MCL allowed for bromate from sodium hypochlorite

NSF Approach and Regulatory Compliance Issues

There are consequences to the limiting dose calculations using the NSF Standard 60 approach due to regulatory concerns. Two of these concerns, bromate in sodium hypochlorite and consequences of the arsenic MCL, are discussed below.

Bromate in sodium hypochlorite was not analyzed in this research project since that is the specific forms of other ongoing research. Using mean data reported by Delcomyn (2000), the limiting dose for sodium hypochlorite was 19 mg/L as Cl_2. After this time, careful selection of raw materials and monitoring and control of the production process have reduced bromate levels to the point where typical limiting doses for sodium hypochlorite are closer to 80 mg/L as Cl_2. Before the NSF Standard 60 was modified to allow sodium hypochlorite to contribute 50 percent of bromate MCL rather than 10 percent, the Delcomyn data would have resulted in a calculated limiting dose of 3.8 mg/L as Cl_2. This would have severely limited the use of sodium hypochlorite products in most U.S. drinking water applications. Each of these cases are illustrated below:

Case 1	Case 2
Traditional NSF std. = <10 percent of bromate MCL can come from sodium hypochlorite	Modified NSF std. = <50 percent of bromate MCL can come from sodium hypochlorite
Bromate content = 264 µg/g Cl_2	Bromate content = 264 µg/g Cl_2
Max. allowable sodium hypochlorite dose = 3.8 mg/L as Cl_2	Max. allowable sodium hypochlorite dose = 19 mg/L as Cl_2

Based on this research, and using the NSF Standard 60 approach, arsenic was the limiting constituent in hydrofluorosilicic acid. Using the highest arsenic result from this research, a maximum allowable dose of 4.3 mg/L as F was calculated. If the arsenic MCL had been reduced to 3 µg/L instead of the current 10 µg/L, the limiting dose would have been 1.3 mg/L as F. This example and the example of bromate in sodium hypochlorite show that very low MCLs for certain contaminants could impact selection of chemical products and/or force manufacturers to lower levels of particular trace contaminants. Comparison of these two situations is presented below:

Case 1	Case 2
Arsenic MCL = 10 µg/L	Arsenic MCL = 3 µg/L
Arsenic content = 231 µg/g F	Arsenic content = 231 µg/g F
Max. allowable fluoride dose = 4.3 mg/L as F	Max. allowable fluoride dose = 1.3 mg/L as F

Although the bromate in sodium hypochlorite and arsenic in hydrofluorosilicic acid examples show how trace contaminant levels in water treatment chemicals can be a significant problem with respect to meeting drinking water MCLs, this research showed that these are unusual cases. These two problems were related to a contaminant that remains in the water phase through treatment (bromate) and a contaminant present in a chemical added after coagulation and filtration (hydrofluorosilicic acid). Most other contaminants are contributed by chemicals added early in the treatment process, especially coagulants, and these contaminants mostly partition to the residuals streams rather than the finished water.

ESTIMATING IMPACT OF CONTAMINANTS IN TREATMENT CHEMICALS ON RESIDUALS QUALITY

The analogous mass-balance relationship used to evaluate pilot- and full-scale data can also be manipulated to develop a relationship to estimate the maximum allowable chemicals composition in coagulants and other treatment chemicals based upon residuals quality goals. For example, a reasonable goal for all utilities would be to minimize levels of regulated metals in finished water. Another goal would be to limit residuals quality to permitted levels. These two assumptions would produce a mass balance relationship as follows:

$$\text{Chemicals} = \text{Residuals} - \text{Untreated Water}$$

If the chemical dose is known, the equation can be modified as follows:

$$\text{Chemical Composition} = \frac{\text{Residuals} - \text{Untreated Water}}{\text{Dose}}$$

This can be expressed symbolically as follows:

$$X = \frac{L - R}{\text{Dose}} = \frac{(M * \text{limit}) - R}{\text{Dose}}$$

where X = Allowable metal concentration in coagulant so that residuals land application limits or other goals are not exceeded (mg/kg)

L = Allowable metal level in sludge per million gallons (MG) of finished water produced (lb/MG)

R = Metal concentration in raw water (mg/L)

Dose = Coagulant dose (mg/L)

M = Dry sludge production per volume of finished water produced (e.g., lb/MG)

limit = Trace metal limit in sludge (mg contaminant/kg of dry sludge)

Coagulant dose is established based on treatment goals and raw water quality. Utilities may or may not have goals for metals levels in water plant residuals, but the research team developed a simple methodology for calculating limiting chemical dose based on specific residuals quality objectives. Using the technique shown below, a utility could input its chemical composition and residuals goal to calculate maximum coagulant or other chemical dose restrictions. Molybdenum (Mo) is used in these sample calculations, though calculations would be similar for other trace metals of concern. The dose and turbidity are based on data reported from the PWD field study.

Assumptions:

- Ferric chloride dose = 11.4 mg/L as Fe or 33.1 mg/L as $FeCl_3$
- Raw turbidity = 6 ntu
- Sludge production from ferric chloride = 2.9 kg dry sludge per kg Fe dose = 1 kg dry sludge per kg $FeCl_3$ (see Appendix E)
- b factor = 1.8 mg/L TSS per ntu removed (see Appendix E)
- Assume no molybdenum in raw water
- 40 CFR 503 sludge limit = 75 mg/kg for molybdenum

Example calculations:

Step 1: Calculate M (see Appendix F) - dry sludge production

$$M = \left[6.0\ \text{ntu}\left(\frac{1.8\ \text{mg/L TSS}}{\text{ntu}}\right)\frac{8.34\ \text{lb/MG}}{\text{mg/L}}\right]$$

$$+\left[\frac{11.4\ \text{mg as Fe}}{\text{L}}\left(\frac{2.9\ \text{mg sludge}}{\text{mg Fe}}\right)\frac{8.34\ \text{lb/MG}}{\text{mg/L}}\right]$$

$$= 366\ \text{lb/MG} = 166\ \text{kg/MG}$$

Step 2: Calculate L (land application limit x residuals generation)

L = M*limit = 75 mg/kg x 166 kg/MG

L = 12,500 mg/MG

Step 3: Calculate X (Allowable metal concentration in $FeCl_3$)

$$X = \frac{(12{,}500\ -\ 0)\ \text{mg/MG}}{33\ \text{mg/L as}\ FeCl_3} * \frac{\text{MG}}{3.78\times 10^6\text{L}} * \frac{10^6\text{mg}}{\text{kg}}$$

X = 99.5 mg Mo/kg $FeCl_3$ (289 mg Mo/kg Fe)

Step 4: Compare to chemical composition data

The ferric chloride product used at PWD had a molybdenum composition of about 18 mg per kg of dry product, which is approximately 5.5 times below the maximum allowable level calculated in this example. Consequently, this ferric chloride product would not be expected to produce residuals with molybdenum levels exceeding a 75 mg/kg sludge biosolids limit.

Table 5.13 is an example of how a spreadsheet could be used to calculate allowable metals levels in a coagulant at a given facility. The raw water concentrations, coagulant dose, and sludge production in this example were based on the PWD full-scale study. These calculations can easily be modified for other doses, coagulants, raw water quality, or residuals goals. The last two columns in the table compare the maximum allowable trace metal composition (X) predicted versus the measured composition of the ferric chloride product used in the PWD full-scale study. The most sensitive metals in this example were mercury and molybdenum, but these were about four times lower than the limiting value. In fact, measured compositional data for the ferric chloride product indicate that the full strength chemical itself would not exceed typical residuals quality limits. This finding is consistent with the results for residuals generated during the pilot-scale studies, which were composed of mostly coagulant sludge.

Therefore, a facility using any of the treatment chemicals described in this report would not exceed residuals limits at their facility unless one or more of the following occurs:

- The residuals limits at the facility are lower than the Federal 40 CFR 503 limits
- Raw water or other sources contribute contamination pushing the residuals quality over the limit
- The treatment chemicals are more contaminated than those indicated in this report, or
- Analytical errors during measurement of sludge composition result in overestimation of trace metal content of the sludge

Table 5.13

Techniques for estimating allowable metals levels in coagulants based on residuals quality goals

			Constituent levels in sludge				
Constituent	Raw water concentration R (mg/L)	Residuals Limit* (mg/kg dry)	Total L† (mg/MG)	Contribution from raw water R (mg/MG)	Maximum contribution from coagulant L-R (mg/MG)	Max conc. allowed in coagulant X‡ (mg metal/kg dry)	Composition of coagulant (mg metal/kg dry)
Arsenic	<0.001	41	6,805	3,785	3,020	24	<3
Cadmium	<0.001	39	6,473	3,785	2,688	21	1
Chromium	<0.001	1,200	199,182	3,785	195,397	1,561	100
Copper	0.004	1,500	248,977	15,140	233,837	1,868	6
Lead	<0.001	300	49,795	3,785	46,010	368	<16
Mercury		17	2,822		2,822	23	5
Molybdenum	<0.001	75	12,449	3,785	8,664	69	18
Nickel	0.001	420	69,714	3,785	65,929	527	11
Selenium	<0.001	100	16,598	3,785	12,813	102	<3
Zinc	0.011	2,800	464,757	41,635	423,122	3,381	258

*40 CFR 503 Federal limits for sewage biosolids

†L = M * limit

‡X = (L-R)/dose

Coagulant dose = 33 mg/L as $FeCl_3$

M = Sludge production = 366 lb/MG (166 kg/MG)

Using calculations described in this report, a utility can compare the calculated maximum allowable composition of a treatment chemical to the measured composition of that treatment chemical. Since the pure treatment chemical can be analyzed fairly accurately using appropriate analytical procedures, the utility can predict the approximate composition of the resulting residuals.

CONCLUSIONS

- Some treatment chemicals contain appreciable levels of certain trace metals in the full-strength product, but these chemicals are typically applied at low enough doses that the mass of contaminants added are insignificant compared to the levels of metals added by metal salt coagulants or by the raw water.
- Treatment chemicals such as iron- or aluminum-based coagulants can contribute appreciable amounts of many trace metals, such as cadmium, chromium, cobalt, manganese, mercury, molybdenum, nickel, titanium, vanadium, and zinc.
- Other metals such as arsenic, lead, selenium, and silver were not typically detected in raw water or treatment chemicals during studies described in this report.
- Most trace metals in the full- and pilot-scale studies partitioned into the residuals stream rather than the finished water.
- Utilities can use the NSF Standard 60 approach along with chemical compositional data, like that presented in Chapter 4, to predict impact of treatment chemicals on finished water, although this will be conservative.
- Results showed that drinking water MCLs would not be exceeded due to the trace contaminants in water treatment chemicals.
- This research provides calculation methods to determine the impact of trace contaminants on residuals quality. These could be used to specify composition of specific metals in chemicals so that residuals quality goals of utilities can be met.
- Lowering regulatory limits for parameters such as arsenic or bromate can affect chemical selection by utilities.

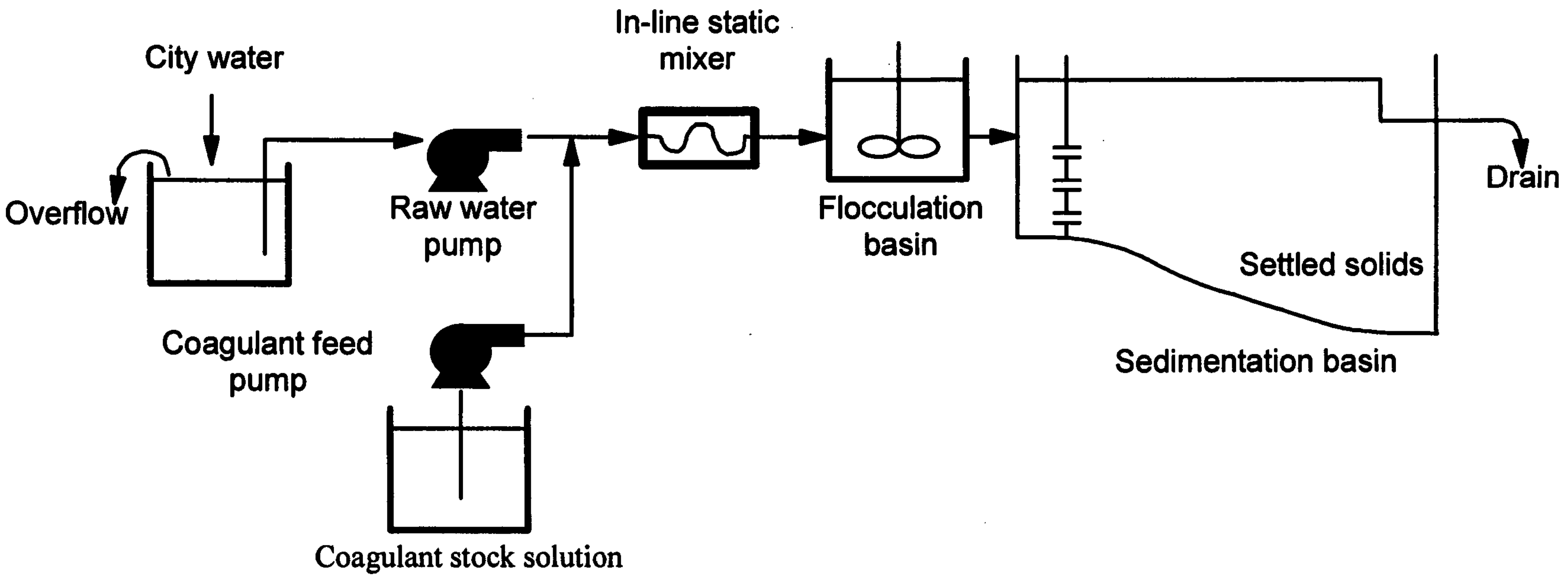


Figure 5.1 Process used for pilot-scale partitioning studies

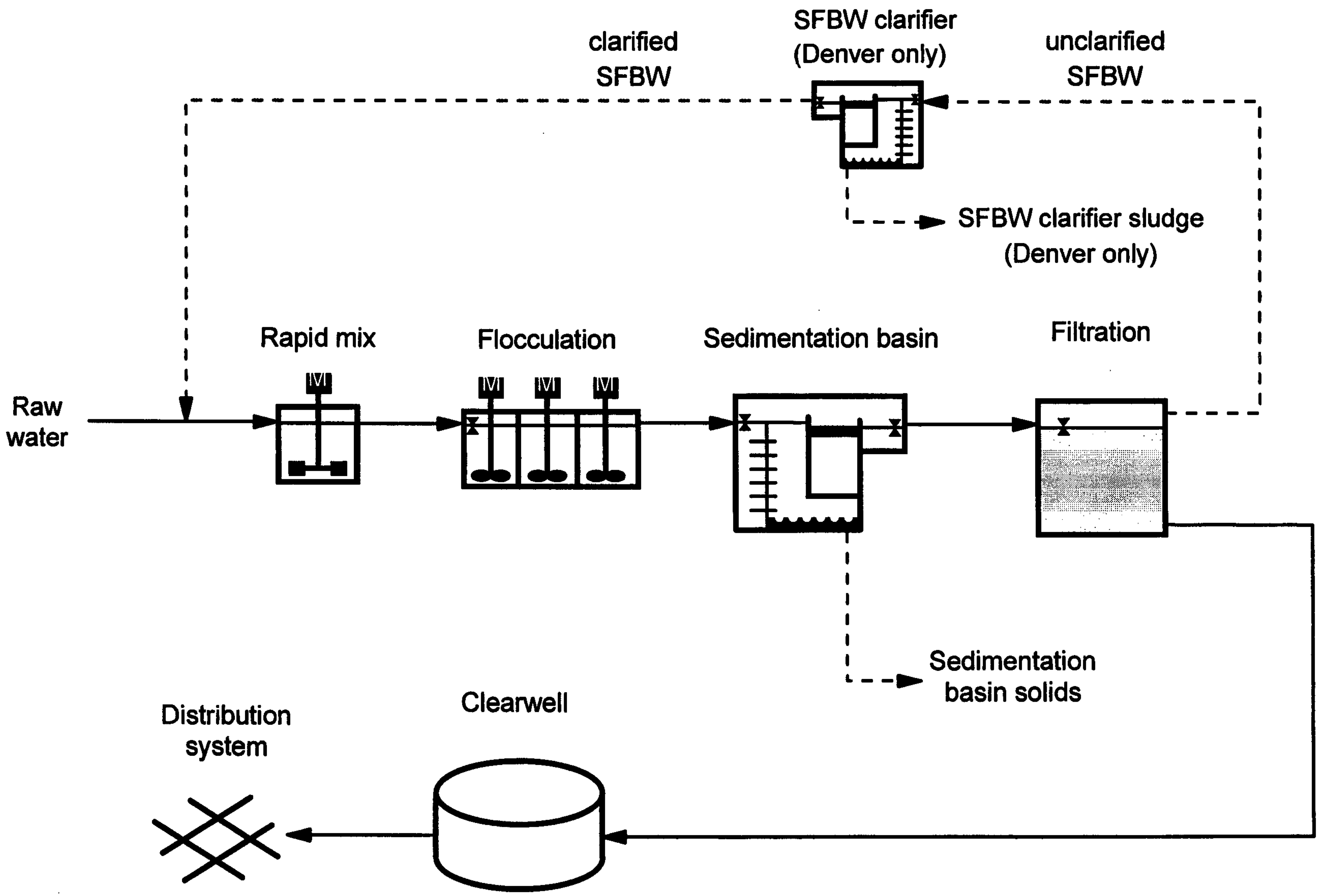


Figure 5.2 Schematic of treatment processes at Philadelphia Water Department (PWD) and Denver Water (DW)

CHAPTER 6

CONTROL OF CONTAMINATION IN TREATMENT CHEMICALS USED AT DRINKING WATER TREATMENT FACILITIES

OVERVIEW

Chapters 3, 4, and 5 provide insight into the composition of trace constituents in different treatment chemicals, how the choice of treatment chemical or method of manufacture can impact trace contaminants added to the treatment process, and whether chemical type or dose can be limited based on drinking water MCLs or residuals quality goals. The results in Chapters 4 and 5 generally indicate that manufacturer quality assurance/quality control (QA/QC) procedures for selection of raw materials and control of the manufacturing process are capable of producing treatment chemicals of acceptable quality for use in drinking water treatment. This chapter focuses on contamination issues and control measures related to transportation and on-site storage at the treatment plant.

Chapter 2 showed that contamination problems associated with treatment chemicals delivered to water treatment plants are rarely traced to an inadequacy in the manufacturing or refining process. In fact, the most severe and most frequently identified problems associated with delivery and use of water treatment chemicals were transport-related, either due to blunders during delivery or inadequately or improperly cleaned, non-dedicated delivery vehicles.

There are exceptions where improperly monitored or improperly controlled manufacturing and refining processes have lead to the production of poor quality products. Instances were noted in the utility survey where such products made it past the manufacturer's QA/QC procedures and were delivered to a water treatment facility. Many utilities with inspection programs in place were able to identify and reject these deliveries before the chemicals were used for treatment, even by using simple visual product inspection or by checking paperwork. Facilities with some type of inspection process were able to identify most of the transport-related problems before they impacted water treatment operations. Conversely, utilities without chemical inspection procedures sometimes had problems that impacted water plant operations, and occasionally impacted finished water quality. Therefore, utilities ought to develop and implement basic Standard Operating Practices (SOPs) for inspection and evaluation of chemical shipments in order to confirm that they received the chemicals ordered, and to verify that chemical quality was not affected during transport. This should be in addition to SOPs already in place for controlling contamination and degradation of treatment chemicals during on-site storage.

Figure 6.1 and Table 6.1 show that contamination of treatment chemicals can occur during manufacture, transport, or on-site storage. The utility may be able to control contamination and degradation during on-site storage; however, contamination that occurs during chemical manufacture and transport are not under the direct control of the utility. Although the water utility does not have direct control of these sources of contamination, it can exercise indirect control through its chemical specifications and SOPs for inspection of chemical deliveries. The remainder of this chapter describes how the quality of chemicals used for drinking water treatment can be controlled through tighter specifications and standard operating procedures.

Table 6.1

Examples of contamination sources for drinking water treatment chemicals

Contamination source depicted in Figure 6.1	Examples
Contamination of raw materials used to manufacture treatment chemicals	• Trace metals in ores and recycled materials used for metal coagulant manufacture • Contaminated acids used for coagulant manufacture • Bromide in salt used for chlor-alkali manufacture (sodium hydroxide, chlorine, sodium hypochlorite) • Arsenic in hydofluorosilic acid • Nickel, copper, and/or iron in reactants used for sodium hypochlorite manufacture (these metals catalyze later decomposition of hypochlorite into chlorite and then chlorate)

(continued)

Table 6.1 (continued)

Contamination source depicted in Figure 6.1	Examples
Contamination during manufacture, processing, or treatment chemical refinement	• Insufficient temperature or reaction time during oxidation of ferrous metals during manufacture of ferric coagulants • Carbon tetrachloride in chlorine • Bromate in sodium hypochlorite • Lack of a filtration step as part of manufacturing process for liquid forms of metal coagulants, or during processing of sodium hypochlorite
Contamination during transport	• Improperly or inadequately cleaned delivery vehicles • Inadequately cleaned or maintained delivery hoses
Contamination during storage at water treatment plant	• Delivery of a chemical incompatible with others already stored in that area • Leakage and other contamination
Chemical degradation	• High temperature, low pH, presence of catalyzing metals, or long storage times leading to degradation of sodium hypochlorite

TREATMENT CHEMICAL SPECIFICATIONS

General Issues

Individual utilities use different approaches when establishing chemical specifications. For example, some utilities have one specification document with all of the general requirements that apply to all treatment chemicals, then separate sections with specific requirements for individual treatment chemicals. By contrast, other utilities develop separate specification documents for each individual treatment chemical. In either of these forms, the specifications can range from simple "bare bones" approaches with a few paragraphs or pages for each treatment chemical, versus more detailed specifications with multiple pages per chemical. Although some utilities prefer to use simpler specifications, bad experiences with chemical deliveries have resulted in more elaborate and detailed specifications to prevent some problems from re-occurring. For example, one of the utilities noted in Chapter 2 reported difficulties when liquid polymer products were off-loaded with mechanical delivery pumps. This utility now mandates pneumatic (pressurized air) delivery of all bulk liquid chemicals. This is a common practice reported by other utilities as well.

Specifications for water treatment chemicals include some common elements applicable to all treatment chemicals, plus some sections that are unique to specific products. The following list includes some commons elements recommended to prevent or limit contamination in all treatment chemicals. The example specification language listed below in *italics* is for a contract between the "Water Department" and the "Contractor".

- Description of product, including active strength (e.g., 25 versus 50 percent caustic soda)

  Example:

  Product shall be commercial grade and shall contain approximately ____ percent by weight of _____.

- Shipping and billing addresses

  Example:

  All deliveries shall be made by truck between the hours of 8:00 am and 4:30 pm on regular working days of the Water Department, F.O.B., to the following address:

Alpha Treatment Plant
1110 South River Road
Your Town, State xxxxx-xxxx
Phone 555-555-5555

- Product certification

Example:

Product shall conform with ANSI/AWWA _____. Affidavit of compliance must be furnished by supplier. Product must also be certified as meeting ANSI/NSF Standard 60. Documentation of this certification must be provided by supplier. NSF will be notified by the Water Department in the event any NSF certified product arrives at the treatment facility and appears to be contaminated.

- Packaging requirements for non-bulk deliveries

a. Container size and type

Examples:

- *Products packaged in bags must be palletized and shrink wrapped. Products in drums must be on pallets*
- *Product must be delivered in bin/tote containers only — no bulk deliveries will be accepted at this location. Bins/totes must be capable of being lifted from either side with a 4,000 pound capacity forklift*
- *Packed in multi-wall paper bags of 50 pounds each (net weight) with bags shrink wrapped and palletized*

b. Labeling requirements

Example:

All products supplied in bag, drum, or bin/tote must have container clearly marked with product designation, name of chemical manufacturer, net weight, and manufacturing lot number. Any product without this labeling may be rejected with vendor to pay freight for return.

5. Shipping and off-loading requirements

a. Shipping company must provide evidence of either washout slips or use of dedicated vehicles

Example:

The supplier must either use a delivery vehicle dedicated to transporting the product or must supply a washout ticket with information indicating prior material shipped in this vehicle.

b. Bid price to include delivery and off-loading specified by authorized water utility personnel

Example:

The bid prices for bulk or containerized material shall be submitted as delivered to the respective facility. No charges shall be incurred by the Water Department for either additional equipment needed to make the delivery (i.e., hose charges) or for separate shipping charges.

c. Department of Transportation (DOT) compliance

Example:

Delivery vehicles must be properly labeled and must comply with US Department of Transportation (DOT) specifications

d. Material Safety Data Sheet (MSDS) documentation

Example:

The Water Department has determined that in order to satisfy its Hazard Communication Plan, waste disposal efforts, and regulatory requirements, the Contractor must furnish all available MSDS documentation. This documentation must be provided with the initial delivery, plus after a change in composition of the product, a change in the manufacturing process, a change in supplier, or a change in labeling/packaging (e.g., change in brand name) of the product.

e. Amount of advance notice to give water plant prior to impending delivery

Example:

A lead time of three working days will be provided by the Water Department. When a minimum three day notice is provided to the supplier, it is expected that the supplier will be able to provide shipment on the day requested by the Water Department.

f. Appropriate safety/protective equipment, clothing, and practices

Example:

Delivery personnel shall wear appropriate personnel protective equipment (PPE) when off-loading product.

g. Require delivery personnel to be present during all stages of off-loading, and that off-loading needs to be directed by authorized utility personnel

Example:

Driver will be required to remain at the water treatment plant during unloading. Material may not be off-loaded until authorized by the Water Department.

h. Require contractor to provide all necessary equipment to off-load chemicals

Example:

- *Product must be delivered to the Water Department in a self unloading pneumatic tank truck capable of pumping against twenty-five feet of headloss.*
- *Contractor shall make deliveries in single-unit cargo trailers of 4,500 gallon capacity. The trailer shall be equipped with an appropriate air compressor and pumping system to effectively transfer chemical into the Water Department's storage tanks. The cargo trailer transfer system shall be considered the primary transfer system for off-loading this chemical, with any Water Department owned transfer system considered as a secondary or backup system.*
- *Contractor shall provide a 2-inch female cam-lock coupling which will be compatible with the Water Department's 2-inch male cam-lock coupling.*

6. Verification of chemical composition

Examples:

- *Each shipment must contain bill of lading identifying source of supply and a certificate of analysis or "C of A" of the material being shipped by the manufacturer. Information in the C of A must include .....*
- *Every delivery of _______ will be inspected and evaluated by Water Department personnel using tests and test methods chosen at the sole discretion of the Water Department. Each delivery must be approved by Water Department personnel prior to unloading. Material not meeting specifications will be rejected and must be removed at the Contractor's expense.*
- *The bidder shall furnish, by attachment to the proposal, a typical analysis of the product, which shall include analysis of the following constituents and parameters: .... The Contractor shall submit such a typical analysis throughout the term of the contract on an annual basis or at the request of the Water Department.*
- *Upon request, the bidder may be required to furnish a typical sample of not less than one liter of product.*

7. Require plant trials before product is approved, or require bids on pre-approved products (such as, a specific polymer formulation or an iron-free alum rather than a standard alum)

Example:

Some products must be tested in a plant trial prior to being awarded any bid. Contact _____, Superintendent, at 555-555-5555 to confirm whether a product must undergo a plant trial. Plant trial must be completed prior to bid closing date.

8. Exclude all products produced from recycled raw materials

Example:

Liquid alum sulfate (alum) shall be manufactured from aluminum hydrate ($Al(OH)_3$) *and virgin sulfuric acid in a standard digestion process. Alum manufactured from waste products of other processes shall not be accepted. The successful bidder shall submit affidavits indicating compliance with NSF Standard 60 and AWWA Standard B403-98 and with the requirements regarding raw materials specified in this paragraph. The affidavit concerning raw material processes must be submitted annually.*

9. Provisions for utility to return shipments of unacceptable quality, including damaged containers

Examples:

- *Ton containers or 150 pound cylinders of liquid chlorine which cannot be opened with reasonable force by plant personnel will be returned to the supplier for exchange at no additional charge. Valves shall not require a force greater than 35 foot-pounds to open.*
- *The Water Department reserves the right to reject any shipment that does not include the proper documentation or that does not match the Water Department's screening tests. In the event a delivery is rejected, the Contractor shall provide a replacement shipment meeting the requirements of this specification within 24 hours.*

Chemical Specific Issues

Certain chemicals require special provisions that are not applicable to other treatment chemical products. For example, liquid chlorine deliveries require special handling, safety precautions, and special concern that containers are not damaged. Similarly, as noted in the utility survey in Chapter 2, because unloading caustic soda that is too hot (115°F, 46°C) can melt plastic pipe during off-loading, a utility needs to check the temperature of incoming caustic soda shipments. Likewise the vendor needs to know that the utility will not accept any product deliveries with temperatures above specified levels.

There also differences in required specifications for different products that are provided in solid forms versus other products that are either liquids or gases. For gaseous products, important considerations are that containers containing compressed gases are undamaged and that they include valves that can be opened using reasonable force. For solids, a common concern is moisture content (e.g., potassium permanganate) so that the product will be free flowing in order for chemical feed systems to operate properly. For liquid products, solids content is also important. A further complication for liquid products, such as polymers, is that they need to be kept above freezing during transport and during unloading at the treatment plant. The utility can improve the situation by ordering sufficient quantities early enough in the season to limit deliveries during colder parts of the year. However, the specifications need to be clear that the vendor and shipping company are responsible to schedule shipments and provide any equipment necessary to keep the chemicals from freezing before or during off-loading at the water treatment plant.

Cooperative Purchasing Agreement

Several utilities consulted during the survey indicated that they have entered into cooperative regional purchasing agreements with other nearby utilities. This included agreements between several utilities of approximately the same size, as well as cases where one large utility was working with several nearby smaller utilities. Responsibilities for ordering chemicals and taking care of paperwork was often shared on a rotating basis among utilities of similar size, versus much of the responsibility handled by the larger utility when the agreement was between one large and several small utilities. These cooperative regional purchasing agreements are normally entered into for economic reasons, or to simplify and centralize ordering and purchasing procedures for treatment chemicals. Experiences reported suggest that such arrangements can positively impact the quality of products delivered to all of the member water utilities, even though that might not have been one of the intended consequences.

Smaller utilities have the greatest potential gain from such arrangements because there is increased clout associated with collectively requiring stricter specifications. Economies of scale due to ordering collectively rather than individually means that a utility can order a higher quality product at a lower unit cost.

In order for regional cooperative agreements to work, all member utilities must: 1) agree on specification provisions and ordering procedures, 2) be in appropriate regional proximity, and 3) be willing to cooperate in order to make this kind of agreement work. All affected utilities interviewed in the utility survey were pleased with their particular arrangement and would endorse the use of similar arrangements by other utilities. These regional agreements have also some potential benefits for the manufacturers because they simplify and centralize ordering and billing procedures, but could cause lower overall profits because of the bargaining strength of the collective group.

Dedicated Delivery Vehicles

Several utilities interviewed during the survey indicated that they were evaluating whether they should require use of dedicated delivery vehicles for certain categories of treatment chemicals, or perhaps for all chemicals. Some chemicals are already delivered in dedicated containers (e.g., chlorine) or specialized delivery vehicles (e.g., lined hydrofluorosilicic acid delivery vehicles). However, potential problems associated with using dedicated vehicles for delivery of treatment chemicals to water plants include the following:

- Cost implications are unknown
- May not be feasible for some chemicals or for more remote regions
- Resistance from manufacturers and shipping companies

- Documentation attesting that delivery vehicle has been "dedicated" is subject to error or falsification
- The vehicle still requires cleaning due to residue from previous delivery of the same chemical, especially solid residue at bottom of tank
- Some products that are nominally the same can have vastly different quality or strength

PROCEDURES FOR INSPECTION AND EVALUATION OF INCOMING TREATMENT CHEMICAL DELIVERIES

Several of the project participants and some of the survey respondents provided information regarding practices and procedures they use to evaluate incoming chemical deliveries. One of the project participants has published a journal article outlining some of the findings and recommendations based upon practices at their facilities (Casale 2001). The collective experiences of the project research team and participating utilities were relied upon heavily in developing the recommendations outlined in this chapter.

Standard operating procedures (SOPs) for evaluating incoming chemical deliveries should be prepared in writing and should typically include the following three primary elements: 1) careful scrutiny of the delivery paperwork, 2) assessment of contents of shipment (visual and analytical evaluations), and 3) verification of the connection to and available storage space remaining in the receiving tank. Scrutiny of paperwork helps to confirm that the proper chemical in the correct amount and the correct strength is delivered to the appropriate facility. Generally, review of the paperwork is a good indicator of the identity of the delivered product, and the product quantity, quality, and strength.

Verification of the connection from the delivery vehicle to the receiving tank is a vital element in safe chemical unloading practices. Written procedures should stipulate that plant personnel verify to which tank the product will be transferred in order to establish that the tank has enough available space to hold the amount of chemical scheduled for delivery, and to identify the correct fill line to be used for unloading purposes. Connections to chemical storage tanks should be locked at all times. Tank connections should only be unlocked by authorized plant personnel in order to prevent unloading a chemical into the wrong bulk storage tank or overfilling a bulk storage tank.

Table 6.2 includes a summary of the types of evaluations or analytical tests performed by one of the major project participating utilities during delivery of water treatment chemicals. Evaluations typically included visual inspection for color, clarity, and presence of sediment and checking for odors, plus simple physical tests like specific gravity. These tests are intended to indicate whether the correct chemical was delivered, and whether contamination occurred during manufacture or shipping.

At about 40 percent of their facilities (77 of 185), some kind of assessment is performed prior to authorizing the unloading of some chemicals. For the most part, this testing is only done on bulk-liquid chemicals, including metal coagulants, fluoridation chemicals, caustic soda, and polymers. Bulk solids (such as lime) are not usually sampled. Compressed liquids and gases, such as chlorine gas, are usually not sampled due to safety concerns and difficulty in collecting a sample. Containerized chemicals (drums, totes, or compressed gas cylinders) are typically inspected for container condition, but not for the quality of the chemical contents. Damaged containers should rarely, if ever, be accepted if there is evidence that the integrity of the chemical has been compromised.

Most of these inspection and evaluation activities are not intended to identify minor discrepancies in treatment chemical composition. The objective is to identify gross contamination or gross discrepancies. This would include incidents such as major malfunctions in the manufacturing process, gross contamination from sediment or other residual materials remaining in delivery vehicle from previous delivery, or attempted delivery of the wrong chemical.

Table 6.2

Suggested inspection procedures for treatment chemical deliveries

Chemical	Specific gravity	Visual appearance	Odor	pH	Temp	Other
Alum (liquid)	X	X	X	X		Color
Caustic soda	X	X	X	X	X	
Ferric chloride	X	X	X			
Hydrofluorosilicic acid	X	X	X	X	X	Verify fluoride
Sodium hypochlorite	X					
Lime						Sieve Test
Corrosion inhibitor	X	X	X	X	X	
Phosphoric acid	X	X				Verify Phosphate
Polyaluminum chloride	X	X	X	X	X	
Polyaluminum sulfate	X	X	X			Viscosity
Polymer and blends	X	X	X			
Polyacrylamide	X	X				Conductivity
Sodium silicate	X					
Sodium thiosulfate	X	X	X			
Other chemicals						
Visual appearance only -	Dry alum, chlorine, cutrine (copper complex), hydrated lime, potassium permanganate, powdered activated carbon, sodium chloride, sodium chlorite					
No testing -	Anhydrous ammonia, carbon dioxide, copper sulfate, calcium hypochlorite, pebble lime, liquid oxygen, potassium hydroxide, sodium aluminate, sodium carbonate (soda ash), sodium fluoride					

Most of the simple inspection activities should be considered mandatory for all U.S. drinking water facilities. A facility that desires to have even more rigorous chemical composition requirements, or wants to perform a more detailed chemical analysis of the delivered chemical products, could perform additional testing. Due to the complex matrix effects associated with analyzing composition of concentrated treatment chemicals, the utility would either need to develop appropriate in-house capability to perform the desired analyses, or more likely find an outside laboratory to do the work. In order to implement such an analytical testing program, a utility would ideally have sufficient chemical storage capacity in case of the need for rejection after unloading. Available on-site chemical storage would need to be sufficient to allow the chemical to be continuously fed to the treatment plant while the newly delivered chemical product is being evaluated.

Detailed chemical analyses do not need to be performed on every chemical delivery. Periodic analyses conducted yearly or every six months and unscheduled analyses are probably sufficient and should be encouraged if utilities can afford this testing. Furthermore, the chemical analyses for a given shipment need not include an extensive list of metals. Analysis of a few trace constituents of most concern (arsenic, mercury, etc.), or an assay of the main active ingredient in a given chemical (i.e., aluminum in alum), may be adequate if the analytical capability exists. For example, one respondent during the utility survey reported success with on-site analysis of aluminum content for each delivery of alum to the site. This does not give an assessment of other trace constituents, but is one measure to verify that the quality of delivered product is close to what was expected.

If an NSF-certified product arrives at a treatment facility and appears to be contaminated, the treatment facility should contact NSF directly to file a formal complaint. The required formal complaint form is available at www.nsf.org/regulatory/request.html. An NSF auditor will be sent to the location to sample the shipment. The sample will be analyzed by the NSF laboratory to determine if the product is contaminated and at what level. In addition, NSF policy requires that an NSF-certified company retain a record of written complaints. The record of written complaints may be reviewed by an NSF auditor at the time of an annual audit.

CONTROL OF CONTAMINATION AND DEGRADATION OF TREATMENT CHEMICALS DURING ON-SITE STORAGE

As long as water treatment plant operations personnel follow reasonable standard operating procedures and sound housekeeping practices, the potential for contamination during on-site storage may not be as great as the other potential contamination sources that could impact the quality before the treatment chemical is delivered to the water plant. However, some important recommendations to consider include the following:

- Visually inspect tanks, storage areas, and chemical equipment on a regular basis
- At least once per year, visually inspect screens on air vents for liquid and solid storage areas, and repair if damaged
- Segregate dry products in separate storage areas, especially non-bulk storage, in order to limit cross-contamination and chemical feed mix-ups
- Use bulk storage when possible
- When feasible, do not mix newly delivered products with previously delivered products. Keep products from different shipments segregated as long as possible in case some deficiency is uncovered with respect to the recently delivered product.
- Store chemical in areas with controlled access, in order to limit potential for cross-contamination
- Retain a sample of previously delivered material, if product is not degradable, in order to compare composition or appearance with next delivery
- To decrease dependance on shipper to provide chemical transfer hoses, a utility could choose to purchase and maintain its own transfer hoses (cleaning and maintenance of hoses will need to be added to the utility's SOP list)
- Evaluate plant performance, feed equipment operations, and other aspects of treatment plant operations that indicate that specifications need to be tightened in the future to keep out substances causing problems (e.g., sediment in liquid chemicals)

SUMMARY

Overall, activities that utilities should implement to reduce or eliminate the presence of contaminants in water treatment chemicals used at drinking water treatment plants include these basic steps:

1. Use NSF Standard 60-certified chemical products
2. Utilities should estimate the maximum allowable metals levels for coagulants used at their treatment plants. This can be established using guidance and example calculations provided in this report. Required information to make these calculations include coagulant dose, raw water trace metal levels, dry sludge production, and residual disposal limits applicable to these facilities
3. Include more rigorous compositional requirements, as needed, for site-specific concerns (e.g., limiting residuals quality)
4. Develop and implement detailed inspection and evaluation procedures for each shipment of treatment chemicals delivered to a water plant. At a minimum this should include careful review of paperwork, visual and other inspection of chemical and delivery vehicle, and simple physical/chemical tests (e.g. specific gravity)
5. Keep recently delivered products separated from previously delivered products in case any discrepancies or irregularities are uncovered later associated with the new chemicals
6. Utilities with the required capability and financial means can benefit from more detailed chemical compositional analysis of delivered products. Even if utilities cannot afford a detailed compositional analysis on every shipment, they should consider doing so on a periodic basis
7. Utilities should provide incentives or otherwise encourage use of dedicated delivery vehicles, if feasible. Some utilities have already gone one step further by mandating use of dedicated delivery vehicles for certain products
8. Investigate opportunities to enter into regional cooperative chemical purchasing agreement with other nearby water utilities

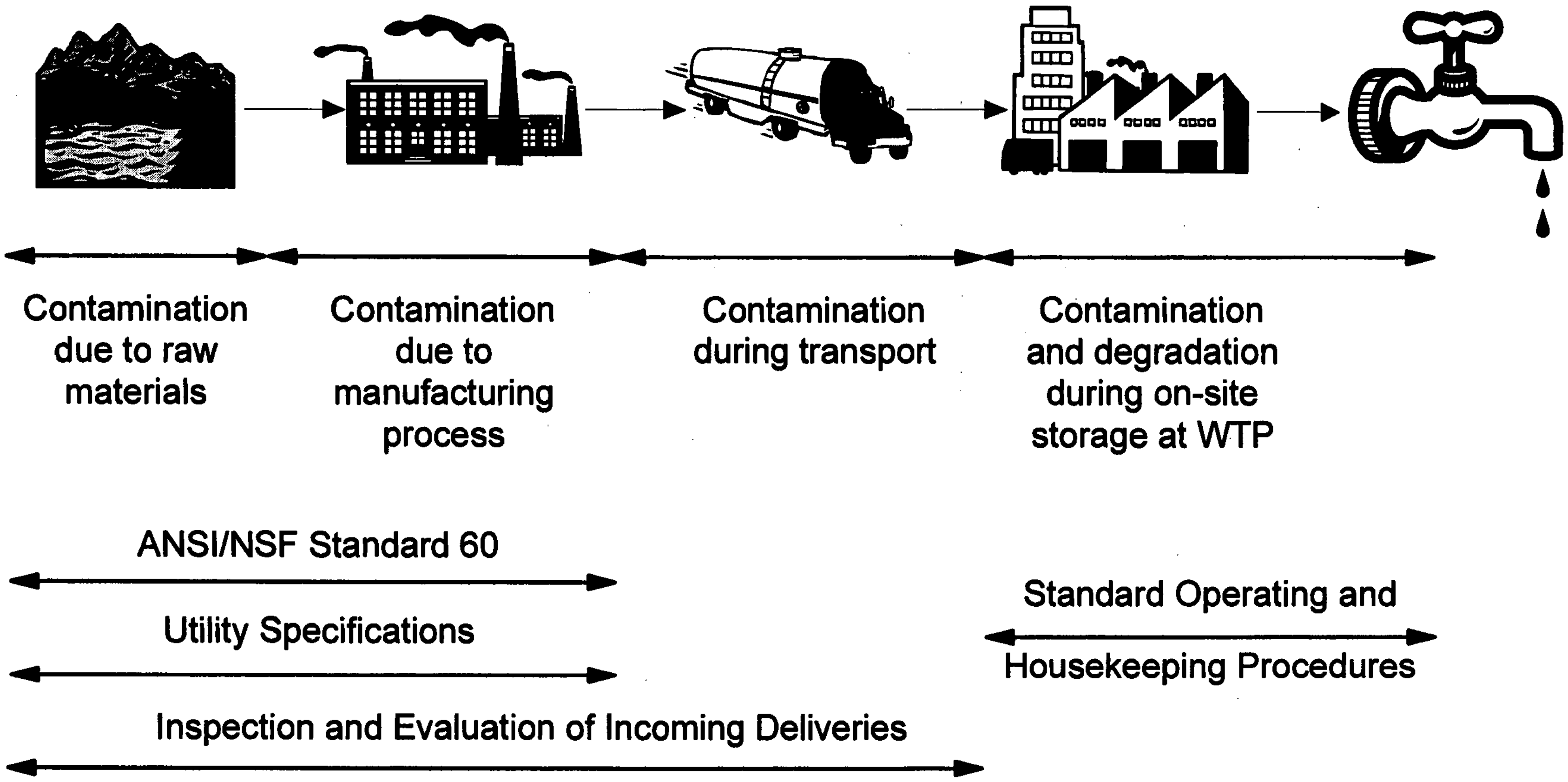


Figure 6.1 Sources of treatment chemical contamination and control options

APPENDIX A

CALCULATIONS TO CONVERT CONCENTRATIONS OF DIFFERENT PRODUCTS TO DIFFERENT UNITS

Composition of different products can be expressed in a number of ways. Some typical examples for some of the products discussed in this report are listed below.

ALUM

For liquid alum, even though standard (bauxitic) and low-iron alum are made by slightly different processes, the characteristics of the final products are similar, except for higher iron and trace metal content in standard alum. Low-iron and standard liquid alum typically have the following characteristics:

Specific gravity	~1.33
Wet density	$= \dfrac{11.1 \text{ lb liquid product}}{\text{gal liquid product}} = \dfrac{1.33 \times 10^6 \text{ mg liquid product}}{\text{L liquid product}}$
Dry density	$= \dfrac{5.4 \text{ lb dry product}}{\text{gal liquid product}}$
Percent dry product	$= \dfrac{5.4}{11.1} = \dfrac{48.5 \text{ lb dry product}}{100 \text{ lb liquid product}}$
Molecular weight	$\dfrac{\sim 600 \text{ mg alum}}{\text{mmol alum}}$
Al composition	~8.2 percent Al_2O_3 (wet basis) or ~17 percent Al_2O_3 (dry basis)

Therefore, the strength (Al composition) of a standard or low-iron liquid alum can be expressed on a wet weight or dry weight basis, or as alum (product), as Al, or as Al_2O_3 as indicated below:

$$\text{Alum Composition} = \frac{8.2 \text{ mg } Al_2O_3}{100 \text{ mg wet alum}} \cdot \frac{\text{mmol } Al_2O_3}{102 \text{ mg } Al_2O_3} \cdot \frac{2 \text{ mmol Al}}{\text{mmol } Al_2O_3} = \frac{0.00161 \text{ mmol Al}}{\text{mg wet alum}}$$

$$= \frac{0.00161 \text{ mmol Al}}{\text{mg wet alum}} \cdot \frac{27 \text{ mg Al}}{\text{mmol Al}} \cdot \frac{10^6 \text{ mg}}{\text{kg}} = \frac{43{,}000 \text{ mg Al}}{\text{kg wet alum}}$$

$$= \frac{43{,}000 \text{ mg Al}}{\text{kg wet alum}} \cdot \frac{100 \text{ kg wet alum}}{48.5 \text{ kg wet alum}} = \frac{89{,}500 \text{ mg alum}}{\text{kg dry alum}}$$

$$= \frac{1.33 \times 10^6 \text{ mg wet product}}{\text{L}} \cdot \frac{0.043 \text{ mg Al}}{\text{mg wet product}} = \frac{58{,}000 \text{ mg Al}}{\text{L}}$$

$$= \frac{8.2 \text{ mg } Al_2O_3}{100 \text{ mg wet alum}} \cdot \frac{100 \text{ mg wet alum}}{48.5 \text{ mg dry alum}} = 17\% \; Al_2O_3 \text{ (dry basis)}$$

Since dry or granular alum is actually dehydrated liquid alum, the composition of dry alum is the same as the composition of liquid alum expressed on a dry-weight basis. Consequently, Al composition of dry alum is ~89,500 mg Al per kg dry alum or ~17 percent Al_2O_3 on a dry basis.

Composition of liquid alum or dry alum for constituents other than Al are variable, depending upon how the product is made. However calculations are similar to those above for Al. For example, if composition of Cr in a liquid alum product is 1.5 ppm on a wet-weight basis (i.e., 1.5 mg Cr per kg wet alum), and since liquid alum is typically ~ 48.5 percent dry product, the dry weight composition of Cr in this product is 3.1 ppm on dry-weight basis (i.e., 3.1 mg Cr per kg dry alum). Furthermore, if Cr composition of liquid alum is as indicated above, since specific gravity of liquid alum is ~1.33, concentration of Cr in this liquid alum product would be 4.0 mg/L as Cr.

IRON SALTS

Liquid ferric chloride used for drinking water typically has the following characteristics:

Specific gravity	~1.4
Molecular weight	~162 mg $FeCl_3$ per mmol $FeCl_3$

Percent dry product $= \frac{39 \text{ mg dry FeCl}_3}{100 \text{ mg liquid FeCl}_3} \sim \frac{13.5 \text{ mg dry Fe}}{100 \text{ mg liquid FeCl}_3}$

Fe composition ~12 to 13.5% (wet basis)

$$= 120{,}000 \text{ to } 135{,}000 \ \frac{\text{mg dry Fe}}{\text{kg wet FeCl}_3}$$

$$= \frac{390{,}000 \text{ mg dry FeCl}_3}{\text{kg wet FeCl}_3}$$

$$= \frac{135{,}000 \text{ mg Fe}}{\text{kg wet FeCl}_3} \cdot \frac{100 \text{ mg wet FeCl}_3}{39 \text{ mg dry FeCl}_3} = \frac{346{,}000 \text{ mg Fe}}{\text{kg dry FeCl}_3}$$

$$= \frac{13.5 \text{ mg Fe}}{100 \text{ mg wet FeCl}_3} \cdot \frac{1.4 \times 10^6 \text{ mg wet FeCl}_3}{\text{L}} = \frac{189{,}000 \text{ mg dry Fe}}{\text{L}}$$

$$= \frac{39 \text{ mg FeCl}_3}{100 \text{ mg wet FeCl}_3} \cdot \frac{1.4 \times 10^6 \text{ mg wet FeCl}_3}{\text{L}} = \frac{546{,}000 \text{ mg dry FeCl}_3}{\text{L}}$$

Liquid ferric sulphate typically contains 10-12 percent soluble Fe and has other characteristics as summarized below:

Specific gravity 1.58

Molecular weight ~400 mg product/mmol product

Percent dry product $= \frac{12 \text{ mg dry Fe}}{100 \text{ mg liquid product}} \cdot \frac{\text{mmol Fe}}{55.85 \text{ mg Fe}} \cdot \frac{\text{mmol product}}{2 \text{ mmol Fe}} \cdot \frac{400 \text{ mg product}}{\text{mmol product}}$

$$= \frac{0.43 \text{ mg dry product}}{100 \text{ mg wet product}} \sim 43\% \text{ dry product}$$

Fe composition $= \frac{120{,}000 \text{ mg Fe}}{\text{kg wet product}}$

$$= \frac{430{,}000 \text{ mg product}}{\text{kg wet product}}$$

$$= \frac{280{,}000 \text{ mg Fe}}{\text{kg dry product}}$$

$$= \frac{1.58 \times 10^6 \text{ m wet product}}{\text{L}} \cdot \frac{12 \text{ mg dry Fe}}{100 \text{ mg wet product}} = \frac{189{,}000 \text{ mg dry Fe}}{\text{L}}$$

$$= \frac{189{,}000 \text{ mg dry Fe}}{\text{L}} \cdot \frac{400 \text{ mg dry product}}{2\ (55.85 \text{ mg dry Fe})} = \frac{678{,}000 \text{ mg dry product}}{\text{L}}$$

Caustic soda

Though caustic soda (Caustic soda) is typically used at 50 percent strength, products with other strengths can be used for water treatment. Typical characteristics of 50 percent Caustic soda are as follows:

Specific gravity = 1.53

Wet density $= \frac{12.76 \text{ lbs liquid NaOH}}{\text{gal NaOH}} = \frac{1.53 \times 10^6 \text{ mg liquid NaOH}}{\text{L}}$

Percent product $= \frac{50 \text{ lbs dry NaOH}}{100 \text{ lbs wet NaOH}}$

Molecular weight $= \frac{40 \text{ mg NaOH}}{\text{mmol Na OH}}$

Na composition (wet) $= \frac{1.53 \times 10^6 \text{ mg Na OH}}{\text{L}} \cdot \frac{23 \text{ mg Na}}{40 \text{ mg NaOH}} = \frac{880{,}000 \text{ mg wet Na}}{\text{L}}$

Na composition (dry) $= \frac{50 \text{ mg dry NaOH}}{100 \text{ mg wet NaOH}} \cdot \frac{23 \text{ mg Na}}{40 \text{ mg NaOH}} \cdot \frac{10^6 \text{ mg}}{\text{kg}} = \frac{288{,}000 \text{ mg dry Na}}{\text{kg wet NaOH}}$

$$= \frac{23 \text{ mg Na}}{40 \text{ mg NaOH}} \cdot \frac{10^6 \text{ mg}}{\text{kg}} = \frac{575{,}000 \text{ mg Na}}{\text{kg dry NaOH}}$$

APPENDIX B

COMBINED RESULTS FROM THIS AwwaRF PROJECT AND FROM THE MANUFACTURER'S SURVEY FOR ALUMINUM BASED COAGULANTS AND FOR ORGANIC POLYMERS

Table B.1 includes data for aluminum-based coagulants in units of mg/kg on a dry weight basis. Table B.2 has identical data for aluminum-based coagulants, except units are µg metal/g Al (or mg metal/kg Al). Table B.3 includes data for organic polymers in units of mg/kg wet weight basis.

Table B.1
Compositional data for aluminum-based expressed on a dry weight basis

Constituent	Units	Standard Alum							Summary Statistics				
		#1	#2	#3	#4	#5	#6	#7	count	min	max	median	mean
Aluminum	mg/kg dry	88,660	90,000	92,118	90,491	91,037	84,924	89,509	7	84,924	92,118	90,000	89,534
Calcium	mg/kg dry	54	60	37	99	93	72	62	7	37	99	62	68
Iron	mg/kg dry	1,794	1,300	1,400	1,093	1,010	598	1,381	7	598	1,794	1,300	1,225
Potassium	mg/kg dry	12.4	5.7	7.5	3.3	7.4	30.9	14.2	7	3.3	30.9	7.5	11.6
Magnesium	mg/kg dry	19	55	6	103	17	85	33	7	6	103	33	45
Manganese	mg/kg dry	2.5	5.2	2.2	10.9	7.0	1.0	1.6	7	1.0	10.9	2.5	4.4
Sodium	mg/kg dry	74	210	63	990	722	680	247	7	63	990	247	427
Antimony	mg/kg dry <	0.82							1	0.82	0.82	0.82	0.82
Arsenic	mg/kg dry <	0.82 <	2.00	2.10 <	2.06 <	2.06 <	2.06 <	2.06	7	0.82	2.10	2.06	1.88
Barium	mg/kg dry	0.41 <	0.10 <	0.10 <	0.10	0.41 <	0.10	0.41	7	0.10	0.41	0.10	0.23
Cadmium	mg/kg dry <	0.08 <	0.10 <	0.10 <	0.10 <	0.08 <	0.10 <	0.10	7	0.08	0.10	0.10	0.10
Chromium	mg/kg dry	61.86	80.00	81.00	65.98	57.73	26.80	86.60	7	26.80	86.60	65.98	65.71
Cobalt	mg/kg dry	0.21	0.30 <	0.20	0.41 <	0.16 <	0.14 <	0.14	7	0.14	0.41	0.20	0.22
Copper	mg/kg dry	1.86	8.40	2.80	8.04 <	0.08	0.41	1.88	7	0.08	8.40	1.86	3.35
Lead	mg/kg dry <	4.12 <	4.00 <	4.00 <	4.12 <	4.12	<	4.12	6	4.00	4.12	4.12	4.08
Mercury	mg/kg dry <	0.82							1	0.82	0.82	0.82	0.82
Molybdenum	mg/kg dry	0.16 <	2.00 <	1.50 <	1.65 <	1.65 <	1.65 <	1.65	7	0.16	2.00	1.65	1.47
Nickel	mg/kg dry	3.09	14.00	0.90	37.11	0.62	0.41	0.41	7	0.41	37.11	0.90	8.08
Yttrium	mg/kg dry	0.41 <	0.30 <	0.30 <	0.41 <	0.41 <	0.41 <	0.41	7	0.30	0.41	0.41	0.38
Selenium	mg/kg dry <	4.12							1	4.12	4.12	4.12	4.12
Silver	mg/kg dry <	0.82 <	0.70 <	0.70 <	0.82 <	0.62 <	0.82 <	0.82	7	0.62	0.82	0.82	0.76
Strontium	mg/kg dry	1.03							1	1.03	1.03	1.03	1.03
Titanium	mg/kg dry	47.42	18.00	23.00	6.39	45.36	53.61	26.80	7	6.39	53.61	26.80	31.51
Vanadium	mg/kg dry	39.18	56.00	60.00	39.18	22.68	20.62	59.79	7	20.62	60.00	39.18	42.49
Zinc	mg/kg dry	1.44	4.20	2.30	4.33	3.09	3.30	1.44	7	1.44	4.33	3.09	2.87
Zirconium	mg/kg dry	8.87	12.00	12.00	10.72	11.96	6.80	11.96	7	6.80	12.00	11.96	10.62
Silicon	mg/kg dry	51.55							1	51.55	51.55	51.55	51.55
Tin	mg/kg dry <	0.82	13.00 <	2.00	47.42 <	2.06 <	2.06 <	4.12	7	0.82	47.42	2.06	10.21
Phosphorus	mg/kg dry	82.47	100.00	100.00	123.71 <	0.82	53.61	88.66	7	0.82	123.71	88.66	78.47

(continued)

Table B.1
(continued)

Constituent	Units	Low-Fe Alum (continued on following page)									
		#1	#2	#3	#4	#5	#6	#7	#8	#9	#10
Aluminum	mg/kg dry	84,536	90,928	89,509	88,199	88,636	93,176	90,529	91,059	89,400	88,745
Calcium	mg/kg dry	54	74	148	148	103	46	42	33	58	62
Iron	mg/kg dry	111	19	45	198	27	45	41	29	39	31
Potassium	mg/kg dry	4.7	6.6	5.2	19.4	12.8	7.7	11.0	7.7	8.0	10.1
Magnesium	mg/kg dry	29	11	31	330	37	9	9	3	14	5
Manganese	mg/kg dry	3.9	0.8	0.6	20.6	0.8	1.1	0.9	1.1	0.8	2.7
Sodium	mg/kg dry	845	433	454	3,918	639	680	600	580	474	412
Antimony	mg/kg dry <	0.82 <	0.82								
Arsenic	mg/kg dry <	0.82 <	0.82 <	2.06 <	2.06 <	2.06 <	2.00 <	2.00 <	2.00 <	2.06 <	2.06
Barium	mg/kg dry	0.12	0.01 <	0.10	0.12 <	0.10 <	0.09 <	0.09 <	0.10 <	0.10	0.21
Cadmium	mg/kg dry	0.21 <	0.08 <	0.10 <	0.10 <	0.10 <	0.09 <	0.09 <	0.10 <	0.10 <	0.10
Chromium	mg/kg dry	3.30	0.41	0.41	2.68	0.82	0.60	0.40	0.50	0.82	0.62
Cobalt	mg/kg dry <	0.16 <	0.16 <	0.14	0.21 <	0.14 <	0.15 <	0.15 <	0.15 <	0.14 <	0.14
Copper	mg/kg dry	5.98	0.82 <	0.14	10.31	0.19	0.20 <	0.10	3.10 <	0.12 <	0.12
Lead	mg/kg dry <	4.12 <	4.12	<	4.12 <	4.12 <	4.00 <	4.00 <	4.00 <	4.12 <	4.12
Mercury	mg/kg dry	1.03	1.03								
Molybdenum	mg/kg dry	0.62 <	0.16 <	1.65 <	1.65 <	1.65 <	2.00 <	2.00 <	2.00 <	1.65 <	1.65
Nickel	mg/kg dry	9.07	0.41	0.62	15.88	0.41	0.50	0.30 <	0.30	0.62	0.41
Yttrium	mg/kg dry <	0.16 <	0.16 <	0.41 <	0.41 <	0.41 <	0.30 <	0.30 <	0.30 <	0.41 <	0.41
Selenium	mg/kg dry <	4.12 <	2.06								
Silver	mg/kg dry <	0.82 <	0.82 <	0.82 <	0.82 <	0.82 <	0.80 <	0.80 <	0.80 <	0.82 <	0.82
Strontium	mg/kg dry	0.41	0.41								
Titanium	mg/kg dry	1.65	0.62	1.65	9.48	1.03	1.20	1.10	0.80	1.24	1.03
Vanadium	mg/kg dry	0.62 <	0.16	0.41	1.24 <	0.16	0.20	0.20	0.20	0.21	0.41
Zinc	mg/kg dry	16.70	247.42	0.41	3.51	19.59	17.00	16.00	16.00	14.85	16.29
Zirconium	mg/kg dry	0.21 <	0.16	0.41	0.62	0.41	0.40	0.30	0.30	0.41	0.21
Silicon	mg/kg dry	39.18	6.60								
Tin	mg/kg dry	1.44 <	0.82 <	2.06	7.42 <	2.06 <	2.00 <	2.00	2.80 <	2.06 <	2.06
Phosphorus	mg/kg dry	134.02 <	4.12	4.12 <	4.12 <	4.12 <	4.00 <	4.00	4.20 <	4.12	6.39

(continued)

Table B.1
(continued)

Constituent	Units	Low-Fe Alum (continued)			Summary Statistics				
		#11	#12	#13	count	min	max	median	mean
Aluminum	mg/kg dry	87,435	89,727	89,290	13	84,536	93,178	89,400	89,321
Calcium	mg/kg dry	72	35	124	13	33	148	82	77
Iron	mg/kg dry	64	27	20	13	19	198	39	54
Potassium	mg/kg dry	12.4	6.0	3.5	13	3.5	19.4	7.7	8.9
Magnesium	mg/kg dry	25	11	39	13	3	330	14	43
Manganese	mg/kg dry	0.8	0.8	0.6	13	0.6	20.8	0.8	2.7
Sodium	mg/kg dry	577	577	351	13	351	3,918	577	811
Antimony	mg/kg dry	<	0.82 <	0.82	4	0.82	0.82	0.82	0.82
Arsenic	mg/kg dry <	4.12 <	0.82 <	0.82	13	0.82	4.12	2.00	1.83
Barium	mg/kg dry <	0.10	0.06	0.14	13	0.01	0.21	0.10	0.10
Cadmium	mg/kg dry <	0.10 <	0.08 <	0.08	13	0.08	0.21	0.10	0.10
Chromium	mg/kg dry <	0.16	0.62	0.41	13	0.16	3.30	0.60	0.91
Cobalt	mg/kg dry <	0.16 <	0.16 <	0.16	13	0.14	0.21	0.15	0.16
Copper	mg/kg dry	0.21	0.21	0.21	13	0.10	10.31	0.21	1.87
Lead	mg/kg dry <	4.12 <	4.12 <	6.19	12	4.00	8.19	4.12	4.26
Mercury	mg/kg dry	<	0.82	1.03	4	0.82	1.03	1.03	0.98
Molybdenum	mg/kg dry <	1.44 <	0.16 <	0.16	13	0.16	2.00	1.65	1.29
Nickel	mg/kg dry <	0.41	0.41	0.41	13	0.30	15.88	0.41	2.29
Yttrium	mg/kg dry <	0.41 <	0.16 <	0.16	13	0.16	0.41	0.30	0.31
Selenium	mg/kg dry	<	8.19 <	6.19	4	2.06	6.19	5.15	4.64
Silver	mg/kg dry <	0.82 <	0.82 <	0.82	13	0.80	0.82	0.82	0.82
Strontium	mg/kg dry		0.10	0.41	4	0.10	0.41	0.41	0.34
Titanium	mg/kg dry	1.03	3.92	2.27	13	0.62	9.48	1.20	2.08
Vanadium	mg/kg dry	0.41 <	0.16 <	0.16	13	0.16	1.24	0.20	0.35
Zinc	mg/kg dry	14.43 <	0.08 <	0.08	13	0.08	247.42	16.00	29.41
Zirconium	mg/kg dry	0.41	0.41	0.41	13	0.16	0.62	0.41	0.36
Silicon	mg/kg dry		18.76	10.10	4	8.60	39.18	14.43	18.66
Tin	mg/kg dry <	2.06 <	0.82 <	0.82	13	0.82	7.42	2.06	2.19
Phosphorus	mg/kg dry <	4.12 <	4.12 <	0.82	13	0.82	134.02	4.12	14.02

(continued)

Table B.1
(continued)

Constituent	Units	ACH #1	ACH #2	ACH #3	PACl #1	PACl #2	PACl #3	PACl-OH-S #1	PACl-OH-S #2	Summary Statistics count	min	max	median	mean
		PACl												
Aluminum	g/kg dry	255,428	252,153	249,970	114,615	186,659	118,981	121,164	117,890	8	114,615	255,428	153,911	177,107
Calcium	g/kg dry	392	80	120	62	179	74	1,608	5,155	8	62	5,155	149	959
Iron	g/kg dry	167	138	99	29	29	82	20	3,299	8	20	3,299	91	483
Potassium	g/kg dry	9.5	30.9	12.0	9.5	6.6	8.9	15.3	433.0	8	6.6	433.0	10.7	65.7
Magnesium	g/kg dry	95	25	52	17	10	31	1,732	1,216	8	10	1,732	41	397
Manganese	g/kg dry	4.7	6.4	2.1	1.0	4.3	1.6	1.6	35.1	8	1.0	35.1	3.2	7.1
Sodium	g/kg dry	132	433	330	660	1,113	412	55,670	15,258	8	132	55,670	546	9,251
Antimony	g/kg dry						<	1.24		1	1.24	1.24	1.24	1.24
Arsenic	g/kg dry<	6.19 <	4.12 <	4.12 <	1.03 <	4.12 <	1.03 <	1.24 <	1.03	8	1.03	6.19	2.68	2.86
Barium	g/kg dry<	0.21 <	0.21	0.21	0.10	1.44	0.12	0.41	4.33	8	0.10	4.33	0.21	0.88
Cadmium	g/kg dry<	0.21 <	0.21 <	0.41 <	0.10 <	0.21 <	0.10 <	0.12	0.16	8	0.10	0.41	0.19	0.19
Chromium	g/kg dry	7.22	1.44 <	0.62	0.41 <	0.41	0.62	0.41	4.54	8	0.41	7.22	0.62	1.96
Cobalt	g/kg dry<	0.41 <	0.41 <	0.62 <	0.21 <	0.41 <	0.21 <	0.41	2.27	8	0.21	2.27	0.41	0.62
Copper	g/kg dry	4.33	0.21	1.86 <	0.10	0.62	0.82	20.62	61.86	8	0.10	61.86	1.34	11.30
Lead	g/kg dry<	12.37 <	10.31 <	4.12		<	2.06 <	4.12		5	2.06	12.37	4.12	6.60
Mercury	g/kg dry			2.68 <	1.03		1.44	1.44		4	1.03	2.68	1.44	1.65
Molybdenum	g/kg dry<	4.12 <	4.12 <	0.62	0.21 <	4.12 <	2.06	0.41	0.82	8	0.21	4.12	1.44	2.06
Nickel	g/kg dry	4.54 <	0.62	3.71	0.62 <	0.62	2.68	0.41	35.05	8	0.41	35.05	1.65	6.03
Yttrium	g/kg dry<	0.82 <	0.62 <	0.62 <	0.21 <	0.62 <	0.21 <	0.41 <	0.41	8	0.21	0.82	0.52	0.49
Selenium	g/kg dry						<	2.06		1	2.06	2.06	2.06	2.06
Silver	g/kg dry<	2.06 <	1.65 <	1.86 <	0.82 <	1.65 <	0.82 <	1.03	2.27	8	0.82	2.27	1.65	1.52
Strontium	g/kg dry			0.41	0.41		0.41	1.44		4	0.41	1.44	0.41	0.67
Titanium	g/kg dry	5.98	30.93	2.89	1.03	1.44	3.09	2.06	47.42	8	1.03	47.42	2.99	11.86
Vanadium	g/kg dry	11.96	18.97	7.84	0.41	0.41	5.15	4.12	5.98	8	0.41	18.97	5.57	6.86
Zinc	g/kg dry	16.08	9.69	8.66	17.94	35.05	12.37	6.39	15.88	8	6.39	35.05	14.12	15.26
Zirconium	g/kg dry	10.72	4.54	1.03	0.41	0.82	0.82	2.27	0.21	8	0.21	10.72	0.93	2.60
Silicon	g/kg dry			82.47			30.93	41.24	70.10	4	30.93	82.47	55.67	56.19
Tin	g/kg dry<	6.19 <	4.12 <	4.12 <	1.03 <	4.12 <	1.03 <	1.24 <	1.03	8	1.03	6.19	2.68	2.86
Phosphorus	g/kg dry	13.40 <	8.25 <	10.31 <	4.12	783.51 <	4.12 <	41.24 <	1.03	8	1.03	783.51	9.28	108.25

Table B.2

Composition of aluminum-based coagulants relative to aluminum (Al) content

Constituent	Units	Standard Alum							Summary Statistics				
		#1	#2	#3	#4	#5	#6	#7	count	min	max	median	mean
Aluminum	µg/g Al	1,000,000	1,000,000	1,000,000	1,000,000	1,000,000	1,000,000	1,000,000	7	1,000,000	1,000,000	1,000,000	1,000,000
Calcium	µg/g Al	605	667	402	1,094	1,018	850	691	7	402	1,094	691	761
Iron	µg/g Al	20,233	14,444	15,198	12,076	11,098	7,041	15,434	7	7,041	20,233	14,444	13,646
Potassium	µg/g Al	139.5	63.3	81.4	36.5	61.5	364.2	158.9	7	36.5	364.2	81.5	132.2
Magnesium	µg/g Al	212	611	66	1,139	186	995	389	7	68	1,139	369	511
Manganese	µg/g Al	27.9	57.8	23.9	120.8	77.0	12.1	18.4	7	12.1	120.8	27.9	46.3
Sodium	µg/g Al	637	2,333	684	10,937	7,927	8,012	2,764	7	684	10,937	2,764	4,785
Antimony	µg/g Al <	9.30							1	9.30	9.30	9.30	9.30
Arsenic	µg/g Al <	9.30 <	22.22	22.80 <	22.79 <	22.65 <	24.28 <	23.04	7	9.30	24.26	22.79	21.01
Barium	µg/g Al	4.65 <	1.11 <	1.09 <	1.14	4.53 <	1.21	4.61	7	1.09	4.65	1.21	2.62
Cadmium	µg/g Al <	0.93 <	1.11 <	1.09 <	1.14 <	0.91 <	1.21 <	1.15	7	0.91	1.21	1.11	1.08
Chromium	µg/g Al	697.67	888.89	879.31	729.12	634.16	315.62	967.46	7	315.62	967.48	729.12	730.32
Cobalt	µg/g Al	2.33	3.33 <	2.17	4.56 <	1.81 <	1.70 <	1.61	7	1.61	4.58	2.17	2.50
Copper	µg/g Al	20.93	93.33	30.40	88.86 <	0.91	4.88	20.73	7	0.91	93.33	20.93	37.14
Lead	µg/g Al <	46.51 <	44.44 <	43.42 <	45.57 <	45.30	<	48.07	6	43.42	46.51	45.43	45.22
Mercury	µg/g Al <	9.30							1	9.30	9.30	9.30	9.30
Molybdenum	µg/g Al	1.86 <	22.22 <	18.28 <	18.23 <	18.12 <	19.42 <	18.43	7	1.88	22.22	18.23	18.37
Nickel	µg/g Al	34.88	155.56	9.77	410.13	8.79	4.88	4.81	7	4.61	410.13	9.77	89.51
Yttrium	µg/g Al	4.65 <	3.33 <	3.26 <	4.56 <	4.53 <	4.86 <	4.61	7	3.28	4.86	4.56	4.26
Selenium	µg/g Al <	46.51							1	46.51	46.51	46.51	46.51
Silver	µg/g Al <	9.30 <	7.78 <	7.60 <	9.11 <	8.79 <	9.71 <	9.21	7	6.79	9.71	9.11	8.50
Strontium	µg/g Al	11.63							1	11.63	11.63	11.63	11.63
Titanium	µg/g Al	534.88	200.00	249.68	70.63	498.27	631.25	299.46	7	70.63	631.25	299.46	354.88
Vanadium	µg/g Al	441.88	622.22	651.34	432.92	249.13	242.79	668.02	7	242.79	868.02	441.86	472.61
Zinc	µg/g Al	18.26	46.67	24.97	47.65	33.97	36.85	16.12	7	18.12	47.85	33.97	32.10
Zirconium	µg/g Al	100.00	133.33	130.27	118.48	131.36	80.12	133.60	7	80.12	133.60	130.27	118.17
Silicon	µg/g Al	581.40							1	581.40	581.40	561.40	561.40
Tin	µg/g Al <	9.30	144.44 <	21.71	524.06 <	22.65 <	24.28 <	48.07	7	9.30	524.08	24.28	113.22
Phosphorus	µg/g Al	930.23	1,111.11	1,065.57	1,367.11 <	9.06	631.25	990.51	7	9.06	1,367.11	990.51	874.96

(continued)

Table B.2
(continued)

Constituant	Units	Low-Fe Alum (continued on following page)									
		#1	#2	#3	#4	#5	#6	#7	#8	#9	#10
Aluminum	µg/g Al	1,000,000	1,000,000	1,000,000	1,000,000	1,000,000	1,000,000	1,000,000	1,000,000	1,000,000	1,000,000
Calcium	µg/g Al	634	816	1,659	1,683	1,163	494	464	362	623	697
Iron	µg/g Al	1,317	209	507	2,244	302	483	453	318	438	349
Potassium	µg/g Al	58.1	72.6	57.6	219.7	144.2	82.6	121.5	84.6	89.9	113.8
Magnesium	µg/g Al	341	122	346	3,740	419	91	99	33	157	60
Mangenese	µg/g Al	46.3	9.1	6.9	233.8	9.3	11.8	9.9	12.1	9.2	30.2
Sodium	µg/g Al	10,000	4,762	5,068	44,417	7,211	7,298	6,628	6,370	5,305	4,647
Antimony	µg/g Al <	9.76 <	9.07								
Arsenic	µg/g Al <	9.76 <	9.07 <	23.04 <	23.38 <	23.26 <	21.46 <	22.09 <	21.98 <	23.06 <	23.23
Barium	µg/g Al	1.46	0.14 <	1.15	1.40 <	1.16 <	0.97 <	0.99 <	1.10 <	1.15	2.32
Cadmium	µg/g Al	2.44 <	0.91 <	1.15 <	1.17 <	1.16 <	0.97 <	0.99 <	1.10 <	1.15 <	1.16
Chromium	µg/g Al	39.02	4.54	4.61	30.39	9.30	6.44	4.42	5.49	9.23	6.97
Cobalt	µg/g Al <	1.95 <	1.81 <	1.61	2.34 <	1.63 <	1.61 <	1.66 <	1.65 <	1.61 <	1.63
Copper	µg/g Al	70.73	9.07 <	1.61	116.89	2.09	2.15 <	1.10	34.04 <	1.38 <	1.39
Lead	µg/g Al <	48.78 <	45.35	<	46.75 <	46.52 <	42.93 <	44.18 <	43.93 <	46.13 <	46.47
Mercury	µg/g Al	12.20	11.34								
Molybdenum	µg/g Al	7.32 <	1.81 <	18.43 <	18.70 <	18.61 <	21.46 <	22.09 <	21.96 <	18.45 <	18.59
Nickel	µg/g Al	107.32	4.54	6.91	180.01	4.65	5.37	3.31 <	3.29	6.92	4.65
Yttrium	µg/g Al <	1.95 <	1.81 <	4.61 <	4.68 <	4.65 <	3.22 <	3.31 <	3.29 <	4.61 <	4.65
Selenium	µg/g Al <	46.78 <	22.68								
Silver	µg/g Al <	9.76 <	9.07 <	9.21 <	9.35 <	9.30 <	8.59 <	8.84 <	8.79 <	9.23 <	9.29
Strontium	µg/g Al	4.88	4.54								
Titanium	µg/g Al	19.51	6.80	18.43	107.54	11.63	12.88	12.15	8.79	13.84	11.62
Vanadium	µg/g Al	7.32 <	1.81	4.61	14.03 <	1.86	2.15	2.21	2.20	2.31	4.65
Zinc	µg/g Al	197.56	2,721.09	4.61	39.74	220.99	182.45	176.74	175.71	166.06	183.55
Zirconium	µg/g Al	2.44 <	1.81	4.61	7.01	4.65	4.29	3.31	3.29	4.61	2.32
Silicon	µg/g Al	463.41	72.56								
Tin	µg/g Al	17.07 <	9.07 <	23.04	84.16 <	23.26 <	21.46 <	22.09	30.75 <	23.08 <	23.23
Phosphorus	µg/g Al	1,585.37 <	45.35	46.07 <	46.75 <	46.52 <	42.93 <	44.18	46.12 <	46.13	72.02

(continued)

Table B.2
(continued)

Constituent	Units	Low-Fe Alum (continued)			Summary Statistics				
		#11	#12	#13	count	min	max	median	mean
Aluminum	µg/g Al	1,000,000	1,000,000	1,000,000	13	1,000,000	1,000,000	1,000,000	1,000,000
Calcium	µg/g Al	825	391	1,385	13	362	1,683	697	861
Iron	µg/g Al	731	299	224	13	209	2,244	438	606
Potassium	µg/g Al	141.5	66.6	39.3	13	39.3	219.7	84.6	99.2
Magnesium	µg/g Al	283	122	439	13	33	3,740	157	481
Manganese	µg/g Al	7.1	6.9	6.9	13	6.9	233.8	9.3	30.7
Sodium	µg/g Al	6,603	6,434	3,926	13	3,926	44,417	6,434	9,128
Antimony	µg/g Al		< 9.19	< 9.24	4	9.07	9.76	9.21	9.31
Arsenic	µg/g Al	< 47.16	< 9.19	< 9.24	13	9.07	47.16	22.09	20.45
Barium	µg/g Al	< 1.18	0.69	1.62	13	0.14	2.32	1.15	1.18
Cadmium	µg/g Al	< 1.18	< 0.92	< 0.92	13	0.91	2.44	1.15	1.17
Chromium	µg/g Al	< 1.89	6.89	4.62	13	1.89	39.02	6.44	10.29
Cobalt	µg/g Al	< 1.89	< 1.84	< 1.85	13	1.61	2.34	1.66	1.77
Copper	µg/g Al	2.36	2.30	2.31	13	1.10	116.89	2.30	19.03
Lead	µg/g Al	< 47.16	< 45.96	< 69.27	12	42.93	69.27	46.30	47.79
Mercury	µg/g Al		< 9.19	11.55	4	9.19	12.20	11.44	11.07
Molybdenum	µg/g Al	< 16.51	< 1.84	< 1.85	13	1.81	22.09	18.45	14.43
Nickel	µg/g Al	< 4.72	4.80	4.62	13	3.29	180.01	4.65	26.22
Yttrium	µg/g Al	< 4.72	< 1.84	< 1.85	13	1.81	4.72	3.31	3.48
Selenium	µg/g Al	2.36	< 68.94	< 69.27	5	2.36	69.27	48.78	42.41
Silver	µg/g Al	< 9.43	< 9.19	< 9.24	13	8.59	9.76	9.23	9.18
Strontium	µg/g Al		1.15	4.62	4	1.15	4.88	4.58	3.80
Titanium	µg/g Al	11.79	43.66	25.40	13	6.80	107.54	12.88	23.39
Vanadium	µg/g Al	4.72	< 1.84	< 1.85	13	1.81	14.03	2.21	3.86
Zinc	µg/g Al	165.07	< 0.92	< 0.92	13	0.92	2,721.09	175.71	325.80
Zirconium	µg/g Al	4.72	4.60	4.62	13	1.81	7.01	4.60	4.02
Silicon	µg/g Al		209.11	113.15	4	72.56	463.41	161.13	214.56
Tin	µg/g Al	< 23.58	< 9.19	< 9.24	13	9.07	84.16	23.04	24.55
Phosphorus	µg/g Al	< 47.16	< 45.96	< 9.24	13	9.24	1,585.37	46.12	163.37

(continued)

Table B.2
(continued)

Constituent	Units	PACl								Summary Statistics				
		ACH #1	ACH #2	ACH #3	PACl #1	PACl #2	PACl #3	PACl-OH-S #1	PACl-OH-S #2	count	min	max	median	mean
Aluminum	µg/g Al	1,000,000	1,000,000	1,000,000	1,000,000	1,000,000	1,000,000	1,000,000	1,000,000	8	1,000,000	1,000,000	1,000,000	1,000,000
Calcium	µg/g Al	1,534	319	478	540	961	624	13,273	43,724	8	319	43,724	792	7,682
Iron	µg/g Al	654	548	398	252	155	693	165	27,984	8	155	27,984	472	3,858
Potassium	µg/g Al	37.1	122.7	47.8	82.8	35.3	74.5	125.9	3,672.8	8	35	3,873	79	525
Magnesium	µg/g Al	371	98	206	149	54	260	14,294	10,319	8	54	14,294	233	3,219
Manganese	µg/g Al	18.8	25.3	8.2	9.0	23.2	13.9	13.8	297.3	8	8	297	16	51
Sodium	µg/g Al	517	1,717	1,320	5,757	5,965	3,468	459,459	129,424	8	517	459,459	4,811	75,953
Antimony	µg/g Al							10.21		1	10.2	10.2	10.2	10.2
Arsenic	µg/g Al	24.22	16.35	16.50	8.99	22.09	8.66	10.21	8.74	8	8.7	24.2	13.3	14.5
Barium	µg/g Al	0.81	0.82	0.82	0.90	7.73	1.04	3.40	36.73	8	0.8	38.7	1.0	8.5
Cadmium	µg/g Al	0.81	0.82	1.65	0.90	1.10	0.87	1.02	1.40	8	0.8	1.6	1.0	1.1
Chromium	µg/g Al	28.25	5.72	2.47	3.60	2.21	5.20	3.40	38.48	8	2.2	38.6	4.4	11.2
Cobalt	µg/g Al	1.81	1.64	2.47	1.80	2.21	1.73	3.40	19.24	8	2	19	2	4
Copper	µg/g Al	18.95	0.82	7.42	0.90	3.31	8.93	170.17	524.69	8	1	525	7	91
Lead	µg/g Al	48.43	40.89	16.50			17.33	34.03		5	18	48	34	31
Mercury	µg/g Al			10.72	8.99		12.13	11.91		4	9	12	11	11
Molybdenum	µg/g Al	18.14	16.35	2.47	1.80	22.09	17.33	3.40	7.00	8	2	22	12	11
Nickel	µg/g Al	17.78	2.45	14.85	5.40	3.31	22.53	3.40	297.33	8	2.5	297.3	10.1	45.9
Yttrium	µg/g Al	3.23	2.45	2.47	1.80	3.31	1.73	3.40	3.50	8	1.7	3.5	2.9	2.7
Selenium	µg/g Al							17.02		1	17.0	17.0	17.0	17.0
Silver	µg/g Al	8.07	6.54	7.42	7.20	8.84	8.93	8.51	19.24	8	6.5	19.2	7.7	9.1
Strontium	µg/g Al			1.65	3.60		3.47	11.91		4	1.8	11.9	3.5	5.2
Titanium	µg/g Al	23.41	122.66	11.55	8.99	7.73	25.99	17.02	402.28	8	8	402	20	77
Vanadium	µg/g Al	46.82	75.23	31.34	3.60	2.21	43.32	34.03	50.72	8	2	75	39	36
Zinc	µg/g Al	62.96	38.43	34.64	156.51	187.78	103.98	52.75	134.67	8	35	188	83	98
Zirconium	µg/g Al	41.98	17.99	4.12	3.60	4.42	6.93	18.72	1.75	8	2	42	6	12
Silicon	µg/g Al			329.94			259.94	340.34	594.65	4	260	595	335	381
Tin	µg/g Al	24.22	18.35	18.50	8.99	22.09	8.66	10.21	8.74	8	9	24	13	14
Phosphorus	µg/g Al	52.47	32.71	41.24	35.98	4,197.53	34.66	340.34	8.74	8	9	4,198	39	593

Table B.3
Compositional data for organic polymers on a wet weight basis

Constituent	Units	Polymer #1	Polymer #2	Polymer #3	Polymer #4	Polymer #5	Polymer #6
		mg/kg on wet weight basis					
Aluminum	Al	< 1	< 0.5	< 78	< 120	< 0.5	< 110
Calcium	Ca	67	20	< 76	< 120	0.5	< 110
Iron	Fe	< 0.4	< 0.2	< 31	< 49	1	< 44
Potassium	K	< 8	< 4	< 620	< 970	28	< 870
Magnesium	Mg	24	4.2	< 5	< 8	0.3	< 7
Manganese	Mn	< 0.04	< 0.02	< 3	< 5	< 0.02	< 5
Sodium	Na	160	85	190	1,100	27,000	13,000
Antimony	Sb	< 2	< 1	< 150	< 240	< 1	< 220
Arsenic	As	< 2	< 1	< 150	< 240	< 1	< 220
Barium	Ba	0.1	< 0.01	< 2	< 3	0.1	< 3
Cadmium	Cd	< 0.2	< 0.1	< 16	< 25	< 0.1	< 22
Chromium	Cr	< 0.4	< 0.2	< 31	< 49	< 0.2	< 44
Cobalt	Co	< 0.4	< 0.2	< 31	< 49	< 0.2	< 44
Copper	Cu	< 0.2	< 0.1	< 16	< 25	< 0.1	< 22
Lead	Pb	< 1	< 5	< 150	< 240	< 5	< 220
Mercury	Hg	< 2	< 1	< 150	< 240	< 1	< 220
Molybdenum	Mo	< 0.4	0.2	< 31	< 49	< 0.2	< 44
Nickel	Ni	< 0.04	< 0.2	< 31	< 49	< 0.2	< 44
Yttrium	Y	< 0.4	< 0.2	< 31	< 49	< 0.2	< 44
Selenium	Se		2.9	< 160	< 240	1.5	< 220
Silver	Ag	< 2	< 0.8	< 120	< 190	< 0.8	< 170
Strontium	Sr	0.9	0.02	< 2	< 3	0.04	< 3
Titanium	Ti	< 0.4	0.2	< 16	< 25	0.6	< 44
Vanadium	V	< 0.4	< 0.2	< 31	< 49	< 0.2	< 44
Zinc	Zn	7.7	1	< 18	< 25	0.2	< 22
Zirconium	Zr	2.2	< 0.2	< 31	< 49	< 0.2	< 44
Silicon	Si	< 1	1.9	< 100	< 120	14	< 110
Tin	Sn	< 2	< 1	< 150	< 240	1.4	< 220
Phosphorus	P	< 8	36	< 620	< 970	< 4	< 870
Sulfur	S	110	13	< 390	1,200	970	2,200
specific gravity	sg	1.002	1.141	0.994	1.023	1.093	1.046
Total Organic Carbon	C	4,178					
Percent polymer as dadmac		1.76					
Percent polymer as epi		1.60					
pH			5.2	5.2	4.6	4.2	6.6

(continued)

Table B.3
(continued)

		mg/kg on wet weight basia					
Constituent	Symbol	Polymer #7	Polymer #8	Polymer #9	Polymer #10	Polymer #11	Polymer #12
Aluminum	Al	< 100	< 89	< 0.5	2,200	< 0.5	< 0.5
Calcium	Ca	< 100	< 89	1.2	< 120	0.8	23
iron	Fe	< 40	< 36	3	340	< 0.2	1.5
Potassium	K	< 800	< 700	11	< 920	< 4	< 4
Magnesium	Mg	< 7	< 6	0.4	54	0.4	7.4
Manganese	Mn	< 4	< 4	0.2	8	< 0.02	2.1
Sodium	Na	< 100	4,800	1800	120	780	1,100
Antimony	Sb	< 200	< 180	< 1	< 230	< 1	< 1
Arsenic	As	< 200	< 180	< 1	< 230	< 1	< 1
Barium	Ba	< 2	< 2	0.02	< 3	0.01	0.04
Cadmium	Cd	< 20	< 18	< 0.1	< 23	< 0.1	< 0.1
Chromium	Cr	< 40	< 36	< 0.2	< 46	< 0.2	< 0.2
Cobalt	Co	< 40	< 36	< 0.2	< 46	< 0.2	< 0.2
Copper	Cu	< 20	< 18	0.2	< 23	< 0.1	< 0.1
Lead	Pb	< 200	< 180	< 5	< 460	< 5	< 1
Mercury	Hg	< 200	< 180	< 1	< 230	< 1	< 1
Molybdenum	Mo	< 40	< 36	< 0.2	< 46	< 0.2	< 0.2
Nickel	Ni	< 40	< 36	< 0.2	< 47	< 0.2	< 0.2
Yttrium	Y	< 40	< 36	< 0.2	< 47	< 0.2	< 0.2
Selenium	Se	< 200	< 180	< 1	< 230	< 1	< 1
Silver	Ag	< 160	< 140	< 0.8	< 180	< 0.8	< 0.8
Strontium	Sr	< 2	< 2	0.06	< 3	0.02	0.1
Titanium	Ti	< 20	< 18	< 0.2	490	< 0.1	< 0.2
Vanadium	V	< 40	< 36	< 0.2	< 46	< 0.2	< 0.2
Zinc	Zn	< 20	< 18	< 0.1	230	1.9	0.3
Zirconium	Zr	< 40	< 36	< 0.2	140	< 0.2	< 0.2
Silicon	Si	< 100	< 89	3.9	130	2.1	8.8
Tin	Sn	< 200	< 180	< 1	< 230	< 1	< 1
Phosphorus	P	< 800	< 700	< 1	< 230	< 1	1.1
Sulfur	S	< 500	< 440	1,700	4,100	540	850
specific gravity	sg		1.060	1.042	1.039	1.02	1.016
Total Organic Carbon	C						
Parcent polymer as dadmac							
Percent polymer as epi							
pH			5.7	6.8		6.5	6.6

(continued)

Table B.3
(continued)

Summary Statistics for Polymers
(mg/kg wet weight)

Constituent	Symbol	count	min	max	median
Aluminum	Al	12	0.50	2,200	40
Calcium	Ca	12	0.50	120	73
Iron	Fe	12	0.20	340	17
Potassium	K	12	4.00	970	324
Magnesium	Mg	12	0.30	54	7
Manganese	Mn	12	0.02	8	3
Sodium	Na	12	85	27,000	940
Antimony	Sb	12	1	240	76
Arsenic	As	12	1	240	76
Barium	Ba	12	0.01	3	1
Cadmium	Cd	12	0.10	25	8
Chromium	Cr	12	0.20	49	16
Cobalt	Co	12	0.20	49	16
Copper	Cu	12	0.10	25	8
Lead	Pb	12	1	460	78
Mercury	Hg	12	1	240	76
Molybdenum	Mo	12	0.20	49	16
Nickel	Ni	12	0.04	49	18
Yttrium	Y	12	0.20	49	16
Selenium	Se	11	1	240	160
Silver	Ag	12	0.80	190	61
Strontium	Sr	12	0.02	3	1
Titanium	Ti	12	0.10	490	8
Vanadium	V	12	0.20	49	18
Zinc	Zn	12	0.10	230	12
Zirconium	Zr	12	0.20	140	17
Silicon	Si	12	1	130	52
Tin	Sn	12	1	240	76
Phosphorus	P	12	1	970	133
Sulfur	S	12	13	4,100	695
specific gravity	sg	11	0.99	1.14	1.04
Total Organic Carbon	C	1	4,178	4,178	4,178
Percent polymer as dadmac		1	1.76	1.76	1.78
Percent polymer as epi		1	1.60	1.60	1.60
pH		9	4.2	6.8	5.7

APPENDIX C

COMPOSITION OF TREATMENT CHEMICALS REPORTED FROM UTILITY SURVEY

Data presented in Table C.1 was collected during the utility survey. Some of the information supplied by the utilities was compositional data provided to them by manufacturers and suppliers. Other data was analyzed by the water utility or by an outside contract laboratory, typically on a one-time basis. Since the analytical methods employed to generate this data are unknown, it is not known if appropriate techniques were used in all cases in order to account for the complicated sample matrix in these chemicals. This would explain why some of the data reported in this table are outside the ranges seen from other sources, including this study.

Table C.1:
Compositional data for commonly used water treatment chemicals as reported in the utility survey

(units are mg/kg on dry weight basis, unless stated otherwise)

Constituent	Units	obs	min	max	median	mean
Lime, hydrated [Ca(OH)$_2$]						
Aluminum	mg/kg	4	1,830	2,420	2,060	2,092
Antimony	mg/kg	2		< 100		
Arsenic	mg/kg	3	< 5	16	13	11
Barium	mg/kg	3	24	89	50	54
Beryllium	mg/kg	2		< 10		
Boron	mg/kg	2	< 10	13		
Cadmium	mg/kg	1		< 5		
Calcium	mg/kg	4	449,800	727,400	619,650	604,125
Chromium	mg/kg	3	< 5	24	23	17
Cobalt	mg/kg	1		< 10		
Copper	mg/kg	2	< 2	6		
Iron	mg/kg	4	1,406	2,413	1,776	1,843
Lead	mg/kg	2	< 5	21		
Magnesium	mg/kg	4	490	4,090	3,333	2,811
Manganese	mg/kg	3	< 2	162	28	64
Molybdenum	mg/kg	1		< 50		
Nickel	mg/kg	1		< 50		
Potassium	mg/kg	3	< 1	193	49	81
Selenium	mg/kg	3	< 5	50	42	32
Sodium	mg/kg	3	< 1	197	186	128
Strontium	mg/kg	3	< 20	629	439	363
Thallium	mg/kg	1		< 50		
Vanadium	mg/kg	1		< 50		
Zinc	mg/kg	2	< 5	10		
% Available CaO	%	6	67	92	73	76

(continued)

Table C.1
(continued)

Lime, pebble or ground [CaO], expressed in units of mg/kg as $Ca(OH)_2$

Constituent	Units	obs	min	max	median	mean
Aluminum	mg/kg	1		3,153		
Arsenic	mg/kg	2	2	< 4		
Cadmium	mg/kg	2	< 4	< 4		
Calcium	mg/kg	8	477,838	515,676	499,054	499,020
Cobalt	mg/kg	1		< 8		
Copper	mg/kg	1		< 2		
Iron	mg/kg	1		2,209		
Lead	mg/kg	1		< 4		
Magnesium	mg/kg	1		4,395		
Manganese	mg/kg	1		27		
Molybdenum	mg/kg	1		< 38		
Nickel	mg/kg	1		< 38		
Potassium	mg/kg	1		308		
Sodium	mg/kg	1		341		
Strontium	mg/kg	1		657		
Thallium	mg/kg	1		48		
Vanadium	mg/kg	1		< 38		
Zinc	mg/kg	1		< 4		

% Available CaO	%	10	69	110	92	91
% CO2	%	1		0.4		
% insolubles	%	6	0.7	2.7	1.7	1.8
% Passing 1/8	%	1		5		
3-min Slaking Temp	deg C	7	48	54	52	51

(continued)

Table C.1
(continued)

Constituent	Units	obs	min	max	median	mean

Polyaluminum Chloride (assumed 33% solution)

Constituent	Units	obs	min	max	median	mean
% Al203(Total)	%	2	48	52		
% Basicity	%	2	42	48		
% Iron	%	1		303		
Aluminum	%	2	251,818	274,330		
Hydroxide	%	1		22.73		
pH		1		1.10		
Specific Gravity		7	1.20	1.37	1.22	1.24
Turbidity	ntu	4	4.0	5.0	4.1	4.3
Zinc	mg/kg	1		303		

(continued)

Table C.1
(continued)

Constituent	Units	obs	min	max	median	mean
Organic Polymers						
Arsenic	ppm -wet	3	< 5	14	13	11
Barium	ppm -wet	3	1	< 50	< 5	19
Cadmium	ppm -wet	2	< 0.5	< 5.0		
Chromium	ppm -wet	2	< 0.5	< 5.0		
Copper	ppm -wet	3	< 0.2	< 2.0	1.3	1.2
Iron	ppm -wet	1		3.7		
Lead	ppm -wet	3	< 0.5	< 5.0	2.8	2.8
Nickel	ppm -wet	3	2	< 50	< 5	19
Selenium	ppm -wet	3	< 0.5	11	< 5	5
Zinc	ppm -wet	3	< 0.5	< 5.0	1.8	2.4
% Active Polymer	%	3	20	46	41	36
% Ash	%	1		0.08		
% Moisture	%	1		7.6		
% NaCl	%	1		1.5		
% Residual Monomer	%	2	0.04	0.20		
Brookfield Viscosity at 100 deg F		2	76	1,568		
Brookfield Viscosity at 32 deg F		2	152	1,713		
Conductivity	umhos/cm	10	50	69,300	36,200	34,118
pH		14	2.8	7.7	6.4	6.0
Solids, Total	%	8	10	22	20	18
Specific Gravity		7	1.04	1.37	1.05	1.12
Specific Gravity at 100 deg F		2	0.99	1.04		
Specific Gravity at 32 deg F		2	1.00	1.05		
Specific Weight	lb/gal	2	9	9.0		
Viscosity at 25 deg C (cps)	cps	1		130		

(continued)

Table C.1
(continued)

Constituent	Units	obs	min	max	median	mean
Polymer + Al Blend						
Aluminum	mg/kg	1		42,000		
Iron	mg/kg	2	20	36		
Sodium	mg/kg	2	900	1,200		
Zinc	mg/kg	2	9.0	9.5		
Polymer, Total	mg/kg	1		< 1,000		
Solids, Total	%	2	39	40		
Total Organic Carbon	mg/kg	2	19,000	20,000		

(continued)

Table C.1
(continued)

Constituent	Units	obs	min	max	median	mean
Powdered Activated Carbon						
Arsenic	mg/kg	1		< 5		
Barium	mg/kg	range	45	78		
Cadmium	mg/kg	1		< 5		
Chromium	mg/kg	1		< 5		
Copper	mg/kg	range	6	14		
Lead	mg/kg	1		< 5		
Nickel	mg/kg	1		< 50		
Selenium	mg/kg	1		< 5		
Zinc	mg/kg	range	< 5	8		
Apparent Density		5	0.39	0.90	0.43	0.52
Moisture Content, %	%	5	10	14	12	11

(continued)

Table C.1
(continued)

Constituent	Units	obs	min	max	median	mean

Soda Ash

Constituent	Units	obs	min	max	median	mean
Arsenic	mg/kg	2	0.01	0.04		
% insolubles	%	1		0.012		
% Na2CO3	%	1		99.9		
% Na2O	%	1		58.4		
% Na2SO4	%	1		0.006		
% NaCl	%	1		0.003		
Fe2O3 (total)	mg/kg	1		2.7		

(continued)

Table C.1
(continued)

Constituent	Units	obs	min	max	median	mean
Sodium Hypochlorite (NaOCl)						
Antimony	mg/kg	1		< 0.0006		
Arsenic	mg/kg	2	< 0.0018	< 0.0019		
Barium	mg/kg	2	< 0.0009	< 0.46		
Beryllium	mg/kg	1		< 0.0005		
Cadmium	mg/kg	2	< 0.0003	0.24		
Chromium	mg/kg	2	0.0009	0.05		
Cobalt	mg/kg	1		0.42		
Copper	mg/kg	2	0.0009	0.08		
Iron	mg/kg	1		0.38		
Lead	mg/kg	2	0.0009	0.17		
Mercury	mg/kg	2	0.0002	0.0002		
Nickel	mg/kg	1		0.6		
Selenium	mg/kg	2	0.002	0.006		
Silver	mg/kg	1		0.02		
% Alkalinity (Free)	%	1		0.5		
% Chlorine	%	3	5.3	13.1	12.4	10.3
% NaClO3	%	1		< 0.10		
% NaOH	%	1		0.11		
pH		1		13		
Specific Gravity		3	1.08	1.21	1.20	1.16
Color		1		113		
Total THM	mg/kg	1		60		
Chloroform	mg/L	1		741		

(continued)

Table C.1
(continued)

Constituent	Units	obs	min	max	median	mean
Liquid Alum						
Aluminum	mg/kg	9	75,670	138,763	89,509	100,755
Antimony	mg/kg	2	1.9	< 3.1		
Arsenic	mg/kg	3	< 0.02	10	1	4
Barium	mg/kg	2	< 0.1	< 1		
Beryllium	mg/kg	1		< 1		
Boron	mg/kg	1		< 0.4		
Cadmium	mg/kg	3	0.1	< 1	0.45	0.51
Calcium	mg/kg	2	39	61		
Chromium	mg/kg	3	3	31	7	14
Cobalt	mg/kg	1		< 10		
Copper	mg/kg	2	0.2	< 1		
Iron	mg/kg	1		1,912		
Lead	mg/kg	3	0.1	8	5	5
Manganese	mg/kg	2	0.4	6		
Mercury	mg/kg	3	< 0.002	< 0.021	< 0.002	0.008
Molybdenum	mg/kg	1		0.2		
Nickel	mg/kg	2	1	< 2		
Potassium	mg/kg	2	< 8	< 8		
Selenium	mg/kg	3	0.1	2	1.3	1
Silver	mg/kg	3	< 0.01	< 10	0.1	3
Sodium	mg/kg	2	928	969		
Sulfate (Na_2SO_4)	mg/kg	5	418,557	917,526	577,320	621,443
Vanadium	mg/kg	1		< 1		
Zinc	mg/kg	2	0.5	< 10		
% Alum	%	2	48.0	48.1		
Alum (lbs dry/gal)	lb/gal	2	5.3	5.3		
% Al_2O_3(Free) - wet weight basis	%	6	0.04	< 0.20	0.13	0.12
% Al_2O_3(Total) - wet weight basis	%	10	7	13	8	9
% Fe_2O_3 (Total) - wet weight basis	%	1		0.07		
% H_2SO_4	%	1		1		
% Insolubles	%	3	< 0.001	0.050	0.003	0.018
Baume		1		36		
pH		5	2	4	2	3
Specific Gravity		3	1.327	1.332	1.330	1.330
Specific Weight	lb/gal	1		11		

(continued)

Table C.1
(continued)

Constituent	Units	obs	min	max	median	mean
Ammonia						
Arsenic	mg/kg	1		0.7		
Barium	mg/kg	1		< 0.1		
Cadmium	mg/kg	1		< 0.1		
Chloride (NaCl)	mg/kg	1		0.1		
Chromium	mg/kg	1		< 0.3		
Iron	mg/kg	1		< 0.3		
Lead	mg/kg	1		< 0.2		
Mercury	mg/kg	1		< 0.1		
P2O5	mg/kg	1		< 0.0		
Selenium	mg/kg	1		< 0.3		
Silver	mg/kg	1		< 0.5		
Sulfate (Na2SO4)	mg/kg	1		0.04		
% NH4	%	1		19		
Specific Gravity		1		0.93		
Specific Weight	lb/gal	1		7.7		

(continued)

Table C.1
(continued)

Constituent	Units	obs	min	max	median	mean

Sulfuric Acid

Constituent	Units	obs	min	max	median	mean
Antimony	mg/kg	1		< 0.3		
Arsenic	mg/kg	1		< 0.3		
Barium	mg/kg	1		< 0.3		
Cadmium	mg/kg	1		< 0.3		
Chloride (NaCl)	mg/kg	1		< 10		
Chromium	mg/kg	1		< 0.3		
Copper	mg/kg	1		< 0.3		
Iron	mg/kg	1		5.3		
Lead	mg/kg	1		< 0.3		
Manganese	mg/kg	1		< 0.3		
Mercury	mg/kg	1		< 0.0001		
NH4	mg/kg	1		< 10		
Nickel	mg/kg	1		< 0.3		
Nitrate	mg/kg	1		< 5.0		
Selenium	mg/kg	1		< 0.1		
Silver	mg/kg	1		< 0.3		
Zinc	mg/kg	1		2.6		

Constituent	Units	obs	min	max	median	mean
Baume		1		66		
Color		1		10		
Specific Gravity		1		1.8		

(continued)

Table C.1
(continued)

Caustic Soda (NaOH)

Constituent	Units	obs	min	max	median	mean
Aluminum	mg/kg	7	0.1	189	0.5	51
Antimony	mg/kg	range	< 2	< 100		
Arsenic	mg/kg	6	< 0.01	< 1.8		
Barium	mg/kg	8	0.1	< 10	0.8	2.4
Beryllium	mg/kg	2	< 0.2	< 1.0		
Boron	mg/kg	6	0.2	456	1.5	142
Cadmium	mg/kg	5	< 0.10	< 1.80		
Calcium	mg/kg	6	0.4	4.8	3.3	2.9
Chromium	mg/kg	7	< 0.2	< 1.8	0.8	0.8
Cobalt	mg/kg	3	< 0.10	< 1.00		
Copper	mg/kg	5	< 0.04	< 0.40		
Iron	mg/kg	11	1	844	6	82
Lead	mg/kg	6	0.4	< 1.8	< 0.4	0.0
Magnesium	mg/kg	4	< 0.1	2.6	1.4	1.4
Manganese	mg/kg	2	< 0.04	< 0.20		
Manganese	mg/kg	2	0.12	0.14		
Mercury	mg/kg	3	< 0.004	< 0.010	0.008	0.007
Molybdenum	mg/kg	2	< 1	< 5		
Nickel	mg/kg	6	0.1	< 10	1.2	3.1
Potassium	mg/kg	5	174	2,160	370	689
Selenium	mg/kg	5	< 0.2	< 1.8		
Silicon	mg/kg	3	14	21	16	17
Silver	mg/kg	2	< 0.2	< 1.8		
Sodium	mg/kg	3	372,100	921,600	384,700	559,467
Strontium	mg/kg	5	< 0.4	4.6	2.0	2.1
Thallium	mg/kg	2	< 1	< 5		
Vanadium	mg/kg	3	< 0.1	< 10		
Zinc	mg/kg	6	< 0.1	< 1.0	0.2	0.4

Constituent	Units	obs	min	max	median	mean
Total Alkali - wet basis	%	15	35	40	39	38
Strength	%	14	45	51	50	49
Na2CO3 - wet basis	mg/kg	13	0.03	8.6	0.6	1.8
Chlorate (NaClO3)	mg/kg	4	3,600	5,400	4,300	4,400
NaCl - wet basis	mg/kg	6	0.01	1.00	0.94	0.64
Sulfate (Na2SO4)	mg/kg	5	380	8,000	440	2,248

Constituent	Units	obs	min	max	median	mean
Specific Gravity		2	1.53	1.54		
Specific Weight	lb/gal	1		12.7		
NaOH	lb/gal	1		6.4		

(continued)

Table C.1
(continued)

Constituent	Units	obs	min	max	median	mean

Corrosion Inhibitor (Zn & PO_4 based)

Arsenic	mg/kg	3	9	82	25	39
Barium	mg/kg	2	5	< 50		
Cadmium	mg/kg	2	< 5	14		
Chromium	mg/kg	2	26	83		
Copper	mg/kg	2	< 2	4		
Lead	mg/kg	2	44	158		
Nickel	mg/kg	2	< 50	64		
Selenium	mg/kg	2	35	118		
Zinc	mg/kg	4	46,000	114,600	86,200	83,250

Phosphate, ortho, %	%	3	30	35	33	33
Phosphorus	mg/kg	2	44,535	51,000		
Specific Gravity		8	1.37	1.56	1.44	1.45
Specific Weight	lb/gal	1		11		

(continued)

Table C.1
(continued)

Constituent	Units	obs	min	max	median	mean
Chlorine						
Arsenic	mg/kg	1		< 0.1		
Barium	mg/kg	1		< 0.1		
Cadmium	mg/kg	1		< 0.1		
Chromium	mg/kg	1		< 0.1		
Iron	mg/kg	1		0.3		
Lead	mg/kg	1		0.07		
Mercury	mg/kg	2	0.0004	< 0.0050		
Selenium	mg/kg	1		< 0.1		
Silver	mg/kg	1		< 0.1		
% Chlorine	%	2	99.7	99.9		
Bromine	mg/kg	1		128		
Oxygen	mg/kg	1		46		
moisture	%	2	4	5		
Non Volatile Residue	mg/kg	1		12		
CCl4	mg/kg	1		0.7		
Total THM	mg/kg	1		52		
NCl3	mg/kg	1		0.3		

(continued)

Table C.1
(continued)

Fluorosilicic Acid (H_2SiF_6) - data reported on wet weight basis

Constituent	Units	obs	min	max	median	mean
Aluminum	mg/kg	1		154		
Antimony	mg/kg	1		< 1		
Arsenic	mg/kg	range	9	59		
Barium	mg/kg	range	< 0.1	9		
Beryllium	mg/kg	1		< 0.1		
Boron	mg/kg	1		49		
Cadmium	mg/kg	range	< 1	3		
Calcium	mg/kg	1		87		
Chloride	%	1		0.40		
Chromium	mg/kg	range	< 1	3		
Cobalt	mg/kg	1		< 0.1		
Copper	mg/kg	range	< 0.2	1		
Iron	mg/kg	1		32		
Lead	mg/kg	8	0.83	55	< 20	20
Magnesium	mg/kg	1		23		
Manganese	mg/kg	1		0.4		
Molybdenum	mg/kg	1		1		
Nickel	mg/kg	2	< 0.1	< 5		
Phosphorus	%	8	0.020	0.190	0.055	0.071
Potassium	mg/kg	1		3		
Selenium	mg/kg	range	< 1	20		
Silver	mg/kg	1		< 1		
Sodium	mg/kg	1		385		
Strontium	mg/kg	1		< 1		
Thallium	mg/kg	1		< 2		
Vanadium	mg/kg	1		20		
Zinc	mg/kg	range	< 2	5,672		

% H2SiF6 - APHA	%	6	18.0	35.0	24.5	26.2
% H2SiF6, hydrogen titration	%	11	22.2	29.3	25.5	25.4
% H2SiF6, Specific gravity	%	6	23.1	25.0	23.4	23.8
% HF	%	4	0.39	0.49	0.42	0.43
Free Acid	%	5	0.3	< 1	0.5	0.5
Specific Gravity		17	1.20	1.40	1.23	1.23
Color		6	5	39	18	19.8

(continued)

Table C.1
(continued)

Constituent	Units	obs	min	max	median	mean
Ferric Chloride						
Antimony	mg/kg	1		3		
Arsenic	mg/kg	17	0.2	410	8	179
Barium	mg/kg	14	0.3	250	13	66
Beryllium	mg/kg	5	0.1	0.8	0.3	0.3
Cadmium	mg/kg	11	0.1	198	0.5	63
Chromium	mg/kg	16	28	1,913	357	695
Cobalt	mg/kg	1		10		
Copper	mg/kg	14	0.5	2,830	82	366
Lead	mg/kg	17	0.6	1,118	13	282
Magnesium	mg/kg	6	31	350	44	93
Manganese	mg/kg	4	592	724	676	667
Manganese	mg/kg	2	1,695	1,875		
Mercury	mg/kg	6	0.01	1.20	0.08	0.27
Molybdenum	mg/kg	7	3	30	10	14
Nickel	mg/kg	12	5	385	30	82
Phosphorus	mg/kg	5	38	123	54	74
Selenium	mg/kg	15	1	505	7	190
Silver	mg/kg	7	0.3	28	0.8	5
Sulfur	mg/kg	6	72	290	123	148
Titanium	mg/kg	6	9	7,125	11	1,203
Vanadium	mg/kg	7	5	1,388	7	206
Zinc	mg/kg	18	1	26,900	96	1,657
% FeCl2	%	4	0.3	0.8	0.4	0.5
% FeCl3	%	9	32	45	41	39
% HCl (Free)	%	3	0.02	0.83	0.80	0.55
% Insolubles	%	2	0.02	0.11		
Specific Gravity		17	1.33	1.48	1.43	1.42
Specific Weight	lb/gal	2	11.8	12.3		
Baume		1		44		

(continued)

Table C.1
(continued)

Ferric Sulfate

Constituent	Units	obs	min	max	median	mean
Antimony	ppm -wet	1		< 0.003		
Arsenic	ppm -wet	1		< 0.001		
Barium	ppm -wet	1		< 0.2		
Beryllium	ppm -wet	1		< 0.001		
Cadmium	ppm -wet	1		< 0.012		
Calcium	ppm -wet	1		3		
Copper	ppm -wet	1		0.04		
Lead	ppm -wet	1		0.17		
Magnesium	ppm -wet	1		78		
Manganese	ppm -wet	1		10		
Molybdenum	ppm -wet	1		< 0.2		
Nickel	ppm -wet	1		1		
Selenium	ppm -wet	1		< 0.002		
Silver	ppm -wet	1		< 0.002		
Sodium	ppm -wet	1		3		
Titanium	ppm -wet	1		28		
Zinc	ppm -wet	1		1		

(continued)

Table C.1
(continued)

Potassium Permanganate

Constituent	Units	obs	min	max	median	mean
Aluminum	mg/kg	2	67	69		
Antimony	mg/kg	2	< 0.8	0.8		
Arsenic	mg/kg	3	3.3	< 5.0	4.8	4.4
Barium	mg/kg	3	13	71	20	35
Beryllium	mg/kg	2		< 0.8		
Bismuth	mg/kg	2	0.8	2.0		
Boron	mg/kg	2	0.4	11		
Cadmium	mg/kg	2	< 0.4	< 5.0		
Calcium	mg/kg	2	50	126		
Chromium	mg/kg	3	2.4	131	14	49
Cobalt	mg/kg	1		0.8		
Copper	mg/kg	3	8.0	371	11	130
Iron	mg/kg	2	18	36		
Lead	mg/kg	3	1.2	101	2.8	35
Lithium	mg/kg	2	2.4	3.4		
Magnesium	mg/kg	2	3.2	15		
Mercury	mg/kg	1		0.04		
Molybdenum	mg/kg	2	8.3	10.0		
Nickel	mg/kg	3	1.2	< 50	3.2	18
Selenium	mg/kg	3	0.1	182	0.8	61
Silicon	mg/kg	2	1,000	3,200		
Silver	mg/kg	2	< 0.1	< 0.4		
Sodium	mg/kg	2	270	475		
Strontium	mg/kg	1		0.4		
Thallium	mg/kg	1		5		
Vanadium	mg/kg	1		12		
Zinc	mg/kg	3	3.6	6.8	5.0	5.1
Chloride	%	2	0.006	0.010		
Nitrogen	%	2	0.0002	0.0030		
Phosphorus	mg/kg	2	1.6	4.0		
Sulfate	%	2	0.015	0.020		
Sulfur	mg/kg	1		133		
Insolubles	mg/kg	2	0.3	0.7		
KMnO4	%	1		98.6		
pH , 5% solution		2	9.7	9.8		
Water Tolerance	%	1		0.3		

(continued)

Table C.1
(continued)

Constituent	Units	obs	min	max	median	mean
Liquid and Granular Alum (data from one utility)						
Arsenic	mg/kg	range	555	821		
Barium	mg/kg	3	< 0.1	< 50	10	20
Boron	mg/kg	1		5		
Cadmium	mg/kg	3	< 1	21	5	9
Calcium	mg/kg	1		532		
Chromium	mg/kg	3	< 5	66	43	38
Copper	mg/kg	3	< 0.4	14	2	6
Lead	mg/kg	2	< 1	< 5		
Magnesium	mg/kg	1		140		
Nickel	mg/kg	2	< 10	< 50		
Potassium	mg/kg	1		153		
Selenium	mg/kg	range	< 5	285		
Silver	mg/kg	1		0.1		
Sodium	mg/kg	1		56		
Strontium	mg/kg	1		16		
Zinc	mg/kg	4	< 1	19	9	9

APPENDIX D

SAMPLE CALCULATIONS FOR DBP PRECURSOR DETERMINATIONS FOR COMMONLY USED COAGULANTS

DBP formation potential determinations were performed by EE&T in order to estimate the potential contribution to THM and HAA formation from trace amounts of organic material found in commonly used water treatment coagulants. Coagulants tested included two iron (Fe)-based products, ferric chloride ($FeCl_3$) and ferric sulfate ($Fe_2(SO_4)_3$), and three aluminum (Al)-based products, a standard alum and two polyaluminum chloride (PACl) products. Coagulant samples used for THM and HAA formation potential included a fixed amount of coagulant exposed to free chlorine for a seven-day period. Coagulant dose used in all of these studies was approximately 1.5 mmol/L of coagulant metal, i.e., 1.5 mmol/L of Fe or Al.

Calculations used to determine the source concentration of the full-strength material, and the corresponding amount of this material needed to be added to produce the desired experimental dose, are described separately below for each of the five coagulants used. Please note that coagulants used for these THM and HAA formation potential determinations were the same samples analyzed for TOC. However, these samples were not necessarily the same coagulants used in the laboratory partitioning studies described in other sections of this report.

ALUM DOSE CALCULATIONS

$Al_2(SO_4)_3 \cdot 14.3\ H_2O$ = molecular weight of 600 mg/mmol

Alum source specific gravity = 1.335

Alum strength = 48.5 percent as alum

$$\text{source concentration} = 1.335 * \frac{8.34\text{ lb}}{\text{gal}} * \frac{\text{gal}}{3.785\text{ L}} * \frac{454{,}000\text{ mg}}{\text{lb}} * \frac{48.5\text{ mg dry alum}}{100\text{ mg wet alum}} = \frac{6.5 \times 10^5\text{ mg as alum}}{\text{L}}$$

$$= \frac{6.5 \times 10^5\text{ mg as alum}}{\text{L}} * \frac{\text{mmol alum}}{600\text{ mg alum}} * \frac{2\text{ mmol Al}}{\text{mmol alum}} * \frac{27\text{ mg Al}}{\text{mmol Al}} = \frac{5.8 \times 10^4\text{ mg as Al}}{\text{L}}$$

Adding 350 μL of alum source to a vial containing 500 mL DI water will result in an experimental dose of:

$$\text{Experimental dose} = \frac{6.5\times10^{5}\ \text{mg as alum}}{\text{L}} * \frac{350\ \mu\text{L alum}}{500\ \text{mL vial}} * \frac{\text{mL}}{1{,}000\ \mu\text{L}}$$

$$= \frac{453\ \text{mg as alum}}{\text{L}}$$

$$= \frac{453\ \text{mg as alum}}{\text{L}} * \frac{2\ \text{mmol Al}}{\text{mmol alum}} * \frac{\text{mmol alum}}{600\ \text{mg alum}}$$

$$= \frac{1.51\ \text{mmol Al}}{\text{L}}$$

FERRIC SULFATE DOSE CALCULATIONS

$Fe_2(SO_4)_3$ = molecular weight of 400 mg/mmol

Ferric sulfate source specific gravity = 1.58

Ferric sulfate strength = 12.15 percent as Fe^{+3}

$$\text{Source concentration} = 1.58 * \frac{8.34\ \text{lb}}{\text{gal}} * \frac{\text{gal}}{3.785\ \text{L}} * \frac{454{,}000\ \text{mg}}{\text{lb}} * \frac{12.15\ \text{mg dry Fe}}{100\ \text{mg wet product}}$$

$$= \frac{192{,}000\ \text{mg dry Fe}}{\text{L}}$$

Adding 220 μL of ferric sulfate source to a vial containing 500 mL DI water will result in an experimental dose of:

$$\text{Experimental dose} = \frac{192{,}000\ \text{mg as Fe}}{\text{L}} * \frac{220\ \mu\text{L ferric}}{500\ \text{mL vial}} * \frac{\text{mL}}{1{,}000\ \mu\text{L}}$$

$$= \frac{84.5\ \text{mg as Fe}}{\text{L}}$$

$$= \frac{84.5\ \text{mg as Fe}}{\text{L}} * \frac{\text{mmol Fe}}{55.85\ \text{mg Fe}}$$

$$= \frac{1.51\ \text{mmol Fe}}{\text{L}}$$

FERRIC CHLORIDE DOSE CALCULATIONS

$FeCl_3$ = molecular weight of 162 mg/mmol

Ferric chloride source specific gravity = 1.432

Ferric chloride strength = 39.67 percent as $FeCl_3$

$$\text{Source concentration} = 1.432 * \frac{8.34\text{ lb}}{\text{gal}} * \frac{\text{gal}}{3.785\text{ L}} * \frac{454{,}000\text{ mg}}{\text{lb}} * \frac{39.67\text{ mg dry FeCl}_3}{100\text{ mg wet FeCl}_3}$$
$$= \frac{568{,}000\text{ mg dry FeCl}_3}{\text{L}}$$

Adding 215 μL of ferric chloride source to a vial containing 500 mL DI water will result in an experimental dose of:

$$\text{Experimental dose} = \frac{568{,}000\text{ mg as FeCl}_3}{\text{L}} * \frac{215\ \mu\text{L ferric}}{500\text{ mL vial}} * \frac{\text{mL}}{1{,}000\ \mu\text{L}}$$
$$= \frac{244\text{ mg as FeCl}_3}{\text{L}}$$
$$= \frac{244\text{ mg as FeCl}_3}{\text{L}} * \frac{\text{mmol FeCl}_3}{162\text{ mg FeCl}_3}$$
$$= \frac{1.51\text{ mmol Fe}}{\text{L}}$$

PACl DOSE CALCULATIONS

Product is listed as 49 percent basicity, which means formula of this product is approximately $Al_2(OH)_3Cl_3$

Product strength = 10.8 percent Al_2O_3

Specific gravity = 1.3

Product strength is:

$$\text{Strength} = \frac{10.8\text{ mg Al}_2\text{O}_3}{100\text{ mg product}} * \frac{1.3*10^6\text{ mg product}}{\text{L of product}} * \frac{2\text{ mmol Al}}{\text{mmol Al}_2\text{O}_3} * \frac{\text{mmol Al}_2\text{O}_3}{102\text{ mg Al}_2\text{O}_3} * \frac{27\text{ mg Al}}{\text{mmol Al}}$$

$$\approx \frac{74{,}000\text{ mg Al}}{\text{L of product}}$$

Adding 270 μL of this PACl to a vial containing 500 mL of DI water will result in an experimental dose of:

$$\text{Experimental dose} = \frac{270\ \mu\text{L of product}}{500\text{ mL vial}} * \frac{74{,}000\text{ mg Al}}{\text{L of product}} * \frac{\text{mmol Al}}{27\text{ mg Al}} * \frac{\text{mL}}{1{,}000\ \mu\text{L}}$$

$$\approx \frac{1.5\text{ mmol of Al}}{\text{L}}$$

ACH DOSE CALCULATIONS

PACl product is listed as 84 percent basicity, which means formula of this product is approximately $Al_2(OH)_5Cl$—in other words, aluminum chlorohydrate (ACH).

Product strength = 23.7 percent Al_2O_3
Specific gravity = 1.3
Product strength is:

$$\text{Strength} = \frac{23.7\text{ mg Al}_2\text{O}_3}{100\text{ mg product}} * \frac{1.3*10^6\text{ mg product}}{\text{L of product}} * \frac{2\text{ mmol Al}}{\text{mmol Al}_2\text{O}_3} * \frac{\text{mmol Al}_2\text{O}_3}{102\text{ mg Al}_2\text{O}_3} * \frac{27\text{ mg Al}}{\text{mmol Al}}$$

$$\approx \frac{163{,}000\text{ mg Al}}{\text{L of product}}$$

Adding 125 μL of this PACl to a vial containing 500 mL of DI water will result in an experimental dose of:

$$\text{Experimental dose} = \frac{125\ \mu\text{L of product}}{500\ \text{mL vial}} * \frac{163{,}000\ \text{mg Al}}{\text{L of product}} * \frac{\text{mmol Al}}{27\ \text{mg Al}} * \frac{\text{mL}}{1{,}000\ \mu\text{L}}$$

$$\approx \frac{1.5\ \text{mmol of Al}}{\text{L}}$$

APPENDIX E

SLUDGE PRODUCTION FROM COAGULANTS AND OTHER TREATMENT CHEMICALS

Work by Cornwell (1999) has demonstrated that sludge production can be estimated by summing up the relative contributions from each potential source, including solids produced from raw water turbidity or solids contribution from added treatment chemicals. This relationship is summarized in the following expression.

$$M_T = S/Q = \sum M_i = w * \sum \left(K_i * C_i\right)$$

where M_T = total solids production per volume of raw water treated

S = daily solids production

Q = raw water flow rate

w = $8.34 \dfrac{\text{lb}/10^6\text{gal}}{\text{mg/L}} = \dfrac{10^6\ \text{kg/L}}{\text{mg/L}}$

M_i = $w \cdot K_i \cdot C_i$ = contribution from component "i" to mass of solids produced per volume of raw water treated

K_i = sludge production coefficient

C_i = concentration of component "i" removed, i.e., either a treatment chemical or raw water constituent

CONTRIBUTION OF DIFFERENT COMPONENTS TO SOLIDS PRODUCTION

The units for "K_i" and "C_i" must match, i.e., dry weight versus wet weight, alum versus Al, $FeCl_3$ versus Fe, etc., as appropriate. For example, please note that contribution to sludge production from each of the following components:

Alum

$$M_{alum} = w \cdot K_{alum} \cdot C_{alum} = w \cdot K_{Al} \cdot C_{Al}$$

$$K_{alum} = \frac{0.44 \text{ lb dry sludge}}{\text{lb dry alum}}$$

$$K_{Al} = \frac{4.89 \text{ lb dry sludge}}{\text{lb dry alum as Al}}$$

PACl

$$M_{PACl} = w \cdot K_{Al} \cdot C_{Al} = w \cdot K_{PACl} \cdot C_{PACl}$$

$$K_{Al} = \frac{4.89 \text{ lb dry sludge}}{\text{lb dry PACl as Al}}$$

$$K_{PACl} = K_{Al} \cdot \frac{54 \text{ lb Al}}{102 \text{ lb } Al_2O_3} \cdot \frac{\% \text{ dry product}}{100 \text{ lb wet product}}$$

Therefore, for a liquid PACl product that is 33 percent PACl on a dry weight basis:

$$K_{PACl} = 4.89\left(\frac{54}{102}\right)\left(\frac{33}{100}\right) = \frac{0.85 \text{ lb dry sludge}}{\text{lb wet PACl as } Al_2O_3}$$

Iron Salts

$$M_{Fe} = w \cdot K_{Fe} \cdot C_{Fe} = w \cdot K_{FeCl_3} \cdot C_{FeCl_3} = w \cdot K_{Fe_2(SO_4)_3} \cdot C_{Fe_2(SO_4)_3}$$

$$K_{Fe} = \frac{2.9 \text{ lb dry sludge}}{\text{lb of dry ferric salt as Fe}}$$

$$K_{FeCl_3} = \frac{2.9 \text{ lb dry sludge}}{\text{lb of dry ferric as Fe}} \cdot \frac{55.85 \text{ lb Fe}}{162 \text{ lb } FeCl_3} = \frac{1.0 \text{ lb dry sludge}}{\text{lb dry } FeCl_3}$$

$$K_{Fe_2(SO_4)_3} = \frac{2.9(2)(55.85)}{\left[2(55.85) + 3(96)\right]} \frac{\text{lb dry sludge}}{\text{lb dry } Fe_2(SO_4)_3} = \frac{0.81 \text{ lb dry sludge}}{\text{lb dry } Fe_2(SO_4)_3}$$

Raw Turbidity or Suspended Solids

$$M_{solids} = M_{Turb} = M_{TSS} = w \cdot K_{Turb} C_{Turb} = w \cdot C_{TSS}$$

$$K_{Turb} = \frac{0.77 \text{ to } 2.2 \text{ mg/L TSS}}{\text{ntu removed}}$$

K_{Turb} varies depending upon characteristics of the raw water. For calculations in this appendix, a value of K_{Turb} = 1.8 mg/L TSS per ntu removed will be used.

Softening

$$M_{Soft} = w \cdot \left[(K_{Ca} \cdot C_{Ca}) + (K_{Mg} \cdot C_{Mg})\right]$$

$$K_{Ca} = \frac{2.0 \text{ lb dry sludge}}{\text{lb of Ca hardness removed as } CaCO_3}$$

$$K_{Mg} = \frac{2.6 \text{ lb dry sludge}}{\text{lb of Mg hardness removed as } Mg(OH)_2}$$

$$= \frac{4.48 \text{ lb dry sludge}}{\text{lb of Mg hardness removed as } CaCO_3}$$

Please note that Ca hardness removal includes amount of raw water hardness removed + amount of lime added.

Therefore:

C_{Ca} = total Ca hardness removed = $Ca_{raw} + Ca_{lime} - Ca_{filtered}$

where Ca_{raw} = raw water Ca hardness

Ca_{filt} = filtered water Ca hardness

Ca_{lime} = amount of Ca hardness added via lime addition

Therefore, the above equation for M_{Soft} can be re-stated as follows:

$$M_{Soft} = w\left[K_{Ca}\left(Ca_{raw} - Ca_{filt}\right) + K_{Mg}\left(Mg_{raw} - Mg_{filt}\right)\right] + \left[K_{Ca}\left(Ca_{lime}\right)\right]$$

$$= M_{hardness} + M_{lime}$$

where $M_{hardness}$ = mass of Ca and Mg hardness removal from raw water

M_{lime} = mass of lime added

Other Chemicals

$$M_{other} = w \cdot K_{other} \cdot C_{other}$$

$$K_{other} = \frac{1 \text{ lb dry sludge}}{\text{lb of other chemical agent}}$$

This includes all chemicals added prior to sedimentation basin, plus all chemicals added after sedimentation and before filtration if SFBW is recycled. This would include polymers, pH control chemicals, PAC, $_{\text{Potassium permanganate}}$, and other chemicals not otherwise accounted for.

RELATIVE CONTRIBUTION OF TREATMENT CHEMICALS TO TOTAL SOLIDS PRODUCTION

The first equation in this appendix for "M_T" can be re-stated as follows:

$$M_T = M_{chemicals} + M_{treatment}$$

and

$$M_{treatment} = M_{hardness} + M_{solids}$$

$M_{chemicals} = M_{coagulant} + M_{lime} + M_{other}$

$M_{coagulant} = M_{alum}$ or M_{PACl} or M_{Fe}

In order to illustrate the use of these relationships, the following examples will be presented below:

- Conventional (clarification plus filtration) system with low raw water turbidity (example 1) and high raw water turbidity (example 2) using the following coagulants:
  - Alum
  - Iron salt
  - PACl
- Softening plant with low raw water turbidity (example 3a and 3b)
  - No coagulant
  - Iron salts
- Softening plant with high raw water turbidity (example 3c)
  - Iron salts
- Direct filtration (example 4) with same conditions as for low turbidity example used for conventional clarification plus filtration system
  - Iron salts

Example 1: Conventional Treatment, Low Raw Water Turbidity

Figure E.1 includes a schematic of the treatment system for this hypothetical example. Listed below are the source water characteristics and the chemical feed responses which impact sludge production in this example.

Influent turbidity = 10 ntu
Effluent turbidity = ~0 ntu
Hardness removed = ~0 mg/L as $CaCO_3$
Pre-rapid mix (RM) polymer dose = 0.1 mg/L as product

Pre-filter polymer dose = 0.01 mg/L as product

$KMnO_4$ dose = 1.0 mg/L as $KMnO_4$

Dose of post-filter chemicals(F, PO_4, NaOCl, NaOH) are irrelevant in this example

If the $FeCl_3$ dose in this situation is 15 mg/L as $FeCl_3$, then sludge production for this example would be calculated as follows:

$$C_{FeCl_3} = \frac{15 \text{ mg as } FeCl_3}{L}$$

$$C_{FeCl_3} = \frac{15 \text{ mg as } FeCl_3}{L} \cdot \frac{\text{mmol } FeCl_3}{162 \text{ mg } FeCl_3} \cdot \frac{\text{mmol Fe}}{\text{mmol } FeCl_3}$$

$$= \frac{0.093 \text{ mmol Fe}}{L} \cdot \frac{55.9 \text{ mg Fe}}{\text{mmol Fe}} = \frac{5.2 \text{ mg Fe}}{L}$$

Therefore,

$$M_{Fe} = \frac{8.34 \text{ lb}/10^6 \text{ gal}}{\text{mg/L}} \cdot \frac{1.0 \text{ lb dry sludge}}{\text{lb dry } FeCl_3} \cdot \frac{15 \text{ mg as } FeCl_3}{L} = \frac{125 \text{ lb dry sludge}}{10^6 \text{ gal}}$$

or

$$M_{Fe} = \frac{8.34 \text{ lb}/10^6 \text{ gal}}{\text{mg/L}} \cdot \frac{2.9 \text{ lb dry sludge}}{\text{lb dry } FeCl_3} \cdot \frac{5.2 \text{ mg as Fe}}{L} = \frac{125 \text{ lb dry sludge}}{10^6 \text{ gal}}$$

Similarly, for other treatment chemicals ($KMnO_4$ and two polymers), the contribution to sludge production is as follows:

$$M_{Mn} = \frac{8.34 \text{ lb}/10^6 \text{ gal}}{\text{mg/L}} \cdot \frac{1.0 \text{ lb dry sludge}}{\text{lb dry } KMnO_4} \cdot \frac{1.0 \text{ mg as } KMnO_4}{L} = \frac{8.3 \text{ lb dry sludge}}{10^6 \text{ gal}}$$

$$M_{\text{pre-RM polymer}} = \frac{8.34\ \text{lb}/10^6\ \text{gal}}{\text{mg/L}} \cdot \frac{1.0\ \text{lb dry sludge}}{\text{lb product}} \cdot \frac{0.1\ \text{mg as product}}{\text{L}} = \frac{0.8\ \text{lb dry sludge}}{10^6\ \text{gal}}$$

$$M_{\text{pre-filter polymer}} = \frac{8.34\ \text{lb}/10^6\ \text{gal}}{\text{mg/L}} \cdot \frac{1.0\ \text{lb dry sludge}}{\text{lb product}} \cdot \frac{0.01\ \text{mg as product}}{\text{L}} = \frac{0.08\ \text{lb dry sludge}}{10^6\ \text{gal}}$$

Therefore, the total sludge produced from all added treatment chemicals in this example is:

$$M_{\text{chemicals}} = M_{\text{Fe}} + M_{\text{Mn}} + M_{\text{pre-RM polymer}} + M_{\text{pre-filter polymer}}$$

$$= \frac{125 + 8.3 + 0.8 + 0.08\ \text{lb dry sludge}}{10^6\ \text{gal}}$$

$$= \frac{134\ \text{lb dry sludge}}{10^6\ \text{gal}}$$

The total sludge due to removal of turbidity in this example is 150 lb/10^6 gal as calculated below:

$$M_{\text{Turb}} = \frac{8.34\ \text{lb}/10^6\ \text{gal}}{\text{mg/L}} \cdot \frac{1.8\ \text{lb dry sludge}}{\text{ntu removed}} \cdot 10\ \text{ntu removed} = \frac{150\ \text{lb dry sludge}}{10^6\ \text{gal}}$$

Therefore, the total sludge production in this example is about 284 lbs of dry sludge per 10^6 gallons of water produced, with ~47 percent of sludge coming from added treatment chemicals, as shown below:

$$M_T = M_{\text{chemicals}} + M_{\text{turb}}$$

$$= \frac{134 + 150\ \text{lb dry sludge}}{10^6\ \text{gal}} = \frac{284\ \text{lb dry sludge}}{10^6\ \text{gal}}$$

$$Y_{\text{chemical}} = \frac{M_{\text{chemical}}}{M_T} \times 100\% = \frac{134}{284} \times 100\% = 47\%$$

where Y_{chemical} = percent of total dry sludge production contributed by added treatment chemicals

If the alum dose needed for the same situation is 30 mg/L alum, then:

$$C_{alum} = \frac{30 \text{ mg as alum}}{\text{L}}$$

$$C_{Al} = \frac{30 \text{ mg as alum}}{\text{L}} \cdot \frac{\text{mmol alum}}{600 \text{ mg as alum}} \cdot \frac{2 \text{ mmol Al}}{\text{mmol alum}}$$

$$= \frac{0.10 \text{ mmol Al}}{\text{L}} \cdot \frac{27 \text{ mg Al}}{\text{mmol Al}} = \frac{2.7 \text{ mg Al}}{\text{L}}$$

$$M_{alum} = \frac{8.34 \text{ lb}/10^6 \text{ gal}}{\text{mg/L}} \cdot \frac{0.44 \text{ lb dry sludge}}{\text{lb dry alum}} \cdot \frac{30 \text{ mg as alum}}{\text{L}} = \frac{110 \text{ lb dry sludge}}{10^6 \text{ gal}}$$

or

$$M_{alum} = \frac{8.34 \text{ lb}/10^6 \text{ gal}}{\text{mg/L}} \cdot \frac{4.89 \text{ lb dry sludge}}{\text{lb dry alum as Al}} \cdot \frac{2.7 \text{ mg as Al}}{\text{L}} = \frac{110 \text{ lb dry sludge}}{10^6 \text{ gal}}$$

Replacing M_{Fe} in previous calculations with M_{Al}, the resulting sludge production on a dry weight basis using alum instead of $FeCl_3$ is calculated as follows:

$$M_{chemical} = M_{alum} + M_{Mn} + M_{Pre\text{-}RM\ polymer} + M_{Pre\text{-}filter\ polymer}$$

$$= \frac{110 + 8.3 + 0.8 + 0.08 \text{ lb dry sludge}}{10^6 \text{ gal}} = \frac{119 \text{ lb dry sludge}}{10^6 \text{ gal}}$$

$$M_T = M_{chemical} + M_{turb}$$

$$= \frac{(119 + 150) \text{ lb dry sludge}}{10^6 \text{ gal}} = \frac{269 \text{ lb dry sludge}}{10^6 \text{ gal}}$$

$$Y_{chemicals} = \frac{119}{269} \times 100\% = 44\%$$

If a PACl is used instead of alum or $FeCl_3$, and if the amount of PACl necessary to meet the same degree of coagulation (for TOC and particle removal) is 2.7 mg/L of PACl as Al (i.e., 15.5 mg/L of wet PACl as Al_2O_3 for a PACl that was 33 percent product on a dry weight basis), then sludge production would be identical to sludge production calculated above for alum, calculated as follows:

$$M_{PACl} = \frac{8.34\ \text{lb}/10^6\ \text{gal}}{\text{mg/L}} \cdot \frac{4.89\ \text{lb dry sludge}}{\text{lb dry PACl as Al}} \cdot \frac{2.7\ \text{mg as Al}}{\text{L}} = \frac{110\ \text{lb dry sludge}}{10^6\ \text{gal}}$$

or

$$M_{PACl} = \frac{8.34\ \text{lb}/10^6\ \text{gal}}{\text{mg/L}} \cdot \frac{0.85\ \text{lb dry sludge}}{\text{lb dry PACl as wet product}} \cdot \frac{15.5\ \text{mg as wet product}}{\text{L}}$$

$$= \frac{110\ \text{lb dry sludge}}{10^6\ \text{gal}}$$

All of the above calculations are summarized in Table E.1. Overall, a little less than 50 percent of sludge on a dry weight basis in each of these instances was contributed by added treatment chemicals. Please note that above calculations are for sludge production on a dry weight basis. Volume of sludge and sludge production on a wet weight basis may be different for PACl versus alum versus Fe sludges.

Table E.1

Contribution of treatment chemicals to total sludge production in some typical drinking water treatment situations

			Coagulant dose (mg/L)			Softening (mg/L asCaCO$_3$)			Other chemicals (mg/L as product)		Sludge production (lbs dry sludge/10^6 gal water produced)				
Ex.	Description	Turb. removal (ntu)	Fe	Al	Polymer	Ca-hard	Mg-hard	Lime dose	KMnO$_4$	Pre-filter polymer	Chemicals	Turbidity	Softening	Total	Sludge contribution from chemicals (percent)
1a	Clarification + Filtration Low turbidity Iron + Polymer	10	5.2		0.1				1.0	0.01	134	150		284	47
1b	Clarification + Filtration Low turbidity Alum + Polymer	10		2.7	0.1				1.0	0.01	119	150		269	44
1c	Clarification + Filtration Low turbidity PACl + Polymer	10		2.7	0.1				1.0	0.01	119	150		269	44
2a	Clarification + Filtration High turbidity Iron + Polymer	150	10.4		0.5				1.0	0.05	263	2,250		2,513	10
2b	Clarification + Filtration High turbidity Alum + Polymer	150		5.4	0.5				1.0	0.05	233	2,250		2.483	9
2c	Clarification + Filtration High turbidity PACl + Polymer	150		5.4	0.5				1.0	0.05	233	2,250		2,483	9
3a	Lime softening Low turbidity No coagulant	10				80	20	100			1,668	150	2,082	3,900	43
3b	Lime softening Low turbidity Iron + Polymer	10	2.8		0.1	80	20	100			1,740	150	2,082	3,972	44
3c	Lime softening Low turbidity Iron + Polymer	150	5.6		0.5	80	20	100			1,810	2,250	2,082	6,142	29
4	Direct filtration Low turbidity Iron + Pre-filter Polymer	10	5.2		0.1				1.0		134	150		284	47

Example 2: Conventional Treatment, High Raw Water Turbidity

Example 2 is identical to example 1, except that turbidity is higher and coagulant dose is correspondingly higher. Examples 2a, 2b, and 2c include the following characteristics:

Influent turbidity = 150 ntu
Effluent turbidity = ~0 ntu
Hardness removed = ~0 mg/L as $CaCO_3$
Pre-rapid mix (RM) polymer dose = 0.5 mg/L as product
Pre-filter polymer dose = 0.05 mg/L as product
$KMnO_4$ dose = 1.0 mg/L as $KMnO_4$
Dose of post-filter chemicals (F, Phosphate, NaOCl, Caustic soda) = Irrelevant to sludge production in this example

The following coagulant doses are sufficient under these conditions:

$$C_{Fe} = \frac{10.4 \text{ mg as Fe}}{L}$$

$$C_{alum} = C_{PACl} = \frac{5.4 \text{ mg as Al}}{L}$$

At these coagulant doses, and at level of turbidity removal indicated, the quantity of sludge produced was about 2,500 lbs dry sludge per 10^6 gal of water produced and the contribution from treatment chemicals was about 10 percent, as summarized in Table E.1.

Example 3: Lime Softening, Low and High Turbidity

Example 3 is similar to Examples 1 and 2 except that 100 mg/L as $CaCO_3$ of lime is added and 80 mg/L $CaCO_3$ of raw water calcium and 20 mg/L as $CaCO_3$ of raw water magnesium are removed (i.e., a total of 180 mg/L as $CaCO_3$ of calcium hardness and 20 mg/L $CaCO_3$ of magnesium hardness are removed). Except for the lime addition and the hardness removal noted above:

- Example 3a is similar to example 1a, except for no coagulant addition
- Example 3b is similar to example 1a, including coagulant addition
- Example 3c is similar to example 2a, including coagulant addition

Results summarized in Table E.1 indicate that at low turbidity, about 4,000 lbs of dry sludge is produced per 10^6 gallons, slightly more than 50 percent coming from raw water Ca and Mg removal and slightly less than 50 percent from added treatment chemicals, including mostly lime. In the higher turbidity example, about 6,000 lbs dry sludge production per 10^6 gallons was calculated, about one-third from softening, greater than one-third from turbidity removal, and slightly less than one-third from addition of treatment chemicals (including lime).

Please note that a lime softening plant can have a single clarification basin prior to filtration (called single-stage lime softening), similar to system depicted in Figure E.1, or it can have two clarification basins (two-stage softening) or more (multi-stage softening) prior to filtration. The sludge production from each individual clarification basin in a multi-stage process will be different and the relative contribution of treatment chemicals, turbidity removal, and hardness removal will be different in each basin, depending upon characteristics of the treatment process. However, whether a single-stage or multi-stage process, the total sludge production from all clarification basins will be similar to the above examples if the coagulant doses and turbidity + hardness removals are the same. Furthermore, since softening plants co-mingle sludge prior to disposal, the relative contribution of turbidity removal, hardness removal, and chemical addition will be similar to the above examples if the chemical doses and turbidity plus hardness removal are the same.

Example 4: Direct Filtration, Low Raw Water Turbidity

If water with similar characteristics to example 1a is treated with a direct filtration process like that depicted in Figure E.2 using similar chemical doses (except pre-filter polymer) to produce similar finished water quality, the sludge production would be almost identical to the conventional system. Comparison of calculations for example 1a versus calculations for example 4 indicate ~280 lbs of dry sludge per 10^6 gallons of water produced, including slightly less than a 50 percent contribution from treatment chemicals in each example (see Table E.1).

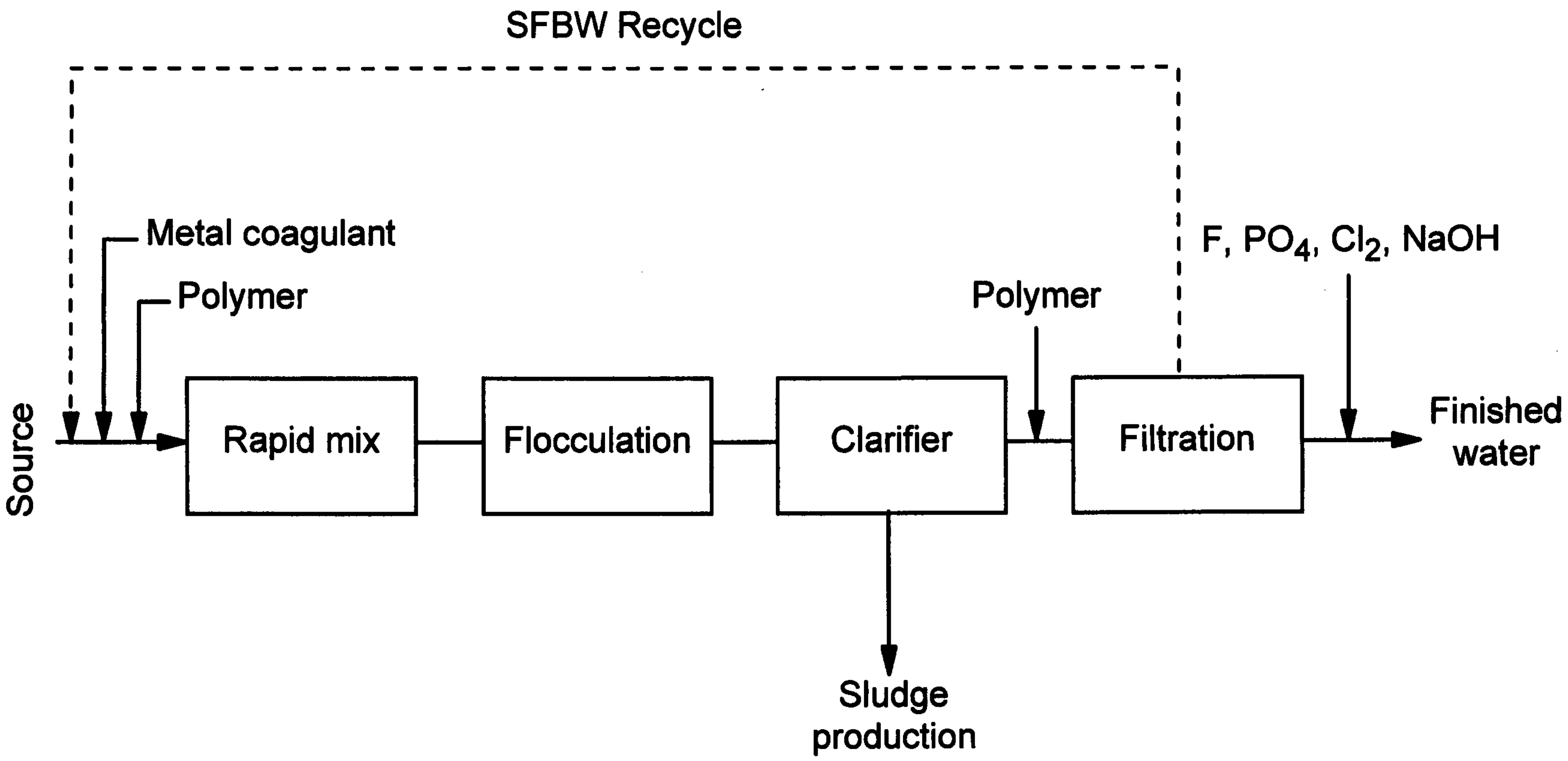


Figure E.1 Clarification plus filtration treatment of surface water

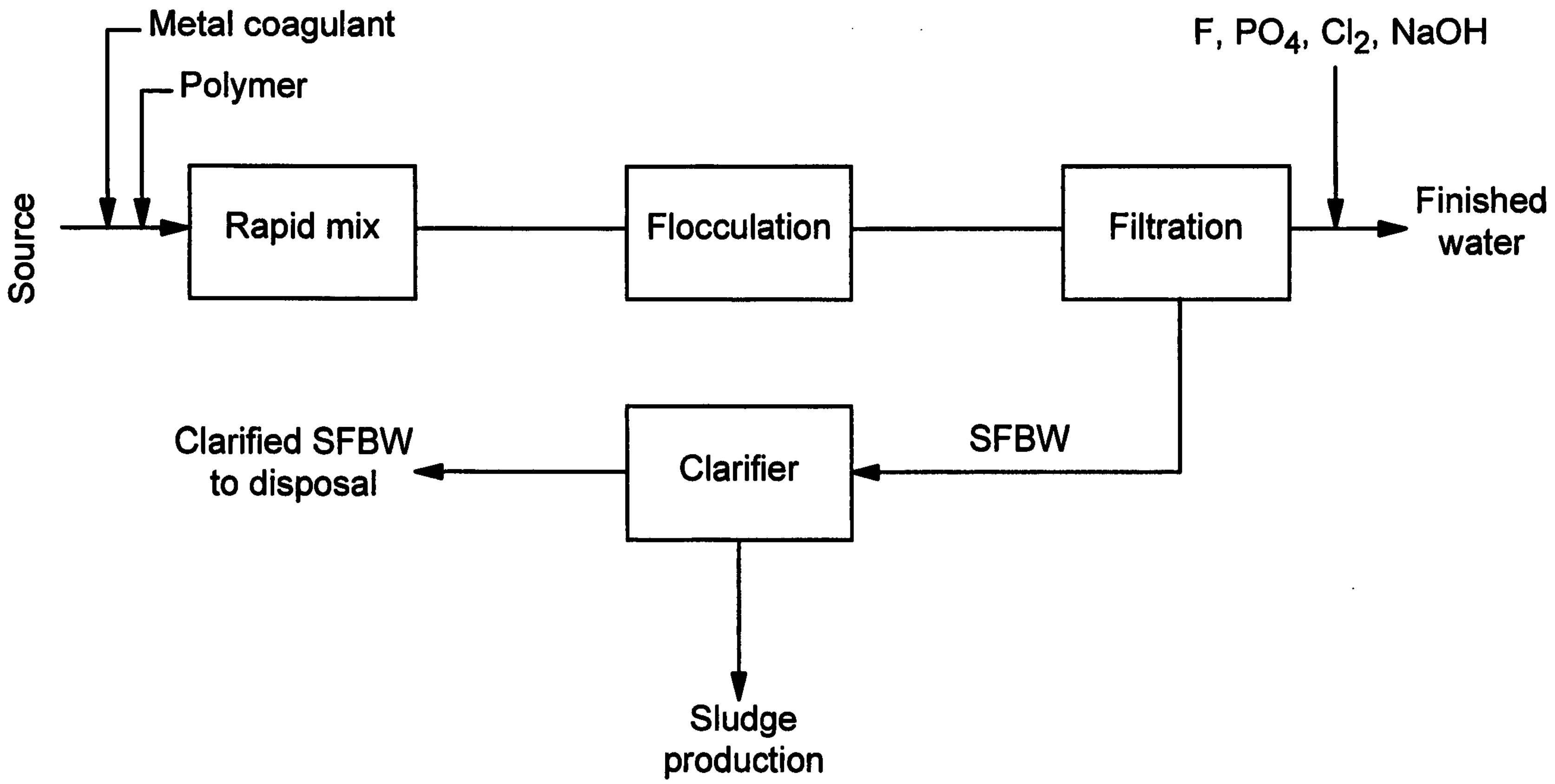


Figure E.2 Direct filtration treatment of surface water

APPENDIX F

RESULTS FROM PILOT-SCALE PARTITIONING STUDIES

Tables F.1, F.2, and F.3 list results for laboratory studies using alum, ferric chloride, and aluminum chlorohydrate (ACH). Aluminum chlorohydrate is also often referred to as a "high-basicity" PACl. Sample calculations used to generate the data listed in this appendix are summarized below, using aluminum data from the lowest ACH dose as an example:

- Aluminum in untreated tap water was 0.101 mg/L
- Aluminum in effluent from pilot-scale clarifier was 0.143 mg/L
- Flow rate during the study was 423 mL/min during a study duration of 76 hours
- Coagulant dose was 4.6 mg/L as Al
- Calculated mass of aluminum contributed by tap water during study was calculated at follows: 0.101 mg/L * 423 mL/min * 76 hours * 60 min/hr * L/1,000 mL * 1,000 μg/g = 195,000 μg of Al
- Calculated mass leaving the system in effluent from clarifier was 276,000 μg as Al, calculated in a similar fashion
- Mass of aluminum added by coagulant was: 4.6 mg/L * 423 mL/min * 76 hours * 60 min/hr * L/1,000 mL * 1,000 μg/g = 8,800,000 μg of Al
- The estimated mass of sludge produced (see Appendix E) was calculated a follows (turbidity ~0): 4.6 mg/L * 423 mL/min * 76 hours * 60 min/hr * L/1,000 mL * 4.89 mg sludge/mg Al = 43,000 mg sludge
- The sludge slurry had an aluminum concentration of 360 mg/L as Al and a total suspended solids composition of 2,080 mg/L, resulting in a dry weight sludge composition of about 173,000 mg Al per kg dry sludge
- Mass of aluminum in sludge phase was: 170,000 mg Al/kg sludge * 43,000 mg * 1,000 μg/g * kg/10^6 mg = 7,400,000 μg of Al
- Total input of aluminum (tap water + coagulant) = 195,000 + 8,800,000 μg = 9,000,000 μg
- Total output of aluminum (clarifier sludge + clarifier effluent water) = 275,000 + 7,400,000 μg = 7,700,000 μg

- Total output of aluminum (clarifier sludge + clarifier effluent water) = 275,000 + 7,400,000 μg = 7,700,000 μg
- Percent of aluminum contributed by ACH = 8.8/9 = 98 percent
- Percent of aluminum ending up in sludge = 7.4/7.7 = 96 percent

Table F.1

Partitioning of trace constituents in pilot-scale studies using aluminum chlorohydrate (ACH)

		Raw Water	Finished Water Samples			Sedimentation Basin Solids		
Description		influent	low	high	spike	low	high	spike
Dose (as Al)	mg/L	none	4.6	9.9	9.7	4.6	9.9	9.7
As-Pb-Cu spike?		no	no	no	yes	no	no	yes
Constituent	Unit							
Aluminum	mg/L	0.101	0.143	< 0.01	0.023	360	480	208
Antimony	mg/L	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Arsenic	mg/L	< 0.001	< 0.001	< 0.001	0.001	0.014	0.012	1.68
Barium	mg/L	0.019	0.021	0.02	0.022	0.105	0.072	0.058
Beryllium	mg/L	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Cadmium	mg/L	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Calcium	mg/L	25.4	30.3	28.3	27.3	152.5	138.2	38.9
Chromium	mg/L	0.004	< 0.001	0.003	< 0.001	< 0.001	< 0.001	< 0.001
Cobalt	mg/L	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Copper	mg/L	0.005	< 0.001	< 0.001	0.304	0.518	0.479	15.14
Iron	mg/L	0.014	0.033	< 0.01	< 0.01	5.75	4.4	2.82
Lead	mg/L	< 0.001	< 0.001	< 0.001	< 0.001	0.004	0.002	0.78
Magnesium	mg/L	1.509	1.479	1.313	1.364	4.17	3.923	2.304
Manganese	mg/L	0.011	0.015	0.011	0.02	1.38	1.399	0.382
Molybdenum	mg/L	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Nickel	mg/L	< 0.001	< 0.001	< 0.001	< 0.001	0.008	0.005	0.006
Potassium	mg/L	2.82	1.47	1.88	1.82	5.57	6.34	2.37
Selenium	mg/L	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Silver	mg/L	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Sodium	mg/L	7.83	7.54	7.68	8.85	19.1	20	9.76
Thallium	mg/L	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Titanium	mg/L	< 0.001	< 0.001	< 0.001	< 0.001	0.042	0.026	0.066
Total Phosphorus	mg/L	0.263	0.212		0.028	61	45.1	32.8
Vanadium	mg/L	< 0.001	< 0.001	< 0.001	< 0.001	0.049	0.041	0.042
Zinc	mg/L	0.072	0.031	0.011	0.055	21.4	17.8	8.259
Suspended Solids	mg/L					2,080	2,260	2,162
Flow rate	mL/min		423	423	429	423	423	429
Coagulant feed	mL/min		6.6	7.1	7.1	6.6	7.1	7.1
Duration	hours		76	35	32	76	35	32

Table F.2

Partitioning of trace constituents in pilot-scale studies using alum

		Raw Water	Finished Water Samples			Sedimentation Basin Solids		
Description		influent	low	high	spike	low	high	spike
Dose (as Al)	mg/L	none	2.5	5.0	4.7	2.5	5.0	4.7
As-Pb-Cu spike?		no	no	no	yes	no	no	yes
Constituent	Unit							
Aluminum	mg/L	0.101	0.212	0.16	0.447	167	198	907
Antimony	mg/L	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.002
Arsenic	mg/L	< 0.001	< 0.001	< 0.001	< 0.001	0.044	0.066	15.8
Barium	mg/L	0.019	0.019	0.02	0.018	0.125	0.039	0.065
Beryllium	mg/L	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Cadmium	mg/L	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Calcium	mg/L	25.4	26.1	25	27.6	35.5	40.2	73.3
Chromium	mg/L	0.004	0.003	0.003	0.001	< 0.001	< 0.001	0.016
Cobalt	mg/L	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Copper	mg/L	0.005	0.002	0.005	0.943	1.687	0.842	31.49
Iron	mg/L	0.014	0.011	0.012	0.011	4.38	4.56	25.8
Lead	mg/L	< 0.001	< 0.001	< 0.001	0.006	< 0.001	< 0.001	1.645
Magnesium	mg/L	1.509	1.5	1.47	1.52	1.734	1.72	4.44
Manganese	mg/L	0.011	0.013	0.017	0.011	1.296	0.693	4.684
Molybdenum	mg/L	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.005
Nickel	mg/L	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.006
Potassium	mg/L	2.82	1.77	2.11	2.33	2.63	2.41	7.49
Selenium	mg/L	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.004
Silver	mg/L	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Sodium	mg/L	7.83	7.52	8.6	7.68	8.12	8.54	20
Thallium	mg/L	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Titanium	mg/L	< 0.001	< 0.001	< 0.001	< 0.001	0.083	0.147	0.268
Total Phosphorus	mg/L	0.263	0.205		0.39	92.8	53.2	314
Vanadium	mg/L	< 0.001	< 0.001	< 0.001	< 0.001	0.016	0.028	0.097
Zinc	mg/L	0.072	0.074	0.137	0.095	6.461	1.957	8.67
Suspended Solids	mg/L					2,160	1,940	6,100
Flow rate	mL/min		429	432	425	429	432	425
Coagulant feed	mL/min		7.7	7.9	7.3	7.7	7.9	7.3
Duration	hours		69	73	48	69	73	48

Table F.3

Partitioning of trace constituents in pilot-scale studies using ferric chloride

		Raw Water	Finished Water Samples			Sedimentation Basin Solids		
Description		influent	low	high	spike	low	high	spike
Dose (as Fe)	mg/L	none	4.5	9.1	9.1	4.5	9.1	9.1
As-Pb-Cu spike?		no	no	no	yes	no	no	yes
Constituent	**Unit**							
Aluminum	mg/L	0.101	7.16	0.176	0.384	87.3	40.1	5.57
Antimony	mg/L	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Arsenic	mg/L	< 0.001	< 0.001	0.001	< 0.001	0.062	0.042	5.66
Barium	mg/L	0.019	0.021	0.022	0.024	0.196	0.194	0.03
Beryllium	mg/L	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Cadmium	mg/L	< 0.001	< 0.001	< 0.001	< 0.001	0.01	< 0.001	0.005
Calcium	mg/L	25.4	29.3	28.7	26.7	44.8	39.4	27.8
Chromium	mg/L	0.004	< 0.001	0.004	< 0.001	1.444	1.38	1.357
Cobalt	mg/L	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Copper	mg/L	0.005	< 0.001	0.006	1.43	2.802	1.595	4.892
Iron	mg/L	0.014	0.018	0.052	0.034	856	735	703
Lead	mg/L	< 0.001	< 0.001	< 0.001	0.002	1.031	0.911	3.138
Magnesium	mg/L	1.509	1.623	1.448	1.572	1.465	1.445	1.452
Manganese	mg/L	0.011	0.063	0.096	0.125	0.274	0.253	0.569
Molybdenum	mg/L	< 0.001	< 0.001	< 0.001	< 0.001	0.155	0.148	0.186
Nickel	mg/L	< 0.001	< 0.001	< 0.001	0.001	0.011	0.01	< 0.001
Potassium	mg/L	2.82	1.82	1.41	2.07	2.09	2.71	2.46
Selenium	mg/L	< 0.001	< 0.001	< 0.001	< 0.001	0.028	0.03	0.036
Silver	mg/L	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Sodium	mg/L	7.83	8.03	7.46	7.91	7.26	7.81	8.09
Thallium	mg/L	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Titanium	mg/L	< 0.001	< 0.001	0.002	< 0.001	20.1	17.6	17.3
Total Phosphorus	mg/L	0.263	0.177	0.229	0.165	29.8	49.4	41.2
Vanadium	mg/L	< 0.001	< 0.001	< 0.001	< 0.001	4.41	3.91	3.82
Zinc	mg/L	0.072	0.157	0.115	0.219	3.331	2.817	0.654
Suspended Solids	mg/L					7,700	6,800	6,500
Flow rate	mL/min		449	441	431	449	441	431
Coagulant feed	mL/min		6.9	7.0	6.9	6.9	7.0	6.9
Duration	hours		50	30	34	50	30	34

APPENDIX G
FULL-SCALE PARTITIONING STUDY RESULTS

Table G.1 includes data from the full-scale study at Denver Water (DW) and Table G.2 includes data from the study at the Philadelphia Water Department (PWD). Calculated values in these tables are reported in units of kg/day. The following examples describe how these value were calculated.

- Mass flow rate in water phase samples, including SFBW, was calculated by multiplying flow rate by concentration and apply appropriate conversion factors.

  Example:
  Flow rate and barium concentration at rapid mix influent at Denver were 262 mgd and 0.04 mg/L as Ba, respectively. The resulting mass flow rate of barium at this point in the process was 40 kg/day, calculated as follows:

  $262 \text{ MG/day} * 0.04 \text{ mg/L} * 3.785 \times 10^6 \text{ L/MG} * \text{kg}/10^6 \text{ mg}$

- Mass flow rate added by treatment chemicals was calculated by multiplying flow rate by chemical dose and composition of constituent of interest in the treatment chemical.

  Example:
  Flow rate at point where alum was added at Denver was 262 mgd. Alum does was 15 mg/L as alum or 1.35 mg/L as Al. Barium composition in alum was 0.14 mg Ba per kg Al. Resulting contribution of barium from alum addition was 0.0002 kg/day, calculated as follows:

  $262 \text{ MG/day} * 1.35 \text{ mg/L} * 0.14 \text{ mg Ba/kg Al} * 3.785 \times 10^6 \text{ L/MG} * (\text{kg}/10^6 \text{ mg})^2$

- Mass flow rate leaving the system in clarifier residuals was calculated by multiplying residuals production rate by composition of the residuals sample.

Example:
Sedimentation basin at Denver produced 7,814 lb/day of dry solids with a composition of 240 mg Ba/kg dry solids. Resulting mass flow rate of barium in clarifier residuals was about 1 kg/day, calculated as follows:

$7{,}814 \text{ lb lb/day} * 240 \text{ mg Ba/kg} * 0.454 \text{ kg/lb} * \text{kg}/10^6 \text{ mg}$

Table G.1
Full-scale partitioning study results at DW

			Treatment Chemicals‡				Residuals		
Sample Description			Alum	Cationic Polymer	Nonionic Polymer	NaOH	Sludge Blowdown	SFBW	SFBW Clarifier Sludge†
Chemical Dose			15 mg/L as alum	1.8 mg/L as product	0.055 mg/L as product	3.9 mg/L as NaOH			
Flow Rate (mgd)			262	262	262	256		6	
Solids Production (lb/day)							7,814		
Constituent	**Symbol**	**Unit**							
Calcium	Ca	kg/day	1.1	0.0009	< 0.20	0.004	35	781	
Magnesium	Mg	kg/day	0.16	0.0005	< 0.01	0.002	12	270	5
Potassium	K	kg/day	0.10	0.05	< 1.55	5.03	13	43	
Sodium	Na	kg/day	6	48	23	2,173	9	654	11
Aluminum	Al	kg/day	1,339	< 0.0009	< 0.20	0.023	642	840	772
Iron	Fe	kg/day	0.28	0.002	< 0.08	0.009	50	49	45
Manganese	Mn	kg/day	0.012	0.00004	< 0.01	< 0.0002	22	43	39
Barium	Ba	kg/day	0.0002	< 0.0002	< 0.005	< 0.0001	1	2	1
Zinc	Zn	kg/day	3.6	0.0004	< 0.04	< 0.0009	0.8	1.6	1.4
Antimony	Sb	kg/day	< 0.012	< 0.002	< 0.39	< 0.009	< 0.16	0.07	<
Arsenic	As	kg/day	< 0.012	< 0.002	< 0.39	< 0.009	< 0.16	0.27	0.25
Cadmium	Cd	kg/day	< 0.001	< 0.0002	< 0.04	< 0.0009	< 0.01	< 0.01	
Chromium	Cr	kg/day	0.006	< 0.0004	< 0.08	< 0.002	0.05	< 0.02	
Copper	Cu	kg/day	0.012	< 0.0002	< 0.04	< 0.001	< 0.02	0.2	< 0.1
Lead	Pb	kg/day	< 0.06	< 0.009	< 0.39	< 0.009	0.43	0.16	0.11
Mercury	Hg	kg/day	0.015	< 0.002	< 0.39	< 0.009	< 0.17	0.002	<
Molybdenum	Mo	kg/day	< 0.002	< 0.0004	< 0.08	< 0.002	< 0.05	0.16	0.05
Nickel	Ni	kg/day	0.006	< 0.0004	< 0.08	< 0.002	0.12	0.07	0.02
Selenium	Se	kg/day	< 0.030	0.003	< 0.39	< 0.009	< 3.55	0.05	<
Silver	Ag	kg/day	< 0.012	< 0.001	< 0.30	< 0.007	< 0.16	< 0.005	

(continued)

Table G.1
(continued)

Sample Description			Raw Water	WW Return	Rapid Mix Influent	Rapid Mix Effluent	Settled Water	Filtered Water	Post Clearwell
			Water Samples from Treatment Process						
Chemical Dose									
Flow Rate (mgd)			256	6	262	262	262	256	256
Solids Production (lb/day)									
Constituent	**Symbol**	**Unit**							
Calcium	Ca	kg/day	33,817	783	34,510	34,609	34,510	33,623	33,623
Magnesium	Mg	kg/day	11,628	266	11,801	11,900	11,801	11,531	11,434
Potassium	K	kg/day	1,841	43	1,884	1,884	1,884	1,841	1,841
Sodium	Na	kg/day	27,034	643	27,668	27,568	27,568	26,937	28,487
Aluminum	Al	kg/day	29	68	218	992	893	58	68
Iron	Fe	kg/day	48	5	69	79	50	19	19
Manganese	Mn	kg/day	24	4	43	39	34	< 5	< 5
Barium	Ba	kg/day	39	1	40	40	50	39	39
Zinc	Zn	kg/day	< 3.9	0.25	< 4.0	7.9	11.9	< 3.9	15.5
Antimony	Sb	kg/day	< 2.9	< 0.07	< 3.0	< 3.0	< 3.0	< 2.9	< 2.9
Arsenic	As	kg/day	< 1	0.02	< 1	< 1	< 1	< 1	< 1
Cadmium	Cd	kg/day	< 0.5	< 0.0	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
Chromium	Cr	kg/day	< 1.0	< 0.02	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0
Copper	Cu	kg/day	23	< 0.1	< 5	< 5	< 5	< 5	6
Lead	Pb	kg/day	< 1.9	< 0.05	< 2.0	< 2.0	< 2.0	< 1.9	< 1.9
Mercury	Hg	kg/day	< 0.1	< 0.002	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Molybdenum	Mo	kg/day	3.9	0.11	4.0	4.0	5.0	3.9	3.9
Nickel	Ni	kg/day	< 1.9	< 0.05	< 2.0	< 2.0	< 2.0	< 1.9	< 1.9
Selenium	Se	kg/day	< 1.9	< 0.05	< 2.0	< 2.0	< 2.0	< 1.9	< 1.9
Silver	Ag	kg/day	< 0.2	< 0.005	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2

Table G.2
Full-scale partitioning study results at PWD

Sample Description			Treatment Chemicals						Residuals	
			KMnO$_4$	Ferric Chloride	Zn PO$_4$	lime	H$_2$SiF$_6$	NaOCl	Clarifier Sludge	SFBW Composite
Chemical Dose			1 mg/L as KMnO$_4$	11.4 mg/L as Fe	0.46 mg/L as P	38.4 mg/L as Ca	1.1	6		
Flow Rate (mgd)			157	175	157	175	157	63		2.33
Solids Production (lb/day)									57,429	
Constituent	**Symbol**	**Unit**								
Calcium	Ca	kg/day	0.02	4	0.03	13,749	0.24	0.18	1,330	333
Magnesium	Mg	kg/day	< 0.0002	8	0.02	236	0.08	0.001	216	69
Potassium	K	kg/day	148	1	0.09	20	0.04	0.18	214	22
Sodium	Na	kg/day	0.2	21	0.13	1	0.05	463	26	158
Aluminum	Al	kg/day	0.3	76	0.01	72	0.01	< 0.004	287	10
Iron	Fe	kg/day	0.2	7,551	0.003	34	0.04	< 0.001	8,109	197
Manganese	Mn	kg/day	207	61	0.0004	1	0.0004	< 0.0001	88	10
Barium	Ba	kg/day	0.007	0.4	0.0001	0.55	< 0.001	< 0.0001	8	0.4
Zinc	Zn	kg/day	0.001	6.2	14.5	0.3	0.003	0.009	15	8.0
Antimony	Sb	kg/day	< 0.006	0.2	< 0.0004			< 0.007	< 1.2	< 0.009
Arsenic	As	kg/day	< 0.006	< 0.1	< 0.0004	< 0.06	0.02	< 0.007	< 1.2	0.018
Cadmium	Cd	kg/day	< 0.001	0.0	0.0001	< 0.06	0.001	< 0.001	0.11	0.009
Chromium	Cr	kg/day	0.027	2.4	0.003	0.067	0.001	< 0.001	4	< 0.009
Cobalt	Co	kg/day	< 0.001	0.5	< 0.0001	< 0.06	< 0.001	< 0.001	0.9	0.026
Copper	Cu	kg/day	< 0.001	0.1	0.0001	< 0.06	< 0.001	< 0.001	1.1	0.088
Lead	Pb	kg/day	< 0.03	< 0.3	< 0.002	< 0.06	< 0.001	< 0.01	< 1.1	0.088
Mercury	Hg	kg/day	0.05	0.1	< 0.0004			< 0.007	< 1.2	
Molybdenum	Mo	kg/day	0.015	0.4	0.0006			< 0.001	1.1	0.026
Nickel	Ni	kg/day	0.02	0.3	0.0004	0.11	< 0.001	< 0.001	1.0	0.035
Selenium	Se	kg/day	0.045	< 0.1	< 0.0004	< 0.06	< 0.001	< 0.007	< 1.1	0.009
Silver	Ag	kg/day	0.1	< 0.1	< 0.0003	< 0.06	< 0.001	< 0.006	< 1.2	< 0.009
Titanium	Ti	kg/day	0.003	258	0.0010	3.8	0.06	< 0.001	313	5.477
Vanadium	V	kg/day	< 0.001	37	< 0.00007	0.164	0.014	< 0.001	42	0.988

(continued)

Table G.2
(continued)

Sample Description			Raw Water	Pre-Rapid Mix	Post-Rapid Mix	Pre-Filter	Combined Filter Effluent	Reservoir
			Water Samples from Treatment Process					
Chemical Dose								
Flow Rate (mgd)			175	175	175	175	157	157
Solids Production (lb/day)								
Constituent	Symbol	Unit						
Calcium	Ca	kg/day	13,049	13,645	26,031	25,634	21,512	21,690
Magnesium	Mg	kg/day	4,736	4,717	4,928	4,962	4,400	4,504
Potassium	K	kg/day	1,835	1,788	1,795	1,848	1,705	1,533
Sodium	Na	kg/day	16,824	11,790	11,989	12,121	10,696	10,280
Aluminum	Al	kg/day	370	130	340	85	46	45
Iron	Fe	kg/day	689	318	7,419	412	12	14
Manganese	Mn	kg/day	46	22	79	11 <	6 <	6
Barium	Ba		24	20	20	11	11	11
Zinc	Zn	kg/day	39	14	20	9	7	89
Antimony	Sb	kg/day <	0.7 <	0.7 <	0.7 <	0.7 <	0.6 <	0.6
Arsenic	As	kg/day	1 <	1 <	1 <	1 <	1 <	1
Cadmium	Cd	kg/day <	1 <	1 <	1 <	1 <	1 <	1
Chromium	Cr	<	1 <	1 <	1 <	1 <	1	3
Cobalt	Co	kg/day <	1 <	1 <	1 <	1 <	1 <	1
Copper	Cu	kg/day	4	3	24 <	1	2	2
Lead	Pb	kg/day	3	1	4 <	1 <	1 <	1
Mercury	Hg	kg/day						
Molybdenum	Mo		1	1	1	1 <	1 <	1
Nickel	Ni	kg/day	3	1	1	1	1	1
Selenium	Se	kg/day <	1 <	1 <	1 <	1 <	1 <	1
Silver	Ag	kg/day <	1 <	1 <	1 <	1 <	1 <	1
Titanium	Ti	kg/day	11	5	219	13 <	1 <	1
Vanadium	V	kg/day	1	1	36	2 <	1 <	1

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ABBREVIATIONS

40 CFR 503	Title 40 (Protection of Environment), Code of Federal Regulations, Part 503 (Standards for the use or disposal of sewage sludge)
AA	atomic adsorption spectroscopy
ACH	aluminum chlorohydrate, high basicity PACl
$Al(OH)_3$	aluminum hydroxide
Al_2O_3	aluminum oxide
ANSI	American National Standards Institute
AWWA	American Water Works Association
AwwaRF	Awwa Research Foundation
AWWSC	American Water Works Service Company (Voorhees, NJ)
Br_2	bromine gas
BrCl	bromine chloride (disinfectant)
BrO_3^-	bromate
C of A	certificate of analysis
$Ca_5(PO_4)_3F$	Fluorapatite, phosphate rock
CAA	atomic adsorption spectroscopy preceded by chelation extraction
$CaCl_2$	calcium chloride
$CaCO_3$	calcium carbonate, limestone mineral
CaF_2	calcium fluoride, fluorospar ore
$CaMg(OH)_2$	dolomite mineral
CaO	quicklime
$Ca(OCl)_2$	calcium hypochlorite
$Ca(OH)_2$	hydrated or slaked lime
CCl_4	carbon tetrachloride
C_2Cl_6	hexachloroethane

C_6Cl_6	hexachlorobenzene
$CHCl_3$	chloroform
CH_2Cl_2	methylene chloride, dichloromethane
CIC	ion chromatography preceded by chelation
Cl^-	chloride ion
Cl_2	chlorine gas/liquid
ClO_2^-	chlorite
ClO_3^-	chlorate
cm	centimeter
CO_2	carbon dioxide
CWW	Cincinnati Water Works (Cincinnati, OH)
DBP	disinfection by-product
DBPR	disinfectants/disinfection by-products rule
DW	Denver Water (Denver, CO)
Dose	coagulant dose
e^-	electron
EE&T	Environmental Engineering & Technology
EFMA	European Fertilizer Manufacturers Association
ES	Executive Summary
$FeCl_2$	ferrous chloride
$FeCl_3$	ferric chloride
$FeSO_4$	ferrous sulfate
$Fe_2(SO_4)_3$	ferric sulfate
g	gram
GCC	General Chemical Corporation (Syracuse, NY)

H_2	hydrogen gas
H_2O	water
H_2SiF_6	hydrofluorosilicic acid (see Chapter 3 for other synonyms)
HAA	haloacetic acid
HCl	hydrochloric acid
HDPE	high density polyethylene
HF	hydrofluoric acid
HGAF	hydride generation atomic fluorescence
H_3PO_4	phosphoric acid
H_2SO_4	sulfuric acid
IC	ion chromatography
ICP-OES	inductively coupled argon plasma - optical emission spectrascopy
kg	kilogram
$KMnO_4$	potassium permanganate
K_2MnO_4	potassium (VI) manganate
K_3MnO_4	potassium (V) manganate
KOH	potassium hydroxide, caustic potash
L	allowable metal level per million gallons (MG) of finished water
L	liter
lb	pound
limit	value of residuals disposal limit or residuals quality goal
M	dry sludge production per million gallons (MG) of finished water produced
MCL	maximum contaminant level
MG	million gallons
mg	milligram
$MgCO_3$	magnesium carbonate, magnesite

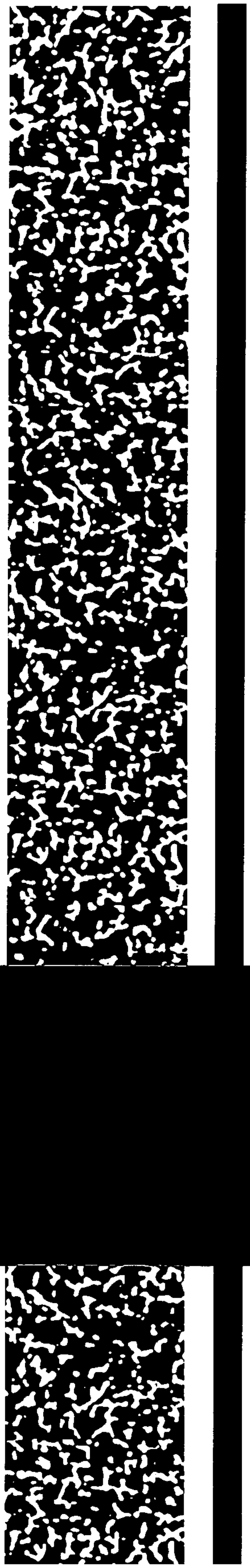
mgd	million gallons per day
μg	microgram
mL	milliliter
mM	millimolar, millimoles per liter
mmol	millimole
MnO_2	manganese dioxide, pyrolusite mineral, manganese (IV)

N_2	nitrogen gas
Na^+	sodium ion
$NaAlO_2$	sodium aluminate
NaCl	sodium chloride salt
$NaClO_2$	sodium chlorite
Na_2CO_3	soda ash
NaF	sodium fluoride
$NaHCO_3$	sodium bicarbonate
Na-Hg	sodium-mercury amalgam
NaOCl	sodium hypochlorite
NaOH	sodium hydroxide, caustic soda
Na_3PO_4	trisodium phosphate, tribasic sodium phosphate
Na_2SiF_6	sodium fluorosilicate
NCl_3	nitrogen trichloride
NDMA	N-nitrosodimethylamine
NH_3	ammonia gas, anhydrous ammonia
NH_4Cl	ammonium chloride
NSF	National Sanitation Foundation
ntu	nephelometric turbidity units

O_2	oxygen gas
OCl^-	hypochlorite ion
OH^-	hydroxide ion

PAC	AwwaRF Project Advisory Committee
PACl	polyaluminum chloride, polymeric aluminum chloride
PACl-OH-S	polymeric aluminum hydroxychlorosulfate
PO_4	phosphate
P_2O_5	phosphorus oxide
PP	polypropylene
PWD	Philadelphia Water Department (Philadelphia, PA)
Q	flow rate
QA/QC	quality assurance / quality control
R	metal concentration in raw water
RDPU	Richmond Department of Public Utilities (Richmond, VA)
SCCRWA	South Central Connecticut Regional Water Authority (New Haven, CT)
SFBW	spent filter backwash water
SiF_4	silicon tetrafluoride, tetrafluorosilane
SiO_2	quartz mineral, silicone dioxide
SNWA	Southern Nevada Water Authority (Boulder City, NV)
SO_4	sulfate
SOP	Standard Operating Practice
SO_x	sulfur oxide
SPL	steel pickle liquor
THM	trihalomethane
TiO_2	titanium dioxide
TSS	total suspended solids
TTHM	total trihalomethanes

U.S. or US	United States of America
UCMR	unregulated contaminants monitoring rule
USEPA	United States Environmental Protection Agency
WPA	wet process acid (phosphoric)
WTP	water treatment plant
X	allowable metal concentration in coagulants so that land application limits or other residuals quality goal is not exceeded
Y	percent of total sludge production contributed by treatment chemical
$ZnSO_4$	zinc sulfate, vitriol



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ISBN 1-58321-247-7
9 781583 212479

1P-4C-90909-9/02-CM