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**REMOVAL OF INORGANIC CONTAMINANTS AND NATURAL ORGANIC  
MATTER BY ENHANCED ALUM COAGULATION: DEFLUORIDATION AT THE  
PILOT SCALE AND APPLICATION TO ARSENIC**

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**BY**

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**THESIS**

Presented to the Faculty of the Graduate School of  
The University of Texas at Austin  
in Partial Fulfillment  
of the Requirements  
for the Degree of

**MASTER OF SCIENCE IN ENGINEERING**

**THE UNIVERSITY OF TEXAS AT AUSTIN**

**DECEMBER 2016**

## **ACKNOWLEDGEMENTS**

I would like to first thank my advisors, Dr. Desmond Lawler and Dr. Lynn Katz, for their invaluable guidance and support throughout the past two years. They are both incredible leaders and teachers, and I will forever be grateful for the opportunity to work with and learn from them. To Mark and Katherine, this project would not have been possible without the amazing foundation your works provided. To Mitch and Jon, there is no one else with whom I would gladly spend 14 hours driving to Colorado. Ki and Trey, I cannot thank you enough for your time and help in the lab; you made the final months fly by. To my family, you are all my constant North Star. And to my second family, EWRE, I never expected to find a community as genuine, welcoming, and supportive as the one I have. I cannot imagine this experience without you all.

## **ABSTRACT**

# **REMOVAL OF INORGANIC CONTAMINANTS AND NATURAL ORGANIC MATTER BY ENHANCED ALUM COAGULATION: DEFLUORIDATION AT THE PILOT SCALE AND APPLICATION TO ARSENIC**

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The removal of inorganic contaminants is a primary concern in drinking water treatment. Fluoride and arsenic both naturally occur in ground and surface waters throughout the world. Recent health concerns regarding extended exposure to high levels of fluoride in drinking water have prompted the United States Environmental Protection Agency (USEPA) to review the fluoride maximum contaminant level (MCL). Arsenic is one of the most well-known and toxic inorganic contaminants regulated by the USEPA. While typically associated with groundwater, arsenic could be an increasing concern for surface water sources in the future. Small water systems may not have the resources to adjust their treatment scheme to accommodate a lower fluoride MCL or target arsenic removal. In this study, enhanced alum coagulation was investigated as a treatment strategy for both fluoride and arsenic. Facilities with surface water sources face a particular challenge, as the presence of natural organic matter (NOM) may interfere with the removal of fluoride and/or arsenic during coagulation.

This work builds upon previous investigation of the interactions between fluoride, NOM, and aluminum during coagulation by comparing two pilot studies in Texas and Colorado. Each pilot study confirmed that enhanced alum coagulation was able to remove fluoride during continuous flow experiments using natural source water; the comparison of the studies revealed that source water composition impacts the maximum efficacy of alum coagulation for fluoride removal. A higher influent organic concentration appears to reduce the maximum efficacy of fluoride removal. However, the use of pH control may also be a contributing factor to the discrepancy in fluoride removal between pilot studies. The pilot study with a lower maximum fluoride removal had a higher influent DOC concentration, but was run without pH control.

Synthetic water jar testing confirmed the ability of alum coagulation to remove arsenic (V). A maximum arsenic removal of 99% was observed for As(V) at alum doses of 100 mg/L and above, and an alum dose of 20 mg/L achieved an As(V) removal of 97%. Aluminum residuals suggest that the presence of As(V) lowers the point of zero charge for aluminum hydroxide solid.

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## CHAPTER 1: INTRODUCTION

### 1.1 Introduction

Traditional drinking water treatment strategies focus on the removal of particles, natural organic matter (NOM), and pathogens. These strategies are necessary to provide clean, safe, and aesthetically pleasing drinking water to communities. Contaminants of concern are regulated by the United States Environmental Protection Agency (USEPA) under the Safe Drinking Water Act of 1974, which gives USEPA the authority to identify potential water contaminants and set enforceable maximum contaminant levels (MCLs) based on available scientific data and health risks. Many drinking water treatment systems struggle to meet current MCLs due to complicated and impaired source water quality. Changes in regulatory standards can also cause problems for drinking water systems, which must change or adapt their treatment strategy to accommodate different treatment goals. Small water systems in particular are at risk of exceeding regulations because small systems may not have the financial or managerial resources necessary to fund and oversee a change in treatment process or infrastructure. Fluoride and arsenic are two inorganic contaminants that may pose a threat to small water systems.

Fluoride is a naturally occurring drinking water constituent that is also commonly added to drinking water supplies for its association with dental health and caries (Mullen, 2005). The USEPA has identified fluoride as a drinking water contaminant and has set a fluoride MCL of 4.0 mg/L. Currently, the fluoride standard is under review by the USEPA due to scientific studies linking chronic exposure to fluoride in excess of 2.0 mg/L to detrimental health impacts such as dental and skeletal fluorosis (Heller et al., 1997; Mandinic et al., 2010). Drinking water facilities should anticipate a reduction in the fluoride MCL. Small systems that currently struggle to meet the existing MCL especially should prepare for stricter regulations; current methods of fluoride reduction can be

costly and ill-suited to small systems with limited personnel and resources. An effective and economic method of fluoride reduction is necessary for small systems to be able to comply with a lower fluoride standard.

Similar to fluoride, arsenic is another naturally occurring background constituent of drinking water. However, arsenic is one of the most well-known drinking water contaminants and carcinogens. The USEPA originally set an MCL for arsenic of 50 µg/L, but lowered the limit to 10 µg/L in 2001 after mounting evidence connecting arsenic to multiple cancers. Arsenic is prevalent in ground waters of the US, particularly in the west (Welch et al., 1988). Surface waters can also contain arsenic from both natural and anthropogenic sources and these waters are also more likely to contain NOM, which could have an impact on the arsenic cycle (Ghosh et al., 2005; Mohora et al., 2012). Arsenic could be a greater concern in the future due to increasingly extreme weather events; larger storms with greater runoff and more severe droughts could result in higher than normal arsenic concentrations for treatment plants (Khan et al., 2015).

Small systems may not have the resources to change their treatment strategy and infrastructure in order to adhere to a tighter fluoride limit or focus on arsenic removal. Alum coagulation is already commonly applied at many small water facilities for particle control; enhanced alum coagulation—the use of doses higher than that that needed for particle removal—is often used at surface water plants to manage both particles and NOM. Enhanced alum coagulation could also be used to remove inorganic contaminants like arsenic and fluoride. Current information surrounding the interaction between arsenic and/or fluoride, NOM, and aluminum during alum coagulation is lacking, and this research was designed to fill in some of the gaps in current knowledge in this arena. Previous researchers at the University of Texas have conducted bench scale tests to investigate the interactions of fluoride, NOM, and aluminum during enhanced alum

coagulation, but pilot scale studies will help evaluate the applicability of enhanced alum coagulation for fluoride reduction at scale (Alfredo, 2012; Stehouwer, 2014). The previous bench-scale work on fluoride needs to be extended to consider arsenic removal in much the same way. A better understanding of how alum treatment removes fluoride and arsenic is necessary to evaluate its efficacy and develop a set of practical treatment guidelines.

## **1.2 Objectives**

This research has two primary objectives: (1) to investigate the applicability of enhanced alum coagulation for the reduction of fluoride at the pilot-scale and (2) to elucidate the interactions between arsenic, NOM, and aluminum during enhanced alum coagulation and determine what levels of each can be achieved in treated drinking water. The specific objectives are as follows:

1. Conduct a pilot study for the reduction of fluoride from drinking water at a small water system that contains fluoride concentrations above the WHO standard or 1.5 mg/L.
2. Investigate the efficacy of enhanced alum coagulation for arsenic removal and optimize removal in synthetic water systems
3. Investigate the interactions between arsenic and organic matter during alum coagulation in synthetic water systems

Bench-scale experiments investigating the reduction of fluoride in both synthetic and natural water systems were previously conducted by a team of researchers at the University of Texas at Austin; results from these experiments are summarized as a part of the literature review provided in Chapter 2. The researchers also completed a pilot study at a small water system in Texas; the results from the Texas pilot study have not

previously been reported, and are therefore included here and are compared to the results from the Colorado pilot study completed as a part of this research in Chapter 4. The materials and methods used in this study are presented in Chapter 3. The bench-scale studies of As(V) removal by alum coagulation are explained in Chapter 5, and a final summary and conclusions are provided in Chapter 6.

## **CHAPTER 2: LITERATURE REVIEW**

### **2.1 Coagulation and Flocculation as a Drinking Water Treatment Strategy**

Coagulation is a chemical process commonly used for particle removal in drinking water treatment. Particles are one of the primary concerns in drinking water treatment because of their potential health and aesthetic impacts. Larger particles can settle out in later treatment steps, but smaller particles do not have a settling velocity high enough to be removed by gravity separation alone in a reasonable time frame. Removal of these smaller particles through gravity settling or filtration requires aggregating them to make larger particles. Due to electrostatic repulsion, however, many particles are naturally stable in water and require a chemical pretreatment process to promote attraction between particles. This process is termed coagulation. Thus, coagulation destabilizes particles so that they can aggregate or attach to another surface and form the larger particles required for gravity separation. The term flocculation is commonly used interchangeably with coagulation, but they refer to two distinct processes; coagulation is the chemical process of destabilizing particles and flocculation is a physical process that promotes particle collision and aggregation (Aguilar et al., 2002; Guo et al., 2009; Khanh Trinh and Seok Kang, 2010; Benjamin and Lawler, 2013).

#### **2.1.1 Alum coagulation**

Alum is a common coagulant used in drinking water treatment to accomplish particle removal through two pathways: charge neutralization and sweep flocculation (Benjamin and Lawler, 2013). Particles in natural waters typically have negative surface charges. This surface charge promotes their stability in suspension because like charges repel one another. Alum, an aluminum salt, forms hydrolysis products when introduced to water. Table 2.1 presents the simpler hydrolysis products formed, although more

complex polymers are also formed and are thought to play a significant role in particle destabilization by charge neutralization. These more complex aluminum-based polymers include single, double, triple, four, five, and up to 19-ring structures (Bi et al., 2004).

TABLE 2.1: HYDROLYTIC REACTIONS FOR THE FORMATION OF ALUMINUM HYDROXIDE PRECIPITATE

Reaction	Log K
$\text{Al}^{3+} + \text{H}_2\text{O} \leftrightarrow \text{AlOH}^{2+} + \text{H}^+$	-5.0
$\text{Al}^{3+} + 2 \text{H}_2\text{O} \leftrightarrow \text{Al}(\text{OH})_2^+ + 2 \text{H}^+$	-9.3
$\text{Al}^{3+} + 3 \text{H}_2\text{O} \leftrightarrow \text{Al}(\text{OH})_3 + 3 \text{H}^+$	-15.0
$\text{Al}^{3+} + 3 \text{H}_2\text{O} \leftrightarrow \text{Al}(\text{OH})_3 (\text{s}) + 3 \text{H}^+$	-8.5
$\text{Al}^{3+} + 4 \text{H}_2\text{O} \leftrightarrow \text{Al}(\text{OH})_4^- + 4 \text{H}^+$	-23

At a low pH, the positively charged species dominate. Adsorption of these positive hydrolysis species by negatively charged particles can neutralize the charged particles, thus destabilizing them and allowing for collision, aggregation, and removal. Sweep flocculation occurs when the solid aluminum hydroxide precipitate is formed. Particle removal by sweep flocculation occurs through enmeshment. When sufficient coagulant is added to form a precipitate, the metal ions adsorb onto the surface of particles in suspension, which act as a nucleus for precipitate formation. Particles then become enmeshed in the amorphous, gelatinous precipitate and are removed along with the precipitate during settling or filtration (Benjamin and Lawler, 2013) .

### 2.1.2 Enhanced Alum Coagulation for Natural Organic Matter Removal

Natural organic matter (NOM) refers to a broad mix of organic compounds, aquatic or terrestrial in origin, commonly found in natural water sources. NOM is composed of hydrophilic and hydrophobic constituents, both in turn comprised of myriad different species with variable molecular compositions, weights, functional groups, and

charges (Leenheer and Croue, 2003; Matilainen et al., 2010; Matilainen et al., 2011; Edzwald, 1993). The hydrophobic constituents, most often humic and fulvic acids, are primarily comprised of aromatic carbon while the hydrophilic components contain more aliphatic carbon and nitrogenous compounds (Matilainen et al., 2011). Commonly, NOM is separated into its dissolved or particulate form; the dissolved fraction of NOM, dissolved organic carbon (DOC), is defined as passing through a 0.45  $\mu\text{m}$  filter while the particulate organic carbon (POC) is retained on the filter (Chow et al., 2009; Edzwald, 1993). DOC is often used to characterize the NOM content of a water; groundwater typically has a DOC content less than 1 mg/L while surface waters can range from 2 – 10 mg/L or higher in rare cases (Morel and Hering, 1993).

Removal of NOM is a concern in drinking water treatment because of aesthetic impacts on water quality such as taste, color, and odor, and also because of detrimental health impacts (Matilainen et al., 2010; Leenheer and Croue, 2003). The biodegradable portion of NOM can promote bacterial growth within treatment and distribution systems by acting as a nutrient source (Volk et al., 2000). Additionally, residual NOM can react with chlorine- or bromine-based disinfectants to produce disinfection by-products (DBPs), which can have carcinogenic as well as reproductive effects (Villanueva et al., 2004; Waller et al., 1998; Dodds et al., 2016). Two groups of DBPs, namely total Trihalomethanes (TTHM) and five Haloacetic acids (HAA5), are regulated; the EPA set maximum contaminant levels (MCLs) of 80  $\mu\text{g/L}$  for TTHM and 60  $\mu\text{g/L}$  for HAA5 (Wu, 2015). NOM removal is an increasing priority for water utilities, especially those using surface waters, to avoid the formation of DBPs and meet the regulatory standards. Indeed, the Disinfection and Disinfection By-Products Rule promulgated in 1998 requires different levels of DOC removal depending on the raw water DOC and alkalinity levels

(USEPA, 1998a). Enhanced alum coagulation is a common technique for meeting the requirements of this regulation and thereby reducing the potential for DBP formation.

Enhanced alum coagulation is the application of alum at concentrations higher than that required for particle removal to remove NOM, and the process is frequently coupled with pH control. Alum coagulation is typically optimized for particle removal, but the NOM content will govern the coagulant dose as long as the turbidity is not excessive; enhanced alum coagulation concentrations are typically between 20 and 50 mg/L alum (Gregor et al., 1997; Edzwald, 1993; Edzwald and Tobiasson, 1999). Alum concentrations are generally below 50 mg/L because of the point of diminishing returns (PODR) during TOC removal; at a certain point, a significant increase in alum dosage will only achieve a modest increase in TOC removal. Because of the highly variable nature of NOM composition, the optimum removal conditions are also variable (Matilainen et al., 2010). Alum dose and pH control are the two most important factors controlling the efficacy of NOM removal (Gregor et al., 1997; Qin et al., 2006; Semmens and Field, 1980).

The primary mechanisms of NOM removal during alum coagulation include adsorption and co-precipitation. NOM adsorbs onto amorphous aluminum hydroxide solid by replacing surface hydroxyl groups through hydrolysis reactions, thus competing as a ligand. During co-precipitation, anionic NOM complexes with cationic aluminum species to form neutral, insoluble products that can precipitate. This mechanism is typically used to explain NOM removal in conditions where aluminum hydroxide precipitation is low (Matilainen et al., 2010; Edzwald, 1993; Yan et al., 2008; Gregor et al., 1997; Volk et al., 2000).

NOM removal can be measured by DOC, total organic carbon (TOC), absorbance of ultraviolet (UV) light, and specific UV absorbance (SUVA). TOC incorporates all of

the organic content, combining DOC and POC. UV absorbance for NOM quantification is commonly measured at a wavelength of 254 nm, which captures the aromatics effectively. UV-254 is thus considered a surrogate measure for DOC, of which a major fraction is hydrophobic aromatics (Edzwald, 1993; Matilainen et al., 2011). Because coagulation tends to favor the removal of the hydrophobic, humic portion of NOM, UV-254 is often used to quantify removal (Chow et al., 2009; Matilainen et al., 2010; Edzwald, 1993). The SUVA value is the ratio of UV-254 absorbance to the DOC content ( $A_{254}/\text{mg C L}^{-1}$ ). SUVA is a popular metric because it describes both the hydrophilic and hydrophobic content of NOM. High SUVA values ( $>4$ ) indicate a more humic, hydrophobic NOM, while low SUVA values ( $<2$ ) indicate a more hydrophilic composition (Matilainen et al., 2011; Matilainen et al., 2010).

## **2.2 Fluoride**

### **2.2.1 History of Fluoride Health Effects and Regulation**

Fluoride is a naturally occurring mineral present in soil, water, plants, animals, and humans (Mandinic et al., 2010). Many drinking water systems currently add fluoride to their water in a process called fluoridation, because fluoride has been shown to help prevent dental caries when consumed in low concentrations (Ozsvath, 2008; Mandinic et al., 2010; Maheshwari, 2006; Mullen, 2005). The practice of fluoridation is relatively new; fluoride has only been added to water supplies since 1945 due to discoveries made by Dr. Frederick McKay (Carstairs, 2015).

In 1901, McKay started a dental practice in Colorado Springs, Colorado and noticed a number of patients had brown stains on their teeth accompanied by a resistance to tooth decay. Fluoride was not specifically identified as the cause of the discoloration until H.V. Churchill, the chief chemist at the Aluminum Company of America (ALCOA),

became involved in 1931 (Mullen, 2005). Churchill discovered that fluoride caused mottling of the teeth in Bauxite, Arkansas, a company town owned by ALCOA, while trying to refute claims that aluminum cookware was poisonous. Churchill discovered fluoride at over 10 mg/L within the water supply, and had McKay send multiple water samples from separate afflicted areas to corroborate the findings (Mullen, 2005). In 1942, a dentist appointed by the US Public Health Service (USPHS), Dr. H.T. Dean, found that mottling and staining were rare below 1 mg/L fluoride, and that this was also the optimum concentration for caries prevention (Mullen, 2005). In 1945, Grand Rapids, Michigan began fluoridating their water supply, and the success led more towns to adopt fluoridation.

Fluoridation of water supplies was initially an easy way to promote dental health in areas that lacked naturally occurring fluoride in their water, but fluoride exposure occurs through many additional routes; humans can intake fluoride through water, air, food, drugs, and cosmetics (Jagtap et al., 2012). Multiple routes of exposure increase the likelihood of an individual ingesting an excess of fluoride and promoting fluorosis.

Fluorosis is caused by high intake of fluoride. Fluoride is strongly electronegative and has a tendency to be attracted to cations such as calcium, which is predominantly found in teeth and bones within the body. Calcium can be found as crystalline hydroxyapatite ( $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ) in tooth enamel and skeletal tissue (Mandinic et al., 2010; Ozsvath, 2008). When fluoride is present, it can replace a hydroxyl group in the crystal lattice and form fluorapatite ( $\text{Ca}_5(\text{PO}_4)_3\text{F}$ ), which is more stable than hydroxyapatite and an order of magnitude less soluble (Ozsvath, 2008; Mandinic et al., 2010; Mohapatra et al., 2009). This reduction in solubility prevents demineralization of tooth enamel in acidic conditions, which are commonly created by ingesting acidic foods or when bacteria in the saliva excrete acids as a part of carbohydrate digestion

(Wongkhantee et al., 2006; Burne and Marquis, 2000). As was discovered in the 20<sup>th</sup> century, fluoride strengthens bones and teeth at low levels (0.7–1.5 mg/L) while higher levels (1.5 – 4 mg/L) promote dental fluorosis (Mandinic et al., 2010; Jagtap et al., 2012; Ozsvath, 2008; Mohapatra et al., 2009; Fawell et al., 2006; Gooch, 2015).

Dental fluorosis can be classified by using Dean’s Index, which is outlined in Table 2.2. Signs of dental fluorosis range from small white flecks to brown stains and corrosive pitting of the teeth. When fluoride forms fluorapatite in the dental enamel, the substitution of fluoride for a hydroxide causes a reduction in crystal volume, leaving large gaps in the crystal structure; teeth become denser, more brittle, and susceptible to mottling (Ozsvath, 2008; Mohapatra et al., 2009). Children with developing teeth are more susceptible to dental fluorosis than adults (Maheshwari, 2006; Ozsvath, 2008; Bhagavatula et al., 2016; Heller et al., 1997).

TABLE 2.2: DEAN’S INDEX FOR THE CLASSIFICATION OF DENTAL FLUOROSIS\*

<b>Criteria</b>	<b>Description</b>
Normal	Enamel is translucent, surface is smooth and glossy
Questionable	Enamel exhibits a few white flecks to occasional white spots
Very Mild	Small opaque, paper white areas covering under 25% of the tooth surface
Mild	More extensive white spots covering under 50% of the tooth surface
Moderate	All enamel surfaces are affected, often featuring brown stains
Severe	All enamel surfaces are affected, form of the tooth may be affected, brown stains are widespread and teeth often exhibit a corroded appearance

\*Table adapted from Mandinic et al., 2010

Prolonged exposure at even higher concentrations of fluoride, 4 – 10 mg/L and above, can cause skeletal fluorosis (Mohapatra et al., 2009). Skeletal fluorosis causes an increase in bone mass and density, called osteosclerosis. Osteosclerosis leads to joint

problems, bone deformation, and paralysis in advanced stages (Ozsvath, 2008; Maheshwari, 2006; Fawell et al., 2006). Mohapatra et al. (2009) catalogued the dental and skeletal health outcomes associated with prolonged exposure to various levels of fluoride in drinking water; their results are presented in Table 2.3. In addition to dental and skeletal effects, prolonged fluoride exposure has been linked to developmental, reproductive, renal neurological, endocrine, gastrointestinal, and possibly carcinogenic detrimental health impacts (Ozsvath, 2008).

TABLE 2.3: EFFECT OF PROLONGED CONSUMPTION OF DRINKING WATER ON HUMAN HEALTH, RELATED TO FLUORIDE CONTENT\*

<b>Fluoride Concentration (mg/L)</b>	<b>Health Impact</b>
<0.5	Dental Caries
0.5 – 1.5	Optimum Dental Health
1.5 – 4.0	Dental Fluorosis
4.0 – 10.0	Skeletal Fluorosis
> 10.0	Crippling Fluorosis

\*Table from Mohapatra et al., 2009

Due to the links between fluoride consumption and fluorosis, the EPA set a non-enforceable Maximum Contaminant Level Goal (MCLG) for fluoride of 4.0 mg/L as a part of the Safe Drinking Water Act (SDWA) of 1974. The SDWA gave the EPA authority to identify and regulate drinking water contaminants. The MCLG of 4.0 mg/L was established as an enforceable MCL in 1986 and remains in place today. A non-enforceable secondary Maximum Contaminant Level (SMCL) was also set at 2.0 mg/L to protect against aesthetic impacts. The regulation for fluoride is currently under review, as the SDWA also requires the EPA to review each MCL every 6 years under the Six-Year Review.

In 2002 the EPA determined there was sufficient health research available to warrant a review of the fluoride MCL, and the NRC conducted a second comprehensive study in 2006. The report concluded that the limit should be lowered to protect against severe dental fluorosis and crippling skeletal fluorosis (NRC, 2006a). The regulation is still under review by the EPA and no report has yet been issued, though a reduction is anticipated. In 2011, the Department of Health and Human Services (HHS) recommended a fluoride limit between 0.7-1.2 mg/L fluoride (HHS, 2011). The World Health Organization (WHO) has recommended a maximum of 1.5 mg/L and this standard has been adopted by many countries (Fawell et al., 2006). A lower fluoride standard than the current 4.0 mg/L would impact current drinking water sources and technologies in the United States.

### **2.2.2 Fluoride Occurrence in Drinking Water**

Fluorine is the most electronegative of the elements and has a strong tendency to acquire a negative charge. Because of its reactivity, fluorine is not found in its elemental state in the environment, but rather exists as inorganic fluoride ions ( $F^-$ ) or inorganic fluoride compounds (Jagtap et al., 2012; Fawell et al., 2006). Fluoride can also exist within organic compounds, where it replaces hydrogen and bonds with carbon (Chambers, 2004). Fluoride is commonly found in water, most often in groundwater supplies where it derives from the dissolution of minerals in rocks and soil. Groundwater concentrations can range from much less than 1 mg/L to greater than 35 mg/L; some areas of the world have reported extremely high concentrations of 2800 mg/L fluoride (Maheshwari, 2006; Fawell et al., 2006). Aquifers with arsenic containing minerals and long residence times are likely to contain groundwater with high fluoride concentrations because of the greater opportunity for water rock interaction. However, the extent of

contamination depends on both the type of rock present and the chemical conditions within the formation.

Fluoride is associated with both igneous and sedimentary rocks as well as volcanic activity; minerals that are major sources of fluoride include fluorospar, cryolite, apatite, rock phosphate, mica, fluorite, and others (Jagtap et al., 2012; Fawell et al., 2006). Fluoride concentration in water is often controlled by the solubility of fluorite in particular (Deng et al., 2011). Many areas with elevated fluoride concentrations ( $>1.5$  mg/L) are characterized by low-calcium igneous and metamorphic rocks, are in areas of volcanic and hydrothermal activity, or are associated with high pH in sodium bicarbonate containing waters (Ozsvath, 2008; Fawell et al., 2006; Deng et al., 2011). Fluoride content in water is highly dependent on conditions such as pH, total dissolved solids (TDS), alkalinity, porosity of formations, temperature, and depth of wells (Mandinic et al., 2010).

Surface waters are also subject to fluoride contamination. Freshwater lakes and rivers generally contain fluoride below 0.5 mg/L, though higher concentrations have been reported from anthropogenic and natural sources (Fawell et al., 2006). Anthropogenic sources of fluoride contamination include aluminum smelters, municipal water discharge, various manufacturing plants, and fluoride-based chemical production (Jagtap et al., 2012). Surface water quality can be impacted by anthropogenic sources directly through runoff or indirectly through precipitation, which can be deposited into surface waters or infiltrate into ground waters. Natural leaching of minerals and groundwater influence may also contribute to fluoride content in surface waters (Fawell et al., 2006; Ozsvath, 2008).

## **2.3 Previous work in fluoride removal**

The UT research team (Katherine Alfredo, Mark Stehouwer and Clayton Ernst) previously investigated the removal of fluoride from drinking water using enhanced alum coagulation (Alfredo, 2012; Stehouwer, 2014). The relationship between fluoride and natural organic matter during removal was also investigated as part of this previous work. As in this study, jar tests were used to simulate the traditional treatment process. Jar tests were performed using both synthetic and natural waters. Studies were conducted with fluoride and/or NOM or a NOM surrogate added to, or present in, the base water. Separate single ligand (NOM or fluoride) jar tests were performed with fluoride and NOM over a range of pH values and alum doses to determine optimal removal conditions. Dual ligand (NOM and fluoride) jar tests were also conducted to investigate the combined impacts. A summary of the results is provided here.

### **2.3.1 Optimum pH for Removal of Fluoride and Organic Surrogates**

Single ligand, synthetic water jar tests were performed to determine the optimum pH for fluoride removal. Maximum fluoride removal was expected to occur at pH 6.5 based on aluminum solubility. The optimum pH for fluoride removal was determined to be between 6 and 7. Circumneutral pH conditions produce a positively charged aluminum hydroxide precipitate surface, which allows negatively charged fluoride ions to adsorb to or complex with the surface. At lower pH values, removal decreases because the solubility of aluminum decreases, and positively charged, soluble fluoro-aluminum complexes form. Above pH 7, hydroxide ions compete with fluoride for adsorption or complexation with the available precipitate. At higher pH conditions, the aluminum hydroxide surface is negatively charged and repels the negatively charged fluoride ions, reducing overall removal efficacy. A maximum fluoride removal of 80-85% was achieved with an alum dose of 500 mg/L in co-precipitation jar tests conducted at pH

6.55. This optimum pH for removal corresponds with maximum Al-F aqueous complexation.

Additional single ligand, synthetic water jar tests were conducted to determine the optimum pH for NOM removal. Three different low-molecular weight (LMW) organic acids were used as surrogates for NOM: salicylic acid, phthalic acid, and pyromellitic acid. Salicylic acid was best removed at pH 6, phthalic acid was best removed at pH 5, and pyromellitic acid was best removed between pH 5 and 6.

Pyromellitic acid was most easily removed with respect to both alum dose and maximum removal. At an alum dose of 100 mg/L, 85% of pyromellitic acid was removed compared to 7-10% of salicylic and phthalic acid. At an alum dose of 500 mg/L, almost 100% of pyromellitic acid was removed, while only 20-30% of salicylic and phthalic acid were removed. The variation in optimum pH and removals can be attributed to the difference in functional groups between the three acids. Functional groups were also expected to control the solubility and charge of organic matter in solution, thus dictating the charge interactions and removal of organic matter by the aluminum hydroxide precipitate during natural water testing.

### **2.3.2 Fluoride and Organic removal in dual-ligand, synthetic water systems**

Dual ligand jar tests were conducted to investigate the interrelationships between fluoride, NOM, and aluminum during alum coagulation. Fluoride removal was not significantly impacted by the presence of LMW organics. Differences in fluoride removals were less than 7% between single and dual ligand tests for alum doses greater than 20 mg/L. In addition, removals from dual-ligand tests were both higher and lower than those of single ligand tests. Fluoride removal results from single and dual ligand synthetic water tests are presented in Figure 2.1.

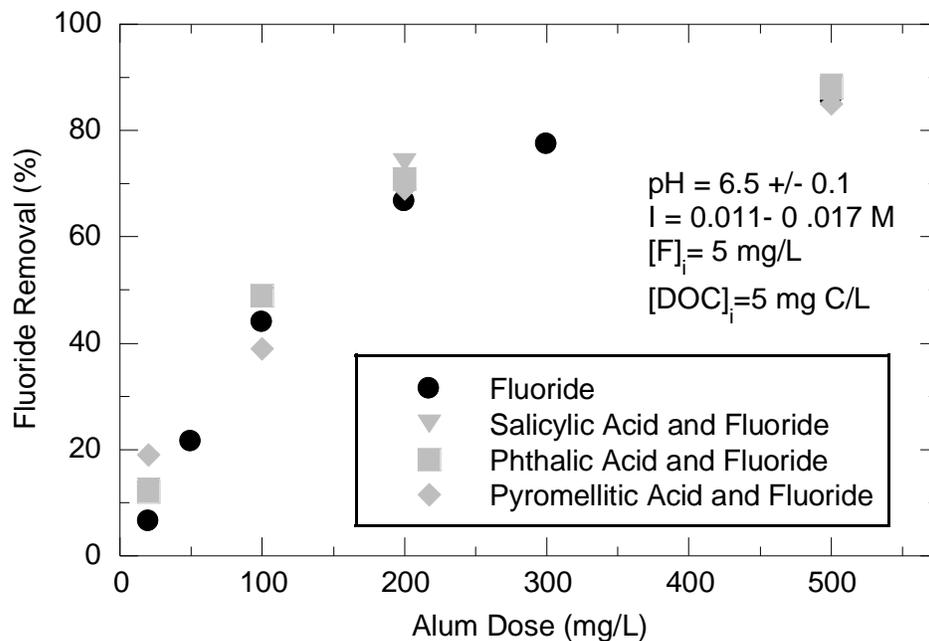


FIGURE 2.1: FLUORIDE REMOVAL IN SINGLE AND DUAL LIGAND SYNTHETIC WATER EXPERIMENTS (TAKEN FROM STEHOUEWER, 2014)

The removal of each LMW organic was reduced in the presence of fluoride. This impact was attributed to the interference of fluoride with aluminum precipitation. Alfredo, 2012 showed that fluoride replaced hydroxyl ions in aluminum hydroxide precipitate structure. This altered precipitate structure impacts the ability of the precipitate to complex with organic matter; inner sphere complexation sites are occupied by fluoride as is it incorporated into the surface structure of the precipitate. It was determined that drinking water systems removing fluoride by alum coagulation are likely to exhibit lower organic removal compared to fluoride free systems. Organic removal results are presented in Figure 2.2.

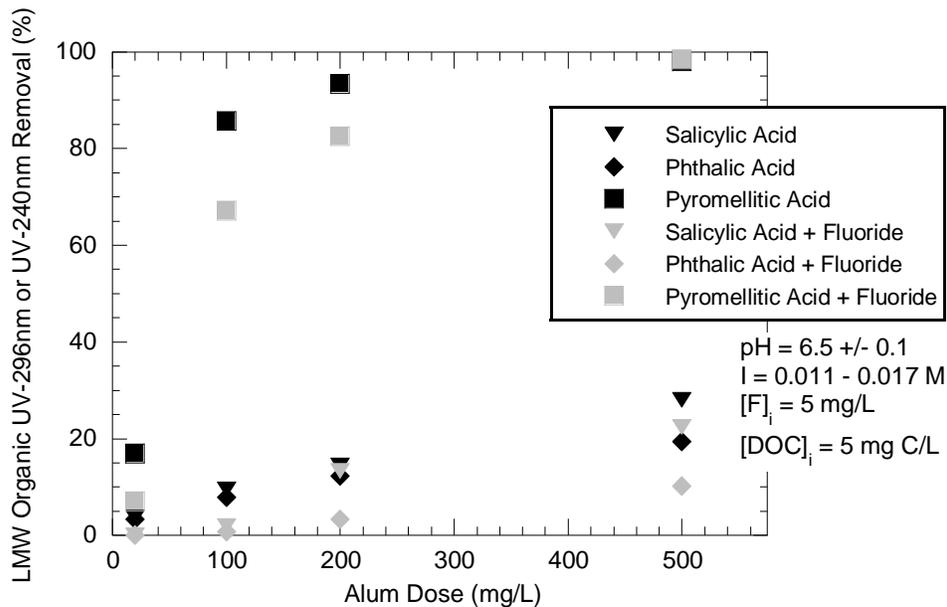


FIGURE 2.2: ORGANIC REMOVAL FROM SINGLE AND DUAL LIGAND SYNTHETIC WATER EXPERIMENTS (TAKEN FROM STEHOUWER, 2014)

### 2.3.3 Aluminum Residuals from Synthetic Water Tests

Aluminum residuals were measured for dual ligand experiments and compared to aluminum residuals from fluoride-only tests and alum-only tests. Aluminum residual results are presented in Figure 2.3. At all alum doses, residuals from fluoride-only and dual ligand systems were greater than those from alum only tests. From these results, it can be inferred that aluminum precipitation was always greater in the alum-only system. For fluoride-only and dual ligand systems, residuals decreased with increasing alum dose. This result can be attributed to the ligand to aluminum (L/A) ratio of the system. In the alum-only system, the L/A ratio is zero and aluminum can form a pure aluminum hydroxide precipitate, thus able to precipitate according to ideal conditions. When ligands are present, the L/A ratio is higher, and a mixed precipitate is formed. The L/A ratio decreases as the alum dose increases, and the precipitate that formed more closely

matches a pure aluminum hydroxide structure, allowing the precipitation behavior to more closely match that of the alum-only system.

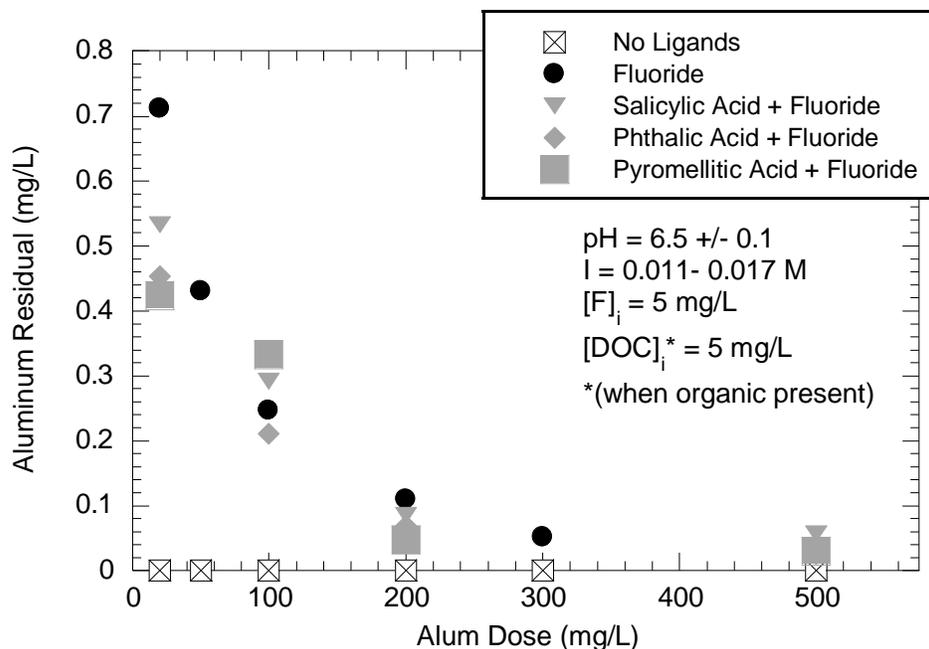


FIGURE 2.3: ALUMINUM RESIDUALS IN DUAL LIGAND SYSTEMS FOLLOWING ALUM COAGULATION (TAKEN FROM STEHOUSER, 2014)

### 2.3.4 Fluoride removal in natural water

Jar tests using natural waters confirmed observations from synthetic water tests. Researchers investigated three waters, two from Texas and one from Colorado. Only two waters are discussed in this section; water from MacKenzie Lake near Silverton, Texas (Water 1 – TX), and water from Manitou Springs, Colorado (Water 3 – CO). This section focuses on water from these two locations because they are the sites of the two pilot studies discussed in the results and discussion section of this study.

Fluoride removal was lower in Water 1 – TX than in synthetic, single ligand jar tests with an initial fluoride concentration of 5 mg/L at the same pH of 6.5 for all alum doses above 20 mg/L, which may be due to a lower initial fluoride concentration in the

pilot study waters compared to synthetic waters. This discrepancy may be due to the high NOM (9.20 mg C/L) concentrations of Water 1 – TX; d NOM may compete with fluoride for adsorption on aluminum hydroxide precipitate. Fluoride removals for both natural waters are compared to fluoride in single and dual ligand systems in Figures 2.4a and 2.4b. In contrast to Water 1 – TX, higher fluoride removals were determined in Water 3 – CO than in synthetic, single ligand jar tests at low alum doses ( $\leq 100$  mg/L), possibly due to a lower initial fluoride concentration. A maximum fluoride removal of over 80% was determined for natural waters.

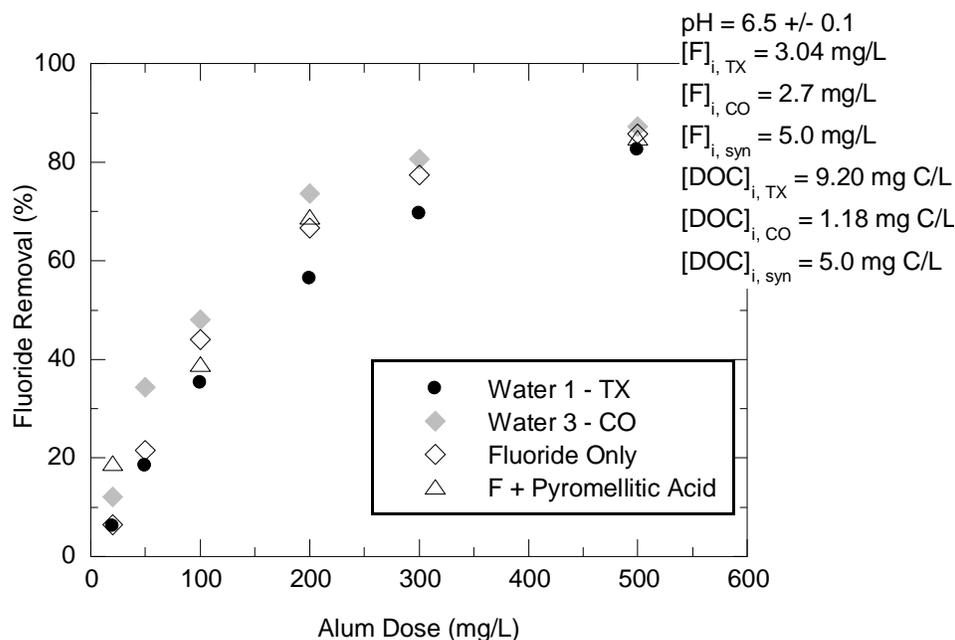


FIGURE 2.4: FLUORIDE REMOVAL IN NATURAL WATERS COMPARED TO SYNTHETIC, DUAL LIGAND EXPERIMENTS FOR (A) WATER 1 – TX AND (B) WATER 3 – CO (TAKEN FROM STEHOUWER, 2014)

The impact of pH control was investigated for Water 1 – TX. It was expected that the high alkalinity of the source water would prevent a substantial pH drop (below pH

6.5) after the addition of large amounts of coagulant. Two series of jar tests were performed, one in which the pH was not adjusted after the addition of coagulant and one in which the system was controlled at pH 6.5. At alum doses below 300 mg/L, no significant difference in fluoride removal was discovered. The pH in the natural system ranged between from 7.94 to 6.17 for these alum doses. For an alum dose of 500 mg/L, the final pH in the natural system fell to 5.04, which is significantly below 6.5. Removal was inhibited at this pH due to the reduction of aluminum solubility. Fluoride removals and system pH values for various alum doses are presented in Table 2.4. These results imply that fluoride removal in this water would not require pH adjustment for alum doses at or below 300 mg/L. While maximum fluoride removal in Water 1 – TX was at pH 6.5, fluoride removals were within 5% of each other between pH 6.5 – 7.0 for alum dose of 200 mg/L and below. Outside of this pH range, removals decreased. This stability in removals can explain why the pH natural and pH 6.5 systems exhibited similar removals across varying pH values. Fluoride removal was also similar at an alum dose of 20 mg/L even though the natural system had a pH of 7.94, which is outside of the stable range. Fluoride removal was similar to that in the pH 6.5 system because the coagulant dose is so low there is minimal removal either way.

TABLE 2.4: FLUORIDE REMOVALS AND FINAL SYSTEM pH VALUES FROM pH 6.5 AND pH NATURAL JAR TESTS USING NATURAL WATER 1 – TX AND ALUM COAGULATION

Alum Dose (mg/L)	Final pH in pH NAT System	Fluoride Removal (%)	
		pH NAT	pH 6.5
20	7.94	6	6
50	7.50	20	18
100	7.10	39	35
200	6.60	61	56
300	6.17	69	70
500	5.04	34	83

### 2.3.5 Organic removal in natural water

A maximum organic removal of approximately 30% was achieved for Water 1 – TX at pH 6. A maximum removal of 100% was achieved for Water 3 – CO, also at pH 6.0. Influent DOC contents for Water 1 – TX and Water 3 – CO were 9.20 mg C/L and 1.18 mg C/L, respectively. Organic removal in natural water tests was measured using both UV-254 and DOC; removals measured by UV-254 were generally within +/- 10% of the removals found from DOC measurements. Organic removals in Water 3 – CO were greater than those in Water 1 – TX and were achieved at much lower alum doses. However, Water 3 – CO was much lower in DOC than Water 1 – TX, which could explain the discrepancy in removals. This discrepancy could also be attributed to a higher SUVA value for Water 3 – CO, indicating the NOM was more humic and aromatic in nature.

### **2.3.6 Summary**

Experiments performed by Katerine Alfredo, Mark Stehouwer, and Clayton Ernst investigated the interactions of fluoride, NOM, and aluminum during alum coagulation. Interactions were investigated in both synthetic and natural waters. Synthetic water experiments confirmed that fluoride could be removed alone and in the presence of organic matter; the presence of fluoride reduced organic matter removal in synthetic water tests while organic matter had no significant effect on fluoride reduction. Results from natural water tests mostly confirmed trends observed in synthetic water tests. In natural waters, a high alkalinity may preclude the necessity of pH control during coagulation, at least up to some alum dose. Overall, it was determined that alum coagulation is a viable method of fluoride reduction in waters where NOM removal is also a concern. Optimal treatment conditions were also identified. Pilot studies were recommended to judge the large-scale applicability of enhanced alum coagulation with process optimization for fluoride reduction at a treatment facility.

## **2.4 Arsenic**

### **2.4.1 History of Arsenic Health Effects and Regulation**

The acute health impacts of arsenic have been well known for centuries, garnering popularity as a poison in both practice and literature. The impacts of chronic exposure to low doses, however, were not as apparent until the 20<sup>th</sup> century (Sambu and Wilson, 2008). Arsenic has been extensively applied throughout history in cosmetics, agriculture, metallurgy, glass-making, insecticides, pesticides, rodenticides, pigments, pyrotechnics, mining, wood preservatives, and even medicine (Sambu and Wilson, 2008; Bentley and Chasteen, 2002; Mandal and Suzuki, 2002). Arsenic was used in low concentration as a medicine for over 2000 years, often to treat syphilis before the invention of penicillin

(Sambu and Wilson, 2008; Jackson and Grainge, 1976; Jolliffe, 1993). Dr. Fowler's solution, containing 1% potassium arsenite, became a popular tonic in the eighteenth century and remained a popular cure-all for over 150 years (Jolliffe, 1993). But as early as 1879, arsenic was linked to lung cancer in miners from Saxony, Germany. Around the same time, continuous use of Dr. Fowler's solution was linked to various cancers (Smith et al., 1994; Sambu and Wilson, 2008). Revelations like these prompted the establishment of an arsenic standard for drinking water.

Evidence supporting the connection between chronic arsenic exposure and cancer kept building throughout the 20<sup>th</sup> century, and in 1942 the United States Public Health Service (USPHS) set an interim drinking water standard of 50 µg/L arsenic, which was adopted by the EPA in 1975 (Smith et al., 1994). After the standard was adopted, new reports continued to strengthen the link between arsenic exposure and cancer. In particular, publicity around findings from Taiwan in 1986 sparked public concern. The study showed an increase in mortality from multiple types of cancers in the same area where a strong prevalence of 'black foot disease,' a terminal gangrene, was recorded in populations drinking water from arsenic-contaminated wells. The cancer rates in Taiwan were unprecedented and added significant pressure to lower the regulated limit (Sambu and Wilson, 2008; Smith et al., 1994). The limit was lowered in 2001 to the current MCL of 10 µg/L arsenic after mounting pressure from the public and publication of a report from the National Research Council (NRC) estimating a cancer mortality risk from arsenic of 1 in 100 at 50 µg/L (Smith et al., 1994). Barringer & Reilly (2013) compiled a summary of presently known arsenic-related health impacts, which is presented in Table 2.5:

TABLE 2.5: SUMMARY OF CHRONIC ARSENIC EXPOSURE EFFECTS\*

System	Health Effects
Cardiovascular	Heart attack, cardiac arrhythmias, thickening of blood vessels, loss of circulation leading to gangrene of extremities, hypertension
Dermal	Hyperpigmentation, abnormal skin thickening, narrowing of small arteries leading to numbness, squamous and basal-cell cancer
Gastrointestinal	Heartburn, nausea, abdominal pain
Hematological	Anemia, low white-blood-cell count
Hepatic	Cirrhosis, fatty degeneration, abnormal cell growth
Neurological	Brain malfunction, hallucinations, memory loss, seizures, coma, peripheral neuropathy
Pulmonary	Chronic cough, restrictive lung disease, cancer
Respiratory	Laryngitis, tracheal bronchitis, rhinitis, pharyngitis, shortness of breath, perforation of nasal septum
Renal	Hematuria, proteinuria, shock, dehydration, cortical necrosis, cancer of kidneys and bladder
Reproductive	Spontaneous abortion, still-births, congenital deformations of fetus, low birth weight

\*Table taken from Barringer & Reilly, 2013, and references therein

Many other countries have adopted 10 µg/L as their arsenic standard after the US adopted it in 2001. The European Union Drinking Water Directive, New Zealand, Japan, Taiwan, and countries throughout Latin America have opted for a limit of 10 µg/L arsenic (Barringer and Reilly, 2013; Mohan and Pittman, 2007). Some places, like New Jersey and Australia, have set lower standards of 5 and 7 µg/L, respectively (Barringer and Reilly, 2013).

#### 2.4.2 Arsenic Occurrence in Drinking Water

Initially, due to its widespread use in mining and pesticides, arsenic contamination of surface and subsurface waters was believed to originate from localized anthropogenic sources. However, it was eventually discovered that natural arsenic

contamination is a more widespread problem (Barringer and Reilly, 2013; Nordstrom, 2002). Areas of high arsenic have been located in Argentina, Chile, Mexico, China, East Asia, the West Bengal basin, and Bangladesh – the latter being of particular concern, causing what has been recognized as one of the worst mass poisonings in human history with an estimated 30,000,000 people affected (Smedley and Kinniburgh, 2002; Welch et al., 2000; Charlet and Polya, 2006; Nordstrom, 2002). Within the US, arsenic is prevalent in the West, New Hampshire, and Maine, and it is particularly prevalent in the southwest region including Arizona, New Mexico, and Texas (Welch et al., 1988; Peters et al., 1999; Ayotte et al., 2003; Robertson; Camacho et al., 2011). Arsenic exists in over 200 mineral forms, including arsenates, arsenites, arsenides, sulfides, oxides, and silicates. These mineral forms can naturally leach into waters depending on pH, redox conditions, temperature, and solution composition (Sambu and Wilson, 2008; Nordstrom, 2002; Mandal and Suzuki, 2002; Baig et al., 2010).

Concentrations in rivers and lakes vary between <0.2 to 1000 µg/L, while concentrations in groundwater can range from <1.0 to well over 1000 µg/L; groundwater concentrations of 15,000 µg/L have been reported in Argentina and 24,000 µg/L in Mexico (Liu, 2007; Barringer and Reilly, 2013). Recently, there has been a resurgence of attention to arsenic in the US. An article in the Texas-based Austin American-Statesman reported that drinking water facilities serving 51,000 individuals in multiple rural Texas communities had exceeded the 10 µg/L arsenic MCL for the past decade (Price, 2016).

Arsenic contamination is most common in three types of environments: (1) closed basins in arid or semi-arid environments (2) strongly reducing alluvial aquifers and (3) geothermal waters. Arsenic is primarily found in groundwater where there is more water-rock interaction and potential for conditions favorable to arsenic mobilization (Smedley and Kinniburgh, 2002). Arsenic-bearing sulfides, most commonly arsenopyrite, tend to

be of concern in groundwater formations. Additionally, arsenic has shown an affinity for pyrite, iron hydroxides, and iron oxides (Barringer and Reilly, 2013).

Oxidation and reduction of arsenic-bearing minerals are common mechanisms of arsenic release; oxidation of sulfides can lead to arsenic contamination through mineral dissolution, while reduction of iron hydroxides can lead to contamination through mineral dissolution or release of sorbed arsenic (Barringer and Reilly, 2013; Wan et al., 2011). The substantial release of arsenic into alluvial aquifers in Bangladesh and West Bengal has been attributed to reductive dissolution of arsenic-rich iron oxyhydroxides, which are themselves derived from weathering of upstream base-metal sulfides (Nickson et al., 1998). Surface water quality can be influenced by groundwater as well as directly impacted by anthropogenic and natural sources (Barringer and Reilly, 2013).

Arsenic speciation is highly dependent on source water redox conditions (Mohan and Pittman, 2007; Vaclavikova et al., 2008). Arsenic most commonly exists in water in two oxidation states: arsenite ( $\text{AsO}_3^{3-}$ ) and arsenate ( $\text{AsO}_4^{3-}$ ), hereafter referred to as As(III) and As(V), respectively. An Eh/pe-pH diagram for arsenic is presented in Figure 2.5. As(V) generally predominates in oxygenated aerobic environments, while As(III) is more common in anaerobic reducing environments (Mohan and Pittman, 2007; Welch et al., 2000; Mudhoo et al., 2011). In the pH range most relevant to municipal water supplies, pH 6-9, As (III) is most commonly found as  $\text{H}_3\text{AsO}_3$ , while As(V) is most commonly found as anionic  $\text{H}_2\text{AsO}_4^{2-}$ . (Kartinen and Martin, 1995).

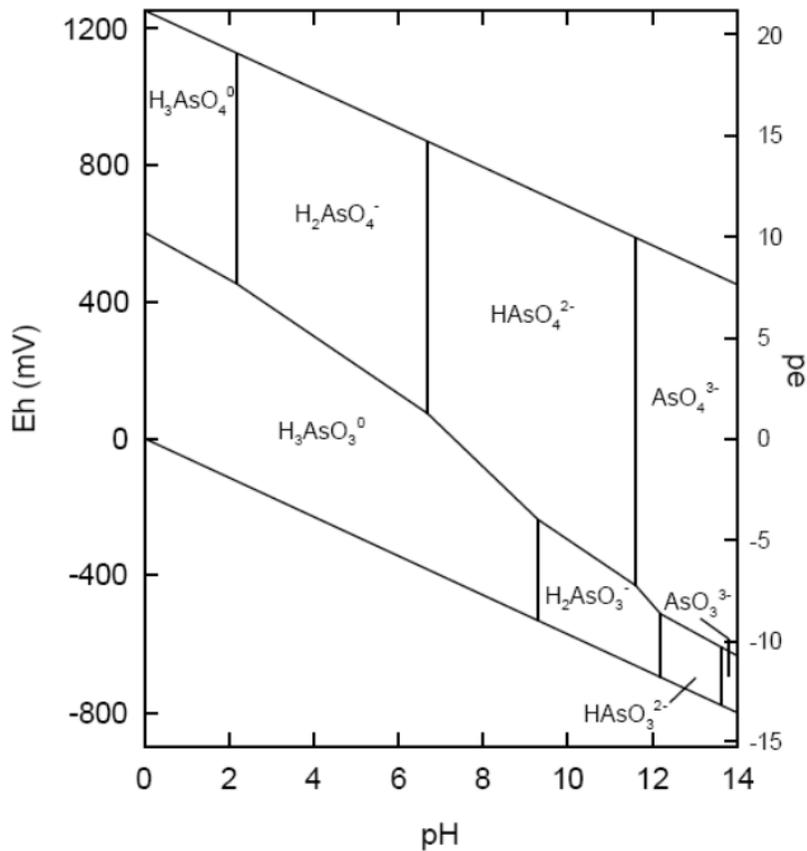


FIGURE 2.5: EH/PE-PH DIAGRAM FOR THE SPECIATION OF ARSENIC (TAKEN FROM CHIBBAN, ZERBET, CARJA, & SINAN, 2012)

As(III) is widely regarded as the more mobile and toxic form of arsenic, while As(V) is found to be easier to remove during treatment (Pallier et al., 2009; Jolliffe, 1993; Mercer and Tobiason, 2008; Bordoloi et al., 2013; Ahmed, 2001). Arsenic speciation, and thus toxicity, can also be influenced by microorganism metabolism through reduction, oxidation, and methylation. Organic (methylated) arsenic does not typically occur at high concentrations, but can be a problem in water affected by industrial pollution (Muller et al., 2007; Smedley and Kinniburgh, 2002; Wan et al., 2011).

### **2.4.3 Existing Technologies for Arsenic Removal from Drinking Water**

Arsenic removal has been extensively studied. The imminent reduction of the arsenic MCL in the late 90's prompted many investigations into the most efficacious and economic methods for arsenic removal in municipal drinking water systems. These methods and new ones continue to be studied, as arsenic remains one of the most dangerous contaminants in drinking water. Multiple technologies have been discussed, including conventional coagulation/flocculation and adsorption processes, as well as more advanced techniques. Adsorption and coagulation are the two most common treatment methods for arsenic removal at present. Because of the acknowledged affinity for iron minerals, existing arsenic literature tends to focus on iron-based coagulants and adsorbents. Aluminum-based adsorbents and coagulants are also investigated to a lesser extent, but most studies look at groundwater sources that are lacking in organic material; knowledge of the interactions between aluminum, arsenic, and NOM during coagulation is lacking. Table 2.6 lists common removal technologies and some of the more prominent studies reported on each technology.

TABLE 2.6: REVIEW OF COMMON TECHNOLOGIES FOR THE REMOVAL OF ARSENIC FROM DRINKING WATER

Technology	Sources
Adsorption	Ahmed, 2001; Jeong et al., 2007; Mohan & Pittman, 2007; Smedley & Kinniburgh, 2002; Vaclavikova, Gallios, Slavomir, Ae, & Jakabsky, 2008
Coagulation and filtration	Ahmed, 2001; Bordoloi et al., 2013; Chwirka, Colvin, Gomez, Mueller, & Mueller, 2004; Kartinen & Martin, 1995; Mudhoo et al., 2011; Pallier et al., 2009; Vaclavikova et al., 2008
Electrocoagulation	Ali, Khan, & Asim, 2011; Mohora et al., 2012; Wan et al., 2011
<i>In situ</i> aquifer oxidation	Ahmed, 2001
Ion-exchange	Ahmed, 2001; Johnston, 2001; Kartinen & Martin, 1995
Lime-softening	Kartinen & Martin, 1995; Mudhoo et al., 2011
Membrane separation	Ahmed, 2001; Johnston, 2001; Kartinen & Martin, 1995; Mercer & Tobiason, 2008; Mudhoo et al., 2011

#### 2.4.4 Studies on Alum Coagulation for Arsenic Removal

Multiple studies have investigated alum coagulation for arsenic removal. Because arsenic is predominantly found in groundwater, most studies focus on groundwater sources. Studies found that alum coagulation is an effective means of arsenic removal from drinking water; the USEPA has identified coagulation and filtration as a best available technology (BAT) for arsenic removal (Chwirka et al., 2004). The primary removal mechanisms for arsenic during alum coagulation are co-precipitation directly with aluminum hydrolysis products and adsorption onto freshly formed amorphous aluminum hydroxide. Direct precipitation of insoluble arsenic-aluminum compounds ( $\text{Al}(\text{AsO}_4)$ ) can also occur, but arsenic removal is dominated by adsorption and co-precipitation (Liu, 2007; Johnston and Heijnen, 2001; McNeill and Edwards, 1997).

McNeil and Edwards (1997) conducted surveys of full-scale drinking water treatment plants to form statistical models for predicting arsenic removal from both iron

and alum coagulation. Plants using alum coagulation had removal efficiencies ranging from 0 – 96%; half of the plants surveyed achieved removal efficiencies near or above 80%. Coagulation pH ranged from 6.85 to 7.8 and alum dose ranged from 6 to 30 mg/L alum over six separate facilities. There was no observed difference in removal efficiency between iron and alum coagulation when the pH was below 7.6. Temperature, pH, competing anions, coagulant dose, and coagulant type were identified as parameters of interest that could potentially impact removal, however, their specific effects are not detailed. Rather, it was reported that these parameters were found to have relatively small effects on As removal as evidenced by low correlation coefficients in the discussed model.

Hering et al. (1997) conducted bench scale tests using natural source waters and synthetic freshwaters to compare both the effects of influent water characteristics on arsenic removal and the impact of coagulant choice. Alum was found to remove greater than 90% of initial arsenic with average initial arsenic concentrations near 22 µg/L. Arsenic removal was greatest at pH 6 – 7 and was not significantly dependent on source water composition. As the alum dose was increased from 10 to 40 mg/L at pH 7, the arsenic removal also increased to a maximum of 98% and brought the final concentration down to < 0.5 µg/L. It was noted that the presence of NOM could have a negative impact on arsenic removal, but the presence of sulfate had no impact on removal over the examined pH range. While both alum and ferric chloride were used in the study, the impacts of NOM were primarily presented with respect to ferric coagulation. The authors also noted that pilot studies at the time reported lower efficacies than expected from bench scale testing.

In 2001, Gregor measured arsenic reduction at three drinking water facilities in New Zealand that draw water from the Waikate River, which has natural and

anthropogenic geothermal sources of arsenic contamination. Ambient pH throughout the year ranged from 7.2 – 8.7, with influent arsenic near 18  $\mu\text{g/L}$  in the winter and almost 28  $\mu\text{g/L}$  in the summer; 85 – 100% of arsenic was soluble, and 90% of soluble arsenic was As(V). Two of the three treatment facilities used alum as their coagulant, and both also employed synthetic flocculation aids. Both facilities achieved effluent arsenic concentrations of  $\leq 5 \mu\text{g/L}$ , though this was exceeded by one plant in the summer. In this study, Gregor highlighted the seasonal variations of arsenic influent concentration and removal efficacy. Gregor also highlighted the importance of particulate arsenic in the treatment process, asserting that it is “key” to low arsenic concentrations; the ultimate goal during coagulation is to convert all soluble arsenic to the particulate form so it can be removed during sedimentation or filtration. Particulate arsenic can be a large portion the total arsenic content in surface waters, ranging from 23 – 54% in some sources (Chen et al., 1999; McNeill and Edwards, 1997). While the authors acknowledge the presence of NOM-bound arsenic, the impact of organic content on treatment effectiveness was not specifically discussed.

Given the importance of arsenic speciation and particulate versus soluble content, NOM is expected to play an important role in arsenic treatment. Indeed, the presence and composition of NOM has been identified as an important parameter during coagulation for arsenic removal (Pallier et al., 2009; Liu, 2007; McNeill and Edwards, 1997; Mohan and Pittman, 2007). Some studies have examined the connection between NOM and arsenic during ferric coagulation, but the relationship between NOM and arsenic during aluminum coagulation requires further investigation (Pallier et al., 2009; Smedley and Kinniburgh, 2002). The presence of NOM has been shown to have a negative effect on arsenic removal during ferric coagulation; Smedley and Kinniburgh (2002) found that

NOM and arsenic compete with each other for adsorption sites on coagulated iron hydroxides (Hering et al., 1997; Pallier et al., 2009).

NOM plays an important role in arsenic cycling in natural waters; it affects arsenic fate and mobility through sorption ability, aqueous complexes, and redox potential (Mudhoo et al., 2011). Liu (2007) confirmed that interactions between NOM and arsenic could directly impact redox potential and speciation of arsenic, which could have a significant impact on removal. In many cases, drinking water plants apply pre-oxidation to convert the more recalcitrant As(III) to the more easily removed As(V) (Pallier et al., 2009; Ahmed, 2001; Bordoloi et al., 2013). Because As(V) typically dominates in aerobic environments, it could be assumed that treatment plants using surface waters would not necessarily require oxidation. However, high As(III) in water has been associated with high NOM content in water, and alum coagulation has been shown to be almost completely ineffective at removing As(III) from water (Liu, 2007; Hering et al., 1997; Gregor, 2001). Additionally, pre-oxidation in organic rich waters would be unwise due to the formation of DBP's (Pallier et al., 2009; Liu, 2007; Matilainen et al., 2010; Leenheer and Croue, 2003). Further investigation of the relationships between arsenic (including its oxidation state), NOM, and aluminum during coagulation is necessary to determine process efficacy and recommend treatment guidelines for optimization.

## **2.5 Summary**

Coagulation and flocculation are the cornerstones of the conventional drinking water treatment. Coagulation is especially important for surface water plants, which tend to be concerned with NOM as well as particle removal. Alum is one of the most commonly used coagulants in practice and is shown to be effective at removing NOM

through enhanced alum coagulation. Alum coagulation can also be used to remove inorganic contaminants from water; previous work conducted by Alfredo, Stehouwer, and Ernst at the University of Texas at Austin confirmed the viability of enhanced alum coagulation for the reduction of fluoride in drinking water at a bench scale (Alfredo, 2012; Stehouwer, 2014). This same methodology could potentially be applied to other inorganic contaminants, such as arsenic, which can also be removed through alum coagulation.

Many small treatment plants that currently use enhanced alum coagulation for NOM and turbidity removal would find it easy to also apply it for the removal of arsenic and fluoride. Given the likely reduction of the fluoride MCL, small treatment facilities with naturally high influent fluoride concentrations could find it difficult to meet new treatment goals. Adjusting their treatment parameters, such as operating pH and alum dose, would be an easier and more economical adjustment than changing their entire treatment process (Chen et al., 1999; Pallier et al., 2009; Piñón-Miramontes et al., 2003). Likewise, enhanced alum coagulation could be applied and optimized for arsenic removal as well.

While some studies have shown that iron-based coagulants are more effective at removing arsenic, alum coagulation can also achieve excellent removals and is often equally as effective as ferric coagulation (see Section 2.3.4). Treatment facilities with alum coagulation already in place could adjust their treatment parameters to target arsenic as well; the ability to optimize fluoride removal conditions lends credence to this potential. Treatment facilities for surface water could also be uniquely poised to apply alum coagulation by not requiring a pre-oxidation step to transform As(III) into As(V), though particulate arsenic and NOM content could complicate the process. Results from this research will determine the applicability of enhanced alum coagulation for fluoride

reduction at a pilot scale as well as elucidate the relationship between arsenic, NOM, and aluminum during alum coagulation.

## CHAPTER 3: MATERIALS AND METHODS

For this study, experiments were completed at both the bench and pilot scale. At the bench scale, jar tests were run to simulate full-scale traditional coagulation-based drinking water treatment. The three sequential phases of rapid mixing, slow mixing, and settling represent the different steps in full-scale systems. Multiple experimental parameters were varied to simulate different conditions and gain insight on contaminant removal during coagulation; these parameters included ligand concentration, alum dose, and system pH. All experiments used either synthetic waters or natural waters sourced from drinking water treatment plants.

Experiments were first run using synthetic waters made from chemical reagents and de-ionized water. Natural waters were used to investigate process efficacy in real, complex systems. Natural waters were obtained from drinking water systems in Texas and Colorado. In addition to the jar tests, pilot studies were conducted at the small systems that provided natural water samples. At these facilities, multiple continuous flow experiments were conducted to simulate coagulation based drinking water treatment at the pilot-scale level. Results were compared to jar tests and between pilot studies to better understand system effectiveness and optimization in real-world applications.

### 3.1 Chemical Reagents

All chemicals and reagents used were of analytical grade or higher. All synthetic water and stock solutions were prepared using de-ionized water. Synthetic water composition was designed to resemble that of natural water with a hardness of 3 meq/L and an alkalinity of 3 meq/L. Synthetic waters were made from a combination of calcium chloride (Calcium Chloride Dihydrate,  $\text{CaCl}_2(\text{H}_2\text{O})_2$ , ACS Powder, Fisher Scientific), sodium bicarbonate (Sodium Bicarbonate,  $\text{NaHCO}_3$ , Certified ACS, Fisher Scientific),

and sodium chloride (Sodium Chloride, NaCl, ACS, Alfa Aesar). The calcium chloride dihydrate provided hardness, the sodium bicarbonate provided alkalinity to buffer the solutions after alum addition in the jar tests, and the sodium chloride adjusted the ionic strength. Ionic strength varied between 0.01 and 0.017 due to the addition of hydrochloric acid or sodium hydroxide for pH adjustment. Synthetic water was made in 2L batches and acidified with 6 mL of 1N hydrochloric acid, which was previously made from concentrated hydrochloric acid (Hydrochloric Acid, 36.5-38.0% V/V, HCl, ACS, EMD Millipore). The recipe for synthetic water and compositions of natural waters used can be found in Section 3.4.

Alum (Aluminum Sulfate Hydrate,  $\text{Al}_2(\text{SO}_4)_3 \cdot 18(\text{H}_2\text{O})$ , 98%, Aldrich Chemical Company) was used as the coagulant during experimentation. During jar tests, the jars were dosed with a stock solution of 13.32 g/L alum; alum stock solutions for jar tests were made in 100 mL batches and acidified with 4 mL of 1N hydrochloric acid. During pilot studies, either one of two solutions were used: a high-concentration solution of 10400 mg/L alum or a low-concentration solution of 2550 mg/L alum; with 18 moles of hydration, the aluminum concentrations were 31 mM and 7.7 mM Al, respectively. Two concentrations of alum were required to account for variations in alum dose and allowable flow rates during testing. Alum stock solutions for pilot studies were made in 4 L batches.

During synthetic water jar tests, ligands were added using chemical solutions of organic matter surrogates, and either fluoride or arsenic (depending on the interest for that test). Three low molecular weight organic acids were used as natural organic matter surrogates. Jars were dosed to 5 mg/L carbon from solutions of 1000 mg/L carbon. Batches of 100 mL were made for each organic acid from reagents (Phthallic Acid,  $\text{C}_8\text{H}_6\text{O}_4$ , 99.5% ACS, Alfa Aesar; pyromellitic Acid,  $\text{C}_{10}\text{H}_6\text{O}_8$ , 96%, Alfa Aesar;

Salicylic Acid, C<sub>7</sub>H<sub>6</sub>O<sub>3</sub>, AR, Mallinckrodt). Jars were dosed to 5 mg/L fluoride using a stock solution of 1000 mg/L fluoride. The stock solution was made from de-ionized water and sodium fluoride (Sodium Fluoride, NaF, Certified ACS, Fisher Scientific). A stock solution was used to dose jars to an initial concentration of 50 µg/L As(V). The As(V) stock solution was made in 100 mL batches using de-ionized water and a certified ICP arsenic 1000 mg/L standard solution purchased from VWR International. The arsenic stock solution was acidified to 2% v/v concentrated nitric acid (Nitric Acid, HNO<sub>3</sub>, OmniTrace).

Hydrochloric acid and sodium hydroxide were used to adjust pH during jar testing. Hydrochloric acid (1N) was made from concentrated hydrochloric acid, and sodium hydroxide (1N) was made from concentrated sodium hydroxide (Sodium Hydroxide, NaOH, 10.0N, BDH). Both solutions were made in 100 mL batches. During jar tests using the natural water from Colorado, a solution of 2.5 g/L sodium carbonate (Sodium Carbonate, Na<sub>2</sub>CO<sub>3</sub>, EM Science) was also used to add buffering capacity and prevent an untenable drop in pH over the course of the test. Sodium carbonate was chosen because it is already used for pH adjustment in drinking water facilities. Jars were dosed to 32.06 mg/L sodium carbonate, and hydrochloric acid and sodium carbonate were used for further pH adjustment. This concentration of sodium carbonate was determined by titration to offset the acid addition associated with a 50 mg/L alum dose. During pilot studies, the pH was controlled using only sodium carbonate. Two solutions of 5 and 20 g/L sodium carbonate were used; two concentrations were required to allow sufficient control and to not significantly dilute the raw water by the chemical additions. The sodium carbonate solutions were made in 4 L batches.

## **3.2 Jar Tests**

Jar tests were used to simulate the coagulation-based treatment process commonly applied in drinking water treatment. A Phipps & Bird PB-700 Jartester was used with six rectangular, custom-made acrylic jars. A seventh jar with no added chemicals was also put through the full mixing and settling process to act as a blank for all analytical methods. All jar tests were either co-precipitation or pre-formed tests. During co-precipitation, ligand(s) and amorphous aluminum hydroxide were allowed to precipitate at the same time; this effect was achieved by ensuring that all ligands were present in the jars before the coagulant was added and mixed. During pre-formed tests, aluminum hydroxide flocs were allowed to form for 48 hours before the addition of ligands. The jar testing procedure for arsenic was the same as for fluoride experiments previously completed by Stehouwer, 2014, whose results are discussed in Section 2.3.

### **3.2.1 Co-Precipitation Jar Tests**

Each jar was initially filled with 200 mL of synthetic or natural water. When synthetic water was used, all ligands were added at the beginning of the test prior to any mixing. Jars were individually placed on a Corning PC-420D stir plate and rapid mixed for 4-8 minutes. During this time, jars were dosed with pre-determined volumes of alum stock and, when required, sodium carbonate, and the pH was adjusted to the desired value using 1N solutions of either hydrochloric acid or sodium hydroxide.

A sodium carbonate solution was used in jar tests involving natural water from Colorado to provide alkalinity so that the desired system pH value in each jar would be maintained throughout the test. A detailed composition of the natural waters used can be found in Section 3.4.2. In all tests the sodium carbonate buffer was added concurrently with alum because this procedure ensures that the pH is never far from the target value and therefore controls the hydrolysis reactions at the desired pH. When further pH

adjustment was required after addition of sodium carbonate and alum, 1N solutions of hydrochloric acid and sodium hydroxide were used to reach the desired pH.

After chemical addition and rapid mixing, each jar was then set to slow mix at 20 rpm with a mean velocity gradient (G) of 12-15 s<sup>-1</sup> for thirty minutes, followed by quiescent settling for forty minutes (Cornwell and Bishop, 1983). The start time of each jar was staggered so that each jar was dosed and set to mix individually and sequentially. This procedure allowed each jar to have the same time frame for chemical addition, mixing, and sampling.

After mixing and settling, the final pH was measured for the jar. Then, samples were taken from the supernatant. The supernatant was drawn from the jars using a wide-mouth pipette. Samples were withdrawn slowly to prevent disturbance and re-suspension of any flocs in the jars, and also to prevent breakup of flocs in the samples prior to measuring the turbidity. The samples were analyzed for turbidity, TOC, UV-254, residual ligand concentration, and residual aluminum concentration. Samples for turbidity were unfiltered, and samples for all other analytical analyses were filtered through a 0.45 µm, Pall Acrodisc, Supor Membrane filter.

### **3.2.2 Pre-Formed Jar Tests**

Pre-formed jar tests allowed for the formation of amorphous aluminum hydroxide solid in the absence of any competing ligands. Pre-formed tests were only used in synthetic water. Jars were filled with 200 mL of synthetic water, dosed with the desired concentration of alum, and brought to pH 6.5. This pH was chosen based on minimum aluminum solubility for maximum solid formation. The jars were then set to slow mix at 20 rpm for 48 hours.

After the formation of the solids, each jar was sequentially taken off of slow mix and placed on the same Corning PC-420D stir plate used in co-precipitation testing. Jars were mixed at slower rate to allow for distribution of added chemicals but prevent floc break-up. Jars were adjusted to the desired pH using 1N solutions of hydrochloric acid and sodium hydroxide. After achieving the desired pH, jars were dosed with 50 µg/L arsenic, and the pH was readjusted if needed. Jars were then returned to slow mix and followed the same procedure as was used during co-precipitation for the remainder of testing. This

### **3.3 Experimental Systems**

#### **3.3.1 Single Ligand Systems**

Jar tests in which only fluoride, arsenic, or a low molecular weight organic acid were classified as single ligand systems. Single ligand systems allowed for co-precipitation of the ligand with amorphous aluminum hydroxide flocs. Results from single ligand systems provided baseline results for each ligand.

#### **3.3.2 Dual Ligand Systems**

Jar tests in which both a low molecular weight organic acid and either fluoride or arsenic were present were classified as dual ligand systems. Dual ligand systems allowed for co-precipitation of ligands with amorphous aluminum hydroxide flocs. Dual ligand system results were compared to single ligand system results to examine any competition and resulting impact on removal efficacy.

### 3.4 Experimental Waters

#### 3.4.1 Synthetic Waters

Synthetic waters were prepared to represent a simple, controlled natural water. Synthetic waters were prepared in 2 L batches in the laboratory using reagents and de-ionized water. A complete recipe for the synthetic water used is provided in Table 3.1.

TABLE 3.1: SYNTHETIC WATER RECIPE (2 L BATCH)

Reagent	Quantity	Unit	Contribution
CaCl <sub>2</sub>	336	mg	Hardness
NaHCO <sub>3</sub>	504	mg	Alkalinity
NaCl	760	mg	Ionic Strength
HCl (1N)	6	mL	Acidification
H <sub>2</sub> O	1.994	L	Background Solute

#### 3.4.2 Natural Waters

A UT research team led by Mark Stehouwer previously identified natural waters for this project. Waters were selected based on fluoride concentration and water source. Drinking water systems with a background fluoride concentration of greater than 2 mg/L and drawing from a surface water source were desired. Surface water was desired as these systems are more likely to have a significant NOM content and a significant turbidity, and therefore were more likely to consider using alum treatment than a groundwater. A minimum background concentration of 2 mg/L fluoride was chosen because it is at or near the minimum concentration at which aesthetic impacts and mild dental fluorosis can occur. Characteristics for the two natural waters utilized in experimentation are found in Table 3.2.

TABLE 3.2: NATURAL WATER CHARACTERIZATION

Parameter	Natural Waters	
	Water 1 – TX Lake MacKenzie	Water 2 – CO Manitou Springs
Water Source	SW	SW
pH	8.60	7.58
[F] (mg/L)	3.04	2.69
DOC (mg/L Carbon)	9.20	1.18
SUVA (L/mg-m)	0.87	1.76
Alkalinity (mg/L CaCO <sub>3</sub> )	294.6	16.8

Contact was made with personnel at the drinking water systems prior to requesting natural water samples. This contact allowed for further information to be gathered about the water systems. Insulated coolers were shipped to each system via ground courier and contained a 20 L Nalgene carboy, ice packs, and filling instructions. Attendants at the systems were instructed to rinse the carboys three times with raw water before filling, and to eliminate headspace in the carboy by filling to the top. The ice packs provided were re-frozen on site and used to pack the returning, full carboys within the coolers. These coolers were then sent back to the laboratory via ground courier. Upon reception, the carboys were taken out of the coolers and placed in a 4°C cold room until use.

### 3.5 Sampling Processes

Unless stated otherwise, all samples were withdrawn using a glass wide-mouth pipette and filtered through a 25 mm, 0.45 µm pore nylon syringe filter (VWR International). Samples were withdrawn slowly from the supernatant to avoid disturbing or re-suspending the settled flocs.

### **3.5.1 pH Analysis**

The pH was measured *in situ* during jar tests using an Orion Ross Ultra pH/ATC Triode Combination Electrode (Fisher Scientific). The probe was calibrated before each test using HACH pH 4.1, 7, and 10.1 buffer solutions. The pH was measured at the beginning of the jar test prior to alum and ligand addition, during pH adjustment, and at the end of each experiment. The probe was maintained with Ross filling solution and was stored in Ross storage solution between uses.

### **3.5.2 Turbidity Sampling and Analysis**

Samples for turbidity were taken at the end of each jar test after the quiescent settling period. A sample was also taken from well-mixed raw water prior to each jar test to provide a turbidity baseline. All turbidity samples were analyzed using a HACH Ratio/XR turbidimeter calibrated with Gelex standards.

### **3.5.3 Organic Sampling and Analysis**

Samples for organic analysis were taken before testing and directly after quiescent settling. Samples were filtered, and absorbance was measured using an Agilent 8453 Spectrophotometer at different wavelengths for the different types of organic matter used in this research. A wavelength of 254 nm was chosen for the natural organic matter, as this is a standard measure in the field. Separate wavelengths were chosen for each organic matter surrogate based on their individual wavelengths of highest absorbance. Standard curves were constructed for all surrogates and sample calibration curves are presented in Figures 3.1a, b, and c. All wavelengths used are presented in Table 3.3.

TABLE 3.3: ORGANIC MATTER WAVELENGTHS USED FOR SAMPLE ANALYSIS

<b>Organic</b>	<b>Water Type</b>	<b>Wavelength (nm)</b>
Natural Organic Matter	Natural	254
Phthalic Acid	Synthetic	240
Salicylic Acid	Synthetic	296
Pyromellitic Acid	Synthetic	296

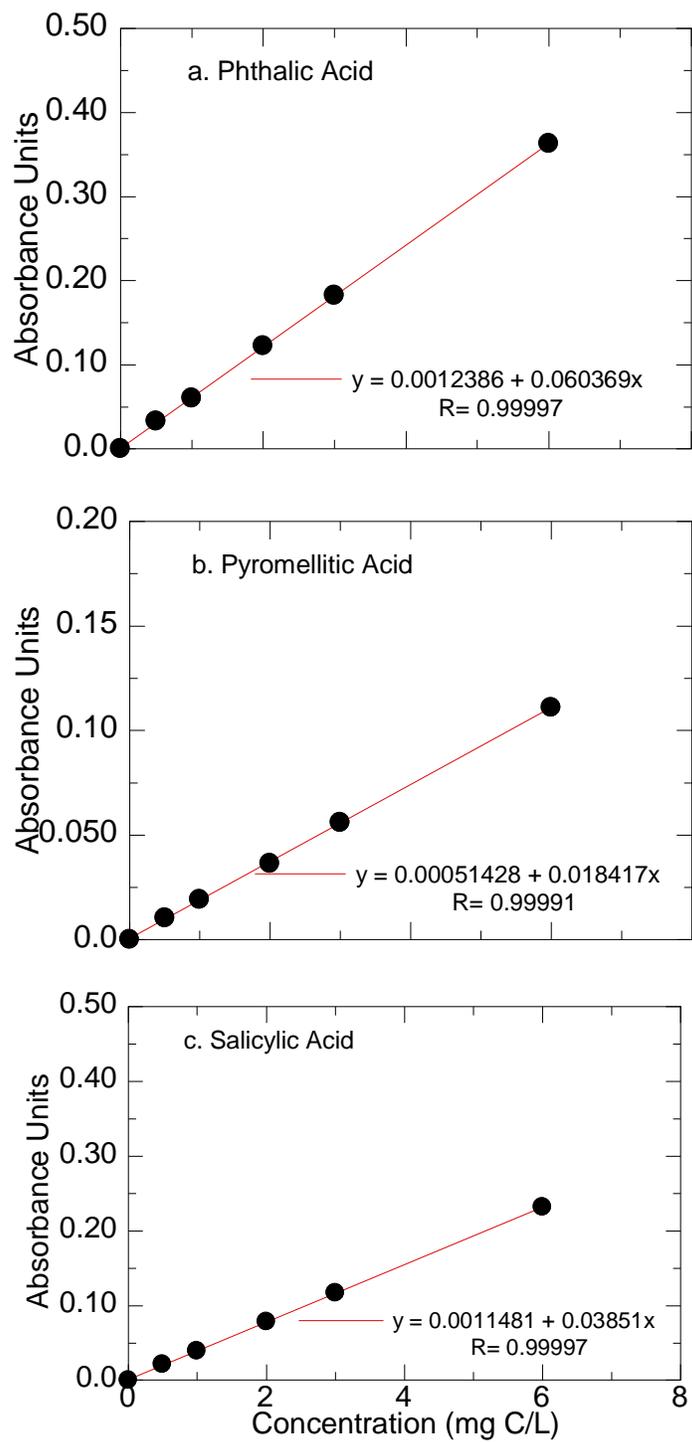


Figure 3.1 Typical Standard Curves for the Organic Acids

### 3.5.4 Aluminum Residual Sampling and Analysis

Aluminum residuals were measured using inductively coupled plasma-optical emission spectroscopy (ICP-OES). Samples for aluminum analysis were taken directly after quiescent settling during each jar test. Samples were filtered and 10 mL of filtrate were placed in a 15 mL plastic centrifuge tube. Samples were acidified with 200  $\mu$ L of concentrated nitric acid per 10 mL of sample and stored at 4°C until analysis. Residual aluminum concentrations were measured using a Varian 710-ES ICP-OES and Autosampler with 2% concentrated nitric acid mobile phase. A standard calibration curve was constructed at the beginning of each run with standards made from an aluminum ICP stock solution. Sample blanks were measured after every five to six samples to rinse the probe and prevent carry-over. A standard calibration curve example is provided in Figure 3.2.

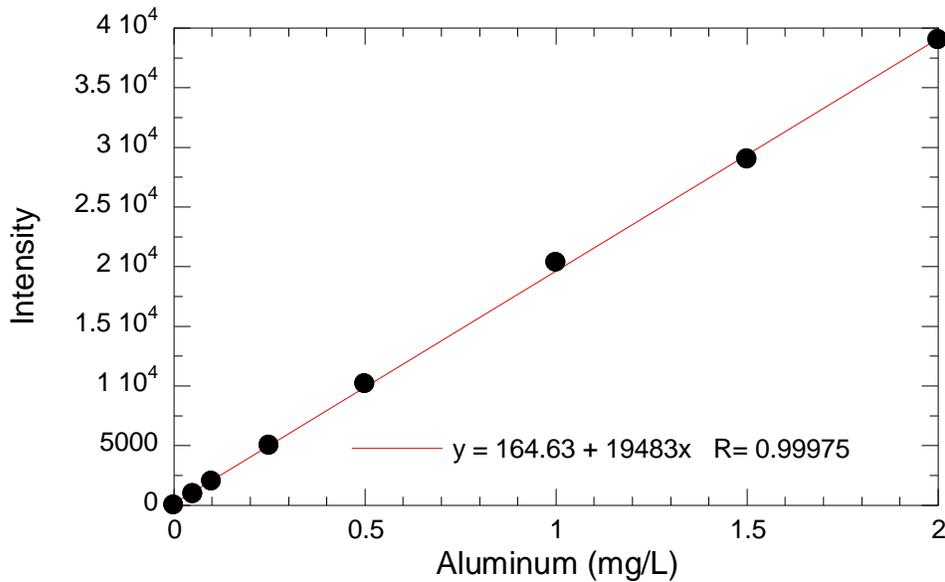


FIGURE 3.2: TYPICAL ALUMINUM STANDARD CURVE

### 3.5.5 Fluoride Sampling and Analysis

Samples for fluoride analysis were taken directly after the quiescent settling period and measured directly after the completion of each jar test. Samples of 10 mL were taken from the supernatant and filtered through a 25 mm, 0.45  $\mu\text{m}$  pore nylon syringe filter (VWR International) before analysis. Fluoride residual samples were adjusted using TISAB II with CDTA (TISAB II, Orion 940909, Thermo Scientific) at a volumetric ratio of 1:1 to prevent complexation and background interference of aluminum with fluoride measurements. An Orion 9609BNWP Ionplus Sure-Flow Fluoride Probe purchased from Thermo Scientific was used for all fluoride measurements. Measurements were taken as milli-volts and converted to mg/L using a fluoride standard calibration curve. A standard curve was constructed prior to each analysis. To ensure measurement accuracy and counteract drift, the probe was re-zeroed after every two samples using the blank calibration standard. An example of a fluoride standard calibration curve is provided in Figure 3.3.

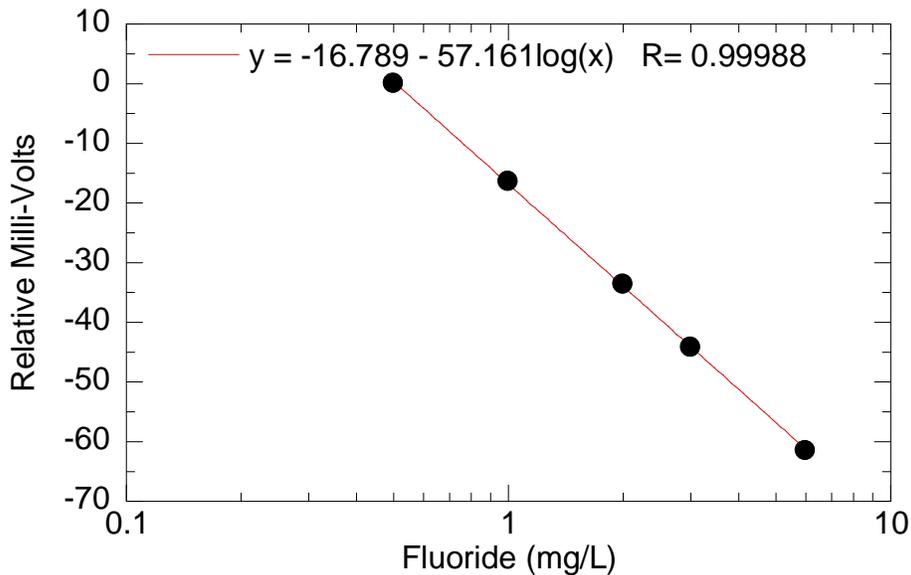


FIGURE 3.3: TYPICAL FLUORIDE STANDARD CURVE

### 3.5.6 Arsenic Residual Sampling and Analysis

Samples for arsenic measurement were taken at the end of the quiescent settling period for analysis. Samples were also taken before coagulant addition to serve as controls. Arsenic was measured by Graphite Furnace Atomic Adsorption (GFAA) using a Perkin Elmer AAnalyst 600 and Autosampler with Zeeman Background Correction. Arsenic samples were acidified with 200  $\mu\text{L}$  concentrated nitric acid per 10 mL sample. A premixed matrix modifier of 0.005 mg palladium and 0.003 mg magnesium nitrate per 5  $\mu\text{L}$  solution, purchased from Environmental Express, was used during arsenic analysis to prevent interference from the background matrix and aluminum. The matrix modifier was added by the Autosampler at a ratio of 5  $\mu\text{L}$  per 20  $\mu\text{L}$  sample withdrawal. A standard calibration curve was constructed before each run using the sample matrix and a certified ICP 1000 mg/L arsenic standard solution purchased from VWR International. A standard calibration curve example is provided in Figure 3.4.

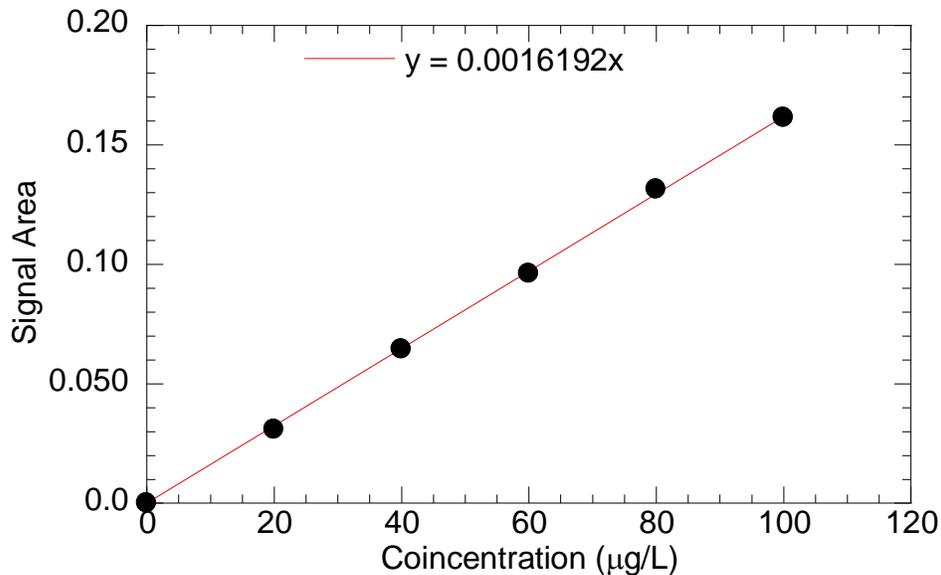


FIGURE 3.4: TYPICAL ARSENIC STANDARD CURVE

## 3.6 Pilot Studies

### 3.6.1 Pilot Study Experimental Set-Up

Two pilot studies were conducted over the course of this research. The pilot studies were located at Lake MacKenzie, TX and Manitou Springs, CO. Each study took place over 4-6 days. Continuous-flow experiments were run using, raw, untreated influent water from the treatment plant where each pilot study took place. Raw water was held in a 50 gallon plastic drum and periodically mixed to prevent any settling or stratification. Masterflex peristaltic pumps and tubing were used throughout the system to control flow. Unless stated otherwise, the experimental set-up consisted of an influent storage drum, rapid mix chamber, and four-chamber flocculation basin. The full experimental set up is presented in Figure 3.5.



FIGURE 3.5: FULL PILOT STUDY EXPERIMENTAL SET UP

The system flow rate was 380 mL/min, consistent with a 30 minute detention time in the flocculation basin. The raw, untreated influent was first pumped from the storage drum into the rapid mix chamber for chemical addition. Stock solutions of the specific chemicals used in each pilot study were kept in individual containers and pumped at pre-determined flow rates through influent ports in the rapid mix chamber. The flow rates for each chemical addition were calculated to achieve desired system conditions and were based on stock solution concentrations, required system concentrations, desired system flow rate, and minimum peristaltic pump flow rates. Figure 3.6 identifies each chemical supply container and the rapid mix chamber.

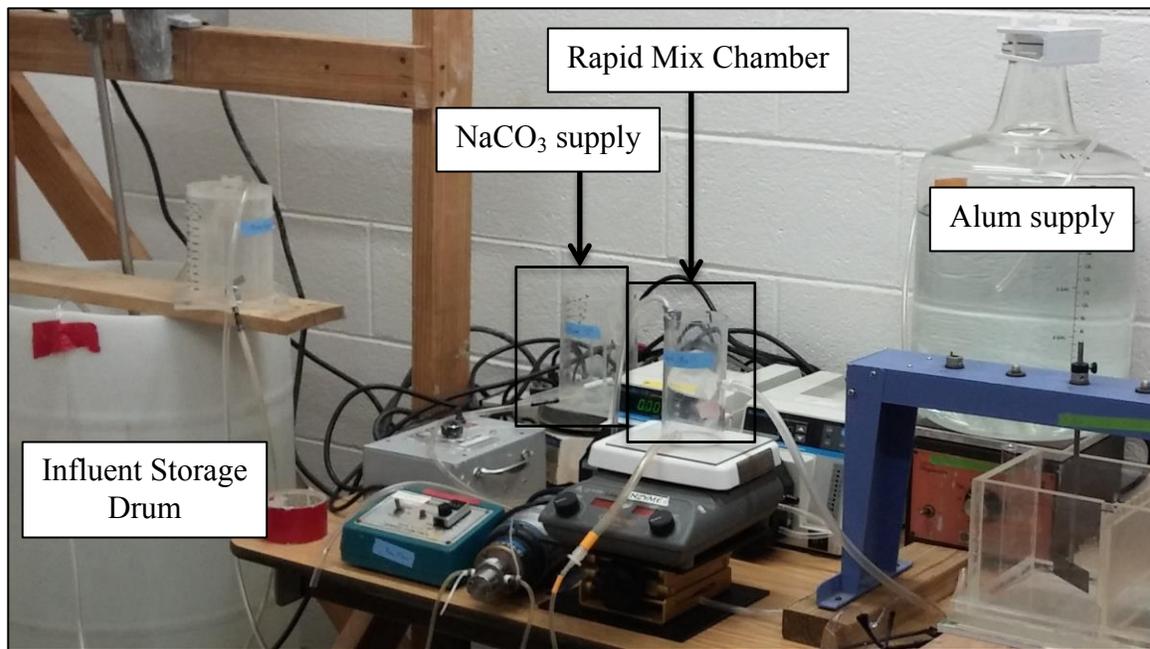


FIGURE 3.6: PILOT STUDY CHEMICAL SUPPLY SYSTEM

From the rapid mix chamber, the water flowed into the flocculation basin. The flocculation basin consisted of four compartments designed so that four of the six mixers of a standard jar test machine could be used by setting the jar tester on top of the unit.

The flocculation basin was mixed using a Phipps & Bird PB-700 Jartester running at 18-20 rpm. Water flowed from chamber to chamber over v-notch weirs. The water left the flocculation basin through two effluent ports. Unless stated otherwise, samples were taken from the influent, rapid mix chamber, first and final flocculation chambers, and flocculation effluent. Figure 3.7 shows the flocculation basin and Table 3.4 describes the dimension of each compartment therein.

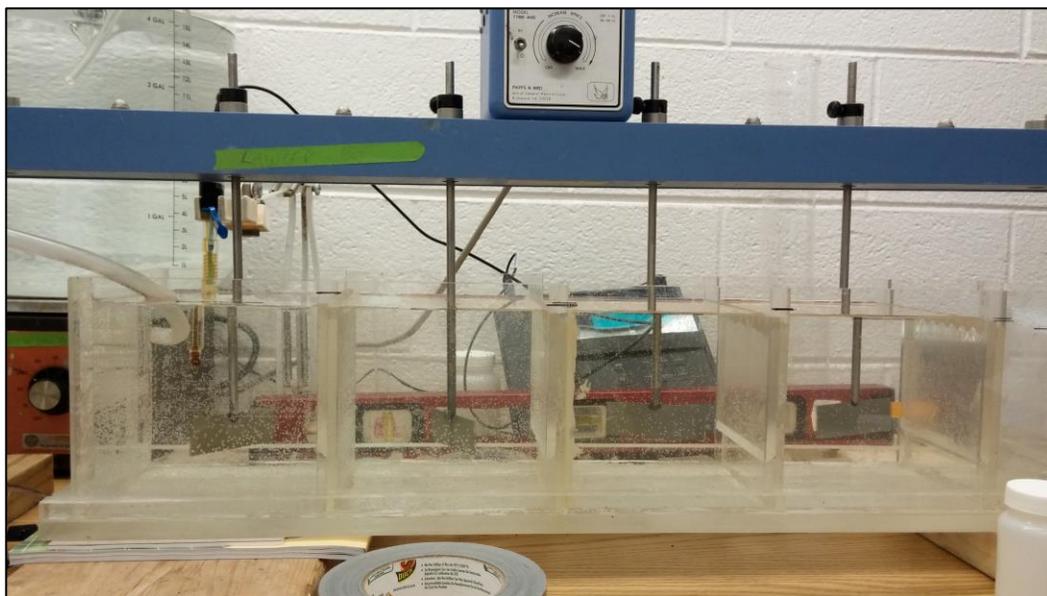


FIGURE 3.7: PILOT STUDY FLOCCULATION BASIN

TABLE 3.4: PILOT STUDY FLOCCULATION BASIN COMPARTMENT DIMENSIONS

<b>Dimensions</b>	<b>Section 1</b>	<b>Section 2</b>	<b>Section 3</b>	<b>Section 4</b>
Length (cm)	14	14	14	14
Width (cm)	15.2	15.2	15.2	15.2
Height (cm)	13.7	13.5	13.2	13
Volume (cm <sup>3</sup> )	2915	2873	2809	2766

## 6.2 Pilot Study Conditions

Researchers from UT, Mark Stehouwer and Clayton Ernst, previously conducted six continuous flow experiments at the Lake MacKenzie drinking water treatment facility near Silverton, TX. None of the experiments were pH controlled, as the natural alkalinity of the influent water allowed for a reasonable operating pH to be maintained throughout each experiment. Initially, the water flowed from the flocculation basin through an additional sedimentation unit. However, no significant difference in fluoride concentration was discovered between the flocculation basin effluent and the sedimentation basin effluent, so the settling basin was not utilized in the remainder of experiments in the interest of time. Figure 3.8 shows the MacKenzie Lake experimental set-up with the sedimentation basin; further details can be found in Section 2.3.4.



FIGURE 3.8: MACKENZIE LAKE PILOT SET-UP WITH SEDIMENTATION BASIN

For this study, seven continuous flow experiments were conducted at the Manitou Springs drinking water treatment facility in Manitou Springs, CO. Six experiments were controlled at pH 6.5, and one experiment was controlled at pH 7.5. The pH was controlled using a stock solution of sodium carbonate; required concentrations for each alum dose were pre-determined in the laboratory through batch titrations.

All samples were analyzed in accordance with the procedures listed in Section 3.5. Samples were analyzed for pH, turbidity, and fluoride on site. Samples for aluminum residuals, UV-254, and TOC were prepared and preserved on-site and transported back to the lab for analysis. Samples to be transported were packed on ice in insulated coolers until back at the University of Texas laboratory, where they were stored at 4°C until analysis.

## **CHAPTER 4: EXPERIMENTAL RESULTS AND DISCUSSION; PILOT STUDIES**

Experimental results from two pilot studies are presented in this section. These pilot studies were conducted to investigate the applicability of enhanced alum coagulation for fluoride removal at the pilot scale. The first study, at MacKenzie Municipal Water Authority, Texas, was previously conducted by Mark Stehouwer and Clayton Ernst from the University of Texas at Austin. The second pilot study, conducted as part of this project, took place in Manitou Springs (MS), Colorado. The same experimental set-up was used for both studies except for two differences: (1) Stehouwer and Ernst used a sedimentation basin following slow mix for the first run (2) Manitou Springs tests were pH controlled using an additional continuous-flow supply of sodium carbonate. The following subsections provide an overview of the results from each study, followed by a comparison of the two.

### **4.1 MacKenzie Lake Pilot Study**

A UT research team led by Mark Stehouwer and Clayton Ernst previously conducted a pilot study at the MacKenzie Municipal Water Authority (MMWA) near Silverton, TX; the results from this study have not previously been reported. MMWA draws water from Lake MacKenzie, and serves a population of 9,837 throughout the towns of Floydada, Silverton, Lockney, and Tulia. The untreated, raw influent is characterized in Table 4.1.

TABLE 4.1: MACKENZIE LAKE, TX WATER QUALITY CHARACTERIZATION

<b>Parameter</b>	<b>Water 1 – TX</b>
Water Source	SW
pH	8.60
[F] (mg/L)	3.04
UV-254nm (cm <sup>-1</sup> )	0.080
DOC (mg/L Carbon)	9.20
SUVA (L/mg-m)	0.87
Alkalinity (mg/L CaCO <sub>3</sub> )	295

Six continuous flow experiments were run with alum concentrations ranging from 20 to 300 mg/L. The overall flow rate was 380 mL/min to yield a 30 minute hydraulic detention time in the four-compartment flocculator. Table 4.2 includes all operating conditions, including steady state system pH values.

TABLE 4.2: MACKENZIE LAKE PILOT STUDY OPERATING CONDITIONS

<b>Alum Dose (mg/L)</b>	<b>pH</b>	<b>Alum Stock Concentration (mg/L)</b>	<b>Alum Flow Rate (mL/min)</b>
20	8.32	2550	3
50	7.98	2550	7.6
100	7.72	10400	3.69
150	7.35	10400	5.51
200	7.20	10400	7.45
300	6.89	10400	11.29

All tests were run without pH control based on results from previous bench scale testing using water from MacKenzie Lake; that previous testing revealed no significant difference in fluoride removal between pH natural and pH controlled systems for alum doses up to 300 mg/L (Section 2.3.4). This result was attributed to the high alkalinity of the raw water (Alkalinity = 295 mg/L as CaCO<sub>3</sub>), which meant that substantial doses of alum could be added without the pH dropping below pH 6.4. In addition, it was thought

that, if alum treatment were to be done at full-scale at this plant, it would be unlikely that pH control would be undertaken due to the expense and the increased operational requirements. Due to the acidity of the alum stock solution, effluent pH values varied between tests based on alum dose. Steady state pH values ranged from 6.89 to 8.32; these pH values were significantly higher than observed in the batch studies conducted at UT Austin, which ranged from 5.04 to 7.94 (see Table 2.4).

#### **4.1.1 MacKenzie Lake Steady State Conditions**

The experimental design for MWWA originally included the use of a sedimentation basin following a slow mix flocculator. A comparison between the flocculator effluent and sedimentation basin effluent, presented in Figure 5.1, revealed no significant difference in steady state fluoride residuals, as would be expected. Additionally, steady state conditions were achieved in the flocculator effluent after approximately 60 minutes whereas it took approximately 150 minutes to achieve steady state in the effluent of the sedimentation tank. In light of these results, the sedimentation basin was removed from the experimental set up and all further residual samples were taken from the flocculator effluent. It should be noted that the initial gap between flocculator and sedimentation basin fluoride residuals seen in Figure 4.1 is because the system was originally filled with raw, untreated water before starting the alum supply, and treated water gradually replaced the raw water in both tanks in succession.

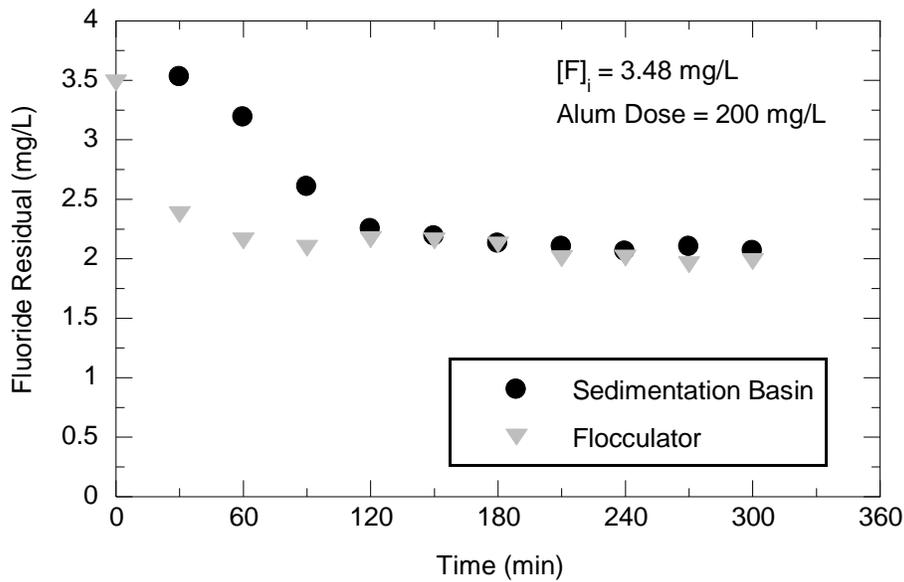


FIGURE 4.1: STEADY STATE FLUORIDE REMOVAL IN THE FLOCCULATION AND SEDIMENTATION BASINS (MMWA, TX)

#### 4.1.2 MacKenzie Lake Fluoride Removal

MMWA raw water had an average influent fluoride concentration of 3.48 mg/L throughout all testing. Fluoride results for all alum doses are presented in Table 4.3. Steady state fluoride reduction ranged from 6 to 56%. These removals were lower than in jar tests, which achieved a maximum removal of 69%. The lowest fluoride residual achieved during pilot testing was 1.53 mg/L at an alum dose of 300 mg/L; no alum dose reduced fluoride to levels below the WHO recommended limit of 1.5 mg/L. Fluoride residuals below the non-enforceable fluoride SMCL, 2.0 mg/L, were only achieved at alum doses of 200 and 300 mg/L.

TABLE 4.3: MACKENZIE MUNICIPAL WATER AUTHORITY PILOT STUDY STEADY STATE FLUORIDE RESULTS

Alum Dose (mg/L)	pH	Fluoride Residuals (mg/L)	Fluoride Reduction (%)
20	8.32	3.24	6
50	7.98	3.14	10
100	7.72	2.88	21
150	7.35	2.42	30
200	7.20	1.98	43
300	6.89	1.57	56

Above a pH of 6.5, the surface of aluminum hydroxide solid is negatively charged. As fluoride is also negatively charged, the like charges repel each other, inhibiting fluoride removal by adsorption and causing a decrease in removal. Moreover, above this pH aqueous Al-F complexation is also reduced, and the increase in hydroxide concentration leads to less substitution of fluoride for hydroxyl groups during co-precipitation. However, previous batch testing showed little difference in fluoride removal between pH natural and pH controlled systems in this water as long as the operating pH was above 6.5, as it was throughout pilot testing. For most doses, the pH values for the pilot test were about 0.5 pH units higher than in the batch testing and well above the optimal range of pH 6 to 7 for fluoride removal reported for batch testing. Thus, fluoride removal in this system would require pH adjustment.

#### 4.1.3 MacKenzie Municipal Water Authority Organic Removal

MMWA raw water had an average influent DOC of 9.20 mg C/L, a value that is quite high in relation to most surface waters in the U.S. Organic results for each alum dose are presented in Table 4.4; DOC removal ranged from 1 to 24%. During bench scale testing, a maximum organic removal of almost 50% was achieved at pH 6. Higher system pH values for pilot testing could affect organic removal. All pilot study alum doses

resulted in an operating pH above 6.5. Alfredo (2012) showed that the presence of both NOM and fluoride resulted in a negative surface charge on aluminum hydroxide between pH 5 and 8. A negative surface charge would repel negatively charged NOM and inhibit removal. Additionally, the sample of MacKenzie Lake NOM used in jar testing had a SUVA value of 0.87 L/mg-m. This suggests a mostly aliphatic, non-humic organic composition, which could explain the low removal, as trends reported in the literature indicate the humic portion of NOM is more easily removed during coagulation.

Given an influent DOC of 9.20 mg C/L and an average influent alkalinity of 298 mg/L as CaCO<sub>3</sub>, determined on-site during pilot testing, the EPA requires a TOC removal of 30% (USEPA, 1999). All alum doses failed to meet this criterion. However, this plant would qualify for an exception from the requirement of 30% removal because the small additional organics removal per extra addition of alum would be beyond the PODR.

TABLE 4.4: MACKENZIE LAKE STEADY STATE ORGANIC REMOVAL IN THE PILOT STUDY

<b>Alum Dose (mg/L)</b>	<b>DOC Residual (mg/L)</b>	<b>% Removal</b>
20	8.9	1
50	8.9	1
100	8.4	7
150	8.0	11
200	7.4	18
300	6.8	24

#### 4.2 Manitou Springs Pilot Study

Seven continuous flow experiments were run at the drinking water treatment facility in Manitou Springs, CO. The city of Manitou Springs draws its water from snowmelt and natural springs on Pikes Peak, which feed the Manitou Springs reservoir. The untreated, raw influent is characterized in Table 4.5. Manitou Springs serves a

population of 4,890 with an average flow rate of about 0.6 MGD. Because Manitou Springs is a popular vacation destination with high seasonal tourist traffic, the treatment facility has the capacity for a maximum flow rate of 2.4 MGD.

TABLE 4.5: MANITOU SPRINGS PILOT STUDY WATER QUALITY CHARACTERIZATION

<b>Parameter</b>	<b>Value</b>
Water Source	SW
pH	7.58
[F] (mg/L)	2.7
UV-254nm (cm <sup>-1</sup> )	0.032
DOC (mg/L Carbon)*	1.18
SUVA (L/mg-m)*	1.76
Alkalinity (mg/L CaCO <sub>3</sub> )	16.8

\*DOC and SUVA values from previous samples used in bench scale testing because no conclusive DOC measurements could be made with the pilot study water

The overall system flow rate was controlled at 380 mL/min to yield a 30 minute hydraulic detention time in the four-compartment flocculator. Alum dose was varied between 20 and 300 mg/L as alum. All experiments were pH controlled using sodium carbonate to target pH 6.5 except one, which was controlled to target pH 7.5 to evaluate the impact of pH on removal efficacy. Measurements for pH were taken from the influent, first flocculation basin, and effluent. Operating conditions for each alum dose are indicated in Table 4.6. The pH values presented were calculated as an average of pH measurements from the flocculation basin or effluent after steady state conditions had been reached; the variation among the measurements was generally <0.05 pH units.

TABLE 4.6: MANITOU SPRINGS PILOT STUDY OPERATING CONDITIONS

Alum Dose (mg/L)	Average Flocculation pH	Average Effluent pH	Alum Stock (mg/L)	Alum Flow Rate (mL/min)	Na <sub>2</sub> CO <sub>3</sub> Stock (mg/L)	Na <sub>2</sub> CO <sub>3</sub> Flow Rate (mL/min)
20	6.50	6.65	2550	3	5	1.9
50	6.49	6.65	2550	7.7	5	6.3
100	6.58	6.79*	10400	3.8	20	1.6
150	6.54	6.74	10400	5.5	20	2.6
200	6.54	6.70	10400	7.6	20	3.5
200	7.47	7.57	10400	7.6	20	4.7
300	6.53	6.79	10400	11.6	20	5.3

\*Effluent pH dropped to 6.58 after 180 minutes, this value was not included in the average

#### 4.2.1 Manitou Springs Fluoride Removal

Manitou Springs' influent water had an average fluoride concentration of 2.7 mg/L. Fluoride reduction was determined between the influent and effluent sampling sites. Results for fluoride reduction are presented in Figure 4.2. Steady state conditions were achieved after approximately 60 minutes for each condition. Fluoride reduction ranged from 14% to 80%. Steady-state fluoride concentrations below 1.5 mg/L were achieved with alum doses 100 mg/L and above. Fluoride residuals below 2.0 mg/L, the fluoride SMCL, were achieved with alum doses of 50 mg/L and above. These results are comparable to those achieved in jar testing. The UV-254nm absorbance for Manitou Springs water increased from 0.02 in bench testing to 0.03 during pilot testing; this change in UV-254nm thus did not have a significant impact on fluoride removal, which was expected given the low DOC concentration for Manitou Springs water as well as previous bench-scale results.

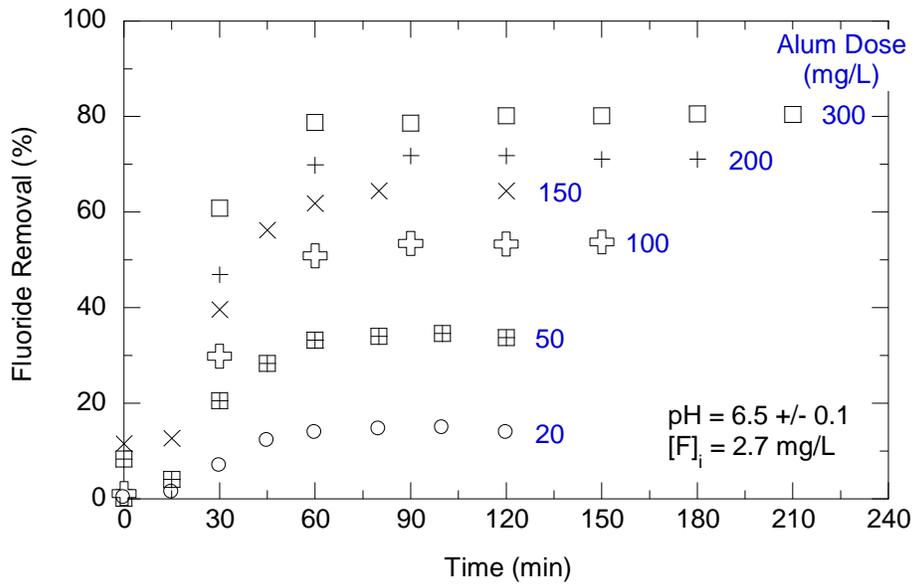


FIGURE 4.2: FLUORIDE REDUCTION AS A FUNCTION OF TIME (MS, CO)

#### 4.2.2 Manitou Springs Aluminum Residuals

Samples were also taken to measure aluminum residuals in the effluent. While the EPA has not set an enforceable MCL for aluminum, a non-enforceable secondary maximum contaminant level (SMCL) is set at 0.2 mg/L. Aluminum residual results are presented in Figure 4.3. Aluminum residuals below 0.2 mg/L were achieved for alum doses of 100 mg/L and above.

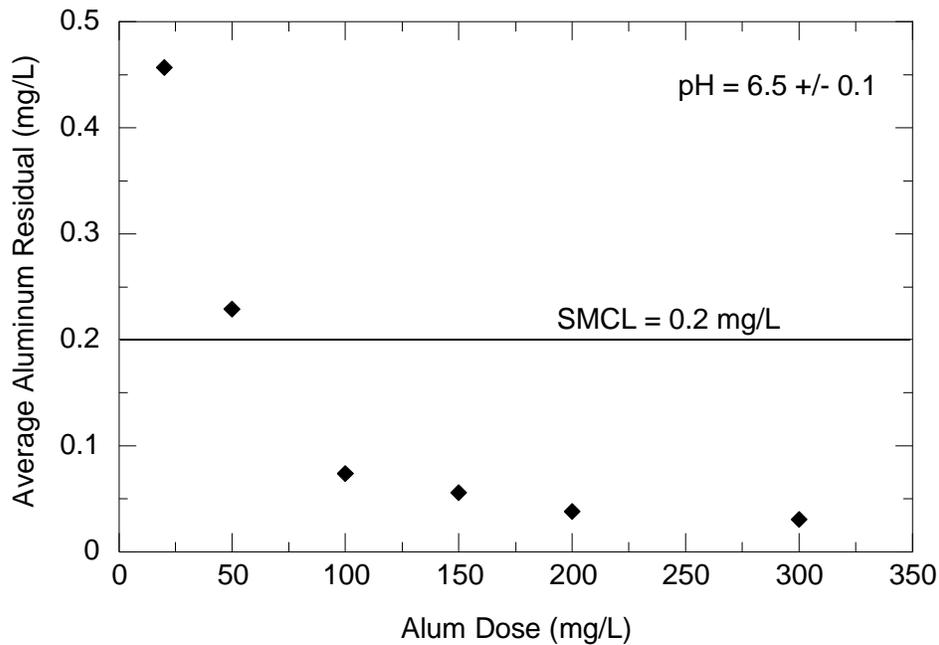


FIGURE 4.3: AVERAGE ALUMINUM RESIDUAL AS A FUNCTION OF ALUM DOSE (MS, CO)

Aluminum residuals decreased as the initial alum dose increased. This trend can be explained in two ways: (1) increased aluminum hydroxide precipitation with increasing alum dose and (2) change in the solid precipitate composition. First, precipitation increases with increasing coagulant dose as the solution reaches supersaturated conditions. The connection between low aluminum residuals and increased precipitation is supported by the increase in fluoride reduction with increasing alum dose; as more precipitate is produced, there are more opportunities for fluoride to adsorb to or precipitate with the amorphous aluminum hydroxide. Second, as discussed in Section 2.3.3, aluminum precipitation deviates from ideal behavior when precipitated in the presence of ligands. The aluminum to ligand ratio increases along with an increasing alum dose, and the precipitate formed is closer to pure aluminum hydroxide, which experiences a minimum solubility at pH 6.5.

The effect of pH was also investigated as a part of this study. Two separate tests were run at the same alum dose of 200 mg/L, but one was controlled at pH 6.5 and the other was controlled at pH 7.5. Fluoride reduction and aluminum residuals from these tests are compared in Figure 4.4.

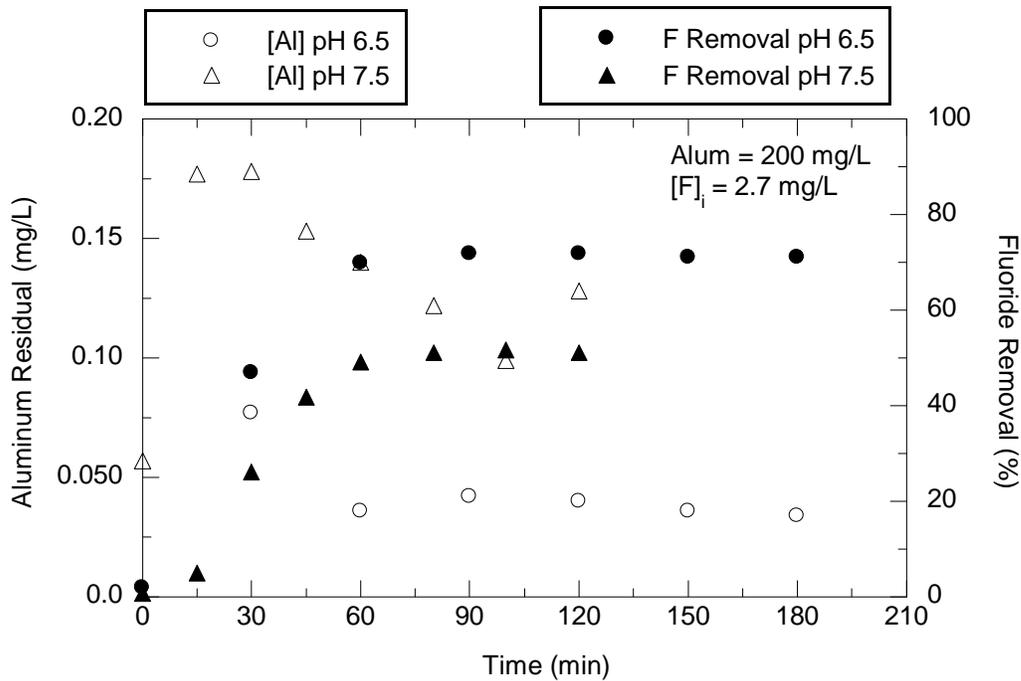


FIGURE 4.4: EFFECT OF pH ON FLUORIDE REDUCTION AND ALUMINUM RESIDUALS (MS, CO)

Steady-state fluoride reduction fell from 71% at pH 6.5 to 51% at pH 7.5, corresponding to effluent fluoride concentrations of 0.78 mg/L and 1.3 mg/L, respectively. This difference highlights the importance of pH control for fluoride reduction; a 200 mg/L alum dose at pH 7.5 achieved the same removal as a 100 mg/L alum dose at pH 6.5. The use of pH control can have a significant impact on the amount of coagulant required to meet treatment goals, impacting the sludge production consequentially. Similarly, when the pH was increased from 6.5 to 7.5, steady state aluminum concentration nearly doubled. Aluminum residuals, while not regulated by an

enforceable standard, are a public health concern because of possible links to Alzheimer's disease (Bhattacharjee et al., 2013; Bondy, 2016).

### 4.2.3 Manitou Springs Organic Removal

Samples were taken for both UV-254nm and DOC measurement at Manitou Springs. UV-254 measurements were made at the University of Texas at Austin laboratory, while samples for DOC measurement were sent to two separate facilities for analysis. The facilities returned conflicting results, so DOC measurements are not included in this section. Organic removal results as measured by UV-254 are presented in Figure 4.5.

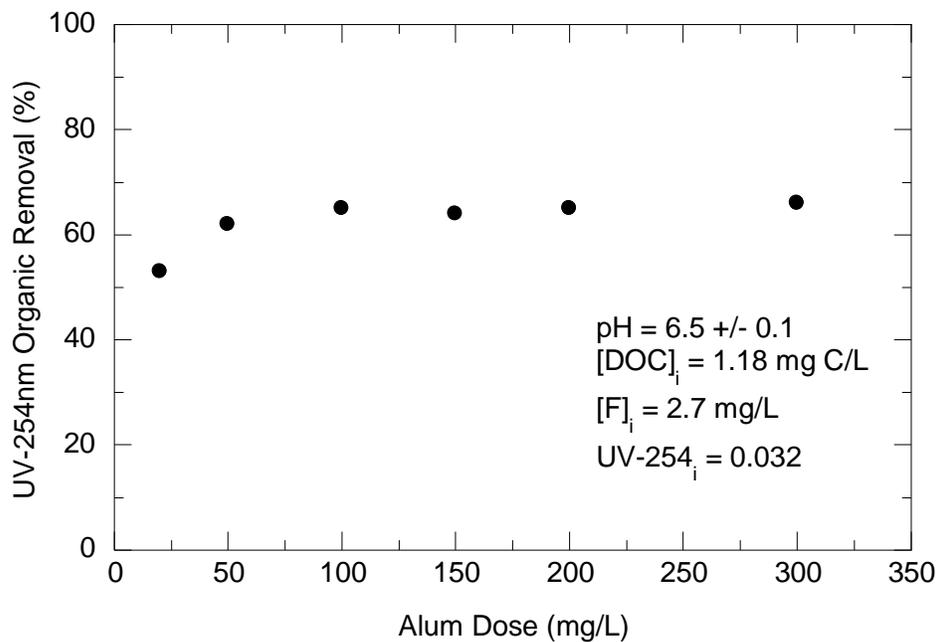


FIGURE 4.5: ORGANIC REMOVAL USING ALUM COAGULATION AS MEASURED BY UV-254NM (MS, CO)

A maximum removal of 66% was achieved at an alum dose of 300 mg/L, with similar removals achieved at much lower doses; 50 mg/L alum resulted in 62% organic

removal, and 20 mg/L alum achieved 53%. However, higher organic removals were observed during jar testing than in the pilot study. A maximum removal of 100% was achieved in jar testing at pH 6.0, which is lower than the optimum pH of 6.5. Influent fluoride concentrations did not factor into the discrepancy in removals, because both batch and pilot testing had an initial fluoride concentration of 2.7 mg/L. The lower removals from the pilot study could be due to seasonal variation of NOM composition.

The composition of organic matter in water is seasonally variable. Samples of water from Manitou Springs were obtained prior to the pilot study for use in jar tests, and the pilot study was later performed in the summer after a period of significant snowmelt. This event, as well as summertime conditions, could have resulted in a NOM content slightly different from that of the previously obtained water sample. The water sample used in jar testing had a SUVA value of 1.76 L/mg-m; SUVA values below 2 L/mg-m indicate a more non-humic composition, while those above indicate a mixed NOM composition of both humic and non-humic substances. Because the SUVA value from Manitou Springs is only somewhat below this limit, the water sample most likely did have a humic component. From trends in the literature, humic substances are more readily removed by coagulation. Lower organic removals during the pilot study could indicate a NOM content even less humic in nature, which is more difficult to remove. Unfortunately, a SUVA value for the pilot study influent water could not be calculated to confirm this hypothesis because of the unreliable DOC measurements.

### **4.3 Pilot Study Comparisons**

#### **4.3.1 Comparison of Pilot Study Fluoride Removal**

Enhanced alum coagulation was effective at reducing fluoride for both MMWA and Manitou Springs. However, no alum dose at MMWA achieved a fluoride residual

below 1.5 mg/L, while Manitou Springs achieved fluoride residuals below 1.5 mg/L at alum doses of 100 mg/L and above. Both Manitou Springs and MMWA had lower fluoride removal in pilot studies than in jar tests using raw water samples from their respective treatment facilities. A comparison for both treatment facilities over the complete alum dose range is provided in Table 4.7. For all alum doses, fluoride results from the Manitou Springs pilot study were more consistent with previous jar testing. The average difference between Manitou Springs pilot study results and corresponding jar test results was 10%. In contrast, MMWA results differed an average of 34% between pilot tests and jar tests most likely due to the increased pH levels in the pilot tests.

TABLE 4.7: FLUORIDE REMOVAL COMPARISON OF PILOT STUDIES AND NATURAL WATER JAR TESTING\*

Alum Dose (mg/L)	TX Jar Tests [F] <sub>i</sub> = 3.04 mg/L			TX Pilot Study [F] <sub>i</sub> = 3.49 mg/L			CO Jar Tests [F] <sub>i</sub> = 2.7 mg/L			CO Pilot Study [F] <sub>i</sub> = 2.7 mg/L		
	pH	F Removal (%)	[F] <sub>r</sub> (mg/L)	pH	F Removal (%)	[F] <sub>r</sub> (mg/L)	pH	F Removal (%)	[F] <sub>r</sub> (mg/L)	Flocc. pH	F Removal (%)	[F] <sub>r</sub> (mg/L)
20	7.94	6	2.9	8.32	6	3.2	6.52	12	2.3	6.50	14	2.3
50	7.50	20	2.5	7.98	10	3.1	6.59	34	1.8	6.49	34	1.8
100	7.10	39	1.9	7.72	21	2.9	6.60	48	1.4	6.58	53	1.3
150	-	-		7.35	30	2.4	-	-	-	6.54	64	1.0
200	6.60	61	1.2	7.20	43	2.0	6.57	74	0.71	6.54	71	0.78
300	6.17	69	0.97	6.89	56	1.6	6.57	81	0.34	6.53	80	0.53

\*TX and CO refer to MacKenzie Lake and Manitou Springs, respectively; [F]<sub>r</sub> refers to residual fluoride concentration

For all alum doses, the fluoride removal was much greater in Manitou Springs than in MacKenzie Lake. It was expected that Manitou Springs would exhibit higher fluoride removals, but the magnitude of the difference between pilot studies was greater than expected based on bench scale results. This discrepancy can be attributed to both process control and source water composition.

Each experiment at Manitou Springs was controlled at pH 6.5, which was previously determined to be the optimum pH for fluoride removal. The use of pH control at Manitou Springs resulted in lower fluoride residuals than expected from bench scale testing, halving the alum dose required to reduce fluoride to 1.5 mg/L and lowering potential chemical requirements. The MWWA operating pH remained above pH 6.5 for all alum doses. Previous bench scale testing of water from MWWA showed that alum additions did not take the waters outside of the optimal range of pH for fluoride removal (between pH 6 and 7). Thus, fluoride removal in this water was relatively stable between pH 6 – 7. For each alum dose, the operating pH was higher in the pilot study than in bench scale testing, which can explain the lower removals. However, a higher initial fluoride concentration in the pilot study compared to jar testing can also partly explain lower removals. Without pH control, extremely high doses of alum (300 mg/L) would be required to achieve even 50% fluoride reduction at MWWA; alum doses above 100 mg/L are unfeasible as they increase chemical costs as well as waste disposal costs from greater sludge production.

Source water composition is also very likely to have a strong effect on fluoride removal efficacy. MacKenzie Lake is considerably higher in NOM than Manitou Springs. NOM could compete with fluoride for adsorption sites on amorphous aluminum hydroxide solid. Additionally, the NOM composition differs between MacKenzie Lake and Manitou Springs; Manitou Springs NOM has a higher SUVA value than MacKenzie

Lake. NOM composition could impact the amount of aluminum precipitate formed by promoting the formation of smaller flocs and thus influencing the potential for further nucleation sites. Herrboldt (2016) found that the presence of fluoride during alum coagulation resulted in smaller particles, and the presence of NOM during alum coagulation resulted in the formation of a larger number of particles and larger total particle volume. When both fluoride and NOM were present, the particle volume distribution shifted so as to indicating both a smaller average particle diameter and a larger total particle volume.

#### **4.3.2 Comparison of Pilot Study Organic Removal**

A comparison of organic removals from both MWWA and Manitou Springs confirms bench scale results; higher removals were observed at Manitou Springs than MWWA for all alum doses. Higher removals were achieved at lower alum doses in Manitou Springs; at a dose as low as 20 mg/L, organic removal was 53% at Manitou Springs, while only 1% at MWWA. Organic removals are compared in Figure 4.6. It is, however, important to note the difference in initial DOC values for each system; MWWA is much richer in DOC than Manitou Springs. A lower initial DOC concentration lends itself to greater organic removals.

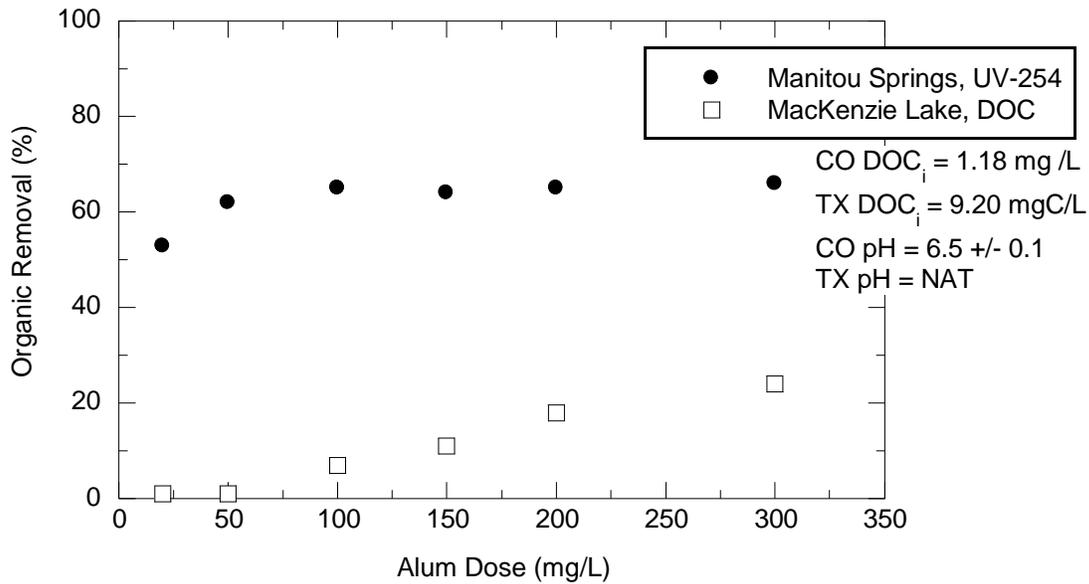


FIGURE 4.6: PILOT STUDY ORGANIC REMOVALS AS MEASURED USING UV-254

The discrepancy in organic removals between the two pilot studies can be explained by the previously discussed disparate SUVA values and DOC concentrations. Manitou Springs NOM has a higher SUVA, indicating a more humic composition. Trends in literature indicate that organic content with a more humic composition is more readily removed through coagulation. MWWA has a lower SUVA value, which indicates a more non-humic composition and thus a NOM that is not as easily removed through coagulation. Additionally, the lower organic content at Manitou Springs allows for greater relative removal compared to MWWA. The capacity of the aluminum precipitate is finite, and a system with a larger organic content will exhaust that capacity with a smaller portion of its overall organic concentration. This results in a smaller relative removal.

## **CHAPTER 5: INTERACTIONS BETWEEN ARSENIC, NOM, AND ALUMINUM DURING COAGULATION**

Experimental results from jar tests are presented here. The results are divided into two main sections. The first covers single ligand experiments, and the second covers dual ligand experiments. Within each, subsections delve further into interactions between As(V), aluminum, and organic constituents. All experiments were performed with As(V).

### **5.1 Single Ligand Experiments**

Jar tests were conducted to examine the efficacy of enhanced alum coagulation for arsenic removal and determine the optimum removal conditions without the presence of any ligands. Dependence of As(V) removal on pH and alum dose are discussed in this section. Both co-precipitation (CPT) and pre-formed (PRF) conditions were investigated.

#### **5.1.1 Arsenic Removal – Dependence on pH**

Throughout the entire pH range studied, As(V) was better removed during CPT than PRF experiments. Figure 5.1 contains As(V) removal results. PRF tests achieved a maximum As(V) removal of 91%, reducing the concentration of As(V) to  $< 5 \mu\text{g/L}$ . Testing under CPT conditions achieved a maximum removal of 100%. The optimum pH for PRF conditions occurred between pH 5 – 5.5, with a continuous decline in removal as the pH increased. CPT conditions achieved maximum As(V) removal between pH 5 – 8, with a steep drop off in removal at the edges. Between pH 5 and 8, removal remained steady near 100%. This is a wide pH range for such high removals, but similar removals and pH ranges have been reported in the literature using lower alum doses (McNeill and Edwards, 1997; Gregor, 2001).

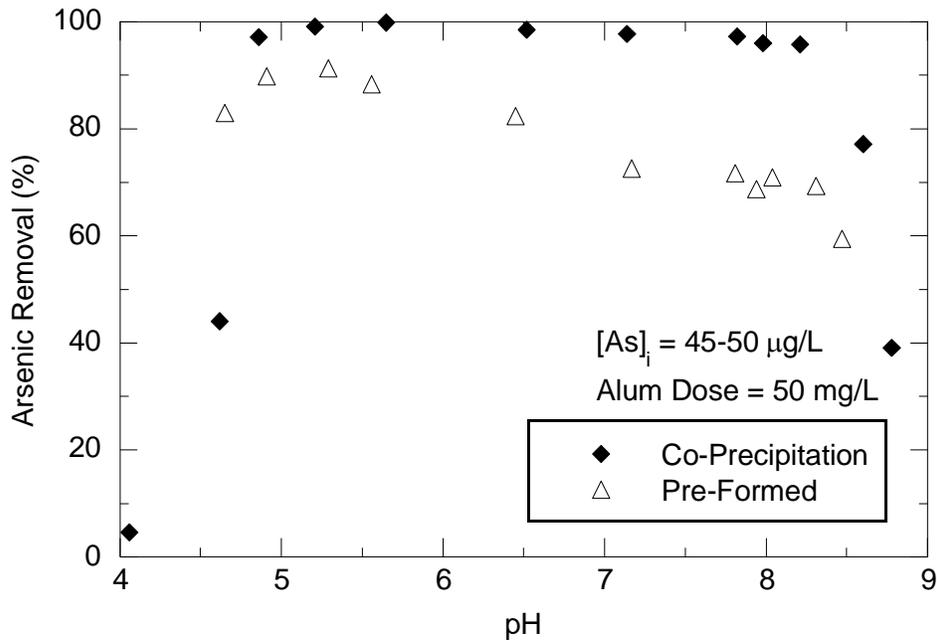


FIGURE 5.1: AS(V) REMOVAL DEPENDENCE ON pH UNDER CO-PRECIPIATION AND PRE-FORMED CONDITIONS IN SYNTHETIC WATER

Alfredo (2012) suggested that a larger surface area of solid may have been produced during CPT conditions compared to PRF experiments, although no verification of this hypothesis was provided. Greater solid surface area can explain why higher As(V) removals were achieved through CPT conditions compared to PRF conditions because of a corresponding increase in adsorption sites. The decline in As(V) removal under PRF conditions is consistent with its behavior with other aluminum oxide adsorption studies; adsorption is fairly stable at low pH values, and declines with increasing pH (Anderson et al., 1976).

### 5.1.2 Arsenic Removal – Dependence on Alum Dose

When controlled at pH 6.5, a slight increase in As(V) removal was observed with increasing alum dose. However, removals ranged from 97 to 99%, and are illustrated in

Figure 5.2. Residual As(V) concentration were  $< 0.05 \mu\text{g/L}$  for every dose. These removals, while very high, are not out of the question given the ease with which As(V) specifically can be removed through coagulation. Additionally, similarly high removals have previously been achieved using low alum doses. Herring et al., (1997) achieved an arsenic removal of 98% using an alum dose of 40 mg/L at a pH of 7 and with a lower initial arsenic concentration of  $22 \mu\text{g/L}$ . When the primary form of arsenic is As(V) in source waters, high doses of alum are not necessary, thus preventing excess sludge production and high chemical and disposal costs. At low alum doses, removal increases with increasing dose. However, removals are well above 95% even at low doses.

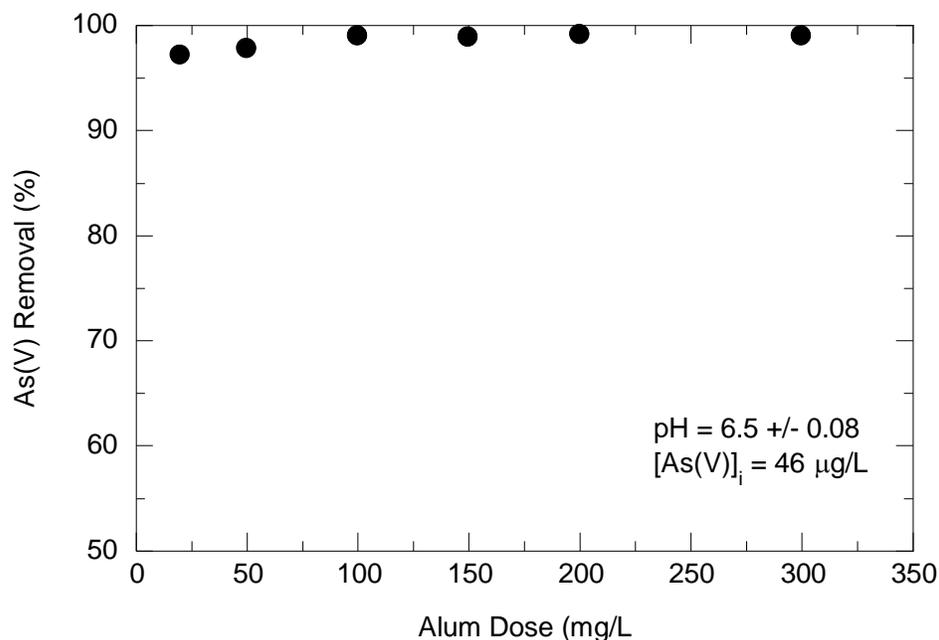


FIGURE 5.2: AS(V) REMOVAL DEPENDENCE ON ALUM DOSE IN SYNTHETIC WATER

### 5.1.2 Aluminum Residuals in Single Ligand Systems

Aluminum residuals were impacted by the presence of As(V); residuals presented in Figure 5.3 show a shift in the pH range of the minimum aluminum residual

concentrations. Aluminum residuals from alum only conditions were either higher or lower than for tests with As(V) depending on the pH. Below pH 6.5, alum only residuals were greater than for tests with As(V), and above pH 6.5 they were lower. This trend is likely due to the effect of As oxyanion adsorption on the surface charge of the precipitates. As(V) may be contributing to charge neutralization of the surface, which leads to a shift in the pH for optimum coagulation (i.e. a shift in the observed solubility during coagulation) to lower pH values. In general, as pH increases, the surface charge of aluminum hydroxide decreases, and the adsorption of negatively charged As(V) oxyanions further decreases the surface charge. This decrease in surface charge may reduce precipitative coagulation and produce higher aluminum residuals compared to the As(V) free system. Alfredo (2012) observed a decrease in the surface charge of aluminum hydroxide due to sorption of fluoride at pH 6.5, which is consistent with the results observed in this work.

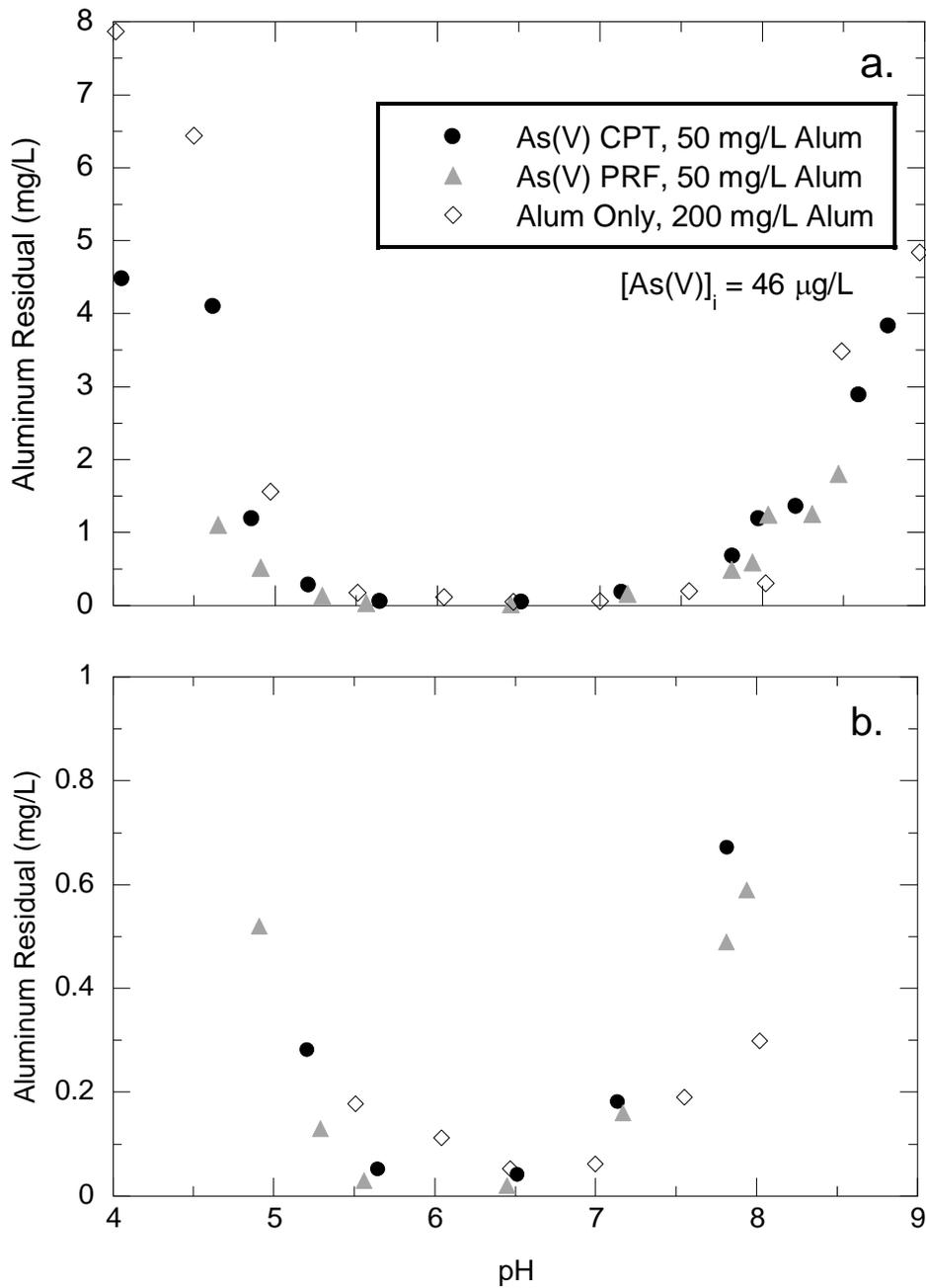


FIGURE 5.3: ALUMINUM RESIDUALS IN SINGLE LIGAND As(V) JAR TESTS UNDER BOTH CO-PRECIPIATION AND PRE-FORMED CONDITIONS (PART B IS A MORE DETAILED VIEW OF THE LOW CONCENTRATION RANGE ACHIEVED)

Figure 5.3 also shows a shift in the pH range of the minimum aluminum residual concentrations. Aluminum residuals from alum only conditions were either higher or lower than for tests with As(V) depending on the pH. Below pH 6.5, alum only residuals were greater than for tests with As(V), and above pH 6.5 they were lower. This is likely due to the effect of As oxyanion adsorption on the surface charge of the precipitates. As(V) may be contributing to charge neutralization of the surface, which leads to a shift in the pH for optimum coagulation (i.e. a shift in the observed solubility during coagulation) to lower pH values. As pH increases, the surface charge of aluminum hydroxide decreases and the adsorption of negatively charged As(V) oxyanions further decreases the surface charge. This decrease in surface charge may reduce precipitative coagulation and produce higher aluminum residuals compared to the As(V) free system. Alfredo (2012) observed a decrease in the surface charge of aluminum hydroxide due to sorption of fluoride at pH 6.5, which is consistent with the results observed in this work.

During PRF testing, alum was added to the system and allowed to mix for 48 hours before the addition of arsenic. This procedure promoted the formation of aluminum hydroxide solid under optimal conditions and thus result in minimal residuals. In contrast, under CPT condition, arsenic was present in the system before the addition of alum and was only mixed for thirty minutes before settling. Both the presence of ligands and shorter coagulation period could explain the higher aluminum residuals from co-precipitation. The difference in testing conditions could also explain why PRF aluminum residuals in the presence of As(V) are lower than the alum only system; alum solubility was determined using CPT conditions.

## 5.2 Dual Ligand Experiments – Arsenic and Natural Organic Matter

Jar tests were conducted to investigate the relationship between organics and arsenic during coagulation. The impact of a LMW organic acid, pyromellitic acid, and NOM from Lake Austin were both investigated. As(V) removal, organic removal, and aluminum residuals for dual ligand systems are presented here.

### 5.2.1 Arsenic Removal – Impact of NOM

At low alum doses, the presence of both pyromellitic acid and NOM inhibited As(V) removal; As(V) removal results with and without the presence of organics are presented in Figure 5.4.

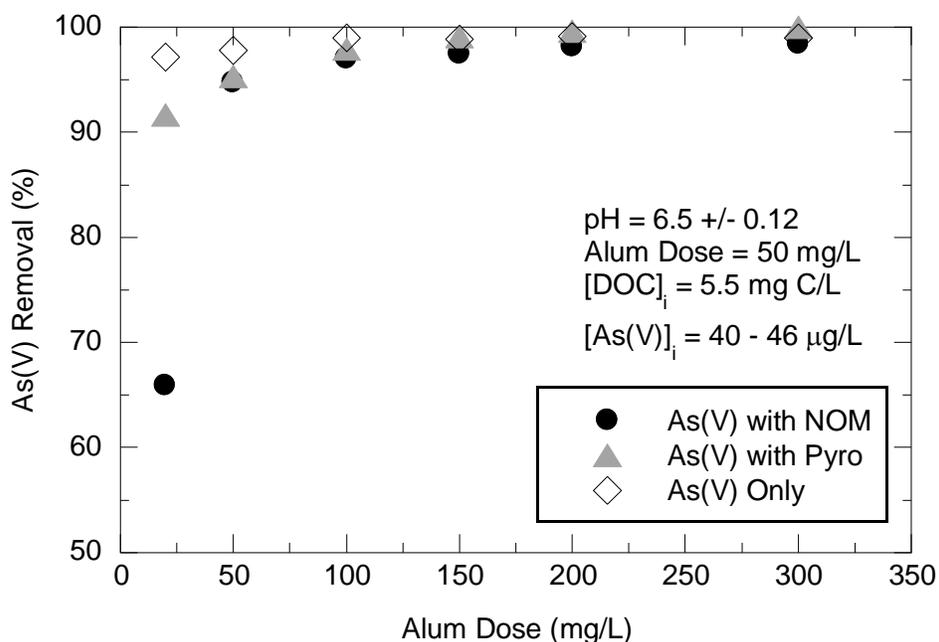


FIGURE 5.4: AS(V) REMOVAL IN THE PRESENCE OF ORGANIC SURROGATES AND NATURAL ORGANIC MATTER

At an alum dose of 20 mg/L, As(V) removal was only minimally inhibited by the presence of pyromellitic Acid. Only slightly lower removals were observed in the

presence of pyromellitic acid, but all alum doses resulted in As(V) residual concentrations below 1 µg/L. As(V) removal was significantly inhibited by the presence of NOM, however; As(V) removal dropped from 96% without NOM to 66% with NOM. This corresponds to an increase in As(V) residuals concentration from 1 µg/L to 16 µg/L, exceeding the arsenic MCL of 10 µg/L. This result is consistent with the zeta potential measurements conducted by Alfredo (2012), in which the presence of NOM led to a negatively charged aluminum hydroxide surface for pH values above approximately pH 6. However, increasing the alum dose to 50 mg/L resulted in more comparable As(V) removals of 98% and 95% with and without NOM present, respectively. Alum doses above 50 mg/L resulted in similar removals with and without the presence of NOM.

NOM inhibits arsenic removal through competition and complexation. At low alum concentrations NOM competes with arsenic for adsorption sites, but higher alum doses may provide enough active sites to reduce the competitive effects. Additionally, NOM can impact the redox behavior and speciation of arsenic, which would have a direct impact on removal efficacy. Other authors have presented evidence of the formation of arsenic-NOM complexes that keep arsenic in the aqueous phase and prevent removal (Liu and Cai, 2010; Fakour and Lin, 2014; Kim et al., 2015).

### **5.2.2 Organic Removal – Impact of Arsenic**

DOC and UV-Vis measurements were also taken for dual ligand experiments to evaluate the effect of arsenic on removal of organic matter. The impact of both pyromellitic acid and NOM were investigated. Removal of pyromellitic acid is presented in Figure 5.5.

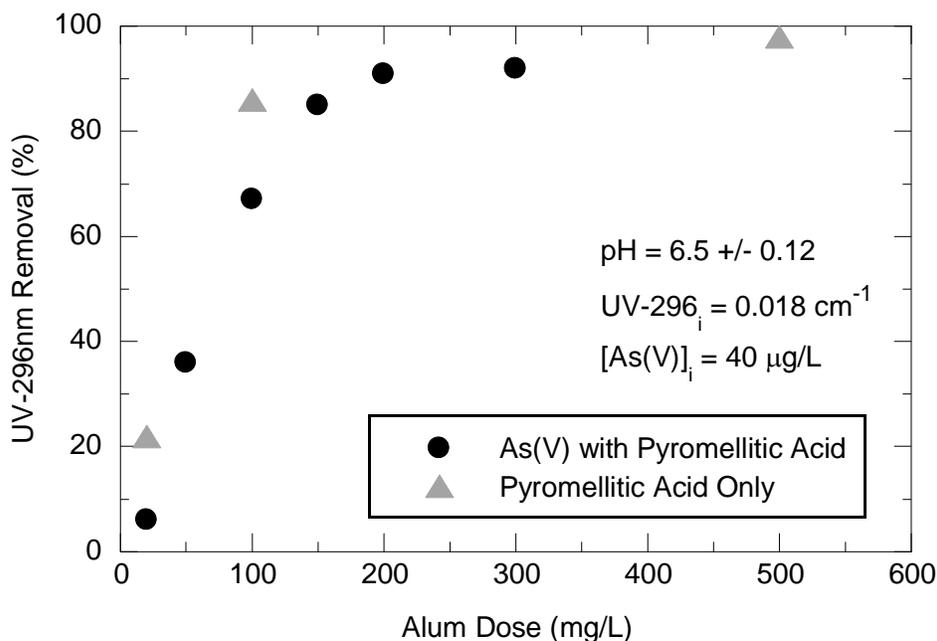


FIGURE 5.5: EFFECT OF AS(V) ON THE REMOVAL OF PYROMELLITIC ACID DURING SINGLE LIGAND CO-PRECIPITATION JAR TESTS

The removal of pyromellitic acid was inhibited by the presence of As(V) at low doses. At 20 mg/L alum, a pyromellitic acid removal of only 6% was achieved in the presence of As(V), compared to 22% without As(V) present. A similar gap in removal was observed at 100 mg/L alum; the presence of As(V) reduced pyromellitic acid removal from 86% to 67%. Greater removals were achieved with higher alum concentrations, but these concentrations are unfeasible in practice due to high chemical costs and waste disposal costs from increased sludge production.

No significant difference in NOM removal was observed with and without the presence of arsenic through UV-254nm or DOC measurements. A DOC removal of 35% was achieved in the presence of As(V) at an alum dose of 100 mg/L. The same alum dose resulted in a DOC removal of 37% in an alum only system. All maximum removals occurred at an alum dose of 300 mg/L, though similar organic removals were achieved at

alum doses of 100 mg/L; Figure 5.6 illustrates the previously discussed point of diminishing returns, as organic removal increases from 20 – 100 mg/L, but does not increase significantly with further increases in alum dose. Alum doses may reduce the competitive effects of arsenic with organic matter through the formation of more bulk solid and a larger number of available adsorption sites.

Lower removals were observed for NOM compared to pyromellitic acid, which was expected because of the complexity of NOM and inclusion of non-humic components that resist removal through coagulation.

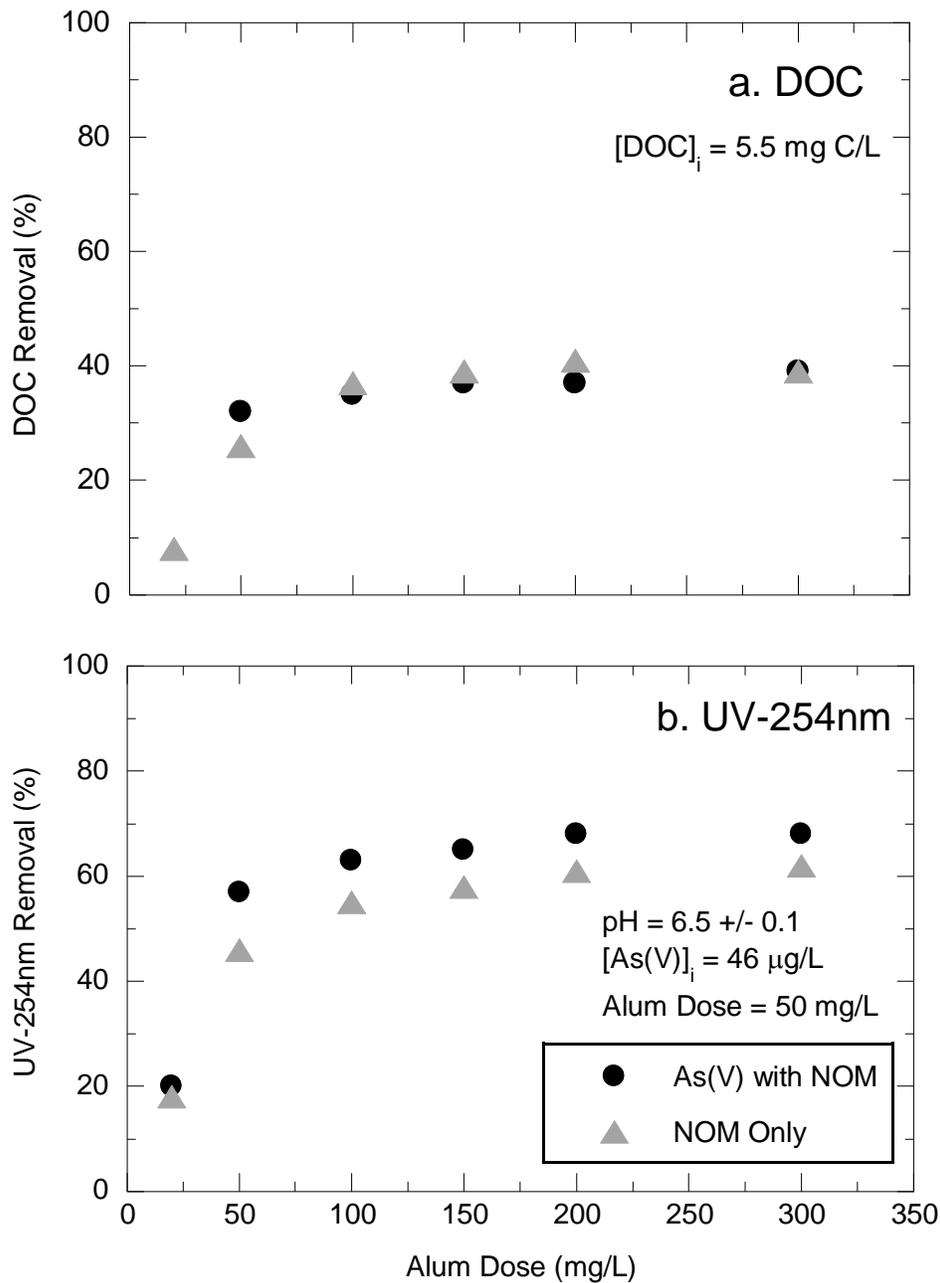


FIGURE 5.6: EFFECT OF AS(V) ON NATURAL ORGANIC MATTER DURING DUAL LIGAND SYNTHETIC WATER JAR TESTING, AS DETERMINED BY (A) DOC AND (B) UV-254NM MEASUREMENT

UV-254nm removals were larger in the presence of As(V) at all alum doses, and NOM removals in the presence of arsenic were slightly higher than those of the NOM-only system for low alum doses. This result was unexpected, and further experiments should be completed to verify these results. Organic removal differed by measurement technique; UV-254nm measurements showed higher removals than DOC measurements, while both following the same general trend. This discrepancy between measurement technique indicates that alum coagulation removed a larger portion of aromatic organic content, as UV-254nm favors aromatic content.

### **5.2.3. Aluminum Residuals in Dual Ligand Systems**

Aluminum residuals from dual ligand experiments, presented in Figure 5.7, were near or below the method detection limit of 0.024 mg/L aluminum for all systems. Aluminum residuals from dual ligand experiments with both As(V) and NOM fall between aluminum residuals from single ligand experiments, with NOM only residuals below the detection limit and As(V) only residuals near 0.03 mg/L. At lower alum doses, aluminum residuals for As(V) only and As(V) with NOM are similar. A larger difference in residual concentrations is observed at higher alum doses. These differences were expected given the negative impact of NOM on arsenic removal at low alum doses. However, the data are likely too close to the detection limit to allow for significant interpretation.

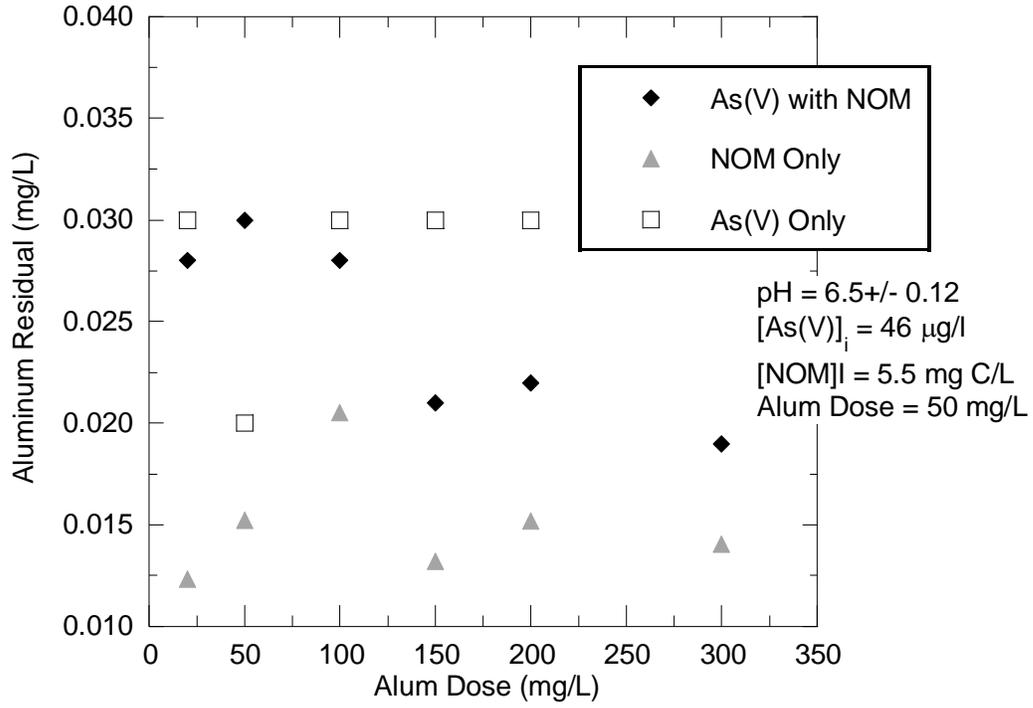


FIGURE 5.7: ALUMINUM RESIDUALS FROM SINGLE AND DUAL LIGAND SYNTHETIC WATER JAR TESTING

## CHAPTER 6: CONCLUSIONS

The removal of particles, natural organic matter, and pathogens is the primary concern of drinking water treatment. These strategies are necessary to provide clean and safe drinking water to the population. Also of concern in regards to drinking water treatment are inorganic contaminants. The USEPA identifies and regulates the presence of inorganic contaminants within drinking water supplies, setting an MCL for each. Fluoride and arsenic are two inorganic contaminants of concern at present.

Recent health concerns associated with high exposure to fluoride in drinking water has prompted USEPA to review its current MCL for fluoride of 4 mg/L, and it is possible that the MCL will be reduced in the near future. Additionally, arsenic is one of the most well-known and toxic inorganic contaminants in drinking water. While more prevalent in groundwater sources, arsenic is also a concern for surface water sources that tend to have a higher organic content. Arsenic may be a larger concern in the future due to increasingly extreme weather events, which could affect surface water plants particularly through excess runoff. Small water treatment facilities may not have the personnel or monetary resources to adjust their treatment process to accommodate new regulatory standards or focus on a new contaminant of interest.

Enhanced alum coagulation is a possible treatment strategy for the reduction of both fluoride and arsenic in drinking waters. Alum coagulation is already commonly applied at many surface water plants for the removal of NOM, and both fluoride and arsenic can be removed by alum coagulation through adsorption to and co-precipitation with aluminum hydroxide solid. Researchers at the University of Texas at Austin, Alfredo, Stehouwer, and Ernst, previously investigated the efficacy of enhanced alum coagulation for the reduction of fluoride as well as the interaction of fluoride with NOM

in surface waters. The majority of previous studies concerning coagulation for the removal of arsenic focus on groundwater sources and ferric coagulants. There is a scarcity of information surrounding the interaction of arsenic, NOM, and aluminum during alum coagulation. The purpose of this research was twofold: (1) to investigate the applicability of enhanced alum coagulation for the reduction of fluoride at the pilot scale and (2) to investigate the reduction of arsenic through enhanced alum coagulation and elucidate the interactions between arsenic, NOM, and aluminum during coagulation.

One pilot study in Colorado was completed for this study and was compared to a previous Texas pilot study completed by Stehouwer and Ernst from the University of Texas at Austin. Jar tests were completed for arsenic experiments to simulate a conventional treatment scheme at a bench scale. Synthetic waters were made in the laboratory to resemble a typical drinking water with a simple background matrix. Single (fluoride, arsenic, pyromellitic acid, or NOM) and dual ligand (fluoride or arsenic and pyromellitic acid, and fluoride or arsenic and NOM) experiments allowed for comparison and clarification of interactions between ligands and coagulant.

## **6.1 Conclusions - Fluoride**

Results from this study confirmed that enhanced alum coagulation is a viable method of fluoride reduction at the pilot scale depending on the water source. Specific conclusions that can be made through the two pilot studies and comparison thereof are as follows:

1. Fluoride was successfully removed from natural water systems during continuous flow experiments. Maximum fluoride removals of 80% and 56% were obtained in CO and TX, respectively. However, the TX water may require alum doses that are not economically reasonable.

2. All alum doses tested during the MMWA (TX) pilot study failed to meet the EPA required 30% TOC removal criterion, which is set based on the source water alkalinity and influent DOC. However, this plant would qualify for an exception because the small additional organics removal per extra addition of alum would be beyond the PODR.
3. Fluoride removal at the pilot scale is influenced by source water composition. Higher DOC can reduce the efficacy of fluoride removal and require larger alum doses to achieve acceptable fluoride residuals.
4. pH control is an important factor for fluoride reduction, especially when source water alkalinity and organic content is low. An increase in pH from 6.5 to 7.5 resulted in a decrease of fluoride removal from 71% to 51%, respectively, during the CO pilot study. Furthermore, higher system pH values during the TX pilot study at MMWA than during jar testing resulted in lower fluoride removals.

## **6.2 Conclusions - Arsenic**

Results from this study confirmed that alum coagulation is effective at removing As(V) from drinking water. No experiments were performed with As(III). Specific conclusions that can be made regarding arsenic removal through alum coagulation as determined from jar tests are as follows:

1. As(V) was successfully removed from synthetic drinking waters. The optimum pH for As(V) removal occurred over a wide range of pH values, from 5 to 8. At pH 6.5, over 90% reduction in As(V) was achieved for all alum doses 20 – 200 mg/L, and essentially 100% was removed at doses of 100 mg/L and above.

2. The presence of pyromellitic acid and NOM inhibited As(V) removal at low alum doses due to competition for adsorption sites and formation of soluble arsenic-NOM complexes.

### **6.3 Future Work**

The interactions between arsenic, NOM, and aluminum are still not completely understood. Experiments using As(III) should be completed to determine the ability of alum coagulation to meet water quality standards without having to oxidize As(III) to As(V). Experiments should also be completed to determine the dominant removal mechanism for As(III) and As(V). Additionally, further experiments with different NOM samples from different sources would help determine the impact of NOM composition on arsenic removal and what, if any, composition may be more of a concern during treatment.

## REFERENCES

- Aguilar, M.I., Saez, J., Llorens, M., Soler, A., and Ortuno, J.F., 2002, Nutrient removal and sludge production in the coagulation–flocculation process: *Water Research*, v. 36, p. 2910–2919.
- Ahmed, M.F., 2001, An Overview of Arsenic Removal Technologies in Bangladesh and India, *in* Proceedings of BUET-UNU International Workshop on Technologies for Arsenic Removal from Drinking Water, Dhaka, p. 55–7.
- Alfredo, K.A., 2012, Drinking Water Treatment By Alum Coagulation : Competition Among Fluoride , Natural Organic Matter , and Aluminum: University of Texas at Austin.
- Ali, I., Khan, T.A., and Asim, M., 2011, Removal of Arsenic from Water by Electrocoagulation and Electrodialysis Techniques Removal of Arsenic from Water by: *Separation & Purification Reviews*, v. 40, no. 2, p. 25–42.
- Anderson, M.A., Ferguson, J.F., and Gavis, J., 1976, Arsenate Adsorption on Amorphous Aluminum Hydroxide: *Journal of Colloid and Interface Science*, v. 54, no. 3, p. 391–399.
- Ayotte, J.D., Montgomery, D.L., Flanagan, S.M., and Robinson, K.W., 2003, Arsenic in Groundwater in Eastern New England: Occurrence, Controls, and Human Health Implications: *Environmental Science and Technology*, v. 37, p. 2075–2083.
- Baig, J.A., Kazi, T.G., Shah, A.Q., Kandhro, G.A., Afridi, H.I., Khan, S., and Kolachi, N.F., 2010, Biosorption studies on powder of stem of *Acacia nilotica*: Removal of arsenic from surface water: *Journal of Hazardous Materials*, v. 178, no. 1, p. 941–948.
- Barringer, J.L., and Reilly, P. a, 2013, Arsenic in Groundwater : A Summary of Sources and the Biogeochemical and Hydrogeologic Factors Affecting Arsenic Occurrence and Mobility: *Intech*,, p. 83–116.
- Benjamin, M.M., and Lawler, D.F., 2013, Water quality engineering: physical/chemical treatment processes: John Wiley & Sons.
- Bentley, R., and Chasteen, T.G., 2002, Arsenic Curiosa and Humanity: *The Chemical Educator*, v. 7, no. 2, p. 51–60.

- Bhagavatula, P., Levy, S.M., Broffitt, B., Weber-Gasparoni, K., and Warren, J.J., 2016, Timing of fluoride intake and dental fluorosis on late-erupting permanent teeth: *Community Dentistry and Oral Epidemiology*, v. 44, no. 1, p. 32–45.
- Bhattacharjee, S., Zhao, Y., Hill, J.M., Culicchia, F., Kruck, T.P.A., Percy, M.E., Pogue, A.I., Walton, J.R., Lukiw, W.J., and Lukiw, W.J., 2013, Selective accumulation of aluminum in cerebral arteries in Alzheimer's disease (AD): *Journal of Inorganic Biochemistry*, v. 126, p. 35–37.
- Bi, S., Wang, C., Cao, Q., and Zhang, C., 2004, Studies on the mechanism of hydrolysis and polymerization of aluminum salts in aqueous solution: correlations between the "Core-links" model and "Cage-like" Keggin-Al13 model: *Coordination Chemistry Reviews*, v. 248, p. 441–455.
- Bondy, S.C., 2016, Low levels of aluminum can lead to behavioral and morphological changes associated with Alzheimer's disease and age-related neurodegeneration: v. 52, p. 222–229.
- Bordoloi, S., Nath, S.K., Gogoi, S., and Dutta, R.K., 2013, Arsenic and iron removal from groundwater by oxidation–coagulation at optimized pH: Laboratory and field studies: *Journal of Hazardous Materials*, v. 260, p. 618–626.
- Burne, R.A., and Marquis, R.E., 2000, Alkali production by oral bacteria and protection against dental caries: *FEMS Microbiology Letters*, v. 193, p. 1–6.
- Camacho, L.M., Gutierrez, M., Alarcon-Herrera, M.T., de Lourdes Villalba, M., and Deng, S., 2011, Occurrence and treatment of arsenic in groundwater and soil in northern Mexico and southwestern USA: *Chemosphere*, v. 83, p. 211–225.
- Carstairs, C., 2015, Debating Water Fluoridation Before Dr. Strangelove: *American Journal of Public Health*, v. 105, no. 8, p. 1559–1569.
- Chambers, R.D., 2004, *Fluorine in Organic Chemistry*: CRC Press.
- Charlet, L., and Polya, D.A., 2006, Arsenic in shallow, reducing groundwaters in southern Asia: an environmental health disaster: *Elements*, v. 2, no. 2, p. 91–96.
- Chen, H., Frey, M.M., Clifford, D., McNeill, L.S., and Edwards, M., 1999, Arsenic Treatment Considerations: *American Water Works Association*, v. 91, no. 3, p. 74–85.

- Chibban, M., Zerbet, M., Carja, G., and Sinan, F., 2012, Application of low-cost adsorbents for arsenic removal\_ A review.pdf: *Journal of Environmental Chemistry and Ecotoxicology*, v. 4, no. 5, p. 91–102.
- Chow, C., van Leeuwen, J., Fabris, R., and Drikas, M., 2009, Optimised coagulation using aluminum sulfate for the removal of dissolved organic carbon: *Desalination*, v. 243, p. 195–207.
- Chwirka, J.D., Colvin, C., Gomez, J.D., and Mueller, P.A., 2004, Arsenic removal from drinking water using the coagulation/microfiltration process Arsenic removal from drinking w water using w the coagulation/microfiltration process: *Source Journal (American Water Works Association)*, v. 96, no. 3, p. 106–114.
- Cornwell, D.A., and Bishop, M.M., 1983, Determining velocity gradients in laboratory and full-scale systems: *Source Journal (American Water Works Association) Financial Planning*, v. 75, no. 9, p. 470–475.
- Deng, Y., Nordstrom, D.K., and McCleskey, R.B., 2011, Fluoride geochemistry of thermal waters in Yellowstone National Park: I. Aqueous fluoride speciation: *Geochemica et Cosmochimica Acta*, v. 75, p. 1176–4489.
- Dodds, L., King, W., Woolcott, C., Pole, J., Dodds, L., King, W., and Wookott, C., 2016, Trihalomethanes in Public Water Supplies and Adverse Birth Outcomes: *Epidemiology*, v. 10, no. 3, p. 233–237.
- Edzwald, J.K., 1993, Coagulation in drinking water treatment: particules, organics and coagulants: *Water Science & Technology*, v. 27, no. 11, p. 21–35.
- Edzwald, J.K., and Tobiason, J.E., 1999, ENHANCED COAGULATION: US REQUIREMENTS AND A BROADER VIEW: *Water Science and Technology*, v. 40, no. 9, p. 63–70.
- Fakour, H., and Lin, T.-F., 2014, Experimental determination and modeling of arsenic complexation with humic and fulvic acids: *Journal of Hazardous Materials*, v. 279, p. 569–578.
- Fawell, J., Bailey, K., and Chilton, J., 2006, Fluoride in Drinking-Water: World Health Organization.
- Ghosh, A., Sáez, A.E., and Ela, W., 2005, Effect of pH, competitive anions and NOM on the leaching of arsenic from solid residuals:.

- Gooch, B.F., 2015, for Fluoride Concentration in Drinking Water for the Prevention of Dental Caries:.
- Gregor, J., 2001, ARSENIC REMOVAL DURING CONVENTIONAL ALUMINIUM-BASED DRINKING-WATER TREATMENT: *Wat. Res*, v. 35, no. 7, p. 1659–1664.
- Gregor, J.E., Nokes, C.J., and Fenton, E., 1997, Optimising natural organic matter removal from low turbidity waters by controlled pH adjustment of aluminium coagulation: *Water Research*, v. 31, no. 12, p. 2949–2958.
- Guo, X., Wu, Z., and He, M., 2009, Removal of antimony(V) and antimony(III) from drinking water by coagulation–flocculation–sedimentation (CFS): *Water Research*, v. 43, p. 4327–4335.
- Heller, K.E., Eklund, S. a, and Burt, B. a, 1997, Dental caries and dental fluorosis at varying water fluoride concentrations.: *Journal of Public Health Dentistry*, v. 57, no. 3, p. 136–143.
- Hering, J.G., Chen, P.-Y., Wilkie, J.A., and Elimelech, M., 1997, ARSENIC REMOVAL FROM DRINKING WATER DURING COAGULATION: *Journal of Environmental Engineering*, v. 123, no. 8, p. 800–807.
- Herrboldt, J.P., 2016, Fluoride , Natural Organic Matter , and Particles : The Effect of Ligand Competition on the Size Distribution of Aluminum Precipitates in Flocculation: University of Texas at Austin.
- Jackson, R., and Grainge, J.W., 1976, Arsenic and Cancer: *The New Zealand Medical Journal*, v. 113, p. 4–7.
- Jagtap, S., Yenkie, M.K., Labhsetwar, N., and Rayalu, S., 2012, Fluoride in Drinking Water and Defluoridation of Water: *Chemical Reviews*, v. 112, no. 4, p. 2454–2466.
- Jeong, Y., Fan, M., Singh, S., Chuang, C.-L., Saha, B., and Van Leeuwen, H., 2007, Evaluation of iron oxide and aluminum oxide as potential arsenic(V) adsorbents: *Chemical Engineering and Processing*, v. 46, p. 1030–1039.
- Johnston, R., and Heijnen, H., 2001, Safe Water Technology for Arsenic Removal: *Technologies for arsenic removal from drinking water*., p. 1–22.
- Jolliffe, D.M., 1993, A History of the Use of Arsenicals in Man: *Journal of the Royal Society of Medicine*, v. 86, no. May 1993, p. 287–289.
- Kartinen, E.O., and Martin, C.J., 1995, An overview of arsenic removal processes:

*Desalination*, v. 103, p. 79–88.

Khan, S.J., Deere, D., Leusch, F.D.L., Humpage, A., Jenkins, M., and Cunliffe, D., 2015, Extreme weather events: Should drinking water quality management systems adapt to changing risk profiles? *Water Research*, v. 85, p. 125–146.

Khanh Trinh, T., and Seok Kang, L., 2010, Response surface methodological approach to optimize the coagulation–flocculation process in drinking water treatment: *chemical engineering research and design*, v. 8, no. 1, p. 1126–1135.

Kim, E.J., Hwang, B.-R., and Baek, K., 2015, Effects of natural organic matter on the coprecipitation of arsenic with iron: *Environmental Geochemistry and Health*, v. 37, p. 1029–1039.

Leenheer, J.A., and Croue, J.-P., 2003, Peer reviewed: characterizing aquatic dissolved organic matter: *Environmental Science & Technology*, v. 37, no. 1, p. 18A–26A.

Liu, G., 2007, THE INTERACTION OF SELECT HEAVY METALS AND NOM DURING: University of Notre Dame.

Liu, G., and Cai, Y., 2010, Complexation of Arsenite with Dissolved Organic Matter: Conditional Distribution Coefficients and Apparent Stability Constants: *Chemosphere*, v. 81, no. 7, p. 890–896.

Maheshwari, R., 2006, Fluoride in drinking water and its removal: *Journal of Hazardous Materials*, v. 137, p. 456–463.

Mandal, B., and Suzuki, K., 2002, Arsenic round the world: a review: *Talanta*, v. 58, no. 1, p. 201–235.

Mandinic, Z., Curcic, M., Antonijevic, B., Carevic, M., Mandic, J., Djukic-Cosic, D., and Lekic, C.P., 2010, Fluoride in drinking water and dental fluorosis: *Science of the Total Environment*, v. 408, p. 3507–3512.

Matilainen, A., Gjessing, E.T., Lahtinen, T., Hed, L., Bhatnagar, A., and Sillanpää, M., 2011, An overview of the methods used in the characterisation of natural organic matter (NOM) in relation to drinking water treatment: *Chemosphere*, v. 83, no. 11, p. 1431–1442.

Matilainen, A., Vepsäläinen, M., and Sillanpää, M., 2010, Natural organic matter removal by coagulation during drinking water treatment: A review: *Advances in Colloid and Interface Science*, v. 159, no. 2, p. 189–197.

McNeill, L.S., and Edwards, M., 1997, Predicting as removal during metal hydroxide

- precipitation: *Journal / American Water Works Association*, v. 89, no. 1, p. 75–86.
- Mercer, K.L., and Tobiason, J.E., 2008, Removal of Arsenic from High Ionic Strength Solutions: Effects of Ionic Strength, pH, and preformed versus in situ formed HFO: *Environmental Science & Technology*, v. 42, no. 10, p. 3797–3802.
- Mohan, D., and Pittman, C.U., 2007, Arsenic removal from water/wastewater using adsorbents-A critical review: *Journal of Hazardous Materials*, v. 142, no. 1-2, p. 1–53.
- Mohapatra, M., Anand, S., Mishra, B.K., Giles, D.E., and Singh, P., 2009, Review of fluoride removal from drinking water: *Journal of Environmental Management*, v. 91, p. 67–77.
- Mohora, E., Rončević, S., Dalmacija, B., Agbaba, J., Watson, M., Karlović, E., and Dalmacija, M., 2012, Removal of natural organic matter and arsenic from water by electrocoagulation/flotation continuous flow reactor: *Journal of Hazardous Materials*, v. 235, no. 236, p. 257–264.
- Morel, F.M., and Hering, J.G., 1993, Principles and Applications of Aquatic Chemistry: John Wiley & Sons.
- Mudhoo, A., Kumar Sharma, S., Kumar Garg, V., Tseng, C.-H., and Tseng, C., 2011, Arsenic: An Overview of Applications, Health, and Environmental Concerns and Removal Processes: *Critical Reviews in Environmental Science and Technology*, v. 41, no. 41.
- Mullen, J., 2005, History of Water Fluoridation: *British Dental Journal*, v. 199, p. 1–4.
- Muller, D., Médigue, C., Koechler, S., Barbe, V., Barakat, M., Talla, E., Bonnefoy, V., Krin, E., Arsène-Ploetze, F., Carapito, C., Chandler, M., Cournoyer, B., Cruveiller, S., Dossat, C., Duval, S., et al., 2007, A tale of two oxidation states: Bacterial colonization of arsenic-rich environments: *PLoS Genetics*, v. 3, no. 4, p. 0518–0530.
- National Research Council (NRC). (2006a). Fluoride in Drinking Water: A Scientific Review of EPA's Standards. Committee on Fluoride in Drinking Water, Board on Environmental Studies and Toxicology, Division on Earth and Life Sciences, National Research Council of the National Academies. Washington, DC: National Academies Press, 205-223.F
- Nickson, R., McArthur, J., Burgess, W., Ahmed, K.M., Ravenscroft, P., and Rahman, M., 1998, Arsenic poisoning of Bangladesh groundwater: *Nature*, v. 395, p. 338.

- Nordstrom, D.K., 2002, Worldwide Occurrences of Arsenic in Ground Water: *Science's Compass*, v. 296, no. June, p. 64–65.
- Ozsvath, D.L., 2008, Fluoride and environmental health: a review:.
- Pallier, V., Feuillade-Cathalifaud, G., Serpaud, B., and Bollinger, J.-C., 2009, Effect of organic matter on arsenic removal during coagulation/flocculation treatment: *Journal of Colloid And Interface Science*, v. 342, p. 26–32.
- Peters, S.C., Blum, J.D., Klaue, B., and Karagas, M.R., 1999, Arsenic Occurrence in New Hampshire Drinking Water: *Environmental Science and Technology*, v. 33, p. 1328–1333.
- Piñón-Miramontes, M., Raúl Bautista-Margulis, ac G., and Pérez-Hernández Chihuahua, A., 2003, REMOVAL OF ARSENIC AND FLUORIDE FROM DRINKING WATER WITH CAKE ALUM AND A POLYMERIC ANIONIC FLOCCULENT: *Fluoride*, v. 36, no. 2.
- Price, A., 2016, Arsenic Persists in Some Texas Water Supplies: *Austin American-Statesman*,.
- "Proposed HHS Recommendation for Fluoride Concentration in Drinking Water for Prevention of Dental Caries," 76 Federal Register 9 (13 January, 2011), pp 2383 - 2388.
- Qin, J.J., Oo, M.H., Kekre, K.A., Knops, F., and Miller, P., 2006, Impact of coagulation pH on enhanced removal of natural organic matter in treatment of reservoir water: *Separation and Purification Technology*, v. 49, no. 3, p. 295–298.
- Robertson, F.N. Arsenic in ground-water under oxidizing conditions, south-west United States:.
- Sambu, S., and Wilson, R., 2008, Arsenic in food and water - a brief history.: *Toxicology and industrial health*, v. 24, no. 4, p. 217–226.
- Semmens, M.J., and Field, T.K., 1980, Coagulation: Experiences in Organics Removal.: *Journal / American Water Works Association*, v. 72, no. 8, p. 476–483.
- Smedley, P.L., and Kinniburgh, D.G., 2002, A review of the source, behaviour and distribution of arsenic in natural waters: *Applied Geochemistry*, v. 17, no. 5, p. 517–568.
- Smith, A.H., Lopipero, P.A., Bates, M.N., and Steinmaus, C.M., 1994, Arsenic

epidemiology and drinking water standards: *Science*, v. 17, no. 6, p. 32–33.

Stehouwer, M., 2014, Defluoridation and Natural Organic Matter Removal in Drinking Waters by Alum Coagulation: University of Texas at Austin.

United States Environmental Protection Agency (USEPA). (1999) Enhanced Coagulation and Enhanced Precipitative Softening Guidance Manual. 815-R-99- 012. Office of Water: Environmental Protection Agency. Washington, DC: Environmental Protection Agency.

Vaclavikova, M., Gallios, G.P., Hredzak, S., and Jakabsky, S., 2008, Removal of arsenic from water streams: An overview of available techniques: *Clean Technologies and Environmental Policy*, v. 10, no. 1, p. 89–95.

Villanueva, C.M., Cantor, K.P., Cordier, S., Jaakkola, J.J.K., King, W.D., Lynch, C.F., Porru, S., and Kogevinas, M., 2004, Disinfection byproducts and bladder cancer: a pooled analysis.: *Epidemiology*, v. 15, no. 3, p. 357–67.

Volk, C., Bell, K., Ibrahim, E., Verges, D., Amy, G., and Lechevallier, M., 2000, Impact of enhanced and optimized coagulation on removal of organic matter and its biodegradable fraction in drinking water: *Water Research*, v. 34, no. 12, p. 3247–3257.

Waller, K., Swan, S.H., DeLorenze, G., and Hopkins, B., 1998, Trihalomethanes in drinking water and spontaneous abortion: *Epidemiology*, v. 9, no. 2, p. 134–140.

Wan, W., Pepping, T.J., Banerji, T., Chaudhari, S., and Giammar, D.E., 2011, Effects of water chemistry on arsenic removal from drinking water by electrocoagulation: *Water Research*, v. 45, no. 1, p. 384–392.

Welch, A.H., Lico, M.S., and Hughes, J.L., 1988, Arsenic in groundwater of the western united states: *Ground Water*, v. 26, no. 3, p. 333–347.

Welch, A.H., Westjohn, D.B., Helsel, D.R., and Wanty, R.B., 2000, Arsenic in Ground Water of the United States: Occurrence and Geochemistry: *Ground Water*, v. 38, no. 4, p. 589–604.

Wongkhantee, S., Patanapiradej, V., Maneenut, C., and Tantbirojn, D., 2006, Effect of acidic food and drinks on surface hardness of enamel, dentine, and tooth-coloured filling materials: v. 34, p. 214–220.

Wu, M., 2015, WARWS Spring Conference, *in* Disinfectants and Disinfection Byproducts Rules (DBPRs) (Stage 1 & 2), Casper, Wyoming.

Yan, M., Wang, D., Ni, J., Qu, J., Chow, C.W.K., and Liu, H., 2008, Mechanism of natural organic matter removal by polyaluminum chloride: Effect of coagulant particle size and hydrolysis kinetics:.