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# TABLE OF CONTENTS

**TABLES**

vi

**FIGURES**

vii

**FOREWORD**

xi

**ACKNOWLEDGMENTS**

xiii

**EXECUTIVE SUMMARY**

xv

## I. INTRODUCTION

1

Research Objectives

1

## II. LITERATURE REVIEW

3

Aqueous Chemistry of Aluminum and Iron(III)

3

Polymeric Inorganic Coagulants

7

Polymeric Iron(III) Coagulants

7

Polymeric Aluminum Coagulants

7

## III. EXPERIMENTAL PROCEDURES

11

Preparation of PAC1

11

Characterization of PAC1

13

Preparation of PIC1

14

Characterization of PIC1

15

Coagulation Tests

15

PAC1 Experiments

16

PIC1 Experiments

17

Direct Filtration Tests

17

Filtration Apparatus

17

PAC1 Experiments

19

PIC1 Experiments

19

## IV. RESULTS

21

Characterization of the Coagulants

21

PAC1 Preparations

21

PIC1 Preparations

23

Coagulation Tests

27

PAC1 Preparations

27

Turbidity Removal

27

High Turbidity

27

Low Turbidity

32

Summary

37

Removal of Humic Substances

37

Summary

38

PIC1 Preparations

38

Turbidity Removal

38

High Turbidity

38

Low Turbidity

45

Summary

51
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Aluminum and Iron(III) Equilibria</td>
<td>4</td>
</tr>
<tr>
<td>2</td>
<td>Experimental Variables and Conditions Examined in PAC1 Preparation</td>
<td>13</td>
</tr>
<tr>
<td>3</td>
<td>Characterization of PACl by Filtration ($r_{OH} = 2.4$)</td>
<td>23</td>
</tr>
<tr>
<td>4</td>
<td>Comparison of Ferron and Ultrafiltration Tests</td>
<td>24</td>
</tr>
<tr>
<td>5</td>
<td>Comparison of Four Aluminum Preparations in Coagulation</td>
<td>72</td>
</tr>
<tr>
<td>6</td>
<td>Comparison of Four Iron(III) Preparations in Coagulation</td>
<td>76</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Solubility of Aluminum at Equilibrium With Gibbsite and Amorphous Aluminum Hydroxide</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>Solubility of Iron(III) at Equilibrium With Goethite and Amorphous Ferric Hydroxide</td>
<td>6</td>
</tr>
<tr>
<td>3</td>
<td>Typical Base Titration of Fe(NO₃)₃ Solution</td>
<td>8</td>
</tr>
<tr>
<td>4</td>
<td>Experimental Apparatus for the Preparation of PACl and PICl</td>
<td>12</td>
</tr>
<tr>
<td>5</td>
<td>Schematic Diagram of Pilot Filtration Apparatus</td>
<td>18</td>
</tr>
<tr>
<td>6</td>
<td>Effects of the Degree of Neutralization (r_{OH}) on the Polymeric Content of PACl Preparations</td>
<td>22</td>
</tr>
<tr>
<td>7</td>
<td>Effects of the Degree of Neutralization (r_{OH}) on the Speciation of PICl Preparations</td>
<td>25</td>
</tr>
<tr>
<td>8</td>
<td>Effects of the Degree of Neutralization (r_{OH}) on the Size Characteristics of PICl Preparations</td>
<td>26</td>
</tr>
<tr>
<td>9</td>
<td>Comparison of Four Aluminum Preparations in the Coagulation of a Turbid Water (pH = 7.0, temperature = 20 °C)</td>
<td>28</td>
</tr>
<tr>
<td>10</td>
<td>Comparison of Four Aluminum Preparations in the Coagulation of a Turbid Water (pH = 5.5, temperature = 20 °C)</td>
<td>29</td>
</tr>
<tr>
<td>11</td>
<td>Comparison of Four Aluminum Preparations in the Coagulation of a Turbid Water (pH = 7.0, temperature = 4 °C)</td>
<td>30</td>
</tr>
<tr>
<td>12</td>
<td>Comparison of Four Aluminum Preparations in the Coagulation of a Turbid Water (pH = 5.5, temperature = 4 °C)</td>
<td>31</td>
</tr>
<tr>
<td>13</td>
<td>Comparison of Four Aluminum Coagulants in the Coagulation of a Low-Turbidity Water (pH = 7.0, temperature = 20 °C)</td>
<td>33</td>
</tr>
<tr>
<td>14</td>
<td>Comparison of Four Aluminum Preparations in the Coagulation of a Low-Turbidity Water (pH = 5.5, temperature = 20 °C)</td>
<td>34</td>
</tr>
<tr>
<td>15</td>
<td>Comparison of Four Aluminum Preparations in the Coagulation of a Low-Turbidity Water (pH = 7.0, temperature = 4 °C)</td>
<td>35</td>
</tr>
<tr>
<td>16</td>
<td>Comparison of Four Aluminum Preparations in the Coagulation of a Low-Turbidity Water (pH = 5.5, temperature = 4 °C)</td>
<td>36</td>
</tr>
</tbody>
</table>
Comparison of Four Aluminum Preparations in the Coagulation of Humic Substances (pH = 7.0, temperature = 20 °C)  

Comparison of Four Aluminum Preparations in the Coagulation of Humic Substances (pH = 5.5, temperature = 20 °C)  

Comparison of Four Aluminum Preparations in the Coagulation of Humic Substances (pH = 7.0, temperature = 4 °C)  

Comparison of Four Aluminum Preparations in the Coagulation of Humic Substances (pH = 5.5, temperature = 4 °C)  

Comparison of Four Iron(III) Preparations in the Coagulation of a Turbid Water (pH = 7.0, temperature = 20 °C)  

Comparison of Four Iron(III) Preparations in the Coagulation of a Turbid Water (pH = 5.0, temperature = 20 °C)  

Comparison of Four Iron(III) Preparations in the Coagulation of a Turbid Water (pH = 7.0, temperature = 4 °C)  

Comparison of Four Iron(III) Preparations in the Coagulation of a Turbid Water (pH = 5.0, temperature = 4 °C)  

Comparison of Four Iron(III) Preparations in the Coagulation of a Low-Turbidity Water (pH = 7.0, temperature = 20 °C)  

Comparison of Four Iron(III) Preparations in the Coagulation of a Low-Turbidity Water (pH = 5.0, temperature = 20 °C)  

Comparison of Four Iron(III) Preparations in the Coagulation of a Low-Turbidity Water (pH = 7.0, temperature = 4 °C)  

Comparison of Four Iron(III) Preparations in the Coagulation of a Low-Turbidity Water (pH = 5.0, temperature = 4 °C)  

Comparison of Three Iron(III) Preparations in the Coagulation of a Moderately Humic Water (pH = 7.0, temperature = 20 °C)  

Comparison of Three Iron(III) Preparations in the Coagulation of a Moderately Humic Water (pH = 5.0, temperature = 20 °C)  

Comparison of Three Iron(III) Preparations in the Coagulation of a Moderately Humic Water (pH = 7.0, temperature = 4 °C)  

Comparison of Three Iron(III) Preparations in the Coagulation of a Moderately Humic Water (pH = 5.0, temperature = 4 °C)  

Comparison of Three Iron(III) Preparations in the Coagulation of a Highly Humic Water (pH = 7.0, temperature = 20 °C)
34 Comparison of Three Iron(III) Preparations in the Coagulation of a Highly Humic Water (pH = 5.0, temperature = 20 °C)  
59
35 Comparison of Three Iron(III) Preparations in the Coagulation of a Highly Humic Water (pH = 7.0, temperature = 4 °C)  
60
36 Comparison of Three Iron(III) Preparations in the Coagulation of a Highly Humic Water (pH = 5.0, temperature = 4 °C)  
61
37 Comparison of Two Aluminum Preparations in the Direct Filtration of a Low-Turbidity Water (pH ≈ 5.4, temperature = 21.5 °C)  
63
38 Comparison of Two Aluminum Preparations in the Direct Filtration of a Low-Turbidity Water (pH = 7.0, temperature = 21.5 °C)  
64
39 Comparison of Two Aluminum Preparations in the Direct Filtration of a Low-Turbidity, Moderately Humic Water (pH ≈ 5.4, temperature = 21.5 °C)  
65
40 Comparison of Two Iron(III) Preparations in the Direct Filtration of a Low-Turbidity Water (pH ≈ 5.0, temperature = 21.5 °C)  
66
41 Comparison of Two Iron(III) Preparations in the Direct Filtration of Low-Turbidity, Moderately Humic Water (pH ≈ 5.0, temperature = 21.5 °C)  
67
FOREWORD

This report is part of the ongoing research program of the AWWA Research Foundation. The research described in this report was funded by the foundation on behalf of its members and subscribers in particular and the water supply industry in general. Selected for funding by AWWARF’s Board of Trustees, the project was identified as a practical, priority need of the industry. It is hoped that this publication will receive wide and serious attention and that its findings, conclusions, and recommendations will be applied in communities throughout the United States and Canada.

The research foundation was created by the water supply industry as its center for cooperative research and development. The Foundation itself does not conduct research; it functions as a planning and management agency, awarding contracts to other institutions such as water utilities, universities, engineering firms, and other organizations. The scientific and technical expertise of the staff is further enhanced by industry volunteers who serve on Project Advisory Committees and on other standing committees and councils. An extensive planning process involves many hundreds of water professionals in the important task of keeping the Foundation’s program responsive to the practical, operational needs of local utilities and to the general research and development needs of a progressive industry.

All aspects of water supply are served by AWWARF’s research agenda: resources, treatment and operations, distribution and storage, water quality and analysis, economics and management. The ultimate purpose of this effort is to provide the highest possible quality of water, economically and reliably. The foundation’s trustees are pleased to offer this publication as a contribution toward that end.

Laboratory scale examination of the characteristics, production and use of polymeric aluminum chloride and polymeric iron chloride in water treatment was the objective of this project. The Surface Water Treatment Rule will require installation of filtration and/or the optimization of existing filtration processes. Better understanding of the production and application of these relatively new coagulants is an important step toward improved water quality.

Richard P. McHugh
Chairman, Board of Trustees
AWWA Research Foundation

James F. Manwaring, P.E.
Executive Director
AWWA Research Foundation

xi
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The authors would like to thank the Project Advisory Committee: Brian Dempsey of Pennsylvania State University, Ray Letterman of Syracuse University, and Alan Stevens of the Environmental Protection Agency.
EXECUTIVE SUMMARY

This report summarizes research conducted at The Johns Hopkins University on the preparation and use of partially neutralized solutions of aluminum and iron(III) chloride in water treatment. These solutions are termed polymeric aluminum chloride (PACI) and polymeric iron chloride (PICl) in this presentation.

The objectives of this research project were (1) to determine appropriate conditions for the preparation of polymeric aluminum and iron(III) coagulants, (2) to identify certain important characteristics of these materials, and (3) to evaluate their potential applications in water treatment.

All experiments were conducted at laboratory scale. PACI and PICl preparations were produced in a batch system that was maintained at constant temperature and mixed vigorously. Concentrated solutions of aluminum or iron(III) chloride were neutralized to various degrees by slow injection of concentrated base. The resulting solutions were characterized chemically by their reactions with ferron and physically with respect to size by membrane and ultrafiltration.

The effectiveness of these partially neutralized aluminum and iron(III) preparations in the removal of turbidity and color by coagulation and sedimentation was evaluated in jar tests. PACI preparations were compared with alum and also with unneutralized aluminum chloride. PICl preparations were compared with unneutralized iron(III) chloride solutions. Submicron latex particles were used to provide turbidity and an aquatic fulvic acid was used to represent humic substances and color. Studies were made with suspensions having high and low turbidities. With iron(III) preparations, two concentrations of humic substances were studied. Experiments were made at neutral pH and also at slightly acidic pHs. All coagulation studies were made at two temperatures, 20 and 4 °C. Removals of contaminants were generally followed spectrophotometrically by absorbance measurements at an appropriate wavelength. In some cases turbidity measurements were made; a limited number of determinations of dissolved organic carbon (DOC) were also obtained.

Direct filtration tests were made using small-scale, continuous-flow laboratory filters containing glass beads as filter media. PACI was compared with alum and PICl was compared with unneutralized, concentrated iron(III) chloride. All experiments were made at room temperature (21.5 °C). Suspensions having low turbidity, with and without the presence of a moderate concentration of fulvic acid, were filtered. Most experiments were conducted at a slightly acidic pH; some were made at neutral pH. Removals were evaluated by absorbance measurements, turbidity determinations, or both.

This report contains an extensive selection of the experimental results obtained in this research but much additional data are available in the form of two doctoral dissertations (Gray 1988; Yao 1987) supported by this project. The discussion and conclusions in the report are derived from all of the data that were obtained and from a consideration of additional information published.

Several conclusions relating to the preparation and characterization of PACI and PICl, the coagulation studies, the direct filtration experiments, and also coagulant and coagulation chemistry are presented in this report. Several conclusions from the report follow.
• Partially neutralized solutions of aluminum chloride that contained a major proportion of stable small cationic polymeric aluminum species could be prepared. Attempts to prepare similar species by partial neutralization of iron(III) chloride were unsuccessful.

• These PACI preparations are particularly effective in the treatment of turbid waters, especially at cold temperatures. They are ineffective in the treatment of low turbidity waters by coagulation and sedimentation but can function well at low dosages in the direct filtration of such suspensions.

• These PACI preparations react with humic substances but are generally less effective than alum. Among the preparations tested, alum is the aluminum coagulant of choice for the treatment of humic waters and for the coagulation and sedimentation of low turbidity waters.

• Unneutralized or conventional iron(III) chloride is an effective coagulant and filter aid over a range of pHs, temperatures, contaminant types, and contaminant concentrations.
CHAPTER 1
INTRODUCTION

In conventional water treatment systems, the removal of particulate and dissolved materials is determined primarily by the effectiveness of coagulation. Coagulation is a process in which chemical reactions and physical transport processes are used to destabilize and aggregate suspended particles and to precipitate or adsorb natural organic substances so that these contaminants can be removed in subsequent sedimentation and filtration facilities.

Particles in natural waters vary widely in origin, concentration, and size. Some are constituents of land-based or atmospheric sources (e.g., clays, pathogenic organisms, asbestos fibers, terrestrial detritus) and some are produced by chemical and biological processes within a water source (e.g., algae, precipitates of CaCO₃, FeOOH, MnO₂, aquatic organic detritus). Particle concentration can vary from 1 mg/L or so to a few thousand milligrams per liter. Particle size may vary by several orders of magnitude, from a few tens of nanometers (e.g., viruses) to a few hundred microns (e.g., zooplankton). All can be removed by properly designed and operated coagulation, sedimentation, and filtration facilities.

Humic substances are the major organic constituent of unpolluted waters. They are derived from soil and are also produced within natural waters and bottom sediments by chemical and biological processes. Humic substances are anionic polyelectrolytes of low-to-moderate molecular weight; their negative charge is due primarily to carboxyl and phenolic groups; they have both aromatic and aliphatic components and can be surface active; they are refractive and can persist for centuries or longer. Humic substances are defined operationally by the methods used to extract them from water or soil. Typically, they are subdivided into the more-soluble fulvic acids (FA) and the less-soluble humic acids (HA), with fulvic acids predominating in most waters. Concentrations in surface waters can range from about 1 mg/L, expressed as dissolved organic carbon (DOC) to more than 50 mg DOC/L, with a median DOC concentration of about 4 mg/L.

The process of coagulation as practiced in water treatment can be considered as three separate and sequential steps: coagulant formation, coagulant reactions with suspended particles and humic substances, and interparticle collisions. Coagulant formation and coagulant reactions with contaminants in surface water sources occur in rapid mixing tanks; interparticle collisions occur predominantly in flocculation tanks and to a lesser but important extent in settling basins.

When alum [Al₂(SO₄)₃•14.3H₂O] or ferric chloride (FeCl₃) are used in coagulation, the actual coagulant species operative in the process are formed during and after these chemicals are mixed with the water to be treated; Al³⁺, SO₄²⁻, Fe³⁺, and Cl⁻ are not directly involved in the coagulation process. Active coagulants can also be formed prior to their addition to rapid mixing facilities. Examples include the use for several decades of activated silica, more recent applications of synthetic organic polymers, and recent introductions of preformed aluminum and iron(III) species (polymeric aluminum chloride [PACl] and polyiron chloride [PICl]). These latter materials are the focus of the research presented in this report.

RESEARCH OBJECTIVES

The objectives of this research project were (1) to determine appropriate conditions for
the preparation of polymeric aluminum and iron(III) coagulants, (2) to identify certain important characteristics of these materials, and (3) to evaluate their applications in potable water treatment. In addressing this latter objective, laboratory jar tests and pilot direct-filtration tests are used to evaluate the effectiveness of various PACI and PICl preparations for the treatment of synthetic waters containing turbidity or natural organic matter at selected temperatures, pH values, and contaminant concentrations, and to compare their performance as coagulants with alum and ferric chloride.
CHAPTER 2

LITERATURE REVIEW

AQUEOUS CHEMISTRY OF ALUMINUM AND IRON(III)

It is useful to begin with thermodynamics; a solubility diagram of aluminum in water is presented in Figure 1. Aluminum equilibria used in constructing this diagram are listed in Table 1. A crystalline aluminum oxide [gibbsite, Al(OH)_3(c), with solubility given by log K_{so} = -33.5] is considered as the solid phase. At alkaline pH (pH > 8), the principal soluble aluminum species present at equilibrium with gibbsite is the monomeric aluminate anion, Al(OH)_4. At lower pH values (pH < 6), the dominant soluble species at equilibrium are cationic monomers such as Al(OH)_{2+}. In this pH range, however, aluminum speciation in water is kinetically controlled and depends on many factors. The freshly precipitated solids formed by addition of an aluminum salt to water are normally amorphous [Al(OH)_3(am), log K_{so} = -31.5] and more soluble than indicated by gibbsite equilibria. A solubility diagram for aluminum considering the formation of Al(OH)_3(am) is shown in Figure 1, part B. Following Baes and Mesmer (1976), aluminum hydrolysis and solubility are evaluated here considering three polymeric species [Al_2(OH)_5^+, Al_3(OH)_4^+, and Al_{13}O_4(OH)_{24}^+] and five monomers [Al^{3+}, Al(OH)^{2+}, Al(OH)_2^+, Al(OH)_3^−, and Al(OH)]] in equilibrium with solid Al(OH)_3(am). Lines for the Al(OH)^{3+} and Al(OH)_3 species are dashed to indicate that their concentrations are questionable because of uncertain thermodynamic data. Aluminum is least soluble at a pH of about 6.2. A 10^{-4} M solution of Al (corresponding to a 30 mg/L dosage of alum), can precipitate Al(OH)_3(am) in the pH range from 5.8 to 8. Below pH 5.7, Al(OH)_3(am) can be quite soluble and cationic polymeric species such as Al_{13}O_4(OH)_{24}^+ can predominate in solution.

The differences in aluminum solubility and speciation between parts A and B of Figure 1 are substantial and important in water treatment practice. Aluminum chemistry at neutral and acidic pH values is generally governed by the kinetics of reactions with water (hydrolysis), with particles, and with natural organic matter. Equilibrium diagrams such as parts A and B of Figure 1 are useful but incomplete. "Polymeric" aluminum species that have been termed PACl and that can range from small cationic polyelectrolytes to colloidal amorphous precipitates can be formed, depending on the methods used in their preparation.

A solubility diagram for Fe(III) in water is presented in Figure 2, based on thermodynamic data listed in Table 1. Two solubility limits are depicted. The lower boundary is for an iron(III) solution at equilibrium with α-FeOOH (goethite, log K_{so} = -41.7). The upper boundary is constructed assuming equilibrium with freshly precipitated Fe(OH)_3(am) (log K_{so} = -38.7). At high pH values (pH > 10), the principal soluble iron(III) specie at equilibrium with either solid is the monomeric anion, Fe(OH)_4. At lower pH levels (pH < 6), the dominant soluble species are cationic monomers such as Fe(OH)_2^+. Iron(III) is least soluble at a pH of about 8. A 10^{-4} M solution of Fe(III) (corresponding to a dosage of ferric chloride, FeCl_3, of 16.2 mg/L) can precipitate Fe(OH)_3(am) above a pH of about 3. Comparing hydrolysis equilibria in Table 1 and solubilities as illustrated in Figures 1 and 2, iron(III) is a stronger acid and is less soluble than aluminum. In addition, there is no evidence to date for the formation of stable large iron(III) polymers analogous to the cationic aluminum polymer represented as Al_{13}O_4(OH)_{24}^+. As with aluminum, however, the chemistry of Fe(III) in water is governed by the kinetics of reactions with water and contaminants.
<table>
<thead>
<tr>
<th>Reaction</th>
<th>log K (25°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Al³⁺ + H₂O = AlOH²⁺ + H⁺</td>
<td>-4.97</td>
</tr>
<tr>
<td>2. AlOH²⁺ + H₂O = Al(OH)₂⁺ + H⁺</td>
<td>-4.3</td>
</tr>
<tr>
<td>3. Al(OH)₂⁺ + H₂O = Al(OH)₃⁻ + H⁺</td>
<td>-5.7</td>
</tr>
<tr>
<td>4. Al(OH)₃⁻ + H₂O = Al(OH)₄⁻ + H⁺</td>
<td>-8.0</td>
</tr>
<tr>
<td>5. 2Al³⁺ + 2H₂O = Al₂(OH)₄⁺ + 2H⁺</td>
<td>-7.7</td>
</tr>
<tr>
<td>6. 3Al³⁺ + 4H₂O = Al₃(OH)₄⁺ + 4H⁺</td>
<td>-13.94</td>
</tr>
<tr>
<td>7. 13Al³⁺ + 28H₂O = Al₁₃O₄(OH)₇⁺ + 32H⁺</td>
<td>-98.73</td>
</tr>
<tr>
<td>8. Al(OH)₃⁰(am) = Al³⁺ + 3OH⁻</td>
<td>-31.5 (estimated)</td>
</tr>
<tr>
<td>9. Al(OH)₃⁰(c) = Al³⁺ + 3OH⁻</td>
<td>-33.5</td>
</tr>
<tr>
<td>10. Fe³⁺ + H₂O = FeOH²⁺ + H⁺</td>
<td>-2.2</td>
</tr>
<tr>
<td>11. FeOH²⁺ + H₂O = Fe(OH)₂⁺ + H⁺</td>
<td>-3.5</td>
</tr>
<tr>
<td>12. Fe(OH)₂⁺ + H₂O = Fe(OH)₃⁻ + H⁺</td>
<td>-6</td>
</tr>
<tr>
<td>13. Fe(OH)₃⁻ + H₂O = Fe(OH)₄⁻ + H⁺</td>
<td>-10</td>
</tr>
<tr>
<td>14. 2Fe³⁺ + 2H₂O = Fe₂(OH)₄⁺ + 2H⁺</td>
<td>-2.9</td>
</tr>
<tr>
<td>15. 3Fe³⁺ + 4H₂O = Fe₃(OH)₅⁺ + 4H⁺</td>
<td>-6.3</td>
</tr>
<tr>
<td>16. Fe(OH)₃⁰(am) = Fe³⁺ + 3OH⁻</td>
<td>-38.7 (estimated)</td>
</tr>
<tr>
<td>17. α-FeOOH(c) + H₂O = Fe³⁺ + 3OH⁻</td>
<td>-41.7</td>
</tr>
</tbody>
</table>

* From Baes and Mesmer (1976)  
+ From Flynn (1984)
FIGURE 1. Solubility of Aluminum at Equilibrium with Gibbsite (A) and Amorphous Aluminum Hydroxide (B) (Thermodynamic data from Table 1)
FIGURE 2. Solubility of Iron(III) at Equilibrium with Goethite (α-FeOOH) and Amorphous Ferric Hydroxide (thermodynamic data from Table 1; arrow denotes base titration of $6.25 \times 10^{-2}$ M Fe(III) solution; regions I, II, III, and IV are discussed in the text)
POLYMERIC INORGANIC COAGULANTS

A recent development in water treatment has been the preparation and use of "polymeric" Fe(III) and Al species as coagulants (Bottéro et al. 1980; Leprince et al. 1984; Dempsey et al. 1985; Buffle et al. 1985; Parthasarathy and Buffle 1985; Tang and Stumm 1987a, 1987b). The following discussion, while focused on polymeric iron(III) preparations, also serves as a basis for considering "polymeric" aluminum preparations.

Polymeric Iron(III) Coagulants

In preparing polymeric ferric species, concentrated solutions of iron(III) salts are partially neutralized by the addition of base, a process indicated in part in Figure 2. A typical neutralization (titration) adapted from the work of van der Woude and de Bruyn (1983) is presented in Figure 3. Solution pH is plotted as a function of base added as denoted by \( r_{OH} \), the number of OH ligands added to the solution per atom of total iron(III) in the solution (\( r_{OH} = \frac{OH_{added}}{Fe_{T}} \)). The addition of base increases \( r_{OH} \) and usually, but not always, raises the pH. In the case illustrated in Figure 3, a solution containing \( 6.25 \times 10^{-2} \text{ M } Fe(NO_3)_3 \) (3.49 g/L of Fe(III)) is titrated or neutralized with sodium hydroxide. Because iron(III) is a rather strong acid, the initial pH is 0.7; this solution is just slightly oversaturated with respect to the precipitation of goethite and is considerably undersaturated with respect to the formation of Fe(OH)\(_3\) (am) (Figure 2). In fact, it is normal for iron(III) solutions prepared by the addition of any ferric salt to water to be oversaturated with respect to goethite in this way; the addition of strong acid is necessary to prepare solutions that are actually thermodynamically stable.

The titration may be divided into four regions, as indicated by van der Woude and de Bruyn (1983). In region I, with \( 0 \leq r_{OH} \leq 0.2 \), the principal Fe(III) species are monomers and small polymers such as Fe\(^{3+}\), FeOH\(^{2+}\), and Fe\(_2\)(OH)\(^4+\). Although the solution becomes increasingly oversaturated with respect to goethite as \( r_{OH} \) is increased, a precipitate is not observed. Polymers larger than the dimer [Fe\(_2\)(OH)\(^4+\)] are not detected. In region II, corresponding to \( 0.2 < r_{OH} < 0.8 \), polymers larger than the dimer are formed. Metastable solutions containing cationic polymeric Fe(III) species may be prepared. The lower boundary of region II (\( r_{OH} = 0.2 \)) corresponds well with the solubility limit of Fe(OH)\(_3\) (am) in Figure 3. Thermodynamically unstable polymeric Fe(III) species are formed when the system becomes unstable with respect to the amorphous solid phase. Polymerization and precipitation kinetics are affected by the concentration of the stock iron(III) solution ([Fe(III)\(_T\)]); the type, concentration, and method of base addition; ionic strength; temperature; and specific anion effects (van der Woude and de Bruyn 1983; Schneider 1984). In region III, for \( 0.8 \leq r_{OH} \leq 2.5 \), van der Woude and de Bruyn report rapid precipitation of Fe(OH)\(_3\) (am). At \( r_{OH} = 2.5 \), precipitation is nearly complete. Additional base (\( r_{OH} > 2.5 \), region IV) may only neutralize positive charge on the precipitate.

Leprince et al. (1984) report the existence of polymeric species of Fe(III) up to \( r_{OH} = 2.5 \) in partially neutralized FeCl\(_3\) solutions, indicating that the upper boundary of region II may not be fixed at \( r_{OH} = 0.8 \). It is possible that a wide variety of "polymeric" iron(III) preparations ranging from small cationic polymers to colloidal amorphous iron(III) precipitates can be obtained, depending on the conditions used in their preparation.

Polymeric Aluminum Coagulants

Partially neutralized solutions of aluminum salts have been used with some success in water treatment. Bottéro et al. (1980) reported that partially neutralized aluminum chloride
FIGURE 3. Typical Base Titration of Fe(NO₃)₃ Solution (Fe(III)ₜ = 6.25 x 10⁻² M; after van der Woude and de Bruyn 1983)
solutions were effective coagulants for clay suspensions. PACl is used extensively in Japan for the treatment of cold, soft, turbid waters. It is also used in potable water treatment in France and Germany, and it is coming into use in the United States. The preparation and use of these materials have many similarities with the iron(III) coagulants described previously. "Polymeric" aluminum species may range from small polymers to colloidal precipitates, depending on many factors in their preparation. Several polymeric aluminum preparations are commercially available with a range of $pOH$ values; some contain additives such as sulfate and cationic organic polyelectrolytes. Some French investigators (Bottéro et al. 1980; Leprince et al. 1984) advocate on-site preparation of these coagulants by partial neutralization or by heating, permitting specific tailoring of the inorganic "polymeric" coagulant to the water to be treated.
CHAPTER 3
EXPERIMENTAL PROCEDURES

PREPARATION OF PACI

PACI preparation is a controlled and conditional hydrolysis of an aluminum chloride solution. Several parameters have been reported to influence the rate and extent of aluminum hydrolysis: (1) the formation function, $r_{OH}$ (Hsu and Bates 1964), (2) the mode of mixing of base with the aluminum salt solution (Vermeulen and de Bruyn 1975), (3) the type and concentration of the added base (Smith 1971), (4) the concentration of the aluminum solution (Stol et al. 1976), (5) aging time (Morgan 1967; Parthasarathy and Buffle 1985), (6) the presence of other anions such as sulfate (de Hek and de Bruyn 1978), (7) ionic strength (Stol et al. 1976), and (8) temperature (Stol et al. 1976).

Experiments were conducted to determine a set of conditions under which a PACI solution containing the maximum proportion of polymeric species could be prepared in the laboratory. This was accomplished through a series of experiments involving injections of base into aluminum chloride solutions under various combinations of selected parameters. Attention was directed toward the effects of the formation function, base (NaOH) concentration, base injection rate, initial concentration of aluminum chloride, aging time, and aging temperature. Various combinations were selected on the basis of a statistical analysis (Yao 1987). A listing of the parameters studied and the levels at which they were investigated is presented in Table 2.

The design of the reaction vessel used in preparing the PACI solutions was adapted from the reactor employed by Vermeulen and de Bruyn (1975). A schematic diagram of the apparatus is presented in Figure 4. A 2-liter, double-walled Pyrex glass vessel was fitted with a plexiglass lid in which five inlets were drilled and to which two plexiglass baffles were glued. The lid and the vessel were sealed together with a rubber gasket and butterfly bolts. A Beckman combination electrode was inserted through one of the ports in the lid. Millivolt readings were obtained with a Fisher pH-mV meter (model 805MP) operated in the millivolt mode; these data were recorded continuously with an automatic digital printer (Alphacom 42). A thermometer was inserted through a second inlet. Another inlet contained a glass capillary through which high-purity N$_2$ gas (99.998 percent) was bubbled vigorously through the solution to prevent CO$_2$ from accumulating in the system and affecting the pH. The nitrogen gas stream was passed through a distilled water solution prior to injection into the reactor in order to saturate it with water vapor and prevent evaporation in the reactor. A glass capillary was inserted through a fourth port and used to inject base (NaOH) into the solution. The aperture at the tip of the capillary was less than or equal to 0.15 mm in diameter to minimize diffusion of aluminum solution into the capillary during the titration. Base was stored in a glass bottle that was connected to a 100-mL Pyrex buret, from which it was pumped to the reactor with a Masterflex peristaltic pump at the desired flow rate. A teflon shaft with a propeller was inserted through the fifth opening in the lid; this shaft was driven by a variable-speed motor (Eastern Mixers, model 5VB-RS) operated at its maximum speed of 2,260 rpm to provide vigorous mixing. The solution in the reactor was maintained at constant temperature by circulating water from a thermostatically controlled water bath (Wilkins-Anderson, Inc.) through the jacket of the double-walled vessel.
FIGURE 4. Experimental Apparatus for the Preparation of PACI and PICl
TABLE 2
Experimental Variables and Conditions Examined in PAC1 Preparation

<table>
<thead>
<tr>
<th>Variable</th>
<th>Level of Investigation</th>
</tr>
</thead>
<tbody>
<tr>
<td>[NaOH] (equivalents/L, N)</td>
<td>0.3 0.5 0.7 1.0</td>
</tr>
<tr>
<td>[Al_T] (moles/L, M)</td>
<td>0.05 0.1 0.2 0.5</td>
</tr>
<tr>
<td>Base injection rate (mL/h)</td>
<td>10 20 30 50</td>
</tr>
<tr>
<td>r_OH (OH added/Al_T)</td>
<td>1.5 1.8 2.2 2.4</td>
</tr>
<tr>
<td>Aging time (days)</td>
<td>&lt;1 2 5 10</td>
</tr>
<tr>
<td>Aging temperature (°C)</td>
<td>4 20</td>
</tr>
</tbody>
</table>

CHARACTERIZATION OF PAC1

Two different and complementary techniques were used to characterize the aluminum speciation in the PAC1 preparations. One procedure used a timed colorimetric reaction with ferron (8-hydroxy-7-iodoquinoline-5-sulfonic acid) to provide a description based on chemical reactivity. The second method used membrane filtration and ultrafiltration to provide a physically based estimate of species size.

Samples were withdrawn from the reaction vessel at selected values of r_OH during a titration and stored at 20 or 4 °C. After a desired period of aging, the speciation of the aluminum in the samples was measured with a timed colorimetric method using ferron orthophenanthroline as the colorimetric reagent. The method is based on differences in the rates of reaction of various aluminum species with ferron. The procedure used in these ferron tests was the same as that employed by Smith (1971). This methodology provides an assessment of the proportions of monomeric aluminum (denoted as Al^a), polymeric aluminum (Al^b), and precipitated aluminum (Al^c) in a sample. Samples containing no more than 0.75 mg Al were pipetted into beakers, and the volume was adjusted to 25 mL with distilled water. In another beaker, 2.0 mL of a sodium acetate - acetic acid buffer solution was added to 5.0 mL of ferron orthophenanthroline reagent. This mixture was then added to the diluted aluminum sample. As rapidly as possible, and within 1 min, 2.0 mL of hydroxylamine hydrochloride solution was added to the test solution and timing was begun. As rapidly as possible, and within 1 min, the mixture was placed into a 1-cm quartz spectrophotometer cell and inserted in a Shimadzu UV-VIS recording spectrophotometer (model UV-160). Absorbance measurements were made continuously at a wavelength of 370 nm against a blank containing all reagents but no aluminum.

The absorbance of the sample 1 min after the reaction was begun was used to determine
the concentration of aluminum monomers \([\text{Al}^a]\) in the PAC1 preparation. The absorbance after a reaction period of 100 min was used to calculate the total concentration of aluminum monomers and polymers, i.e., \([\text{Al}^a] + [\text{Al}^b]\). The concentration of aluminum polymers \([\text{Al}^b]\) was then determined by the difference between these two measurements.

The total aluminum concentration \([\text{Al}_T]\) in a sample was measured by atomic absorption spectrophotometry with a Perkin-Elmer instrument (model 2380) using nitrous oxide and acetylene as the flame gases and a hollow cathode lamp. Aluminum standards and samples were acidified to \(pH < 3\) with concentrated nitric acid. The concentration of precipitated aluminum \([\text{Al}^c]\) was calculated by subtracting \([\text{Al}^a] + [\text{Al}^b]\) from \([\text{Al}_T]\).

The size and size distribution of the aluminum species in the PAC1 preparations were evaluated using membrane filtration and ultrafiltration techniques. Nucleopore polycarbonate membranes with pore sizes of 0.4, 0.2, 0.1, 0.08, 0.05, and 0.03 \(\mu m\) were employed in conjunction with Amicon ultrafiltration membranes having sizes of 130 \(\AA\) (XM300), 20 \(\AA\) (PM10), and 10 \(\AA\) (UMOS). The Nucleopore membranes are made of a polycarbonate film penetrated with cylindrical holes that can produce a sievelike filtering action. The Amicon membranes consist of a thin (0.1 to 1.5 \(\mu m\)) dense "skin" of extremely fine pore structure that opens to a much thicker (50 to 150 \(\mu m\)) open-celled spongy layer of the same polymer.

The Nucleopore filters had a diameter of 25 mm. They were soaked in distilled water, rinsed, and placed in polycarbonate Swin-Lok holders to which disposable polypropylene Luer-Lok syringes were attached. Three to five milliliter aliquots of a PAC1 preparation were pipetted into the syringe, manual pressure was applied, and the first milliliter of filtrate was used for determination of total aluminum concentration by atomic absorption spectrophotometry.

The Amicon filters had a diameter of 43 mm. They were rinsed three times in distilled water and placed in Amicon stirred cells (model 8050). Five to 10 mL of solution were placed in the cell, and pressure was applied with \(N_2\) gas from a pressure cylinder. For the 130 and 20 \(\AA\) membranes, a pressure of 20 psi was applied and, after 1 mL had passed the membrane, a sample was collected for determination of aluminum. A pressure of about 60 psi was used with the 10-\(\AA\) membrane.

All chemicals used in these investigations were analytical-reagent-grade or better unless otherwise noted. Water was glass-distilled unless stated otherwise. Commercially prepared and standardized solutions of NaOH and HCl were used in the titrations. Gases included prepurified nitrogen (99.998 percent pure), A.A. grade acetylene (99.6 percent pure), and A.A. grade nitrous oxide (99.0 percent pure).

PREPARATION OF PIC1

The procedures used in the preparation of PIC1 resembled those described previously for PAC1 preparations. The process is a controlled hydrolysis of a ferric chloride solution. A reaction apparatus essentially identical to the system used for PAC1 preparation was employed (Figure 4).

Titrations were conducted using three different concentrations of ferric chloride—0.1, 0.3, and 0.5 M. These solutions are all oversaturated with respect to the precipitation of goethite, so that additional acid was added to prevent precipitation before the titrations were begun. In all cases, HCl at a final concentration of 0.225 M was used. As with the preparation of PACI, the objective of the titration was to prepare a PIC1 solution containing the maximum proportion
of polymeric species. Sodium carbonate (Na$_2$CO$_3$) was used as the base in these titrations rather than NaOH, because Schwyn (1983) and Schneider and Schwyn (1987) have reported that carbonate reduces the nucleation rate and slows precipitation during the titration. The concentration of Na$_2$CO$_3$ used in the neutralization of the 0.1- and 0.3-M solutions of FeCl$_3$ was 1.0 M; a base concentration of 1.75 M was used in the neutralization of 0.5 M FeCl$_3$.

CHARACTERIZATION OF PIC1

As with PAC1, two different techniques were used to characterize iron(III) speciation in the PIC1 preparations. A timed colorimetric procedure using ferron as developed by Murphy et al. (1975) was used to characterize chemical reactivity, and a series of membrane filtrations such as employed by Buffle et al. (1985) was used for physical characterization.

The use of ferron to characterize iron(III) speciation is similar to its use for aluminum speciation. Absorbance is measured as a function of time, in this case at a wavelength of 600 nm. The reaction of monomeric, dimeric, and perhaps trimeric iron(III) species with ferron is complete within 1 min (Murphy et al. 1975); these species are denoted here as Fe$^a$. Reaction over the next 24 hours is ascribed to polymeric species (Fe$^b$). Any iron(III) that remains unreactive after 24 hours is considered to be precipitated (Fe$^c$). In summary, monomeric and small polymeric iron(III) species are determined from the 1-min absorbance reading. Larger polymeric iron(III) species are determined from the difference between the 24-hour and the 1-min absorbance readings. Precipitated iron(III) is calculated from the difference between the total iron(III) concentration as measured by atomic absorption ([Fe(III)$_T$]) and the 24-hour absorbance measurement.

In the filtration characterizations of iron(III) species, Nucleopore membranes with pore sizes of 0.4, 0.2, 0.1, 0.05, and 0.03 μm were used, as were ultrafiltration membranes with pore sizes of 130 Å, 20 Å, and 10 Å.

Total iron concentrations were measured by atomic absorption spectrophotometry using a hollow cathode Fe lamp and a wavelength of 373.7 nm, with both air and acetylene gases. Iron samples and standards were acidified with nitric acid prior to measurement; samples were allowed to react in the nitric acid for 18 hours before measurement to provide complete dissolution of the iron(III) species.

In each titration, iron(III) speciation was determined initially before the HCl added to suppress hydrolysis was neutralized, and then at values of $r_{OH}$ equal to 0, 0.5, 1.0, 1.5, and 2.0. A value of $r_{OH} = 0$ was assigned to the titration after base was added to neutralize the HCl used to prevent precipitation prior to the beginning of the titration.

COAGULATION TESTS

The effectiveness of the polymeric coagulants in the removal of turbidity and color were evaluated using conventional jar tests. Comparisons were made between the prepared polymeric coagulants and conventional salts such as alum and ferric chloride. Submicron latex particles were used to produce turbidity; fulvic acids isolated from natural waters were used to represent humic substances and color. Experiments were conducted at different concentrations of turbidity in the absence of humic substances, at various concentrations of fulvic acid in the absence of turbidity, and with mixtures of particles (turbidity) and fulvic acid. The effects of pH and temperature on coagulant effectiveness were also investigated. In the following
discussion, the experimental procedure employed in the PACI studies is presented first, followed by a description of the PIC1 procedures.

**PAC1 Experiments**

The PACI experiments were focused on an evaluation of the effectiveness of polymeric aluminum chloride preparations with r_{OH} = 2.4, because these preparations were found to contain a high proportion of polymeric aluminum species and to be fairly stable (see Chapter 4, Results). This coagulant, denoted here as PACI:2.4, was compared with alum (aluminum sulfate), aluminum chloride that had not been neutralized, and a colloidal aluminum hydroxide precipitate prepared by completely neutralizing aluminum chloride (i.e., r_{OH} = 3.0). This latter preparation is termed PACI:3.0 here.

The turbidity in the waters to be treated was produced by spherical and uniform polystyrene latex particles with a diameter of 0.198 μm (Duke Scientific Corporation). The fulvic acid used in this research was isolated from the waters of the Great Dismal Swamp in Virginia (Hundt 1985; Hundt and O'Melia 1988). Fulvic acid is the predominant component of soluble organic matter in unpolluted natural waters, and is present in all surface water supplies. It is a precursor in the formation of trihalomethanes, and its removal is an important objective in modern water treatment.

Latex concentrations were measured with a Shimadzu UV-VIS recording spectrophotometer (model UV-160) operated at a wavelength of 227 nm. Turbidity measurements were made with a Hach turbidimeter (model 2100A). Fulvic acid concentrations are expressed as DOC concentrations (mg DOC/L). In some samples, DOC was measured with a Beckman 915-B organic carbon analyzer. Most fulvic acid concentrations in the jar-test experiments were determined from measurements of UV absorbance using the Shimadzu spectrophotometer operated at a wavelength of 254 nm.

Jar tests were carried out at pH values of 5.5 and 7.0 and at temperatures of 20 and 4 °C. Two concentrations of latex were used to simulate low- and high-turbidity waters; these were 100 mg/L (538 ntu) and 1 mg/L (7.2 ntu). When fulvic acid was studied, it was examined at a concentration of 8.44 mg DOC/L.

The jar tests were conducted in glass beakers having capacities of 600 or 100 mL, with the smaller beakers being used for the turbid waters (100 mg/L of latex) to reduce latex consumption. Tests at 20 °C were conducted in the open laboratory; tests at 4 °C were conducted in a large walk-in constant-temperature room or in a large refrigerator maintained at that temperature. Typically, a total of 495 mL or 79 mL of Milli-Q water was added to each beaker to be used in a jar-test experiment. Sodium bicarbonate was then added to produce an ionic strength of 10^{-3} M. The pH of the solution was then adjusted to 5.5 or 7.0 with HCl. Latex or fulvic acid was added to the beaker to produce the desired turbidity or DOC concentration. A selected dosage of the desired aluminum coagulant was added to the beaker with a digital pipet; aluminum dosages were typically varied from 0 to 1.20 mM in a series of jar-test experiments. The pH of the beaker contents was then readjusted to the desired pH (5.5 or 7.0) with NaOH.

The beakers were mixed rapidly for 1 min and then stirred slowly for 20 or 30 min using a magnetic stirrer (100-mL beakers) or a six-paddle mechanical stirrer (Phipps and Bird, Inc.). Slow mixing or flocculation was followed by 1 hour of sedimentation, after which samples of the supernatant were withdrawn for analysis of latex or fulvic acid concentration. In some experiments, a second sample of the supernatant was withdrawn and filtered through a 0.4-μm
Nucleopore membrane filter. The concentrations of latex and fulvic acid remaining in the filtrate were then determined.

**PIC1 Experiments**

The PIC1 experiments were focused on evaluation of the effectiveness of polymeric iron(III) preparations with $r_{OH} = 0.5$ produced by partial neutralization of acidified 0.3 M FeCl₃ stock solutions. This coagulant, denoted here as PIC1:0.5, was compared with a stock solution of acidified 0.3 M FeCl₃, a concentrated stock solution of unacidified 1.5 M FeCl₃ used to simulate field conditions, and a PIC1 preparation neutralized to a value of $r_{OH} = 1.5$. This last preparation contained a substantial fraction of a colloidal precipitate of iron(III) hydroxide. It is denoted here as PIC1:1.5.

Jar tests were carried out at pH values of 5.0 and 7.0 and at temperatures of 20 and 4 °C. Two latex concentrations were used, 50 and 1 mg/L. Two concentrations were also used in experiments containing fulvic acid, 4 and 10 mg DOC/L. All experiments were performed with 600- or 100-mL beakers and mechanical stirring. The pH of the beaker contents was readjusted after flocculation. In other respects the procedures followed those described for the PAC1 coagulation tests.

**DIRECT FILTRATION TESTS**

Experiments were performed to investigate the effectiveness of PAC1 and PIC1 in the direct filtration of low-turbidity waters in the absence of natural organic matter and also in the presence of a moderate concentration of humic substances. These studies were made with laboratory-scale filtration facilities. This equipment is described first, after which the procedures used for the PAC1 and PIC1 experiments are presented.

**Filtration Apparatus**

A schematic illustration of the filtration apparatus is presented in Figure 5, adapted from the doctoral dissertation by Tobiason (1987). The components are as follows:

1. Raw water reservoir--this contained the water to be treated, and consisted of either a 9-L Pyrex bottle or a polyethylene container with a volume of 60 or 120 L.

2. Raw water pump--piston type, with adjustable flow rate of 0-260 mL/min; (FMI Lab Pump, model RP-G400-2).

3. Surge tank--used to reduce flow fluctuations from the raw water piston pump; Pyrex vacuum flask, 250 mL.

4. Chemical feed pump--a peristaltic, variable-speed, cavity-type pump with a flow rate range of 0-2.5 mL/min (Scientific Industries, model 203) was used for diluted coagulant stock suspensions; a variable-speed syringe pump (Sage Instruments, model 355) was used for concentrated coagulant stock solutions.

5. Filter column--cast acrylic tubing, 2.5 cm inside diameter.

6. Flowmeters--glass-body rotameters were used to monitor all raw water and coagulant flows.
FIGURE 5. Schematic Diagram of Pilot Filtration Apparatus.
7. Tubing and connections—tygon tubing, polypropylene connectors, and polypropylene/teflon valves were used.

The filter columns were filled to a depth of 15 cm with 0.55-mm spherical glass beads (Ferro Corporation, Cataphote Division). A bed porosity of 0.4 was maintained at the start of each run. These media were cleaned prior to each run by repeated rinsing, soaking, and soninating in NaOH, HNO₃, and distilled water. After a final rinse, they were dried in an oven at 70-80 °C prior to use.

PAC₁ Experiments

Two coagulants were compared in these tests, PAC₁:2.4 and alum. The water to be treated had a low turbidity, simulated by the use of a 1-mg/L latex suspension at pH values of 5.5 and 7. Sodium bicarbonate at a concentration of 1 mM was added to each system prior to final pH adjustment. All experiments were conducted at ambient laboratory temperature (21-22 °C).

Suspensions (about 55 L) were prepared the day before a filter run, but the pH was adjusted to the desired level with HCl just prior to the start of an experiment. Two filters were operated in parallel, one receiving PAC₁:2.4 and the other receiving alum. A common raw water reservoir was used to provide a flow rate of 38.1 cm³/min (2 gpm/sq ft or 4.9 m/h) to both filters.

Coagulant was added to the influent of each filter with a peristaltic pump at a flow rate of 0.167 cm³/min. In-line mixing was accomplished by repeated constriction and expansion of the flow. Stock solutions of PAC₁:2.4 and alum were diluted before pumping to achieve the desired dosage. For these chemicals, this dilution was not considered to affect coagulant speciation prior to actual mixing with the water to be treated. Coagulant dosages were selected in two ways. In one procedure, the coagulant dosage for direct filtration was selected as the optimum dosage in the jar tests, and this dosage was maintained throughout the filtration experiment. In other experiments, the initial chemical dosage for filtration was based on jar tests, but was varied systematically after the start of a run. Typically, filter effluent quality changed within 5 min after a change in chemical application, enabling rapid selection of the optimum chemical dosage for direct filtration.

During a filtration run, samples of approximately 30 mL were collected at 5-min intervals during the first 15 min, every 15 min for the remainder of the first hour, and every 30 min for the remainder of an experiment. Effluent quality was monitored by measuring pH, turbidity, and absorbance at 227 nm. Head loss readings were taken at 15-min intervals throughout an experiment. A filtration run proceeded until effluent quality deteriorated considerably or until head loss was excessive.

PIC₁ Experiments

Two coagulants were compared in these tests, PIC₁:0.5 and 1.5 M FeCl₃. Two types of water were treated: (1) low-turbidity waters simulated with 1-mg/L latex suspensions at pH values of 5 and 7, and (2) low-turbidity waters containing moderate amounts of humic substances simulated with 1-mg/L latex suspensions containing aquatic fulvic acid at a concentration of 4 mg TOC/L at pH 5. Sodium bicarbonate at a concentration of 1 mM was added to each system prior to pH adjustment. All experiments were conducted at ambient laboratory temperature (21-22 °C).

Suspensions (about 55 L) were prepared the day before a filter run, but the pH was
adjusted to the desired level with HCl just prior to the start of an experiment. Two filters were operated in parallel, one receiving PACI:0.5 and the other receiving 1.5 M FeCl₃. For experiments with water containing low turbidity and no added humic materials, coagulant dosages were low and coagulant additions did not substantially reduce the pH of the water to be treated. As a result, a common raw water reservoir was used for both filters in the experiments. In waters containing fulvic acid at a concentration of 4 mg DOC/L, the required coagulant dosages were sufficiently high that a substantial decrease in pH accompanied coagulant addition. Because of the different preneutralization of the two coagulants, the pH drop was greater for 1.5 M FeCl₃ than for PACI:0.5 when both were added to similar waters at equal dosages. As a result, two separate raw water reservoirs were used in experiments using fulvic acid; the waters were identical save for a small initial pH difference. After coagulant addition, the pH values of the two systems were comparable. Filters were operated at a flow rate of 2 gpm/sq ft (4.9 m/h).

A coagulant was added to the filter influent with either a peristaltic or a positive-displacement syringe pump. In-line mixing was accomplished by repeated contraction and expansion of the flow. When peristaltic pumps were used in early experiments, the stock coagulant solutions were diluted before pumping to achieve the desired dosage. Because this dilution had the potential to change the chemical characteristics of the iron(III) coagulants, syringe pumps that could operate at a low flow rate (down to about 2 x 10⁻⁵ mL/min) were used in later experiments to pump the undiluted stock coagulant solutions directly to the filter influent. Coagulant dosages were selected as in the tests with PACI, i.e., by jar tests and by systematic changes in the chemical dose during a filter run.

During a filtration run, samples of approximately 30 mL were collected at 5-min intervals during the first 15 min, every 10 min for the remainder of the first hour, and then every 15-30 min for the remainder of an experiment. Effluent quality was monitored by absorbance and turbidity measurements and by pH. Absorbance at 227 nm was used for the low-turbidity waters without fulvic acid; absorbance at 227 and 254 nm was measured for waters containing both latex particles and fulvic acid. Head loss readings were taken throughout an experiment, and a filtration run proceeded until effluent quality deteriorated considerably or until head loss was excessive.
CHAPTER 4

RESULTS

The results of several different experiments are presented in this chapter. Three principal types of studies are reported, viz., characterization of polymeric coagulant species, coagulation using partially neutralized and conventional coagulants, and direct filtration with both partially neutralized and conventional chemicals as filter aids. These results are taken from the research of Yao (1987) and Gray (1988).

CHARACTERIZATION OF THE COAGULANTS

The results of experiments performed to characterize PAC1 preparations (Yao 1987) are presented first, followed by results for PIC1 preparations (Gray 1988).

PAC1 Preparations

The effects of neutralization or base addition ($r_{OH}$), initial aluminum concentration, base concentration, base injection rate, aging time, and aging temperature on the content of polymeric aluminum species in PAC1 preparations were investigated. Some experimental conditions are summarized in Table 2. Aluminum speciation was inferred from ferron tests and from membrane filtration and ultrafiltration experiments.

Effects of neutralization ($r_{OH}$) on the formation of polymeric species as indicated by ferron tests are illustrated in Figure 6. The fraction of polymeric aluminum species in aluminum preparations ($[Al^b]/[Al_T]$) is plotted as a function of base addition expressed as $r_{OH}$. For each of the four points plotted in Figure 6, the polymeric fraction ($[Al^b]/[Al_T]$) is the average of 16 experiments conducted under different combinations of variables (base concentration, aluminum concentration, base injection rate, aging time, and aging temperature) and determined at a particular degree of neutralization ($r_{OH}$).

Statistical analysis of the results indicated that the degree of neutralization, $r_{OH}$, had an effect on the polymeric content of the PAC1 preparations that was significant at the 0.01 level. This is in agreement with many other studies. The effects of all other variables on polymeric content were much less significant.

Some results of filtration tests to describe the size of the polymeric aluminum species are presented in Table 3. These data indicate that the principal aluminum species present in 15 of the 16 preparations passed through the 2-nm ultrafilter but were retained on the 1-nm ultrafilter. In one preparation, experiment 13, a visible aluminum hydroxide precipitate was the principal aluminum species; the polymeric aluminum content $[Al^b]$ as determined with ferron reagent was only 30 percent. This preparation was produced using the highest initial aluminum concentration (0.5 M) and base strength (1 M) in the test series.

The data in Table 3 indicate that the sizes of the polymeric aluminum species in the PAC1 preparations ranged from 1 to 2 nm for all combinations of experimental conditions unless a visible aluminum hydroxide precipitate was formed. The cationic polymeric aluminum species $Al_{13}O_4(OH)_{24}^+$ has a diameter of about 1.2 nm, so that the results of the ultrafiltration tests are consistent with the presence of this species and with the work of Parthasarathy and Buffle (1985). Bottéro et al. (1987) reported that this $Al_{13}$ species is stable in solutions with
Figure 6. Effects of the Degree of Neutralization \( r_{OH} \) on the Polymeric Content of PACI Preparations (aluminum speciation based on ferron tests; each point is the average of 16 experiments conducted under different combinations of variables)
For $r_{OH} < 2.3$, they report the gradual aggregation of these $Al_{13}$ units into linear-shaped clusters. The results presented in Table 3 and by Yao (1987) for $r_{OH} < 2.4$ suggest that either aggregation of the polymeric species did not occur or that the aggregates were broken in the ultrafiltration procedure.

**TABLE 3**

Characterization of PAC1 by Filtration ($r_{OH} = 2.4$)

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>$[Al_T(2 \text{ nm})]/[Al_T(0.4 \text{ \mu m})]^*$</th>
<th>$[Al_T(1 \text{ nm})]/[Al_T(0.4 \text{ \mu m})]^*$</th>
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<tr>
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<td>0.05</td>
</tr>
<tr>
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<td>0.95</td>
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</tr>
<tr>
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<td>0.03</td>
</tr>
<tr>
<td>4</td>
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<td>0.00</td>
</tr>
<tr>
<td>5</td>
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<td>0.01</td>
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</tr>
<tr>
<td>16</td>
<td>0.90</td>
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</table>

*[$Al_T(1 \text{ nm})$, $Al_T(2 \text{ nm})$, and $Al_T(0.4 \text{ \mu m})$] denote the total concentrations of aluminum in the filtrates of 1-nm and 2-nm Amicon membranes and 0.4-μm Nucleopore membranes, respectively.

Based on the experimental characterization of the PAC1 preparations, the following conditions were adopted for preparing polymeric aluminum coagulants for use in subsequent coagulation and direct filtration tests: slow base injection (< 50 mL/h), $r_{OH} = 2.4$ (for polymeric species) and $r_{OH} = 3.0$ (for a colloidal aluminum hydroxide precipitate), moderate initial aluminum chloride concentration (0.2 M), moderate base concentration ([NaOH] = 0.5 M), aging (> 5 days), and low-temperature storage (4 °C). These conditions produced polymeric aluminum solutions (except at $r_{OH} = 3.0$) that contained a large proportion of stable polymeric aluminum species (> 65 percent Al$^{3+}$) with a size between 1 and 2 nm.

**PIC1 Preparations**

Effects of neutralization on the speciation of partially neutralized iron(III) chloride solutions are presented in Figure 7. Iron(III) speciation is based on the results of ferron tests and is classified as (i) monomeric plus dimeric, (ii) polymeric, and (iii) colloidal precipitate. The results in Figure 7 were obtained for the partial neutralization of ferric chloride solutions that had an initial iron(III) concentration of 0.3 M prior to addition of sodium carbonate;
similar results were obtained with solutions that were initially 0.1 and 0.5 M. The results suggest that the iron(III) preparations did not contain a significant fraction of polymeric species.

Some results of filtration tests to describe the size of the iron(III) species in these preparations are presented in Figure 8. Filters in the size range from 2 to 50 nm did not retain a significant fraction of the iron(III) species in these preparations, indicating that stable large polymeric species were not produced. Neutralization to \( r_{\text{OH}} \geq 1.5 \) produced preparations in which the predominant fraction was an iron(III) hydroxide precipitate. Small iron(III) species (i.e., those passing the 2-nm ultrafilter) were the dominant iron(III) fraction only at \( r_{\text{OH}} \leq 1.0 \).

Comparison of the results in Figures 7 and 8 shows close agreement between the ferron and filtration results, adding a rough physical characterization to the chemical characterization. Iron(III) species that react quickly with ferron and that have been considered to be monomeric and dimeric compared well with iron(III) species that passed through 2-nm filters. Iron(III) species categorized as polymeric in the ferron assay compared well with iron(III) species that passed 50-nm filters and were retained on 2-nm filters. Iron(III) that is unreactive with ferron compared well with iron(III) that was retained on filters with pore sizes of 50 nm and larger.

When the filtration tests using 1-nm filters were compared with the ferron assay, a discrepancy was observed. Results obtained for the 0.3 M FeCl₃ solution are presented in Table 4. Monomeric and dimeric iron(III) species should pass through the 1-nm ultrafilter, so that the results of the ferron test were expected to agree well with this fraction. Instead, the data in Table 4 indicate excellent agreement with the iron(III) passing the 2-nm filter. The rapid ferron assay for iron(III) species produced results that were always greater than the 1-nm filter fraction. The comparison in Table 4 indicates that the rapid ferron assay may include iron(III) species that are larger than the dimer in size. This discrepancy is discussed later.

**TABLE 4**

Comparison of Ferron and Ultrafiltration Tests

<table>
<thead>
<tr>
<th>( r_{\text{OH}} )</th>
<th>Ferron*</th>
<th>Ultrafiltration*</th>
</tr>
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<tr>
<td></td>
<td>mono/dimeric</td>
<td>&lt; 2 nm</td>
</tr>
<tr>
<td>0.5</td>
<td>0.81</td>
<td>0.82</td>
</tr>
<tr>
<td>1.0</td>
<td>0.57</td>
<td>0.55</td>
</tr>
<tr>
<td>1.5</td>
<td>0.39</td>
<td>0.39</td>
</tr>
<tr>
<td>2.0</td>
<td>0.15</td>
<td>0.15</td>
</tr>
</tbody>
</table>

*Fraction of total iron(III) in a particular characterization by chemical species (ferron) or size (ultrafiltration); initial iron(III) concentration prior to base addition = 0.3 M.
FIGURE 7. Effects of the Degree of Neutralization ($r_{OH}$) on the Speciation of PICl Preparations (iron(III) speciation based on ferron tests; initial iron concentration = 0.3 M)
FIGURE 8. Effects of the Degree of Neutralization ($r_{OH}$) on the Size Characteristics of PICl Preparations as Determined by Filtration (initial iron(III) concentration = 0.3 M)
Based on the experimental characterization of the PIC1 preparations, the following conditions were adopted for preparing partially neutralized iron(III) coagulants for use in subsequent coagulation and direct filtration tests: moderate initial ferric chloride concentration (0.3 M), prior addition of HCl to an initial concentration of 0.225 M, titrant concentration (Na_2CO_3) = 1 M, slow base injection, \( r_{OH} = 0.5 \) and 1.5, preparation temperature = 20 °C, and no aging (all preparations were used within 24 hours).

**COAGULATION TESTS**

The results of experiments performed to evaluate PAC1 preparations as coagulants (Yao 1987) are presented first, followed by results for PIC1 preparations (Gray 1988).

**PAC1 Preparations**

Four aluminum coagulants were tested: PAC1:2.4 \((r_{OH} = 2.4)\), PAC1:3.0 \((r_{OH} = 3.0)\), aluminum chloride \((\text{AlCl}_3)\), and alum \((\text{Al}_2(\text{SO}_4)\text{O}_3\cdot14.3\text{H}_2\text{O})\). The effectiveness of these chemicals for the removal of particles (turbidity) and humic substances (DOC, color) was evaluated in jar tests.

**Turbidity Removal**

**High turbidity.** Results of jar tests for evaluating the effectiveness of these four coagulants for treating a water with a high turbidity produced by 100 mg/L of latex are presented in Figures 9-12. Residual absorbance after flocculation and sedimentation is plotted as a function of the coagulant dosage (log scale). Coagulant dosages are expressed as moles of aluminum per liter, denoted as M.

Results for a turbid water with a neutral pH (7) and a moderate temperature (20 °C) are presented in Figure 9. The effectiveness of the coagulants under these conditions may be represented as \( \text{AlCl}_3 \approx \text{alum} \approx \text{PAC1:2.4} > \text{PAC1:3.0} \). Alum, \( \text{AlCl}_3 \), and PAC1:2.4 accomplished similar removals of turbidity over a broad range of dosages, from about \( 2 \times 10^{-5} \) M (log \( \text{Al}_T = -4.7; \text{Al}_T = 0.54 \text{ mg/L} \)) to \( 2 \times 10^{-4} \) M (log \( \text{Al}_T = -3.7; \text{Al}_T = 5.4 \text{ mg/L} \)). At higher dosages, alum and \( \text{AlCl}_3 \) continued to be effective while removal with PAC1:2.4 deteriorated, probably because the particles in suspension had become positively charged. PAC1:3.0 was ineffective as a coagulant at aluminum dosages below \( 3 \times 10^{-4} \) M (log \( \text{Al}_T = -3.5; \text{Al}_T = 8.5 \text{ mg/L} \)). These results do not indicate any advantage in the use of PAC1:2.4 under the conditions of these experiments; PAC1:2.4 can be as effective as other aluminum coagulants but not better.

Results for a turbid water coagulated at an acidic pH (5.5) and at moderate temperature (20 °C) are presented in Figure 10. These data indicate that the effectiveness of the four coagulants under these conditions may be represented as PAC1:2.4 > \( \text{AlCl}_3 \) > PAC1:3.0 > alum. PAC1:2.4 was effective over a dosage range from \( 8 \times 10^{-6} \) to \( 4 \times 10^{-5} \) M (log \( \text{Al}_T = -5.1 \) to -4.4; \( \text{Al}_T = 0.2 \) to 1.1 mg/L). It appeared to function as a cationic polyelectrolyte, neutralizing the negative charge on the particles at low dosages and inducing restabilization by producing positively charged particles at higher dosages. Alum produced partial coagulation in the dosage region from \( 10^{-6} \) to \( 10^{-4} \) M (log \( \text{Al}_T = -5 \) to -4; \( \text{Al}_T = 0.27 \) to 2.7 mg/L), but dosages in excess of \( 2.5 \times 10^{-4} \) M (log \( \text{Al}_T = -3.6; \text{Al}_T = 6.8 \text{ mg/L} \)) were required for efficient turbidity removal. PAC1:2.4 can function effectively at dosages lower than the other coagulants for a highly turbid water with a slightly acidic pH.
pH = 7.0; T = 20 °C

- PACI: 2.4
- Alum
- PACI: 3.0
- Aluminum Chloride

**FIGURE 9.** Comparison of Four Aluminum Preparations in the Coagulation of a Turbid Water (100 mg/L of 0.198 μm latex, 538 ntu; residual absorbance at 227 nm after flocculation and sedimentation is plotted as a function of the coagulant dosage expressed as moles of aluminum/L)
**FIGURE 10.** Comparison of Four Aluminum Preparations in the Coagulation of a Turbid Water (100 mg/L of 0.198 μm latex, 538 ntu; residual absorbance at 227 nm after flocculation and sedimentation is plotted as a function of the coagulant dosage expressed as moles of aluminum/L)
FIGURE 11. Comparison of Four Aluminum Preparations in the Coagulation of a Turbid Water (100 mg/L of 0.198 μm latex, 538 ntu; residual absorbance at 227 nm after flocculation and sedimentation is plotted as a function of the coagulant dosage expressed as moles of aluminum/L)
pH = 5.5; T = 4 °C

- PACI:2.4
- Alum
- PACI:3.0
- Aluminum Chloride

FIGURE 12. Comparison of Four Aluminum Preparations in the Coagulation of a Turbid Water (100 mg/L of 0.198 µm latex, 538 ntu; residual absorbance at 227 nm after flocculation and sedimentation is plotted as a function of the coagulant dosage expressed as moles of aluminum/L)
Coagulation of this turbid suspension at neutral pH (7) and low temperature (4 °C) is depicted in Figure 11. The effectiveness of the four coagulants under these conditions can be considered as PACl:2.4 > AlCl₃ > alum > PACl:3.0. Despite the neutral pH, PACl:2.4 functioned as a cationic polyelectrolyte, neutralizing the negative charge on the particles at an applied dosage of about 10⁻⁵ M (log Alₜ = -5; Alₜ = 0.27 mg/L) and causing restabilization by charge reversal at dosages higher than about 2.5 x 10⁻⁶ M (log Alₜ = -4.6; Alₜ = 6.8 mg/L). PACl:3.0 was ineffective at any dose tested. Alum and AlCl₃ functioned well at moderate-to-high dosages. PACl:2.4 offers an advantage compared with the other coagulants; it can function effectively at lower dosages under conditions of high turbidity and cold temperature.

Results obtained for this turbid water at low pH (5.5) and low temperature (4 °C) are presented in Figure 12. Coagulant effectiveness under these conditions may be represented as PACl:2.4 > AlCl₃ ≈ PACl:3.0 > alum. PACl:2.4 was effective at quite low dosages, from 1.6 to 4 x 10⁻⁶ M (log Alₜ from -5.8 to -5.4; Alₜ from 0.04 to 0.11 mg/L). The combination of slightly acidic pH and low temperature appeared to allow the polymeric aluminum species present in PACl:2.4 to persist in solution, act as charge-neutralizing cationic polyelectrolytes, and produce effective coagulation of turbid suspensions at lower dosages than at neutral pH and moderate temperature. PACl:2.4 can function effectively at much lower dosages than the other coagulants under conditions of high turbidity, low temperature, and slightly acidic pH.

Low turbidity. Results of jar tests for evaluating the effectiveness of the four aluminum coagulants for treating a water with a low turbidity produced by 1 mg/L of latex are presented in Figures 13-16. The coagulation of this suspension under conditions of neutral pH (7) and moderate temperature (20 °C) is depicted in Figure 13. The effectiveness of the coagulants may be represented as AlCl₃ ≈ alum ≈ PACl:3.0 ≈ PACl:2.4. Because of the low concentration of particles in this water, the overall process of aggregation was limited by the rate at which interparticle contacts were produced. Effective coagulation was accomplished by precipitation of amorphous Al(OH)₃, which increases the interparticle collision rate, enmeshes the latex particles, and removes them by sedimentation. Dosages of alum or AlCl₃ in excess of about 6 x 10⁻⁵ M as aluminum (log Alₜ = -4.2; Alₜ = 1.7 mg/L) are required under these conditions. PACl:2.4 was completely ineffective as a coagulant for this system.

Results for a low-turbidity water coagulated at an acidic pH (5.5) and moderate temperature (20 °C) are presented in Figure 14. The effectiveness of the four coagulants under these conditions may be described as alum > AlCl₃ ≈ PACl:2.4 ≈ PACl:3.0, with alum being the only coagulant that actually accomplished effective removal by coagulation and sedimentation. Required alum dosages at pH 5.5 were higher than at pH 7.0 (Figure 4-8); it is more difficult to precipitate Al(OH)₃ at pH 5.5 than at pH 7. Alum dosages in excess of 2 x 10⁻⁴ as aluminum (log Alₜ = -3.6; Alₜ = 5.4 mg/L) are needed.

The coagulation of this low-turbidity suspension at neutral pH (7) and low temperature (4 °C) is presented in Figure 15. These data indicate that the effectiveness of the four coagulants under these conditions may be represented as AlCl₃ > alum > PACl:2.4 > PACl:3.0. The dosages of alum and aluminum chloride required to precipitate Al(OH)₃ and remove the turbidity were slightly lower at 4 °C (Figure 15) than at 20 °C (Figure 13). Some removal was accomplished by PACl:2.4 at dosages of about 3 x 10⁻⁵ M (log Alₜ = -4.5; Alₜ = 0.85 mg/L) and by PACl:3.0 at dosages of about 10⁻⁴ M (log Alₜ = -4; Alₜ = 0.27 mg/L), but effective removal was limited by interparticle contacts or flocculation kinetics. It may be that the low temperature retards the precipitation of Al(OH)₃ so that all of the coagulants are more effective at 4 °C than they are at 20 °C.
**FIGURE 13.** Comparison of Four Aluminum Preparations in the Coagulation of a Low-Turbidity Water (1 mg/L of 0.198 μm latex, 7.2 ntu; residual absorbance at 227 nm after flocculation and sedimentation is plotted as a function of the coagulant dosage expressed as moles of aluminum/L)
FIGURE 14. Comparison of Four Aluminum Preparations in the Coagulation of a Low-Turbidity Water (1 mg/L of 0.198 μm latex, 7.2 ntu; residual absorbance at 227 nm after flocculation and sedimentation is plotted as a function of the coagulant dosage expressed as moles of aluminum/L)
FIGURE 15. Comparison of Four Aluminum Preparations in the Coagulation of a Low-Turbidity Water (1 mg/L of 0.198 μm latex, 7.2 ntu; residual absorbance at 227 nm after flocculation and sedimentation is plotted as a function of the coagulant dosage expressed as moles of aluminum/L)
**FIGURE 16.** Comparison of Four Aluminum Preparations in the Coagulation of a Low-Turbidity Water (1 mg/L of 0.198 μm latex, 7.2 ntu; residual absorbance at 227 nm after flocculation and sedimentation is plotted as a function of the coagulant dosage expressed as moles of aluminum/L)
Results obtained for this low-turbidity water at low pH (5.5) and low temperature (4 °C) are presented in Figure 16. The effectiveness of the four coagulants under these conditions may be described as alum » PACI:3.0 > PACI:2.4 > AlCl₃. Precipitation of sufficient Al(OH)₃ to provide effective flocculation kinetics was accomplished only by alum and then only at dosages above about 10⁻³ M (log \( A_{1T} = -3; A_{1T} = 27 \text{ mg/L} \)). The data indicate that PACI:3.0, and perhaps PACI:2.4, can destabilize the particles, but that sufficient interparticle contacts were not available in this low-turbidity water to accomplish removal by coagulation and sedimentation. These results indicate that the partially neutralized aluminum preparations were ineffective as coagulants under these conditions. However, because they can accomplish particle destabilization, they have potential application as filter aids when the filter media provide contact opportunities for particle removal.

**Summary.** The polymeric species in PACI:2.4 can destabilize turbid suspensions by functioning as cationic polyelectrolytes. Under conditions of high turbidity, acidic pH and low temperature, PACI:2.4 can destabilize suspensions at dosages that are less than those required for other aluminum preparations including alum. For turbid suspensions at neutral pH and moderate temperature, PACI:2.4 can be effective as other aluminum coagulants but not better than them. For low turbidity waters, there are insufficient contact opportunities to allow any polyelectrolyte to bring about substantial aggregation; some other particles must be added. This can be accomplished best with alum; the sulfate ion present in alum enhances the kinetics of precipitation of amorphous Al(OH)₃ and thereby enhances the kinetics of flocculation. PACI:2.4 has potential application as a destabilizing chemical ("filter aid") in the direct filtration of low turbidity waters, especially at low temperatures.

**Removal of Humic Substances**

The effectiveness of the four aluminum coagulant preparations in treating a water containing humic substances was evaluated with jar tests on a water containing an aquatic fulvic acid at a concentration of 8.4 mg DOC/L. Results are presented in Figures 17-20. Residual light absorbance at a wavelength of 254 nm is plotted as a function of the coagulant dosage (moles of aluminum/L, log scale).

Results for a water at a neutral pH (7) and a moderate temperature (20 °C) are presented in Figure 17. The effectiveness of the coagulants under these conditions may be represented as AlCl₃ ≈ alum > PACI:2.4 > PACI:3.0. Aluminum chloride and alum accomplished similar removals at aluminum dosages above about 2.5 x 10⁻⁴ M (log \( A_{1T} = -3.6; A_{1T} = 6.8 \text{ mg/L} \)). PACI:2.4 began to become effective at this dosage, but did not achieve the removals observed with both AlCl₃ and alum; it also produced overdosing and probable charge reversal at applications greater than 6 x 10⁻⁴ M (log \( A_{1T} = -3.2; A_{1T} = 17 \text{ mg/L} \)). PACI:3.0 provided modest removal and only at very high dosages. There are no advantages to the use of the partially neutralized preparations under these conditions; they did not do as well as the conventional coagulants.

The coagulation of humic substances at an acidic pH (5.5) and at moderate temperature (20 °C) is presented in Figure 18. The data indicate that the effectiveness of the four coagulants under these conditions may be depicted as alum > AlCl₃ > PACI:3.0 > PACI:2.4. Alum was the only coagulant that yielded acceptable results; alum dosages in excess of 2.5 x 10⁻⁴ M as aluminum (log \( A_{1T} = -3.6; A_{1T} = 6.8 \text{ mg/L} \)) were required. There were differences in effectiveness among the other three coagulants but none produced efficient removal by coagulation and sedimentation. Among the four preparations, aluminum chloride reacted best with the fulvic acid at low dosages (about 10⁻⁴ M; log \( A_{1T} = -4; A_{1T} = 2.7 \text{ mg/L} \)) but it achieved only about 60 percent removal and produced overdosing that was presumably due to the formation of positively charged colloidal particles.
Results for coagulation at neutral pH (7) and at low temperature (4 °C) are presented in Figure 19. The effectiveness of the four coagulants under these conditions can be considered as alum > AlCl₃ > PACl:2.4 > PACl:3.0. Both alum and AlCl₃ produced efficient removals, with alum being effective at somewhat lower dosages than AlCl₃. The partially neutralized preparation termed PACl:2.4 was effective in a narrow range of dosages around 5 x 10⁻⁴ M (log A₁T = -3.3; A₁T = 13.5 mg/L), and produced restabilization at higher applications. Comparing the results at pH 7 in Figures 17 and 19, somewhat lower dosages of alum and AlCl₃ are needed at 4 °C than at 20 °C.

Coagulation at low pH (5.5) and low temperature (4 °C) is depicted in Figure 20. Coagulant effectiveness may be described as alum > PACl:2.4 » PACl:3.0 « A1Cl₃. Alum was the only coagulant that produced acceptable results. Removal of fulvic acid by alum began at alum dosages of about 6 x 10⁻⁵ M as aluminum (log A₁T = -4.2; A₁T = 1.7 mg/L), but dosages of about 2.5 x 10⁻⁴ (log A₁T = -3.6; A₁T = 6.8 mg/L) were required for efficient removal. The difference between alum and A1Cl₃ is surprising, and it indicates that the sulfate anion has an important role in the removal of humic substances by aluminum under these conditions.

Summary. Considering the results in Figures 17-20, PACl:2.4 can interact with fulvic acid and produce removal by coagulation and sedimentation, but the removal was poor and the effective dosage range can be narrow. In contrast, alum performed acceptably under all conditions tested, even at high dosages, and AlCl₃ functioned well under some of the conditions investigated.

PICl Preparations

Four iron(III) coagulants were tested: PICl:0.5 (rOH = 0.5), PICl:1.5 (rOH = 1.5), an acidified 0.3-M solution of ferric chloride (FeCl₃), and a concentrated (1.5-M) solution of FeCl₃. The effectiveness of these chemicals for the removal of particles (turbidity) and humic substances (DOC, color) was evaluated in jar tests. The results are presented in the following sections.

Turbidity Removal

High turbidity. Results of jar tests for evaluating the effectiveness of these four coagulants for treating a water with a high turbidity produced by 50 mg/L of latex (350 ntu) are presented in Figures 21-24. Residual absorbance after flocculation and sedimentation is plotted as a function of the coagulant dosage (log scale). Coagulant dosages are expressed as moles of iron(III) per liter, denoted as M.

Results for the coagulation of a turbid water at a neutral pH (7) and a moderate temperature (20 °C) are presented in Figure 21. The effectiveness of the coagulants under these conditions may be represented as acidified 0.3 M FeCl₃ w 1.5 M FeCl₃ « PICl:0.5 > PICl:1.5. Acidified 0.3 M FeCl₃, concentrated FeCl₃, and PICl:0.5 accomplished similar removals of turbidity at dosages above about 10⁻⁵ M (log FeT = -5.0; FeT = 0.56 mg/L). Slightly higher dosages of PICl:1.5 were required; efficient removal of turbidity with this coagulant occurred at dosages above 1.6 x 10⁻⁶ M ((log FeT = -4.8; FeT = 0.88 mg/L). These results do not indicate any advantage in the use of partially neutralized ferric solutions as a coagulant under the conditions of these experiments.

Results for the coagulation of a turbid water at an acidic pH (5.0) and at moderate temperature (20 °C) are presented in Figure 22. These data indicate that the effectiveness of
FIGURE 17. Comparison of Four Aluminum Preparations in the Coagulation of Humic Substances (aquatic fulvic acid, 8.4 mg DOC/L; residual absorbance at 254 nm after flocculation and sedimentation is plotted as a function of the coagulant dosage expressed as moles of aluminum/L)
**FIGURE 18.** Comparison of Four Aluminum Preparations in the Coagulation of Humic Substances (aquatic fulvic acid; 8.4 mg DOC/L; residual absorbance at 254 nm after flocculation and sedimentation is plotted as a function of the coagulant dosage expressed as moles of aluminum/L)
pH = 7.0; T = 4 °C

- PACI:2.4
- Alum
- PACI:3.0
- Aluminum Chloride

**FIGURE 19.** Comparison of Four Aluminum Preparations in the Coagulation of Humic Substances (aquatic fulvic acid; 8.4 mg DOC/L; residual absorbance at 254 nm after flocculation and sedimentation is plotted as a function of the coagulant dosage expressed as moles of aluminum/L)
FIGURE 20. Comparison of Four Aluminum Preparations in the Coagulation of Humic Substances (aquatic fulvic acid; 8.4 mg DOC/L; residual absorbance at 254 nm after flocculation and sedimentation is plotted as a function of the coagulant dosage expressed as moles of aluminum/L)
**FIGURE 21.** Comparison of Four Iron(III) Preparations in the Coagulation of a Turbid Water (50 mg/L of 0.198 μm latex, 350 ntu; residual absorbance at 227 nm after flocculation and sedimentation is plotted as a function of the coagulant dosage expressed as moles of iron(III)/L)
**FIGURE 22.** Comparison of Four Iron(III) Preparations in the Coagulation of a Turbid Water (50 mg/L of 0.198 μm latex, 350 ntu; residual absorbance at 227 nm after flocculation and sedimentation is plotted as a function of the coagulant dosage expressed as moles of iron(III)/L)
the four coagulants under these conditions may be described as $\text{PIC1:0.5} > \text{acidified 0.3 M FeCl}_3 
\approx 1.5 \text{ M FeCl}_3 > \text{PIC1:1.5}$. \text{PIC1:0.5} was effective over a dosage range of $6 \times 10^{-6}$ to $1.1 \times 10^{-5}$ M ($\log F_e = -5.2$ to $-4.95$; $F_e = 0.35$ to $0.63$ mg/L). Acidified 0.3 M FeCl$_3$ and 1.5 M FeCl$_3$ had optimum dosages similar to PIC1:0.5 but were effective over slightly smaller ranges of coagulant dosage. These three iron(III) preparations appeared to act as cationic polyelectrolytes, neutralizing the negative charges on the latex particles at low dosages and inducing restabilization by adsorption to produce positively charged particles at higher dosages. Electrophoretic mobility measurements (Gray 1988) are consistent with this view. PIC1:1.5 was much less effective than the other iron(III) preparations, requiring dosages above $1.6 \times 10^{-5}$ M ($\log F_e = -4.8$; $F_e = 0.88$ mg/L) to produce efficient particulate removal. These results suggest a minor advantage for PIC1:0.5 over unneutralized FeCl$_3$ solutions as a coagulant under these conditions (high turbidity, slightly acidic pH, moderate temperature).

The coagulation of this turbid suspension at neutral pH (7) and at low temperature (4 °C) is depicted in Figure 23. The effectiveness of the four coagulant preparations under these conditions can be considered as $1.5 \text{ M FeCl}_3 > \text{acidified 0.3 M FeCl}_3 > \text{PIC1:0.5} > \text{PIC1:1.5}$. Concentrated (1.5 M) FeCl$_3$ was effective as a coagulant at dosages greater than about $10^{-5}$ M ($\log F_e = -5.0$; $F_e = 0.56$ mg/L); other coagulants required higher dosages, especially PIC1:1.5. Partial neutralization of ferric chloride solutions retarded coagulant effectiveness under these conditions (high turbidity, neutral pH, low temperature).

Results obtained at low pH (5) and low temperature (4 °C) are presented in Figure 24. Coagulant effectiveness can be stated as follows: acidified 0.3 M FeCl$_3$ $\approx \text{PIC1:0.5} \approx 1.5 \text{ M FeCl}_3 > \text{PIC1:1.5}$. \text{PIC1:0.5} and the two unneutralized FeCl$_3$ solutions were effective at low dosages, ranging from about $5 \times 10^{-5}$ M ($\log F_e = -5.3$ to $-4.95$; $F_e = 0.28$ to $0.63$ mg/L). Coagulation with PIC1:1.5 required higher dosages. The four preparations appeared to act as cationic polyelectrolytes, with optimum dosages corresponding to charge neutralization of the latex particles and with restabilization at higher coagulant dosages accompanied by charge reversal of the latex particles. As with the results at pH 5 and 20 °C (Figure 22), electrophoretic mobility measurements (Gray 1988) are consistent with this interpretation.

Low turbidity. The results of jar tests for evaluating the effectiveness of the four iron(III) coagulants for treating a water with a low turbidity produced with 1 mg/L of latex (7.2 ntu) are presented in Figures 25-28. In these jar tests, an extended flocculation period of 24 hours was used to provide sufficient mass transport or collision opportunities, and thus focus on the chemistry of the four coagulants as destabilizing agents. The results are not representative of flocculation practice in conventional treatment plants, where substantially higher coagulant dosages would be used for a low-turbidity water in order to form a precipitate of iron(III) hydroxide. They are suggestive, however, of coagulant dosages that could be considered in the direct filtration of a low-turbidity water.

The coagulation of this suspension under conditions of neutral pH (7) and moderate temperature (20 °C) is depicted in Figure 25. The effectiveness of the four coagulants may be represented as $1.5 \text{ M FeCl}_3 \approx \text{acidified 0.3 M FeCl}_3 > \text{PIC1:0.5} > \text{PIC1:1.5}$. The two unneutralized iron(III) preparations effectively neutralized the latex particles at very low dosages, above about $8 \times 10^{-7}$ M ($\log F_e = -6.1$; $F_e = 0.04$ mg/L). PIC1:0.5 was apparently effective over a narrow dosage range, whereas PIC1:1.5 was completely ineffective.

Results for a low-turbidity water destabilized at an acidic pH (5) and at moderate temperature (20 °C) are presented in Figure 26. All coagulants exhibited similar effectiveness and provided destabilization at dosages above $5 \times 10^{-7}$ M ($\log F_e = -6.3$; $F_e = 0.028$ mg/L). The results suggest that the four iron(III) coagulants function as destabilizing agents by
FIGURE 23. Comparison of Four Iron(III) Preparations in the Coagulation of a Turbid Water (50 mg/L of 0.198 μm latex, 350 ntu; residual absorbance at 227 nm after flocculation and sedimentation is plotted as a function of the coagulant dosage expressed as moles of iron(III)/L)
**FIGURE 24.** Comparison of Four Iron(III) Preparations in the Coagulation of a Turbid Water (50 mg/L of 0.198 μm latex, 350 ntu; residual absorbance at 227 nm after flocculation and sedimentation is plotted as a function of the coagulant dosage expressed as moles of iron(III)/L)
FIGURE 25. Comparison of Four Iron(III) Preparations in the Coagulation of a Low-Turbidity Water (1 mg/L of 0.198 μm latex, 7.2 ntu; residual absorbance at 227 nm after extended flocculation (24 hours) and sedimentation is plotted as a function of the coagulant dosage expressed as moles of iron(III)/L)
pH = 5.0; T = 20 °C

- **PICl:0.5**
- **acidified 0.3 M FeCl₃**
- **PICl:1.5**
- **1.5 M FeCl₃**

**FIGURE 26.** Comparison of Four Iron(III) Preparations in the Coagulation of a Low-Turbidity Water (1 mg/L of 0.198 μm latex, 7.2 ntu; residual absorbance at 227 nm after extended flocculation (24 hours) and sedimentation is plotted as a function of the coagulant dosage expressed as moles of iron(III)/L)
pH = 7.0; T = 4 °C

- PICl:0.5
- acidified 0.3 M FeCl₃
- PICl:1.5
- 1.5 M FeCl₃

**Figure 27.** Comparison of Four Iron(III) Preparations in the Coagulation of a Low-Turbidity Water (1 mg/L of 0.198 μm latex, 7.2 ntu; residual absorbance at 227 nm after extended flocculation (24 hours) and sedimentation is plotted as a function of the coagulant dosage expressed as moles of iron(III)/L)
forming cationic polyelectrolytes, leading to a dosage range of effective removal within which the charge on the latex particles is neutralized and to overdosing and charge reversal at higher coagulant applications.

The coagulation of this low-turbidity suspension at neutral pH (7) and at low temperature (4 °C) is presented in Figure 27. Under these conditions, the effectiveness of the four coagulants may be represented by 

\[ \text{PIC1:0.5} > \text{PIC1:1.5} > 1.5 \text{ M FeCl}_3 > \text{acidified 0.3 M FeCl}_3 \]

Dosages of 1.5 M FeCl₃ and acidified 0.3 M FeCl₃ above about 9 x 10⁻⁷ M (log Feₜ = -6.05; Feₜ = 0.05 mg/L) accomplished destabilization. With PIC1:0.5, for example, dosages above about 1.6 x 10⁻⁶ M (log Feₜ = -5.8; Feₜ = 0.09 mg/L) are required. Under these conditions (low turbidity, neutral pH, low temperature), partial neutralization of ferric chloride solutions impaired their effectiveness as destabilizing agents for solid particles.

Results obtained for the coagulation of this low-turbidity water at low pH (5) and at low temperature (4 °C) are presented in Figure 28. The effectiveness of the four coagulants under these conditions may be depicted as

\[ \text{PIC1:1.5 > PIC1:0.5 > 1.5 M FeCl}_3 > \text{acidified 0.3 M FeCl}_3 \]

Dosages of PIC1:1.5 as low as 5 x 10⁻⁷ M (log Feₜ = 6.3; Feₜ = 0.03 mg/L) accomplished destabilization, whereas substantially higher dosages of the three other coagulants were required. Under these conditions (low turbidity, low pH, and low temperature), partial neutralization of ferric chloride solutions appears to be useful.

Summary. For turbid waters at neutral pH, partial neutralization either has no effect on or slightly impairs the functioning of iron(III) preparations. For the coagulation of such turbid waters at acidic pH values, it is possible that partial neutralization may slightly broaden the dosage range over which iron(III) functions effectively. In the destabilization of low-turbidity waters for subsequent direct filtration, jar tests suggest that partial neutralization of ferric chloride solutions will not reduce iron(III) dosages.

Removal of Humic Substances

The effectiveness of three of the iron(III) preparations in treating waters containing two concentrations of humic substances was evaluated at two pH values and two temperatures. The coagulants tested were PIC1:0.5, acidified 0.3 M FeCl₃, and 1.5 M FeCl₃. Humic waters were prepared with an aquatic fulvic acid. A fulvic acid concentration characterized by 4 mg DOC/L was taken to represent a moderately humic water; a concentration of 10 mg DOC/L was used to represent a highly humic water. Temperatures were 20 and 4 °C; pH values were 7.0 and 5.0. Results are presented in Figures 29-36. Residual absorbance at a wavelength of 254 nm is plotted as a function of the coagulant dosage (moles of iron(III)/L, log scale).

Moderate humic concentration. Results for a moderately humic water (4 mg DOC/L) coagulated at neutral pH (7) and moderate temperature (20 °C) are presented in Figure 29. The three coagulants had similar effectiveness; all required a dosage of about 1.6 x 10⁻⁴ M (log Feₜ = -3.8; Feₜ = 8.8 mg/L). Partial neutralization of ferric chloride solutions did not enhance treatment under these conditions.

The absorbance of UV light (at 254 nm) by these waters under these conditions increased substantially as iron(III) was added in the dosage range from about 10⁻⁵ to 10⁻⁴ M. This is because iron(III) hydrolysis products are formed in solution, and they absorb light at the wavelength used in these experiments. In addition, solid particles are formed from iron(III) and humic substances. These particles can have sizes and refractive indexes that lead to scattering of the incident UV light, resulting in an apparent light absorbance. Reduction in light absorbance below the initial value (represented as 1.0 in this and similar figures) can, however,
**FIGURE 28.** Comparison of Four Iron(III) Preparations in the Coagulation of a Low Turbidity Water (1 mg/L of 0.198 μm latex, 7.2 ntu; residual absorbance at 227 nm after extended flocculation (24 hours) and sedimentation is plotted as a function of the coagulant dosage expressed as moles of iron(III)/L)
FIGURE 29 Comparison of Three Iron(III) Preparations in the Coagulation of a Moderately Humic Water (4 mg DOC/L; residual absorbance at 254 nm is plotted as a function of the coagulant dosage expressed as moles of iron(III)/L)
FIGURE 30. Comparison of Three Iron(III) Preparations in the Coagulation of a Moderately Humic Water (4 mg DOC/L; residual absorbance at 254 nm is plotted as a function of the coagulant dosage expressed as moles of iron(III)/L)
be taken to indicate removal of the humic substances in these experiments. Stated another way, increases in light absorbance at 254 nm did not indicate a formation of DOC, but reductions below initial values resulted from removal of humic substances by precipitation, aggregation, and sedimentation.

The coagulation of a moderately humic water at an acidic pH (5) and moderate temperature (20 °C) is presented in Figure 30. The three iron(III) coagulant preparations showed similar effectiveness; all produced effective removal of fulvic acid at iron(III) dosages above about 8 x 10^-5 M (log Fe_T = -4.1; Fe_T = 4.4 mg/L). Coagulant requirements were somewhat less than at pH 7 (compare Figures 29 and 30). Partial neutralization did not improve coagulant effectiveness under these conditions (moderate humic concentration, acidic pH, moderate temperature).

The coagulation of a moderately humic water at an acidic pH (5) and moderate temperature (20 °C) is presented in Figure 30. The three iron(III) coagulant preparations showed similar effectiveness; all produced effective removal of fulvic acid at iron(III) dosages above about 8 x 10^-5 M (log Fe_T = -4.1; Fe_T = 4.4 mg/L). Coagulant requirements were somewhat less than at pH 7 (compare Figures 29 and 30). Partial neutralization did not improve coagulant effectiveness under these conditions (moderate humic concentration, acidic pH, moderate temperature).

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Results for coagulation at neutral pH (7) and low temperature (4 °C) are presented in Figure 31. The performances of the three coagulant preparations were similar, although slightly higher dosages of PICl:0.5 may be needed. In general, under these conditions a coagulant dosage of about 10^-4 M (log Fe_T = -4; Fe_T = 5.6 mg/L) or higher was needed to accomplish effective removal.

The coagulation of a moderately humic water at low pH (5) and low temperature (4 °C) is depicted in Figure 32. Although the optimum dosages for the three coagulants are similar, PICl:0.5 was effective over a broader range of application. Effective removal with PICl:0.5 occurred over a dosage range from 4 x 10^-5 to 8 x 10^-5 M (log Fe_T = -4.4 to -4.1; Fe_T = 2.2 to 4.4 mg/L). Partial neutralization may provide some advantages in the coagulation of humic materials under these conditions (moderate humic concentration, low pH, low temperature).

High humic concentration. Results of the coagulation of a highly humic water (DOC = 10 mg/L) at neutral pH (7) and moderate temperature (20 °C) are presented in Figure 33. The effectiveness of the three coagulants may be represented as 1.5 M FeCl_3 ≈ acidified 0.3 M FeCl_3 > PICl:0.5. Dosages of the two unneutralized iron(III) preparations above about 2.2 x 10^-4 M (log Fe_T = -3.65; Fe_T = 12.5 mg/L) produced effective removal. Slightly higher dosages of FeCl:0.5 were required. Partial neutralization of the ferric chloride solutions did not enhance treatment under these conditions (high humic concentration, neutral pH, moderate temperature).

The coagulation of a highly humic water at an acidic pH (5) and moderate temperature (20 °C) is presented in Figure 34. All of the coagulant preparations that were tested yielded remarkably similar results. Effective removal was accomplished with all coagulants at iron(III) dosages above about 1.6 x 10^-4 M (log Fe_T = -3.8; Fe_T = 8.8 mg/L).

Results for coagulation at neutral pH (7) and low temperature (4 °C) are presented in Figure 35. The performances of the three coagulants were similar, although slightly higher dosages of PICl:0.5 may be needed. For the two unneutralized iron(III) preparations, effective coagulation occurred at iron(III) dosages above about 2 x 10^-4 M (log Fe_T = -3.7; Fe_T = 11 mg/L).

The coagulation of a highly humic water at an acidic pH (5) and moderate temperature (20 °C) is presented in Figure 34. All of the coagulant preparations that were tested yielded remarkably similar results. Effective removal was accomplished with all coagulants at iron(III) dosages above about 1.6 x 10^-4 M (log Fe_T = -3.8; Fe_T = 8.8 mg/L).

Results for coagulation at neutral pH (7) and low temperature (4 °C) are presented in Figure 35. The performances of the three coagulants were similar, although slightly higher dosages of PICl:0.5 may be needed. For the two unneutralized iron(III) preparations, effective coagulation occurred at iron(III) dosages above about 2 x 10^-4 M (log Fe_T = -3.7; Fe_T = 11 mg/L).

Coagulation in a highly humic water at low pH (5) and low temperature (4 °C) is depicted in Figure 36. The performance of the three coagulants was again similar, although slightly higher dosages of PICl:0.5 may be required and overdosing was observed in one jar with acidified 0.3 M FeCl_3. Coagulation with 1.5 M FeCl_3 and acidified 0.3 M FeCl_3 was effective at dosages above about 10^-4 M (log Fe_T = -4.0; Fe_T = 5.6 mg/L).
FIGURE 31. Comparison of Three Iron(III) Preparations in the Coagulation of a Moderately Humic Water (4 mg DOC/L; residual absorbance at 254 nm is plotted as a function of the coagulant dosage expressed as moles of iron(III)/L)
FIGURE 32. Comparison of Three Iron(III) Preparations in the Coagulation of a Moderately Humic Water (4 mg DOC/L; residual absorbance at 254 nm is plotted as a function of the coagulant dosage expressed as moles of iron(III)/L)
**FIGURE 33.** Comparison of Three Iron(III) Preparations in the Coagulation of a Highly Humic Water (10 mg DOC/L; residual absorbance at 254 nm is plotted as a function of the coagulant dosage expressed as moles of iron(III)/L)
Comparison of Three Iron(III) Preparations in the Coagulation of a Highly Humic Water (10 mg DOC/L; residual absorbance at 254 nm is plotted as a function of the coagulant dosage expressed as moles of iron(III)/L)
pH = 7; T = 4 °C

- PI: 0.5
- acidified 0.3 M FeCl₃
- 1.5 M FeCl₃

**FIGURE 35.** Comparison of Three Iron(III) Preparations in the Coagulation of a Highly Humic Water (10 mg DOC/L; residual absorbance at 254 nm is plotted as a function of the coagulant dosage expressed as moles of iron(III)/L)
FIGURE 36. Comparison of Three Iron(III) Preparations in the Coagulation of a Highly Humic Water (10 mg DOC/L; residual absorbance at 254 nm is plotted as a function of the coagulant dosage expressed as moles of iron(III)/L)
Summary. Partial neutralization of ferric chloride solutions ($r_{OH} = 0.5$) did not influence the effectiveness of FeCl$_3$ as a coagulant for humic substances in most of the cases tested. In some situations, in fact, partial neutralization appeared to result in a slight increase in coagulant requirements. At low temperature, acidic pH, and moderate DOC concentration, partial neutralization may improve removal efficiency and broaden the dosage range of effective coagulation compared with unneutralized solutions (Figure 32).

DIRECT FILTRATION TESTS

Some results of experiments to evaluate PAC1:2.4 as a "filter aid" in direct filtration are presented first, followed by results for iron(III) preparations (Gray 1988).

**PAC1**

Results of a direct filtration experiment designed to compare the effectiveness of PAC1:2.4 with alum in the treatment of a low turbidity water (1 mg latex/L) at a pH of about 5.4 and at room temperature (21.5 °C) are presented in Figure 37. A low coagulant dosage ($10^{-6}$ M; log $A_{l_T} = -6.0$; $A_{l_T} = 0.027$ mg/L) was selected to destabilize the suspension. With successful destabilization, the particles could then adhere to the glass beads used as filter media and, as filtration proceeded, adhere to previously retained latex particles. The results indicate that both aluminum preparations accomplished destabilization of the influent suspension, with PAC1:2.4 accomplishing slightly better initial removal and better ripening as the run progressed.

Results of a similar direct filtration of a low-turbidity water, this time conducted at a pH of 7.0, are presented in Figure 38. The dosage selected for each coagulant was only $3.2 \times 10^{-7}$ M (log $A_{l_T} = -6.5$; $A_{l_T} = 0.009$ mg/L). In this case PAC1:2.4 accomplished effective destabilization of the latex suspension, permitting attachment of the latex particles to the initial filter media and subsequently to previously retained latex particles as the filter ripened. Alum was not effective as a filter aid under these conditions at a dosage of $3.2 \times 10^{-7}$ M as aluminum.

Results of the direct filtration of a water containing a low turbidity (1 mg latex/L) and a moderate concentration of aquatic fulvic acid (4 mg DOC/L) comparing PAC1:2.4 and alum at a pH of 5.5 and room temperature (21.5 °C) are presented in Figure 39. A dosage of $10^{-4}$ M as aluminum (log $A_{l_T} = -4.0$; $A_{l_T} = 2.7$ mg/L) was used for both coagulants. Absorbance at a wavelength of 227 nm is plotted as a function of filtration time. Measurements of turbidity and of absorbance at 254 nm were also made and provided similar results. These observations confirmed that PAC1:2.4 reacts with and precipitates fulvic acid at a pH of 5.5. Initial removal was good; the ripening period was short; and effluent quality gradually deteriorated over time. Removal with alum was very poor; almost no removal occurred.

**PIC1**

Comparison of two iron(III) preparations as "filter aids" in the direct filtration of a low-turbidity water (1 mg latex/L) at pH 5.0 and room temperature (21.5 °C) is presented in Figure 40. Turbidity remaining in the filter effluent is plotted as a function of filtration time. PIC1:0.5 was compared with 1.5 M FeCl$_3$, a solution representative of commercial ferric chloride. A dosage of $10^{-6}$ M (log $F_{e_T} = -6.0$; $F_{e_T} = 0.056$ mg/L) was used for both iron(III) preparations. Both coagulants produced similar initial removals and similar ripening characteristics during the first 240 min of the experiment. The effluent of the filter receiving iron(III) from a stock solution of 1.5 M FeCl$_3$ stopped ripening and fluctuated after that time. This is thought to be
FIGURE 37. Comparison of Two Aluminum Preparations in the Direct Filtration of a Low-Turbidity Water (1 mg latex/L, 7.2 ntu; absorbance at 227 nm remaining in the filter effluent is plotted as a function of filtration time; dosages of both coagulants = $10^{-6}$ M (log Al estimated $\approx -6.0$; Al concentration $= 0.027$ mg/L))
FIGURE 38. Comparison of Two Aluminum Preparations in the Direct Filtration of a Low-Turbidity Water (1 mg latex/L, 7.2 ntu; absorbance at 227 nm remaining in the filter effluent is plotted as a function of filtration time; dosages of both coagulants = $3.2 \times 10^{-7}$ M ($\log Al_T = -6.5; Al_T = 0.009$ mg/L))
FIGURE 39. Comparison of Two Aluminum Preparations in the Direct Filtration of a Low-Turbidity (1 mg latex/L latex), Moderately Humic (4 mg DOC/L) Water (absorbance at 227 nm remaining in the filter effluent is plotted as a function of filtration time; dosages of both coagulants = $10^{-4}$ M (log $Al_T = -4.0$; $Al_T = 2.7$ mg/L))
FIGURE 40. Comparison of Two Iron(III) Preparations in the Direct Filtration of a Low-Turbidity Water (1 mg latex/L; residual turbidity remaining in the filter effluent is plotted as a function of filtration time; dosages of both coagulants = $10^{-6}$ M as iron(III) ($\log Fe_T = -6.0$; $Fe_T = 0.056$ mg/L))
FIGURE 41. Comparison of Two Iron(III) Preparations in the Direct Filtration of a Low-Turbidity (1 mg latex/L), Moderately Humic (4 mg DOC/L) Water (absorbance at 254 nm remaining in the filter effluent is plotted as a function of filtration time; the dosage of each coagulant was increased in a stepwise manner, from 0 at the start of the run to $1.8 \times 10^{-4}$ M at the end of the experiment)
caused by experimental variations in coagulant dosage and influent pH.

Experimental results for the direct filtration of a low-turbidity (1 mg latex/L), moderately humic (4 mg DOC/L) water at a pH of approximately 5 at room temperature (21.5 °C) are presented in Figure 41. FeCl:0.5 and 1.5 MFeCl₃ were again compared as filter aids. In this experiment, the dosage of each coagulant was increased at about half-hour intervals, beginning at a dosage of 0 and terminating at a dosage of 1.8 x 10⁻⁴ M as iron(III). Absorbance at a wavelength of 254 nm is plotted as a function of filtration time. This type of experiment is useful for determining the dosage requirements of a chemical for use as a filter aid. As the dosage of each coagulant was increased from 0 to 0.72 x 10⁻⁴ M, filtrate quality deteriorated. Iron(III) reacted with the latex particles and also with the fulvic acid, but the resulting products did not filter well. With both iron(III) preparations, an optimum dosage of 0.9 x 10⁻⁴ M as iron(III) (log Fe_T = 5.0 mg/L) was observed. Effluent quality was excellent. As the coagulant dosage was increased above this value, filtrate quality deteriorated substantially. In this experiment, the pH of the influents to the filters varied with the dosage of iron(III), so that the results at the higher dosages represent pH values less than 5. The results do indicate that the optimum dosages of the two preparations for the direct filtration of this water are equal.
CHAPTER 5
DISCUSSION

Evaluations of the studies of characterization of the coagulant species, of coagulant effectiveness, and of direct filtration are presented. For each of the three studies, results for aluminum and iron(III) coagulants are discussed separately and then compared.

CHARACTERIZATION OF THE COAGULANTS

Discussion of the results of the PACl experiments is presented first, followed by evaluation of the PICl experiments and a comparison of the two metal coagulants. Discussions of the PACl and PICl experiments are derived from the works of Yao (1987) and Gray (1988), respectively.

PACl Preparations

The results of the ferron assays show that it was possible to prepare partially neutralized solutions of aluminum chloride comprised primarily of polymeric aluminum species when the degree of neutralization (r OH) was in the order of 2.4. The solutions were stable for several days to a few weeks. Ultrafiltration experiments indicated that the size of the polymeric species was between 1 and 2 nm. Both of these experimental findings are consistent with the formation of "Al13 species" (e.g., Al13O4(OH)24+) in the solutions termed PACl:2.4 in this research. This specie has a size of about 1.2 nm. These results are consistent with many other reports in the literature as exemplified by the work of Parthasarathy and Buffle (1985) and the studies of Bottéro and coworkers (e.g., Bottéro et al. 1980; Bottéro et al. 1982; Bottéro et al. 1987). Based on radiation scattering techniques, Bottéro et al. (1987) concluded that these Al13 species aggregate into linear clusters as r OH is increased above 2.3. This observation was not supported by the ultrafiltration measurements in this research, because the polymeric specie passed through the 2-nm membrane filter. Either aggregates of the Al13 specie did not form in these preparations or the ultrafiltration process broke the aggregates apart during filtration.

Other factors can affect aluminum speciation in partially neutralized aluminum chloride solutions, but are usually less significant. These include the type and concentration of the base used for neutralization, the strength of the aluminum chloride solution, the mixing intensity, the rate of base addition, time, and temperature. These factors were not significant over the range of conditions studied in this research.

Sulfate ions were not present in the preparations produced in this research. At concentrations such as those in alum (molar ratio of sulfate to aluminum equal to 1.5), sulfate causes rapid precipitation of amorphous Al(OH)3 at low values of r OH and prevents the formation of stable aluminum polymers. At much lower concentrations (e.g., at SO4/AlT of 0.1 to 0.2), it is possible that sulfate may facilitate the formation of polymeric aluminum species that differ from the Al13 polymer that was probably formed in this research. The formation and use of such preparations was not studied. A study of the effects of sulfate on partially neutralized aluminum coagulants is being conducted under the sponsorship of the AWWA Research Foundation at the Pennsylvania State University by Brian A. Dempsey.
**Particulate Preparations**

The results of the ferron assays (Figure 7) indicate that it was not possible to prepare partially neutralized solutions of ferric chloride that were comprised primarily of medium to large polymeric iron(III) species. These results, based on chemical reactivity, are consistent with the physical separations in the filtration tests (Figure 8) when iron(III) species that passed through the 2-nm ultrafiltration membrane are considered to be primarily monomers or perhaps dimers and trimers.

Tang and Stumm (1987a, 1987b) studied the preparation and use of partially neutralized iron(III) preparations as coagulants. Their results are most conveniently discussed in terms of the average number of hydroxides bound per iron(III) atom in a preparation, denoted as \( \bar{n} = \frac{\text{OH}_{\text{bound}}}{\text{Fe}_T} \). Because iron(III) solutions hydrolyze without addition of base, \( \text{OH}_{\text{bound}} \) can be greater than \( \text{OH}_{\text{added}} \) in a preparation, with the result that \( \bar{n} \) is somewhat greater than \( r_{\text{OH}} \). The difference is often small, so that in many cases the two measures of neutralization are taken as equal. Tang and Stumm reported that optimum coagulation of turbidity occurred for iron(III) preparations with \( 0.5 < \bar{n} < 1.0 \).

In this research, partially neutralized iron(III) solutions contained either monomers and perhaps small polymers at low values of \( r_{\text{OH}} \) or a colloidal precipitate that dominated iron(III) speciation at \( r_{\text{OH}} \) above about 1.0. Based on these results and the work of Tang and Stumm (1987a, 1987b), two partially neutralized iron(III) preparations were evaluated in the coagulation studies. These preparations had values of \( r_{\text{OH}} \) equal to 0.5 and 1.5. The first contained primarily monomers, and perhaps small polymers, and is considered similar to the preparation found most active by Tang and Stumm. The second was comprised primarily of a rather stable colloidal precipitate of iron(III) hydroxide.

**Comparison**

Partially neutralized solutions of aluminum chloride that contain stable cationic polymeric species such as \( \text{Al}_{13} \) are readily prepared under a variety of experimental conditions as long as the degree of neutralization (\( r_{\text{OH}} \)) is about 2.4 or slightly higher. In contrast, similar solutions could not be prepared by partial neutralization of ferric chloride under a fairly wide range of experimental conditions. It appears that the hydrolysis reactions of aluminum and iron(III) and probably the nucleation and growth of aluminum and iron(III) precipitates have significant differences.

There is substantial agreement in the literature about the kinetic stability of the \( \text{Al}_{13} \) cationic polymeric species in solutions otherwise oversaturated with respect to the precipitation of a crystalline aluminum oxide phase such as gibbsite. This research on aluminum speciation primarily confirms the ability of the investigators to reproduce such polymeric aluminum species for use in coagulation and direct filtration tests.

There is less agreement in the literature about the processes of iron(III) hydrolysis and precipitation. Leprince et al. (1984), for example, reported the presence of small, medium, and large polymers in partially neutralized iron(III) chloride preparations up to \( r_{\text{OH}} = 2.5 \), and indicated that iron(III) performed best as a coagulant when preparations with \( r_{\text{OH}} = 2.5 \) were used. This research suggests that such preparations contain primarily a positively charged colloidal precipitate of an amorphous iron(III) hydroxide.

Schneider has reviewed the processes of hydrolysis, nucleation, growth, and aging of iron(III) species in aqueous systems (Schneider 1984; Schneider and Schwy 1987). Starting
with hydrated ferric ions in aqueous solution \([\text{Fe}(\text{H}_2\text{O})_{\text{j}}^+], \text{positively charged monomeric, dimeric, and polymeric species that undergo a variety of reactions, including some general and specific anion interactions, are formed. In chloride media, these investigators indicate that the formation of mononuclear hydrolysis species and the dimer written as \text{Fe}_2(\text{OH})_2^+ is rapid. At values of \(r_{\text{OH}} \text{ less than about 0.5, this positively charged dimer is rather inert to transition or growth to a trimer. Nevertheless, precipitation is observed in such solutions, and it is ascribed to heterogeneous nucleation by particles in the system. At \(r_{\text{OH}} \text{ values above 0.5, homogeneous precipitation occurs. This is ascribed to the very rapid formation of small polynuclear species with little or no charge [e.g., a trimer such as \text{Fe}_3(\text{OH})_9] in the mixing zone to which base is added in the titration of an acidic iron(III) solution. These small polymers serve as nuclei for the growth of very large polymers and also precipitates in the bulk solution. The distinction between large polynuclear species and a solid precipitate is not a rigorous one; the large polynuclear materials observed by Schneider and coworkers contained from 2,000 to about 40,000 iron(III) atoms and would be classified as colloidal precipitates by the operations procedures used in this research. The conclusions of Schneider and the observations in the present study appear to be consistent. Nuclei are formed in preparing iron(III) solutions with values of \(r_{\text{OH}} \text{ greater than about 0.5, and these nuclei rapidly lead to the formation of materials of colloidal size.}

The speed and complexity of the reactions of iron(III) in forming monomers, dimers, and trimers may account for the apparent disagreement in the characterizations of the iron(III) preparations by ferron and by ultrafiltration in this research (Table 4). The size of iron(III) trimers are near the apparent pore size of the small (1-nm) membrane used in the filtration studies, so that small changes in polymerization or surface-catalyzed reactions at the membrane surface could result in apparent differences in iron(III) speciation as estimated by chemical reactivity (ferron) and physical separation (ultrafiltration).

**COAGULATION**

Discussion of the performance of aluminum preparations is presented first, followed by evaluation of iron(III) preparations and a comparison of the two metal coagulants. For each metal coagulant, effectiveness in removing turbidity and humic materials is considered, as well as the effects of contaminant concentration, pH, and temperature on coagulant selection and performance. Discussions of the aluminum and iron(III) experiments are derived from the works of Yao (1987) and Gray (1988), respectively.

**Aluminum Coagulants**

Some of the results contained in Figures 9–20 are summarized in Table 5. For each set of experimental conditions (turbidity, humic concentration, pH, and temperature), the minimum dosage of each aluminum coagulant required to remove 80 percent of the initial absorbance by coagulation and sedimentation in jar tests is tabulated for comparison and discussion in the following sections of this report. Coagulant dosages are expressed as \(\log A_{1\text{T}}, \text{with } A_{1\text{T}} \text{ in moles of aluminum/L.}

The results in Table 5 indicate the principal applications in the coagulation process of partially neutralized aluminum chloride solutions such as PACl2.4. For the coagulation of waters with high turbidity at low temperatures, PACl2.4 produces effective coagulation at lower dosages than the other coagulants tested. It also offers advantages in the coagulation of turbid waters at acidic pHs, so that turbid, low-alkalinity waters can be treated efficiently with it. For most other water quality conditions, alum is the coagulant of choice among aluminum
preparations when removal by coagulation and sedimentation is desired.

**TABLE 5**

Comparison of Four Aluminum Preparations in Coagulation*

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<tr>
<th>Latex mg/L</th>
<th>DOC mg/L</th>
<th>pH</th>
<th>T °C</th>
<th>Coagulant Dosage (log A1 T)</th>
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<th>Alum</th>
<th>PAC1:3.0</th>
<th>AlCl3</th>
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* Aluminum dosages required to remove 80 percent of the absorbance caused by latex particles (227 nm) or fulvic acid (254 nm) in jar tests, taken from Figures 9-20; aluminum dosages are expressed as the logarithm of the total aluminum concentration (log A1 T), with A1 T in moles/L; for each set of experimental conditions, the lowest coagulant dosage is underlined.

**Turbidity Removal**

PAC1:2.4 is a preparation comprised predominantly of a fairly small cationic polyelectrolyte such as Al13. It has application as a coagulant when particle destabilization, and not interparticle contact opportunities, limits the overall process of particle aggregation. Consequently, it is effective in the treatment of turbid waters (Table 5, Figures 9-12). While the Al13 species is often represented as Al13(OH)24+, it is probable that the actual charge on the molecule varies with pH, decreasing as the pH increases. As a result, the required dosage for neutralization of the charge on negative particles increases as the pH is increased, e.g., from 5.5 to 7 (compare Figure 10 with 9 and also Figure 12 with 11; see also Table 5). For turbid suspensions, it appears that the cationic polymers present in PAC1:2.4 are more effective under most conditions than the coagulant species formed in situ when alum or AlCl3 are used. The advantages of PAC1:2.4 are particularly apparent in the coagulation of turbid waters at low
temperatures, suggesting that the hydrolysis reactions of alum and AlCl₃ are slowed considerably at low temperatures so that the use of preformed aluminum polymers is beneficial.

Cationic polyelectrolytes react with surfaces in a variety of ways in addition to electrostatic interaction, and they normally can adsorb in amounts greatly exceeding the original negative charge on particles. As a result, they can stabilize most suspensions by producing positively charged surfaces at high dosages, a result that is often termed charge restabilization. Such charge restabilization is most effective under conditions that enhance the charge on the cationic polyelectrolyte. For PAC₃:2.4, this occurs at low pH, so that restabilization is most pronounced under these conditions. This is illustrated by a comparison of Figures 9 and 10 and also Figures 11 and 12. For example, a dosage of PAC₃:2.4 of 4 x 10⁻⁵ M (log Al₃ = -4.4; Al₃ = 1.1 mg/L) brings about effective coagulation of a suspension of 100 mg latex/L at a pH of 7.0 and a temperature of 20 °C (Figure 9). The same dosage in the same water at pH 5.5 is much too large, and the system is completely restabilized (Figure 10). The width of the region of optimum dosage narrows as the pH is decreased and the charge on the polyelectrolyte increases. This would require more attention to and control of chemical dosage in a full-scale treatment plant.

A coagulant preparation designed to maintain small cationic polyelectrolytes in solution for a time sufficient to destabilize particles will not function effectively when rapid precipitation of amorphous Al(OH)₃ is desired. As a result, PAC₃:2.4 is not an effective coagulant for the treatment of low-turbidity waters by coagulation and sedimentation. Alum is the coagulant of choice. The sulfate present in alum may increase nucleation, growth, and aggregation in the precipitation of amorphous Al(OH)₃. Results for the coagulation of a low-turbidity water (Figures 13-16) are consistent with this view. Although low pH may impair the kinetics of precipitation of amorphous Al(OH)₃, alum remains the coagulant of choice for the treatment of waters that are low in turbidity under these conditions. Coagulant dosages (Table 5) required to precipitate Al(OH)₃ in a low-turbidity water (1 mg latex/L) are, in general, larger than the dosages needed to destabilize the negative particles in a turbid water (100 mg latex/L).

Humic Substances

The results presented in Figures 17-20 and in Table 5 indicate that alum is the coagulant of choice for the humic water used in these experiments (DOC = 8.4 mg/L) at all pH values and temperatures tested. Possible reasons for this merit discussion.

Humic substances can be considered anionic polyelectrolytes. Studies have shown that they can be precipitated and aggregated by synthetic organic cationic polyelectrolytes (e.g., Narkis and Rebhun 1977; Edzwald et al. 1977; Glaser and Edzwald 1979). Results with PAC₃:2.4 in this research are similar to those produced by synthetic organic cationic polyelectrolytes. At all pH values and temperatures investigated, jar tests with PAC₃:2.4 (Figures 17-20) show a region of underdosing in which removal increases with increasing coagulant dose, an optimum dosage, and a region of overdosing in which removal deteriorates with increasing addition of PAC₃:2.4. Clearly the aluminum species in PAC₃:2.4 react with fulvic acid and do so in a manner characteristic of a cationic polyelectrolyte.

Compared with alum, however, PAC₃:2.4 requires larger dosages to produce maximum effectiveness. It also accomplishes less removal than alum, even when added at its optimum dosage. The first observation, i.e., that alum is effective at lower dosages than PAC₃:2.4, indicates that the species produced by alum are more reactive with humic substances than the Al₁₃ specie in PAC₃:2.4. The second observation, i.e., that PAC₃:2.4 produces less removal than alum at its optimum dosage, may have a physical explanation. The precipitation and
aggregation of the small anionic fulvic polyelectrolytes by the small cationic Al\textsubscript{13} specie (the molecular weights of the two substances are comparable) could produce a loose, porous network of particles that is light and fragile, thereby impairing removal by slow mixing (flocculation) and sedimentation.

The success of alum in accomplishing effective removal of fulvic acid over a wide range of conditions is very important in practice; it is also a complex process that is difficult to explain. The interactions of aluminum and humic substances are reported to be dependent on aluminum dosage, humic concentration, pH, and sulfate concentration (e.g., Dempsey et al. 1984; Dempsey et al. 1985; Hundt and O'Melia 1988). Temperature should probably be added to this list. At low pH, e.g. <5, humic substances can be removed to some extent by direct precipitation with monomeric aluminum species. Between pH 5 and 6, fulvic acid can be precipitated by polymers of aluminum that are either added to the water or formed in situ when the DOC concentration is low, and the required aluminum dosage is correspondingly low. At neutral pH it is generally considered that humic substances adsorb on amorphous aluminum hydroxide that forms readily when alum is added to water at this pH. At pH values from 6 to 7 and also from 5 to 6 in highly humic waters, both of these processes are thought to occur simultaneously.

Additions of aluminum chloride, preformed small cationic polymers (PACI:2.4), and a colloidal precipitate of amorphous Al(OH)\textsubscript{3} (PACI:3.0) were all much less effective than alum in treating the humic water containing fulvic acid at a concentration of 8.4 mg DOC/L (Table 5). This suggests that the presence of sulfate in alum has an important effect in the treatment of such waters. Sulfate is involved in the nucleation, growth, and aggregation of amorphous Al(OH)\textsubscript{3}, and its presence at substantial concentrations is important in the removal of humic substances by aluminum. At an alum dosage of 2.5 x 10\textsuperscript{-4} M (log Al\textsubscript{T} = -3.6; Al\textsubscript{T} = 6.8 mg/L), the concentration of added sulfate is 3.8 x 10\textsuperscript{-4} M or 37 mg/L. The results of this research are consistent with a removal of humic substances from highly humic waters that accompanies the in situ precipitation of amorphous Al(OH)\textsubscript{3} at pH values of 5.5 and 7 and at temperatures of 20 and 4 °C, with this in situ precipitation being catalyzed by sulfate ions.

It is very important to note that the requirements for aluminum coagulants in practice will often be determined by the content of natural organic matter in a water supply rather than by turbidity. At pH 7.0 and a temperature of 20 °C, for example, a water containing 8.4 mg DOC/L requires an alum dosage of 2.5 x 10\textsuperscript{-4} M as aluminum (log Al\textsubscript{T} = -3.6; Al\textsubscript{T} = 6.8 mg/L), whereas a water containing 100 mg latex/L with a turbidity of 538 ntu requires an alum dosage of only 2 x 10\textsuperscript{-5} M as aluminum (log Al\textsubscript{T} = -4.7; Al\textsubscript{T} = 0.54 mg/L; see Table 5).

Temperature Effects

In most of the cases, low temperature either had no effect on coagulation or resulted in a lowering of the required dosage. Considering the coagulation of a turbid water with PACI:2.4, the aluminum coagulant of choice for such waters, a reduction in the temperature from 20 to 4 °C resulted in a lowering of the required coagulant dosages by a factor of about 5 at pH values of both 7.0 and 5.5 (Table 5). Alum is the aluminum coagulant of choice in the treatment of low-turbidity waters and also of humic waters. For the low-turbidity water in which the precipitation of amorphous Al(OH)\textsubscript{3} is needed, the required alum dosage at pH 7 was lower at 4 °C than at 20 °C, whereas at pH 5.5 it was slightly higher (Table 5). In the coagulation of the humic water, alum dosages at 4 °C were equal to or less than those at 20 °C at pH values of 7.0 and 5.5.

These results suggest that slowing the hydrolysis and precipitation reactions of aluminum
in water is beneficial, perhaps by permitting aluminum species to react more extensively with turbidity and with humic substances. Difficulties encountered in practice in treating waters at cold temperatures, at least down to 4 °C, may then be the result of physical limitations such as short-circuiting in such processes as sedimentation or, in some cases, changes in raw water quality.

**pH Effects**

When coagulation is to be accomplished by the destabilization of negatively charged turbidity with positively charged aluminum polymers, as in the treatment of suspensions containing 100 mg latex/L by PACl:2.4 in this research, coagulant dosages are lower at pH 5.5 than at pH 7.0 (Table 5). This is primarily because the charge on the polymeric aluminum species is higher at the lower pH. When coagulation is to be accomplished by the precipitation of amorphous Al(OH)₃ to enhance the kinetics of flocculation, as in the treatment of suspensions containing 1 mg latex/L by alum in this research, coagulant dosages are lower at pH 7.0 than at pH 5.5 (Table 5). This is because the precipitation kinetics of solid Al(OH)₃ are most rapid in the neutral pH region in which the water is most oversaturated with respect to the formation of a solid aluminum oxide or hydroxide phase.

The effects of pH on coagulant dosage in the treatment of the humic water in this research were slight (Table 5). The water that was treated had a fairly high DOC (8.4 mg/L). Although it appears that aggregates are formed by direct precipitation of fulvic acid with aluminum polymers at pH 5.5 (e.g., Figure 20), they do not settle well and removal is limited. It is possible that positive charge to react with the humic substances and the simultaneous formation of an aluminum hydroxide phase are both needed to react with and to remove fulvic acids at this concentration. Charge is promoted at pH 5.5 and precipitation of amorphous Al(OH)₃ is favored at pH 7.0; these effects may counterbalance each other in the humic water being treated, so that the overall effect of pH on coagulant requirements is not large.

**Iron(III) Coagulants**

Some of the results contained in Figures 21-36 are summarized in Table 6. For each set of experimental conditions (turbidity, humic concentration, pH, and temperature), the minimum dosage of each iron(III) coagulant required to remove 80 percent of the initial absorbance by coagulation and sedimentation in jar tests is tabulated for comparison and discussion in the following sections of this report. Coagulant dosages are expressed as log Feₜ, with Feₜ in moles of iron(III)/L.

The results in Table 6 for iron(III) coagulant preparations are much less systematic than those presented in Table 6 for aluminum preparations. Differences in dosage requirements among the iron(III) preparations are much smaller than those observed with aluminum. Although PICl:1.5 is less effective than the three other preparations for the destabilization of the turbid water containing 50 mg latex/L, no other large differences emerged among the four coagulants in the treatment of waters with low turbidity or moderate to high concentrations of aquatic fulvic acid.

**Turbidity Removal**

Coagulation of a turbid water (e.g., 50 mg latex/L, 350 ntu) is expected to be accomplished at low dosages by iron(III) preparations that either contain substantial concentrations of preformed cationic polyelectrolytes or that can form them in situ. Although none of the preparations used in this research contained a high proportion of cationic poly-
TABLE 6
Comparison of Four Iron(III) Preparations in Coagulation*

<table>
<thead>
<tr>
<th>Latex mg/L</th>
<th>DOC mg/L</th>
<th>pH</th>
<th>T °C</th>
<th>PICl:0.5</th>
<th>Acidified 0.3M FeCl₃</th>
<th>PACl:1.5</th>
<th>1.5M FeCl₃</th>
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* Iron(III) dosages required to remove 80 percent of the absorbance caused by latex particles (227 nm) or fulvic acid (254 nm) in jar tests with membrane filtration of the supernatants, taken from Figures 21-36; iron(III) dosages are expressed as the logarithm of the total iron(III) concentration (log Feₜ) with Feₜ in moles/L; for each set of experimental conditions, the lowest coagulant dosage is underlined.

+ Optimum dosage, but removal of absorbance was less than 80 percent; see Figure 32.

Electrolytes, it appears that PICl:0.5, acidified 0.3 M FeCl₃, and 1.5 M FeCl₃ were able to form them in situ, thereby destabilizing the latex particles and allowing their effective aggregation and sedimentation. PICl:1.5, a preparation that contained a significant fraction of iron(III) as a colloidal precipitate, was less effective in the treatment of this turbid suspension (Table 6). Required dosages of the three most effective preparations decrease with a decrease in pH from...
7.0 to 5.0 (Table 6), a trend to be expected when cationic polyelectrolytes are active in the aggregation of negative particles. Required dosages also decrease with a decrease in temperature from 20 to 4 °C, suggesting that low temperatures slow the hydrolysis and precipitation reactions of iron(III) and enable hydrolyzed iron(III) species formed in situ to adsorb and destabilize the latex particles.

Jar tests to evaluate the effectiveness of the four iron(III) preparations in the treatment of a low-turbidity water were modified from normal practice. A period of slow flocculation stirring for 24 hours was used; this is much longer than the normal time of about 0.5 hour. The long flocculation time was adopted to provide sufficient contact opportunities in flocculation so that aggregation would be limited by chemical destabilization rather than physical interparticle mass transport. As a result, the data in Table 6 and in Figures 25–28 can be taken as estimates of chemical requirements for a direct filtration process for this low-turbidity water. The dosages listed for the low-turbidity water in Table 6 could provide particle destabilization, with the media in a packed bed providing contact opportunities for turbidity removal in direct filtration. Under conditions that would promote the unwanted precipitation of amorphous Fe(OH)₃ (pH = 7.0 and temperature = 20 °C), the unneutralized iron(III) preparations (acidified 0.3 and 1.5 M FeCl₃) were more effective at lower dosages than the partially neutralized ones (PICl:0.5 and PICl:1.5). This suggests that partial neutralization enhanced in situ precipitation of amorphous Fe(OH)₃ and impaired particle destabilization under these conditions. Partial neutralization also led to higher chemical requirements in coagulation at 4 °C and pH 7.0 (Table 6). Under acidic conditions at a pH of 5.0 and a temperature of 20 °C, chemical requirements were similar for all coagulants, including PICl:1.5, although overdosing was observed only with the unneutralized preparations (Figure 26). Finally, under conditions that most severely retarded iron(III) hydrolysis and precipitation (pH = 5.0 and temperature = 4 °C), PICl:1.5 performed somewhat better than the other preparations (Figure 28). These results indicate some possible advantages to partially neutralizing iron(III) chloride solutions for the direct filtration of low-turbidity waters under very specific conditions of temperature and pH.

Humic Substances

Results of the coagulation of fulvic acid at two DOC concentrations with three iron(III) preparations at two pH values and two temperatures show many more similarities than differences in coagulant requirements (Table 6, Figures 29–36). There are almost no differences among the dosage requirements of the three coagulants under comparable solution conditions. One possible exception is in the coagulation of the moderately humic water (4 mg DOC/L) at pH 5.0 and a temperature of 4 °C (Figure 32). For each coagulant, a region of underdosing, an optimum dosage, and a region of overdosing are observed, and they occur at similar iron(III) dosages. Optimum dosages are very similar, but PICl:0.5 is the only coagulant to produce a removal of absorbance in excess of 80 percent.

For each coagulant, dosage requirements at a pH of 5.0 are slightly less than at a pH of 7.0, indicating that the charge of the iron(III) species is a factor in their reaction with the fulvic acid (Table 6). For each coagulant, dosage requirements for the highly humic water are slightly greater than for the moderately humic water, indicating some stoichiometry in the processes involved. For each coagulant, dosage requirements at 4 °C are generally the same or very slightly lower than at 20 °C for otherwise comparable conditions, suggesting that rapid precipitation of amorphous Fe(OH)₃ is not a requirement for effective removal.

The overall process by which iron(III) reacts with fulvic acid and permits its subsequent removal by sedimentation cannot be determined unambiguously from the experimental results.
obtained in this research. In the absence of sufficient data, the following is proposed. Iron(III) monomers and small polymers react with fulvic acid and induce its precipitation, especially at low pH. Simultaneously, amorphous Fe(OH)$_3$ is formed in all waters because they are oversaturated with respect to the precipitation of an iron(III) oxide or hydroxide solid phase. A heterocoagulation occurs between these two constituents that produces settleable aggregates under a wide range of temperatures and pH values. Under conditions when the precipitation of amorphous iron(III) hydroxide may be slow (e.g., pH = 5.0 and temperature = 4 °C), a small partial preneutralization of FeCl$_3$ may be useful (Figure 32).

The modest sensitivity of coagulant dosage to the type of iron(III) preparation, DOC concentration, pH, and temperature (Table 6) has utility in practice. These laboratory results suggest that iron(III) coagulants can function effectively in the treatment of humic waters that experience large fluctuations in water quality, because the dosage requirements do not vary widely with temperature, pH, or DOC concentration.

It is very important to note that the requirements for iron(III) coagulants in practice will often be determined by the content of natural organic matter in a water supply rather than by turbidity. At pH 7.0 and a temperature of 20 °C, for example, a water containing 4.0 mg DOC/L requires a dosage of FeCl$_3$ of 1.3 x 10$^{-4}$ M as iron(III) (log Fe$_T$ = -3.9; Fe$_T$ = 7.0 mg/L), whereas a water containing 50 mg latex/L with a turbidity of 350 ntu requires an iron(III) dosage of only 10$^{-6}$ M as iron(III) (log Fe$_T$ = -5.0; Fe$_T$ = 0.56 mg/L; see Table 6).

Temperature Effects

Low temperatures either had no effect on coagulation or resulted in a slight lowering of the required dosage of iron(III) coagulant (Table 6). As with aluminum, these results suggest that slowing the hydrolysis and precipitation reactions of iron(III) in water is beneficial, perhaps by permitting iron(III) species to react more extensively with turbidity and with humic substances. Difficulties encountered at low temperatures in practice are probably the result of changes in pollutant concentrations in the raw water that may accompany temperature reductions in winter or to short-circuiting in the flow patterns in treatment facilities.

pH Effects

A pattern is proposed here that is similar to that suggested previously for aluminum. For the coagulation of turbidity, low pH will be beneficial when destabilization is accomplished by the adsorption of positively charged iron(III) species on negative particles. This is observed (Table 6) in the coagulation of the turbid water (50 mg latex/L). It is also observed in experiments treating the low-turbidity water (1 mg latex/L) with iron(III) because extended flocculation (24 hours) was used to provide contact opportunities for flocculation. If a normal flocculation period had been employed, required dosages of iron(III) coagulants would have been higher at a pH of 5.0 than at pH 7.0 because the precipitation of amorphous Fe(OH)$_3$ would have been required to produce a settleable aggregate.

The effects of pH on the removal of fulvic acid by the iron(III) preparations are more substantial in the treatment of the highly humic water than in the moderately humic one. They are also more substantial for iron(III) coagulants than for aluminum preparations (compare results for humic waters in Tables 5 and 6). In general, requirements for the iron(III) coagulants are lower at low pH values and, in some cases, low temperatures. These are conditions that retard the precipitation of amorphous Fe(OH)$_3$.

As with the aluminum coagulants, it is possible that positive charge on small iron(III)
species is most effective in reacting with humic substances and that the simultaneous formation of an amorphous iron(III) hydroxide is needed to produce an aggregate sufficiently strong and dense enough to withstand flocculation and to settle well. Charge is promoted at low pH and probably at low temperature; precipitation of amorphous Fe(OH)$_3$ is favored at pH 7. Although these effects offset each other somewhat, coagulant requirements for iron(III) are somewhat less at low pH than at pH 7.

**Comparison of Aluminum and Iron(III) Coagulants**

Metastable solutions containing substantial quantities of cationic polyelectrolytes of aluminum can be reproducibly prepared by partial neutralization of aluminum chloride solutions with base. Similar stable iron(III) polyelectrolytes could not be prepared by partial neutralization of ferric chloride solutions.

Solutions of preformed aluminum polymers can retain their identity long enough in water at slightly acidic to neutral pH values to react with turbidity and humic substances in the water. This is advantageous in the treatment of turbid water supplies; it is a disadvantage in treating water with a low turbidity. These aluminum polyelectrolytes can react with fulvic acids but the products are light, porous, probably dendritic, and do not settle well. Some precipitation of amorphous Al(OH)$_3$ is helpful and probably necessary for the efficient removal of humic substances by coagulation and sedimentation under conditions of pH and temperature found in practice. The presence of sulfate ions could be important in this regard.

Iron(III) coagulants can destabilize particles by forming adsorbable and probably small polymeric species in situ in the coagulation of water supplies. These coagulants can also readily precipitate amorphous Fe(OH)$_3$ at neutral pH. Like aluminum, they can be effective in the treatment of waters with high and low turbidities, and they function by adsorption of cationic species in turbid suspensions and by the formation of an amorphous hydroxide or oxide precipitate in low turbidity systems. Cationic polymers of iron(III) formed in situ can react with humic substances. Removal of these reaction products may be enhanced by the concurrent precipitation of amorphous Fe(OH)$_3$. Sulfate ions are not needed to catalyze this precipitation.

Iron(III) may offer advantages over aluminum preparations in the treatment of highly humic waters at acidic pH values (compare Figure 18 with 34 and Figure 20 with 36). Results in this research indicate that under these conditions it can produce better removals at lower dosages (compared on a molar basis) than the aluminum coagulants tested.

**DIRECT FILTRATION**

Discussion of the performance of two aluminum preparations as "filter aids" in direct filtration is presented first, followed by an evaluation of iron(III) preparations and a comparison of the two metal coagulants. Discussion of the iron(III) experiments is based on the work of Gray (1988).

**Aluminum Preparations**

Cationic polyelectrolytes are effective destabilizing chemicals for negatively charged particles, and PACI:2.4 can be expected to function as a "filter aid" in the direct filtration of low-turbidity waters. The results presented in Figures 37 and 38 indicate that PACI:2.4 is, in fact, better than alum for this purpose at pH values of 5.4 and 7.0 at a moderate temperature (21.5 °C).
Selection of the optimum chemical dosage for such a process is not straightforward. Standard jar tests do not perform well for this purpose because the low rates of interparticle contact opportunities in conventional flocculation limit aggregation and subsequent removal of turbidity by sedimentation. The optimum dosage for particle destabilization is often the optimum dosage for the removal of turbidity in direct filtration (Habibian and O'Melia 1975), and jar tests with extended flocculation periods can be used to determine chemical dosages for the destabilization of low-turbidity waters (e.g., Figures 25-28). Alternatively, the dosage of a prospective "filter aid" can be varied systematically over a filtration run, with changes in the quality of the filter effluent used to determine the appropriate chemical dosage (e.g., Figure 41). These two techniques have been found to yield similar results (Habibian and O'Melia 1975). Based on such preliminary tests, a dosage of PAC1:2.4 of 10^{-6} M (\log A_{1T} = -6.0; A_{1T} = 0.027 \text{ mg/L}) was selected for use in a direct filtration experiment at a pH of 5.4 (Figure 37). To provide for a comparison with alum, an identical aluminum concentration in alum was used for a second parallel filter.

The results in Figure 37 indicate that both PAC1:2.4 and alum interacted with the latex particles at a pH of 5.4 and facilitated their removal in direct filtration. PAC1:2.4 provided somewhat better removal as the run progressed, and its effectiveness relative to alum continued to increase over time. The filter receiving PAC1:2.4 continued to ripen throughout the length of the run, indicating that latex particles retained in the bed in early stages of the run were functioning as effective filter media for suspended particles later in the run. The data indicate that the alum produced similar results, but that removal was less effective. This comparison suggests that both aluminum preparations were able to reduce the stability of the latex particles, but that PAC1:2.4 was more effective than alum under the conditions of this experiment.

The length of the ripening period shown in Figure 37 is quite long—more than 10 hours for PAC1:2.4. The filters used in this experiment were shallow (15 cm in depth) in order to produce a filtrate that contained measurable concentrations of contaminants. In practice, a filter with a depth of 1 m or deeper would be needed to produce an acceptable effluent for this water. The data in Figure 37 demonstrate a limitation in the direct filtration of low-turbidity waters that is sometimes overlooked. Waters that are low in turbidity can exhibit a very long ripening period when treated by direct filtration. Deep beds may be needed. This is because the actual filter media operative during most of a filter run in a conventional rapid filtration process are particles removed by the filter in early stages of the run, which serve as filter media for the removal of particles later in the run. When few particles are present in a water, few can be deposited to serve as filter media, and long ripening periods occur.

The results presented in Figure 38 indicate that PAC1:2.4 can function effectively in destabilizing the particles in a low-turbidity water at neutral pH (7), whereas alum applied at an equal aluminum dosage is quite ineffective as a "filter aid" under these conditions. Dosages of both chemicals were only 3.2 \times 10^{-7} M as aluminum (\log A_{1T} = -6.5; A_{1T} = 0.009 \text{ mg/L}). The cationic aluminum polyelectrolytes such as the \text{Al}_{13} species thought to be in PAC1:2.4 are apparently able to retain enough of their positive charge under these conditions to destabilize this dilute suspension of latex at a very low dosage. Alum is unable to form sufficient destabilizing species at this dosage and pH to be an effective filter aid. The removal accomplished by PAC1:2.4 at pH 7 in the direct filtration of this suspension is quite similar to that observed at pH 5.4. Ripening continues throughout the length of the run. Because of the low turbidity and correspondingly low coagulant dosage, the ripening process is slow. Deep filters would be needed to produce efficient treatment of this water in practice.
Figure 39 is a presentation of results from an experiment conducted to compare PAC1:2.4 and alum as filter aids in the direct filtration of a water containing a low turbidity (1 mg latex/L) and a moderate concentration of humic substances (4 mg DOC/L) at a pH of about 5.5 and at room temperature (21.5 °C). The two coagulants were compared at dosages of $10^{-4}$ M as aluminum. The results indicate that PAC1:2.4 was superior to alum as a filter aid under these conditions. A ripening period occurred with PAC1:2.4, beginning as the run commenced and providing efficient removal in the shallow filters. This rapid ripening was due to the high concentration of fulvic acid in the water to be treated and the correspondingly high aluminum dosage required to react with it. The dosage of PAC1:2.4 required in the direct filtration of this water is 100 times greater than that needed for the low-turbidity water at the same pH and temperature (Figure 37). Although filter ripening was rapid, it lasted only about 1 hour. Effluent quality from the filter receiving PAC1:2.4 deteriorated after that time. It is probable that the concentration of natural organic matter in this water is too high to permit direct filtration to function for sufficient run lengths. This is the most common limitation of the process. The chemistry of the system can be adjusted to provide good removals, but bed capacities are too low to provide sufficient filtered-water production.

The performance of alum as a filter aid presented in Figure 39 was poorer than expected. Data for the influent to the filter indicate that the alum did react with the fulvic acid. Three measures of water quality were used in this experiment: absorbance at 227 nm to reflect the concentration of the latex particles, absorbance at 254 nm to evaluate the concentration of the fulvic acid, and turbidity, which is most sensitive to the scattering of visible light by particles with a size of 0.5 μm or so. Measurement of these parameters before and after chemical addition but prior to filtration provided indirect indication of the reaction of the chemicals with the pollutants in the water. Chemical additions reduced the absorbance at 227 nm of the suspensions after chemical addition but prior to filtration only very slightly, less than 5 percent. This suggests that the latex particles had not aggregated extensively in the short flow time between chemical addition and direct filtration. Absorbance measurements at 254 nm were increased slightly by addition of the chemicals, about 8 percent by alum and less by PIC1:2.4. Because of the broad absorbance spectra of humic substances in ultraviolet light, the interpretation of these changes is not clear, but the small effect of chemical additions does suggest that the fulvic acids were not incorporated deep into solid precipitates in the short reaction time available. Turbidity measurements indicated that the addition of alum doubled the turbidity of the water (from 6.3 to 12.5 ntu) prior to filtration, whereas PAC1:2.4 produced a much smaller increase (from 6.3 to 7.3 ntu). Nevertheless, PAC1:2.4 provided for filtration of the water, with effluent turbidity decreasing to 0.33 ntu in the first hour. With alum, effluent turbidity was 12 ntu or greater after 5 min of filtration.

These results suggest that alum reacted with the constituents in the water, primarily the fulvic acid, to produce a finely divided colloidal suspension that was charged and stable. Dempsey and coworkers (Dempsey et al. 1984; Dempsey et al. 1985) conducted studies of the coagulation of fulvic acid solutions containing 3.5 mg DOC/L and consistently observed a region of stability resulting from overdosing at a pH of 5.5 and an alum dose of $10^{-4}$ M as aluminum. Such results suggest that the charge on the colloidal particles in the influent to the filter directly receiving water treated with alum was positive, permitting removal by the negative media in the bed for a short time, and then resulting in the complete passage of this stable suspension through the filter bed. It is possible that an alum dosage less than $10^{-4}$ M as aluminum would have produced more efficient direction filtration of this water.

Iron(III) Preparations

The results presented in Figure 40 indicate that PIC1:0.5 and 1.5 M FeCl₃ can act
effectively as filter aids at low dosages ($10^{-6}$ M; $\log Fe_T = 6.0$; $Fe_T = 0.056$ mg/L) in the treatment of the low-turbidity water (1 mg latex/L). Removals increased over time; the filters ripened. Problems in dosage control were encountered in the small laboratory apparatus; the high strength of the 1.5 M FeCl$_3$ solution and the low dosage requirement ($10^{-6}$ M) caused difficulties in maintaining accurate addition of this chemical solution during the run. The strong acidity of iron(III) also caused problems in controlling pH at 5.0, at which point alkalinity is near zero. These problems in dosage and pH control are thought to be responsible for the fluctuations in the performance of 1.5 M FeCl$_3$ during the latter half of the run. Such problems are primarily a result of the small scale of the experimental apparatus, and would cause less variation in practice. As in the use of aluminum preparations for the direct filtration of this water (Figures 37 and 38), the low turbidity and the accompanying low iron(III) requirement produce a long ripening period. In practice, this would necessitate the use of deep filter beds.

The results presented in Figure 41 are for the removal of absorbance (254 nm) as a function of iron(III) dosage in a direct filtration experiment. Concurrent measurements of turbidity and of absorbance at 227 nm show similar trends. Collectively, these data indicate (1) that iron(III) can provide for the removal of turbidity and humic substances in direct filtration at acidic pH (5) and at moderate temperature ($21.5^\circ$C), (2) that removal in such a direct filtration process is highly dependent on chemical dosage, and (3) that experiments of this type can be used to establish the coagulant requirements for a particular chemical and to compare the dosage requirements of different chemicals.

This experiment and the results in Figure 40 are consistent with dosage requirements observed with aluminum preparations (Figures 37 and 39), in that the chemical requirements for an iron(III) filter aid in the direct filtration of a moderately humic water are two orders of magnitude larger than for the direct filtration of a low-turbidity water. The concentration and probably the type of natural organic matter in a water supply are important and often decisive factors in establishing the chemical requirements and the technical feasibility of direct filtration.

Other direct filtration experiments were conducted (Gray 1988) on this water with a low turbidity and a moderate humic concentration, comparing PIC1:0.5 and 1.5 M FeCl$_3$ at dosages of $10^{-4}$ M ($\log Fe_T = -4.0$; $Fe_T = 5.6$ mg/L). These experiments also encountered difficulties with control of coagulant dosage and, because of the high iron(III) requirements, with pH control in the small laboratory apparatus. When pH and coagulant dosages were maintained at desired levels, PIC1:0.5 and 1.5 M FeCl$_3$ produced effective removals of turbidity and fulvic acid. However, because of the sizable concentration of humic material and the correspondingly high chemical requirements, effluent quality tended to deteriorate over time and head losses were high. It is probable that this water would not be a candidate for direct filtration because of the concentration of humic material that it contained.

Comparison of Aluminum and Iron(III) as "Filter Aids"

Four preparations were tested as filter aids: PAC1:2.4, alum, PIC1:0.5, and 1.5 M FeCl$_3$. Only one of these, PAC1:2.4, contained substantial quantities of preformed cationic polyelectrolytes, and it exhibited somewhat different behavior as a filter aid than the other three preparations.

PAC1:2.4 performed well as a filter aid for the destabilization and direct filtration of suspensions containing low particle concentrations low-turbidity waters at pH values spanning a range from slightly acidic to neutral. Alum can apparently form destabilizing aluminum species
in the direct filtration of low-turbidity waters at a pH of 5.5 and can perform almost as well as PACl:2.4 under these conditions. Alum does not work well in the direct filtration of low-turbidity waters at neutral pH, probably because it forms species with little or no charge and also precipitates amorphous \( \text{Al(OH)}_3 \).

The two iron(III) preparations successfully destabilized the negative particles in the direct filtration of the low-turbidity water at pH 5 (Figure 40) and at pH 7 (Gray 1988). Because neither preparation contained a substantial quantity of stable preformed cationic polyelectrolytes, this success indicates that these solutions formed adsorbable cationic iron(III) species in situ during these experiments. The results indicate that iron(III) chloride solutions can be used successfully without partial preneutralization for the direct filtration of low-turbidity waters over a pH range of at least from 5 to 7.

In the direct filtration of a water containing a moderate concentration of humic substances and a low turbidity, only alum was ineffective under the conditions of the experiments, which were limited to slightly acidic pH values (Figures 39 and 41). The dosage selected for alum was chosen to provide a comparison with PACl:2.4 and may have been too high. PACl:2.4 proved to be relatively more effective in the direct filtration of this water (Figure 39) than it was in coagulation under comparable solution conditions (Figure 18). No studies were conducted to determine the cause of this difference; it is possible that the aggregates formed by the interactions of PACl:2.4 species with fulvic acid in the flocculation step of a coagulation process do not settle well, whereas the products formed in the direct filtration process can be retained in packed beds.

Both preparations of iron(III) chloride reacted with fulvic acid in the direct filtration of the water with low turbidity and moderate humic content, producing products that were filterable as long as the coagulant dosage and pH were properly controlled. This is consistent with the performance of these substances as coagulants. They do not contain preformed polyelectrolytes but they do produce species in situ that react well with both turbidity and humic substances.
CHAPTER 6

CONCLUSIONS

Studies of the characterization of aluminum and iron(III) preparations are considered first, followed by conclusions based on the coagulation studies and then the filtration experiments. Finally, some considerations regarding coagulation and coagulant chemistry that have potential utility in practice are presented.

COAGULANT CHARACTERIZATION STUDIES

1. It was possible to produce stable preparations of partially neutralized aluminum chloride solutions in which cationic aluminum polyelectrolytes predominated. These cationic species resemble an aluminum specie frequently described as $\text{Al}_{13}\text{O}_{4}(\text{OH})_{24}^{2+}$ and written as $\text{Al}_{13}$.

2. Attempts to produce similar stable preparations containing cationic iron(III) polyelectrolytes by partial neutralization of iron(III) chloride solutions were unsuccessful.

3. These differences in the behavior of aluminum and iron(III) chloride solutions during slow partial neutralization with base may reflect differences in the hydrolysis, nucleation, growth, and aggregation of these metals in solution. These, in turn, could be reflected in practice in differences in the reactivity of aluminum and iron(III) with pollutants and, in particular, natural organic substances.

COAGULATION STUDIES

1. Partially neutralized solutions of aluminum chloride, such as the PACl:2.4 used in this research, are effective at dosages lower than other aluminum preparations for the coagulation of high-turbidity waters, particularly at low temperatures or acidic pH values. Such waters can be treated effectively by cationic polyelectrolytes, and PACl:2.4 provides such a material. It is speculated that low temperatures and acidic pH values retard the formation of such cationic polymeric species in situ when other unneutralized aluminum coagulants such as alum are used for the coagulation of turbid waters under these conditions.

2. Among the aluminum coagulants tested, alum is the choice for the coagulation and sedimentation of most other waters. This includes supplies with low turbidity and also waters containing humic substances. Precipitation of solid amorphous $\text{Al(OH)}_3$ is needed to provide contact opportunities in the flocculation of low-turbidity waters for subsequent sedimentation. PACl:2.4, a preparation that contains fairly stable cationic aluminum species, is consequently ineffective in precipitating amorphous $\text{Al(OH)}_3$ and thus ineffective in the treatment of low-turbidity waters by conventional coagulation and sedimentation. The bases for the superiority of alum over PACl:2.4 in the coagulation and sedimentation of humic substances are less clear. Both preparations reacted with humic substances, but alum provided better removals of fulvic acid at lower dosages in jar tests in this research. In fairly humic waters, it is speculated that the aggregates formed by the reactions of PACl:2.4 with fulvic acid are loose, fragile, and difficult to aggregate and settle. Continuing this speculation, it is suggested that the sulfate present in alum is an important factor in the removal of humic substances by aluminum.
3. Additional studies of partially neutralized aluminum preparations as coagulants should be focused on developing preparations that are effective in removing natural organic substances. Sulfate is proposed as an important factor in such a development.

4. Although none of the iron(III) coagulants used in this research contained appreciable quantities of preformed cationic iron(III) polyelectrolytes, three provided effective treatment of a high-turbidity water. Iron(III) coagulants without partial preneutralization can produce adsorbable cationic species in situ and destabilize turbid waters at low dosages. They are effective for this purpose over broad ranges of temperature and pH. Moderate preneutralization of iron(III) chloride ($r_{OH} = 1.5$) precipitated a substantial quantity of colloidal amorphous Fe(OH)$_3$ in this preparation and reduced its effectiveness for the treatment of the high-turbidity water.

5. In the treatment of low-turbidity waters, iron(III) coagulants can precipitate amorphous Fe(OH)$_3$ and accomplish removal by coagulation and sedimentation. Alternatively, they can destabilize the turbidity at low dosages over broad ranges of temperature and pH and have the potential to serve as filter aids in the direct filtration of these waters, even though the original preparations do not contain substantial concentrations of cationic iron(III) polyelectrolytes.

6. Iron(III) preparations were effective in the coagulation and sedimentation of humic waters over wide ranges of pH and temperature. It is proposed that cationic polymers of iron(III) are formed in situ and that these can react with humic substances. Removal of these reaction products by sedimentation may be enhanced by the concurrent precipitation of amorphous Fe(OH)$_3$. Sulfate ions are not needed to catalyze this process.

7. Low temperatures do not impair the coagulation and sedimentation of turbidity or humic substances by aluminum or iron(III) preparations. Dosage requirements are either lower at low temperatures or remain unaffected. Poor performance accompanying low temperatures in full-scale plants may be due to short-circuiting in treatment units caused, for example, by density effects, or to seasonal changes in important water quality parameters. Coagulant chemistry can be at least as favorable for the removal of turbidity and humic substances at low temperatures as it is at moderate temperatures.

DIRECT FILTRATION STUDIES

1. PACi:2.4 is an effective filter aid for low-turbidity waters, providing for destabilization and subsequent filtration of particles at acidic and neutral pH values. This effectiveness is due to the character of the reactive species in the preparation, i.e., adsorbable cationic polyelectrolytes such as Al$_{13}$.

2. Alum provided for some direct filtration of the low-turbidity water at acidic pH but was ineffective at neutral pH. Partial preneutralization improves the effectiveness of aluminum preparations in the direct filtration of low-turbidity waters over a range of pH values at least from 5.5 to 7.

3. Iron(III) preparations without partial preneutralization can serve as destabilizing chemicals or filter aids in the direct filtration of low-turbidity waters.

4. PACi:2.4 and two iron(III) solutions provided for removal of turbidity and fulvic acid in the direct filtration of a moderately humic water with low turbidity. Alum was ineffective
at the dosage tested (chosen to provide a comparison with PAC1:2.4), but might have functioned well at a different (and possibly lower) dosage. Collectively these results suggest that selection of the type of metal coagulant for use in direct filtration, although an important factor, may be less critical than in coagulation and sedimentation. In other words, the direct filtration process may be less sensitive to the type of metal coagulant used than is the coagulation and sedimentation process. For a given chemical, however, process performance in direct filtration can be very sensitive to dosage.

5. There is a lower limit of contamination in a raw water below which direct filtration can become infeasible because of the long ripening period that can be required to produce efficient removal. This can be offset to some extent by the use of deep filter beds.

6. As reported many times in the literature, there is an upper limit of contamination in a raw water above which the direct filtration process is infeasible because of limited capacity of the filter bed to accumulate filtered materials.

7. Considering the last two conclusions, it is possible to speculate about these lower and upper limits of contamination. Some success has been achieved, at least with the upper limit, by indicating upper limits for the turbidity or, less commonly, the DOC or color of the raw water. In a real sense, the chemistry of direct filtration is less complicated than the chemistry of coagulation. Chemicals are always needed, and a direct stoichiometry can be expected between the concentration of contaminants in the water to be treated and the dosage of chemical required to treat that water by direct filtration. For the metal coagulants, it may be useful to describe the upper and lower limits of feasibility of direct filtration by chemical requirements rather than by pollutant concentrations, because these are less defined. Based on the results of this research and some consideration of practice, a first estimate of these limits is as follows. Direct filtration may be infeasible because of slow ripening at metal coagulant dosages below about $10^{-5}$ M (0.3 mg Al/L or 0.6 mg Fe(III)/L). The process may become infeasible because of limitations in bed capacity at metal coagulant dosages above about $10^{-4}$ M (3 mg Al/L or 6 mg Fe/L). These are approximate limits that can be affected to some extent by such factors as bed depth, media size, filtration rate, temperature, and the use of preflocculation. These limits are suggested as preliminary surrogates for knowledge of the properties of contaminants in a water supply.

COAGULANT CHEMISTRY AND COAGULATION PRACTICE

1. The type and concentration of dissolved organic substances in a water supply are frequently the determining factors that establish coagulant requirements. In some and perhaps most cases, the concentration of DOC in a raw water is a useful surrogate for more detailed information about the properties of natural organic substances. It will, in most cases, provide more information about coagulant requirements than turbidity. Aluminum and iron(III) react with some DOC in all waters and with most DOC in some waters. The nature of this iteration involves in large part the formation of metal-ligand complexes between functional groups on the organic substances with iron(III) or aluminum. Removal of the resulting reaction products requires neutralization of the charge on the organic species. In other words, the removal of natural organic matter normally requires neutralization of its charge, but it is useful to understand that the interactions between humic substances and these metals are best viewed as chemical complex formation reactions rather than electrostatic ones. Iron(III) and aluminum salts are frequently preferred over synthetic cationic organic polyelectrolytes for the removal of humic substances because they provide cationic charge less expensively. In addition, they form stronger complexes and thereby can accomplish better removals.
2. Although the aqueous chemistries of iron(III) and aluminum have many similarities, they are not identical. Differences between iron(III) and aluminum observed in this research in the formation of preformed cationic metal polyelectrolytes produce differences in coagulant selection when considering the treatment of turbid waters, especially under cold conditions. Both iron(III) and aluminum can precipitate amorphous metal hydroxides necessary for the treatment of low-turbidity waters by conventional coagulation and sedimentation, but the sulfate ion in alum is necessary for aluminum to function successfully in these cases. These differences may extend to the removal of natural organic matter. Iron(III) is a stronger acid than aluminum; it is also a stronger complex-former than aluminum for many ligands. These differences in reactivity could lead to differences in the interactions of these metals with natural organic matter and also to differences in the properties of the precipitates and aggregates that are formed. Iron(III) should be considered for evaluation and comparison with alum in cases in which the removal of humic substances is an important treatment objective.
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89


