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Defluoridation and Natural Organic Matter Removal in Drinking Waters by Alum Coagulation

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Defluoridation and Natural Organic Matter Removal in Drinking Waters by Alum Coagulation

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Abstract

Defluoridation and Natural Organic Matter Removal in Drinking Waters by Alum Coagulation

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Fluoride naturally occurs in some ground and surface waters at high concentrations all around the world. Due to increasing health concerns about over-exposure to fluoride in drinking water, the United States Environmental Protection Agency (USEPA) has begun to review fluoride as a drinking water contaminant. Should the USEPA decide to lower the fluoride maximum contaminant limit (MCL), many water systems in addition to those already struggling to meet the fluoride MCL will require defluoridation as part of their drinking water treatment process. Alum coagulation was investigated as a defluoridation treatment strategy in this research project. Surface and blended (ground/surface) drinking water sources with high fluoride concentrations pose a unique challenge to defluoridation by alum coagulation because of the presence of both natural organic matter (NOM) and fluoride.

Defluoridation of synthetic and natural waters using jar tests elucidated interactions of fluoride, NOM, and aluminum during alum coagulation. Alum coagulation was able to remove 80% of fluoride from natural waters with a 500 mg/L alum dose;

however, 50% fluoride removal was observed to be possible with an alum dose of 150-170 mg/L. The optimum pH for fluoride removal in synthetic and natural waters was observed to be approximately 6.5 and was found to be an important factor in determining the overall performance of alum coagulation. The presence of fluoride during alum coagulation was found to reduce the removal of three low molecular weight (LMW) organics, acting as surrogates for NOM, to different extents depending on their functionality. The presence of LMW organic acids in synthetic waters did not impact the removal of fluoride; however, increasing NOM concentrations in the natural waters likely accounted for decreasing fluoride removals observed in the natural waters.

Additional jar tests with natural waters revealed that pH adjustment was unnecessary for defluoridation of high pH and high alkalinity waters and that an enhanced precipitation effect occurred at low alum doses when no pH adjustment was made during alum coagulation. The enhanced precipitation effect caused comparable or enhanced removals of fluoride and NOM to be observed despite system pH values being higher than the optimal defluoridation pH of 6.5. Lower aluminum residuals were also observed as part of the enhanced precipitation effect, suggesting that when precipitation begins under high pH conditions, fluoride interference does not occur and therefore promotes more precipitate formation with greater available surface area for adsorption. However, as precipitation occurs, pH drops, and fluoride increasingly interacts with the aluminum precipitate resulting in greater overall fluoride removals.

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Chapter 1: Introduction

1.1 BACKGROUND

Drinking water treatment schemes have traditionally focused on the removal of contaminants including particles, natural organic matter, and pathogenic microorganisms. The removal of these contaminants is of critical importance to provide potable water without health or aesthetic concerns to a community. Not until recently have some traditional water constituents and additives received attention in the United States as compounds that are potentially detrimental to human health. Fluoride is a natural background water constituent that has been found in drinking waters across the United States (US), Ghana, Kenya, China, Pakistan, India, and numerous other countries around the world (Ayoob and Gupta, 2006; Fawell, 2006; Mohapatra et al., 2009; Brindha and Elango, 2011). In addition, many individual communities across the US have introduced fluoride as an additive to their drinking water through a process known as fluoridation. The purpose of fluoridation is to provide beneficially low concentrations of fluoride (under 1 mg/L) in drinking water to prevent dental cavities and protect tooth development especially in young children (Arnold, 1956; Carton, 2006; Fawell, 2006). Research over the years has confirmed the benefits of fluoride to dental health; however, it has also revealed health risks associated with chronic exposure to concentrations of fluoride greater than 2 mg/L (Heller et al., 1997; Ayoob and Gupta, 2006; Carton, 2006; Fawell, 2006; Kakumanu and Sudhaker, 2013).

The United States Environmental Protection Agency (USEPA) has recently begun to review fluoride as a water contaminant due to scientific studies identifying health risks associated with chronic exposure of humans to high fluoride concentrations in drinking water. Regulation of fluoride in US drinking water began in 1974 under the Safe Drinking Water Act. This law required the USEPA to identify water contaminants and subsequently determine maximum contaminant level goals (MCLG) which are non-enforceable goals for water treatment intended to prevent health risks over a lifetime. The MCLG for fluoride was set at 4.0 mg/L. It was not until 1986 that the USEPA established an enforceable standard or maximum contaminant level (MCL) for fluoride of 4.0 mg/L. This fluoride MCL still exists and has not changed to date although a voluntary secondary standard of 2.0 mg/L has been added (USEPA, 2013).

Small water systems that struggle with fluoride contamination must anticipate a lower MCL for fluoride in the future. Current treatment processes used to remove fluoride such as ion exchange, membranes, and adsorption are cost intensive, preventing them from being adopted by small water systems. The successful implementation of an alum coagulation system to remove fluoride depends largely on the inherent parameters of the source water such as pH, alkalinity, and natural organic matter (NOM) content. Current research concerning simultaneous fluoride and NOM removal in water systems is lacking. A better understanding of the coagulation process and the influences of water parameters on fluoride and NOM removal is essential to develop a robust treatment scheme and set of guidelines.

1.2 OBJECTIVES

The main objective of this research was to explore the interactions among fluoride, NOM, and alum during the coagulation process to understand what levels of removal of fluoride and NOM in drinking water can be achieved. The alum coagulation treatment process was simulated at the bench scale level using both synthetic waters created in the laboratory and natural waters that were obtained from small water systems in Colorado and Texas. The specific objectives of this research were as follows:

1. Investigate the interactions of fluoride and three low molecular weight organics acting as NOM surrogates during the alum coagulation treatment process in artificial systems,
2. Study the removal of fluoride in complex systems and verify previous results from artificial systems by performing experiments with natural waters containing NOM and high levels of fluoride,
3. Develop a preliminary set of treatment guidelines for fluoride removal by alum coagulation.

The remainder of the report is structured to provide the reader with a comprehensive understanding of the issues surrounding fluoride as a water contaminant and its removal during alum coagulation. Chapter 2 presents a thorough literature review covering topics relevant to the research performed in this study such as the history of fluoride in drinking water, fluoride in the environment, alum coagulation theory with respect to fluoride and NOM, and prior research focused on fluoride removal through coagulation. The methods and materials used during the experimental phase of the project are documented in Chapter 3. Experimental results are presented in Chapter 4 along with discussions highlighting treatment implications. A final summary and conclusions are contained in Chapter 5.

Chapter 2: Literature Review

2.1 HISTORY OF FLUORIDE IN WATER

The presence of fluoride in water was not known until the 1900's when a young practicing dentist, Frederick McKay, began to investigate the etiology of brownish stains occurring on the teeth of his patients in Colorado Springs, CO. McKay and Green Black, a fellow dental researcher from Chicago, studied the communities around Colorado Springs and were surprised to discover that a significant number of the local population had stains on their teeth, in some cases accompanied by pitting and mottling of the teeth (McKay and Black, 1916; Douglas, 1959). However, only 100 miles away in the town of Boulder, McKay could not find many individuals affected by the brownish stain. The dental condition seemed to be an isolated occurrence and locals of Colorado Springs attributed the dental condition to various factors such as diet, radium exposure, and high calcium concentrations in drinking water (Douglas, 1959). Staining was so prevalent in this area that the dental condition became known commonly as the Colorado brown stain (McKay and Black, 1916; Herschfeld, 1978). Upon further investigation, McKay discovered that select communities located all around the United States (e.g., in Colorado, Kentucky, Illinois, and Arkansas) and even some in Italy exhibited the unusual dental condition his patients in Colorado Springs displayed (Douglas, 1959; Mullen, 2005). Such a discovery led him to consider that a contaminant was present in a community's water supplies which produced the dental staining.

At the same time as McKay's investigation, a similar study was conducted in the small community of Bauxite, AR by Harry Churchill (Mullen, 2005). Churchill was a chemist at the Aluminum Company of America (ALCOA) and was concerned about the potential relationship between his company and the unusual tooth discoloration occurring in the surrounding community in Bauxite. After ruling out many environmental and hereditary factors, Churchill traced the cause of the staining to a contaminant in the community's water supply. Analysis of the samples from the Bauxite water supply revealed that fluoride was present in the water at concentrations of 13.7 mg/L. Until this breakthrough by Churchill, fluoride was not recognized or known to exist in water (Douglas, 1959). Churchill contacted McKay in Colorado Springs and reported his discovery because publicity of both towns and their dental condition had made its way to newspapers. McKay sent water samples from communities afflicted by the Colorado brown stain that he had collected to Churchill for analysis. Results showed all water samples having high concentrations of fluoride similar to the Bauxite community levels. This enabled McKay to confidently link fluoride contamination of water supplies to dental fluorosis, a new dental term describing the discoloration and mottling of teeth previously known as the Colorado brown stain.

McKay's research concerning dental fluorosis did not end after his discovery of fluoride contamination. Population studies amongst children living in Colorado Springs and Boulder showed that children in Colorado Springs had significantly fewer dental cavities despite having dental fluorosis. This attracted the attention of many other dental researchers and in particular that of Henry Dean, head of the Dental Hygiene Unit at the National Institute of Health (NIDCR, 2014). Epidemiological studies performed over the next few years across the nation were focused on understanding the relationship between fluoride concentrations in water and degrees of dental fluorosis. Specifically, research by Dean culminated in a series of studies establishing 1 mg/L fluoride in water as sufficient for cavity prevention in a majority of the United States population without inducing symptoms of dental fluorosis (Dean and Elvove, 1935; Dean et al., 1941; Dean et al., 1942). Dean's findings led many communities lacking fluoride in their current water supply to consider water fluoridation to improve public health. Grand Rapids, MI became the first city to fluoridate their water in 1945 to achieve a beneficial fluoride concentration of 1 mg/L. A continuous fifteen-year study conducted on the 30,000 Grand Rapids school children found that, after eleven years, water fluoridation had reduced the number of cavities by 60%, a significant public health achievement that inspired fluoridation efforts in fluoride deficient water systems nationwide (Arnold, 1957). The target fluoride concentration for fluoridation was initially set at 1 to 1.5 mg/L; however, recently the target fluoride concentration has been lowered to 0.7 to 1 mg/L due to increasing concerns about detrimental health effects of fluoride (USEPA, 2013).

2.2 FLUORIDE PRESENCE IN THE ENVIRONMENT

Fluoride occurs naturally in both terrestrial and aquatic environments around the world. Generally fluoride is found in regions where marine sediments have been deposited near mountainous regions, volcanic activity has occurred or is frequent, and formations defined by calcium-poor igneous and metamorphic rocks including granites and gneisses occur (Edmunds and Smedley, 1996; Gordon et al., 2004; D'Alessandro, 2006; Fawell et al., 2006). High concentrations of fluoride are known to exist in many countries throughout the world such as Iran, Saudi Arabia, Sudan, Turkey, Pakistan, China, Japan, New Zealand, United States, Canada, Mexico, Brazil, Argentina, Ethiopia, Kenya, South Africa, Uganda, India, Germany, Morocco, and others (Lian-Fang et al., 1995; Diaz-Barriga et al., 1997; Kruse and Ainchil, 2003; Mjengera and Mkongo, 2003; Ayoob and Gupta, 2006; Fawell et al., 2006).

Fluoride occurs in both ground and surface waters. Surface water concentrations typically range from less than 0.5 mg/L to 1 mg/L (Fawell et al., 2006; Tebutt, 1983). Freshwater concentrations in lakes and rivers are generally lower than concentrations found in seawater. Fluoride concentrations in groundwater are highly variable and depend on the nature of the surrounding rocks and presence or absence of fluoride-bearing minerals (Fawell et al., 2006). Tebutt (1983) and Hem (1985) in separate studies report that average groundwater concentrations of fluoride are usually in the range of 1-10 mg/L. Positive correlations have been made between elevated fluoride concentrations in groundwaters and thermal groundwaters that have high pH (7.6-8.6) and bicarbonate concentrations (Handa, 1975; Hem, 1985; Edmunds and Smedley, 1996). Low concentrations of fluoride in groundwater occur where there is an absence of fluoride-bearing minerals, circulation of groundwater is rapid, or significant concentrations of calcium (>10-3M Ca^{+2}) occur in the aquifer (Handa, 1975; Hem, 1985).

Natural and artificial sources of fluoride must be considered when addressing the presence of fluoride in the natural environment and its waters. The rocks and minerals constituting aquifers and terrestrial environments influence fluoride concentrations in ground and surface waters by dissolution and leaching. The earth’s crust has approximately 300 mg/kg fluoride. Fluoride in the natural environment occurs in rocks and minerals such as cryolite, biotite, fluorite, fluorospar, fluoroapatite, horneblend, micas, clays, amphiboles, topaz, and others (Douglas, 1959; Tebbutt, 1983; Hem, 1985; Murray, 1986; Edmunds and Smedley, 1996). Average fluoride content for granitic rocks was found to range from 500-1400 mg/kg, which is greater than other rock types (Koritnig, 1972; Krauskopf and Bird, 1995). Rock weathering, dissolution, evaporation, and long aquifer residence times cause elevated concentrations of fluoride in natural waters. Some fertilizers, pesticides, and pharmaceutical contain fluoride and these anthropogenic compounds are introduced to natural waters by direct application, and stormwater runoff (Handa, 1975; NRC, 2006a). Young et al. (2011) found elevated fluoride levels in shallow groundwaters in agricultural regions of Sri Lanka, suggesting a strong correlation between local application of fertilizers and fluoride contamination of groundwater. Volcanic activity generates fluoride-rich gases and ash which contribute fluoride to natural waters in surrounding areas as they partition into rainfall or solubilize in surface waters after settling. Fly ash and gases from the combustion of fossil fuels, especially as coal (fluoride content 85-295 mg/kg), contain fluoride and are transported into natural waters by similar processes as those associated with volcanic gases and ashes (Churchill et al., 1948; Brindha and Elango, 2011). Other fluoride sources include industrial activities such as alumina production, ore processing, and brick and ceramic manufacturing (Haidouti, 1991; WHO, 2002).

2.3 HEALTH EFFECTS OF FLUORIDE

2.3.1 Dietary Intake of Fluoride

Human exposure to fluoride comes in many forms including air, diet, dental products, and drinking water. Drinking water is considered to be the primary contributor to fluoride intake; however, this contribution can vary depending on fluoride concentration, demographic, diet, and climatic conditions (Murray, 1986; USIM, 1997). Trautner and Siebert (1986) found that the bioavailability of fluoride from mineral water was approximately 85%, which is greater than that of many other solid food sources such as fish and algal flour, and supports the significance of fluoride intake through liquids such as water. Estimated average dietary intake of fluoride for children (younger than 12 years old) is in the range of 0.5 to 1.2 mg/day, assuming fluoridated water supplies (0.7-1.2 mg/L fluoride) (McClure, 1943). Slightly higher dietary intakes for children are expected when exposed to waters with naturally occurring elevated fluoride concentrations (>1.2 mg/L fluoride). Adult estimates for the average dietary intake of fluoride range from 1.2 to 2.8 mg/day, assuming fluoridated or natural water with >0.7

mg/L fluoride (San Filippo and Battistone, 1971; Kramer et al., 1974; Osis et al., 1974; Spencer et al., 1981; Dabeka et al., 1987; Standing Committee on the Scientific Evaluation of Dietary Reference Intakes, 1997).

2.3.2 Effects on Dental Health

Intake of fluoride through drinking water and its bioavailability are important because of the impact that fluoride has on dental health, namely cavity prevention and dental fluorosis. Exposure to fluoride at young ages during tooth development and eruption from the gums aids in the formation of a strong enamel structure. Fluoride ions replace hydroxyl groups in the hydroxyapatite structure of the teeth, resulting in a mixed crystalline structure resembling fluoroapatite (Moreno et al., 1977; Ten Cate and Featherstone, 1991). Incorporation of fluoride in dental structures decreases their solubility (Driessens, 1982). Appropriate concentrations of fluoride in water to achieve this dental benefit without risk of fluorosis are 0.7 to 1.2 mg/L (Dean et al., 1941; Dean et al., 1942; Galagan and Vermillion, 1957; USPHS, 1991; Heller et al., 1997; Tylenda et al., 2003). Topical application of fluoride and exposure to water artificially or naturally fluoridated helps repair the softened tooth enamel that can promote the formation of lesions and caries. Tooth enamel is softened by acid-producing oral bacteria that break fermentable carbohydrates such as starches and sugars into organic acids (Moreno et al., 1977; Wefel et al., 1984; Loesche, 1986; Ten Cate and Featherstone, 1991). The presence of low fluoride concentrations around teeth promotes faster remineralization of enamel should caries begin to form (Featherstone, 1999; Glenn, 2002). Fluoride also inhibits the overall activity of carcinogenic bacteria (American Dietetic Association, 2005). Continued topical exposure to low fluoride levels through mediums such as drinking water is recommended to decrease susceptibility in teeth for developing caries (Ten Cate and Featherstone, 1991).

Dental fluorosis can occur when fluoride concentrations in water supplies are greater than 2 mg/L. Severity of the condition depends on demographic, diet, climactic conditions, and other factors (Murray, 1986; USIM, 1997). Conditions of dental fluorosis include discoloration, pitting, and mottling of teeth. The severity of fluorosis in different populations was classified by Dean et al. (1935; 1941). Classification for different conditions of dental fluorosis is shown in Table 2.1, adapted from Dean's original classification scheme. Prolonged exposure to high concentrations of fluoride (>4 mg/L) in drinking water can result in severe cases of dental fluorosis (NRC, 2006b). Increased fluoridation of water supplies, use of new water sources, and changes in the American diet have caused mild cases of fluorosis to become more prevalent in communities throughout the United States since the 1930s and 1940s (Burt et al., 1992).

Table 2.1: Classification of Dental Fluorosis (Adapted from Dean 1942 and Murray 1986).

Degree of Fluorosis	Characteristics
Normal	Smooth, glossy, pale white tooth surface.
Questionable	Appearance of small white flecks or spots on tooth surface.
Very Mild	Scattered and clear white areas scattered over 25% of the tooth surface.
Mild	White spots on teeth are more extensive and cover 25-50% of tooth surface.
Moderate	All teeth are affected by spots some teeth show wearing or brown staining.
Severe	All teeth are affected and some teeth are altered due to pitting. Brown stains are wide spread giving an appearance of corrosion.

2.3.3 Additional Health Effects

High intakes of fluoride over time can cause other adverse health effects in addition to dental fluorosis. Xiong et al. (2007) found that fluoride concentrations greater than 2 mg/L can cause damage to liver and kidney functions in children. The NRC (2006b) and USEPA (2013) stated that chronic exposure to high concentrations of fluoride in drinking water can lead to an increased likelihood of bone fractures accompanied by bone pain and tenderness in adults resulting in a condition known as skeletal fluorosis. Studies investigating links between fluoride and cancer and reproductive hormones are inconclusive at present (NRC, 2006b).

2.4 REGULATION OF FLUORIDE IN DRINKING WATER

The USEPA first identified fluoride as a potential drinking water contaminant in 1974 when the Safe Drinking Water Act was enacted. In 1975, the USEPA established an interim maximum contaminant level (MCL) for fluoride at 1.4-2.4 mg/L because of anticipated health risks, namely dental fluorosis that was associated with exposure to high fluoride concentrations (WRF, 2011). The intent of this interim MCL for fluoride was that subsequent medical research would permit a better understanding of adverse health effects associated with exposure to high concentrations of fluoride in drinking water. The official primary MCL for fluoride that is enforceable was set at 4.0 mg/L in 1986. In addition, the secondary MCL that is not enforceable was set at 2.0 mg/L. Along with these MCLs, a maximum contaminant limit goal (MCLG) was established at 4.0 mg/L to protect against crippling skeletal fluorosis (USEPA, 2013).

The National Research Council (NRC) (1993) reviewed the USEPA's interim MCL for fluoride that was established in 1986 and found it appropriate based on available scientific studies at that time. However, the NRC did recommend the MCL for fluoride be reviewed again when new research and data becomes available. The USEPA (2002; 2003) determined that, due to recent health research associated with detrimental health effects from fluoride, fluoride was available for a risk reassessment. In 2006, the NRC conducted a second comprehensive study to scientifically evaluate the USEPA's MCLG and SMCL for fluoride based on recent clinical data dealing with exposure to fluoride in drinking water. The NRC unanimously concluded in their report that the USEPA's MCLG should be lowered to prevent severe dental fluorosis and long term exposures that can lead to skeletal fluorosis. The NRC did not make a recommendation to change the SMCL of 2 mg/L, but did conclude that, even though severe dental fluorosis was not likely to occur at exposure to fluoride at the SMCL, cases of moderate dental fluorosis could still affect 15% of the population (2006a). As of 2009, the USEPA was performing a health effects assessment on fluoride, but no USEPA report on this subject has been issued at the time of this writing. The World Health Organization and many other countries have fluoride standards set at 1.5 mg/L (Fawell et al., 2006; WHO, 2008; Health Canada, 2012). It seems quite possible that the USEPA will consider lowering the

MCL and SMCL for fluoride after finishing their review. Tighter regulations would hold implications concerning current drinking water treatment strategies and utilization of source waters.

2.5 COAGULATION AS A DRINKING WATER TREATMENT STRATEGY – PARTICLE REMOVAL

2.5.1 Coagulation and Flocculation

Coagulation is a treatment process used in many drinking water treatment plants to remove particles and natural organic matter. The term flocculation is often used synonymously with coagulation, but the processes they describe are slightly different. Flocculation generally refers to the aggregation or formation of larger particles from smaller particles in water, while coagulation describes the chemical interactions that lead to particle destabilization and adsorption or precipitation of soluble materials. Successful removal of particles and NOM from waters involves both coagulation and flocculation processes such that flocs are created with physical properties, namely density and size, that enable their gravity separation from the suspension.

2.5.2 Particle Charges

In natural waters, particles generally have negatively charged surfaces. The like surface charges on the particles cause the particles to repel one another, preventing their aggregation and separation by gravity from solution. London-van der Waal forces also act on particles which are attractive rather than repulsive and can dominate interactions when two particles get quite close to each other. This phenomenon, however, does not usually occur to any substantial extent and particles in water are generally considered stable and repulsive.

The surface charges of particles are derived from three origins, as proposed by Stumm and Morgan (1996). Chemical reactions at the surface of a particle represent the first of these origins. Crystal imperfections, broken surface bonds and isomorphic substitution represent the second origin, and sorption of surface-active ions represents the third. Two end-members characterize the charge developed on particles. Constant surface charge resulting from isomorphic substitution represents one end member. Isomorphic substation occurs during formation of a crystalline lattice (often of clay minerals), when the substitution of another species with different oxidation state into the lattice yields a net charge of the crystalline solid. The other end member which is typical of metal oxides, organic matter and the edges of clay minerals is variable surface charge that results from the presence of surface functional groups. The charge of these functional groups is affected by the interaction of potential determining ions from the surrounding solution. Strongly sorbing metal cations, anions and NOM molecules and their corresponding acid-base functional groups (-OH, -COOH, -COH, -NH2, etc.) can serve as potential determining ions on variable surface charge particles. For hydroxyl functional groups, pH is the most important potential determining ion. Depending on the pH of the solution, protonation of these functional groups can vary, inducing localized or comprehensive surface charges on the particle molecule. Adsorption of NOM molecules on a particle surface provide a range of additional functional group types including, carboxylic groups, hydroxyl groups, and amino groups. Carboxylic groups (which have pKa's below pH 6) tend to dictate the charge of NOM molecules adsorbed to particles because carboxylic groups are often present at higher densities compared to other functional groups comprising NOM. Therefore, NOM molecules are typically negatively charged in natural waters which have pH values in the range of 6.5-8. Adsorption of negatively charged NOM molecules onto all kinds of particles allows for a generalization that all particles in water tend to have a negative surface charge at near neutral pH.

Because particles are charged, an ionic distribution occurs around them when in solution (Benjamin and Lawler 2013). This ionic distribution is characterized by two regions (Figure 2.1). The first region is known as the compact layer which is very thin (~1 nm) and where ions are bound to the surface of the particle. The bound ions are opposite in charge relative to the surface charge of the particle. The second region is known as the diffuse layer which surrounds the compact layer and is larger (~10-100 nm). Co-ions and counter-ions exist in the diffuse layer, but the latter are in excess relative to the bulk concentration, and the former are deficient. Both the compact and diffuse layers can be involved in adsorption reactions of ions or NOM molecules to the surface of a preformed or forming solid.

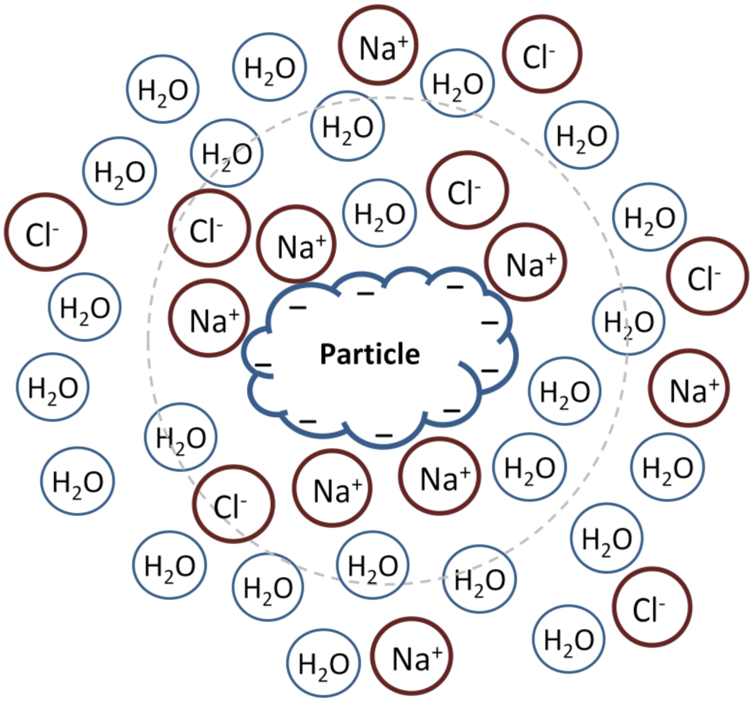

Figure 2.1: Ionic distributions occur around particles in water that have surface charges. Ionic distributions also form around coagulants as they react with soluble species and begin to precipitate out from solution.

Successful removal of particles requires that destabilization of charged particles occurs so that larger, settable flocs can form. Destabilization can be achieved by the addition of a chemical coagulant (destabilizing agent) such as alum or ferric chloride to water. Metal salts dissociate in solution and subsequently begin to form metal hydroxides which may incorporate common anions found in the solution such as phosphate, sulfate, or fluoride into their structure (Benjamin and Lawler, 2013). Organic polymers may also be used as coagulants or floc stabilizers. Each coagulant, whether inorganic or organic, operates best under a specific set of conditions. Alum ($Al_2(SO_4)_3$) is the coagulant of focus for the remainder of this report.

Destabilization of particles can occur by way of four mechanisms upon addition of a coagulant. The first is compression of the diffuse layer surrounding a particle. If salts are added, the ionic strength of a solution increases and the presence of counter ions surrounding a charged particle increases, reducing the thickness of the diffuse layer (Benjamin and Lawler, 2013). A thinner diffuse layer can help particles overcome the energy barrier between them that prevents their collision and aggregation. The second destabilization mechanism of particles is adsorption and charge neutralization (Benjamin and Lawler, 2013). Adsorption of ions of the opposite charge can neutralize the charge of particles, enabling them to collide, aggregate, and settle out of suspension. Restabilization of particles can occur when too much destabilizing chemical has been added and charges are not neutralized, but instead, reversed. The third particle destabilization mechanism is enmeshment (Benjamin and Lawler, 2013). Enmeshment occurs when enough chemical coagulant has been added such that a precipitate forms; usually, the precipitate forms on the surface of the original particles so that those particles are enmeshed in the gelatinous and amorphous precipitate that forms. The enmeshed contaminants are then settled out of suspension with the fresh precipitate. The fourth destabilizing mechanism is adsorption and interparticle bridging which generally involves the addition of high-molecular weight organic polymers (Benjamin and Lawler, 2013). The molecules of the polymers added adsorb to the surface of two or more particles through chemical interactions, forming bridges between them. Through interparticle bridging, the polymers form a floc that is unlikely to break. The success of destabilization by interparticle bridging highly depends on the particle concentration and polymer dose.

2.6 COAGULATION AS A DRINKING WATER TREATMENT STRATEGY – NOM REMOVAL

2.6.1 Nature and Characterization of NOM

NOM is present in natural waters and can be classified as dissolved or particulate. Dissolved organic carbon (DOC) is a common parameter used to describe the amount of NOM in water and is defined operationally as the dissolved fraction of NOM that can pass through a 0.45 µm pore filter. Particulate organic matter is that fraction of organic left on the filter or “undissolved” (Edzwald, 1993). DOC concentrations for freshwaters usually range from 1 to 10 mg/L, though concentrations above 10 mg/L are rare except in bogs, marshes, or similar wetlands (Morel and Hering, 1993). Ground and rainwater DOC concentrations occur at approximately 1 mg/L while surface waters in lakes and rivers can have from 2 to 10 mg/L of DOC (Morel and Hering, 1993). Several classification systems for DOC have been proposed, but the most commonly used is to consider that DOC can be broken down into two components, fulvic and humic acids. Fulvic acids comprise the fraction of DOC that are usually of low molecular weight and are acid-soluble. Humic acids comprise the fraction of DOC that generally has higher molecular weights and precipitate at very low pH values. Besides solubility and molecular weight, fulvic acids are known to have a greater carboxylic content than humic acids and humic acids, are understood to have a higher degree of aromaticity (Rodriguez and Nunez, 2009). Coagulation is understood to remove humic acids far more than fulvic acids (Edzwald, 1993; Edwards, 1997).

The presence of NOM in drinking water may cause taste, odor, and aesthetic issues (Suffet and MacCarthy, 1989). The brown or yellowish discoloration that is often inherent of natural waters is usually directly attributable to the presence of humic NOM in the water. Disinfection byproducts (DBPs) are a concern associated with residual NOM that is present during disinfection using chlorine-based disinfectants. Research has linked DBPs to various forms of cancer and adverse reproductive effects in humans (Morris et al., 1992; Nieuwenhuijsen et al., 2000; Nieuwenhuijsen et al., 2009; Villanueva et al., 2004; Villanueva et al., 2007; Krasner, 2009). Water utilities are under increasing pressure to remove NOM or change disinfectants so that formation of DBPs is minimized. NOM structure and content varies significantly depending on season, age, climate, and source (Stumm and Morgan, 1996). These variations in NOM content coupled with differences in molecular weight, solubility, charge density, and functional groups present impact the removal of NOM from natural waters by coagulation (Goslan et al., 2002; Sharp et al., 2005).

The removal of NOM by alum coagulation is understood to occur through two mechanisms, direct precipitation with aluminum and adsorption to precipitated aluminum hydroxide solids (Dempsey, 1984; Edzwald, 1993; Dennett et al., 1996). Direct precipitation occurs when aluminum complexes with NOM in solution and forms an insoluble phase. Once the overall charge balance between the two species is satisfied, precipitation occurs. Adsorption of NOM to precipitated aluminum hydroxide solids occurs through hydrolysis reactions where NOM displaces hydroxyl groups on the aluminum solid. Thus, competition exists between hydroxyl groups and NOM. Coagulation with metal salts preferentially removes hydrophobic fractions of NOM from solution as opposed to hydrophilic fractions of NOM (Edzwald, 1993; Sharp et al., 2005). Some studies have even suggested dominant removal mechanisms for humic and fulvic acid components of NOM. McKnight et al. (1992) proposed that fulvic acids are primarily removed by adsorption to precipitated aluminum hydroxide solids whereas Huang (1992) and Shiu (1996) proposed that humic acids are removed through both direct precipitation and adsorption reactions.

The amount of NOM in a natural water and its removal is typically measured as total or dissolved organic carbon (TOC or DOC) or absorbance of ultraviolet (UV) light at a wavelength of 254 nm. TOC measurements account for all organic content in a sample while UV-254 measurements quantify the fraction of organic content that is capable of absorbing UV light at that wavelength. UV-254 is a popular quantifier for NOM content in water because its measurement is simple and provides a good indication of how effective coagulation might be for removing NOM from water. Many prominent studies investigating the removal of NOM or specific NOM fractions by coagulation have used UV-254 to quantify NOM removals (Semmens and Field, 1980; Edzwald, 1983; Dempsey et al., 1984; Reckhow and Singer, 1984; Edzwald and Kaminksi, 2008). The fraction of NOM that can absorb UV-254 is typically humic in nature and composed of single or multiple aromatic rings and may have conjugated double bonds. Because coagulation favors the removal of humic acids, UV-254 provides a good measurement to assess the efficacy of coagulation at removing its targeted fraction of NOM in a water (Edzwald et al., 1985). Interference of UV-254 by other aquatic species in water is not common; however, if present at very high concentrations, inorganic species such as nitrite and bromide can absorb UV light (Edzwald, 1983).

When interested in removal of NOM, specific ultraviolet absorbance (SUVA) is a useful concept for classifying NOM and its likelihood of removal by coagulation because it incorporates both DOC and UV-254 measurements (Equation 2.1).

Equation 2.1

$$SUVA = \frac{(UV_{254nm}\ in\ cm^{-1}) \times 100\,\frac{cm}{m}}{(DOC\ in\ mg/L)}$$

High SUVA values generally correspond to NOM that is hydrophobic in nature (predominantly humic acids) while low SUVA values indicate NOM that is hydrophilic (White et al., 1997). Coagulation processes are best at removing NOM with high SUVA values (Edzwald and Kaminski, 2008). Edzwald (1993) found that SUVA can be used to estimate removals of DOC by alum coagulation while investigating the control that NOM can exhibit on coagulation dosages. Reckhow et al. (1997) found DOC removals as high as 70-80% for NOM with high SUVA values, whereas DOC removals of only approximately 10%, could be achieved for NOM with low SUVA values. White et al. (1997) reported residual SUVA values which tended to plateau at approximately 1.0-2.4 L/mg-m following high alum doses (>50 mg/L alum) in thirty one natural waters. Table 2.22.2 summarizes conclusions made from other studies concerning expected removal of NOM based on SUVA values when using coagulation.

Table 2.2: Effect of nature of NOM on Coagulation*.

SUVA	NOM Composition	Coagulation Impact
<2	Mostly non-humic Low hydrophobicity Low molecular weight Mostly aliphatic	Poor DOC removal NOM has little influence on coagulant dosages
2 - 4	Mixture of aquatic humics and other NOM Mixture of hydrophobic and hydrophilic NOM Mixture of molecular weights Mixture of aliphatic and aromatic	Fair to good DOC removal NOM may influence coagulant dosages
> 4	Mostly humic High hydrophobicity High molecular weight Mostly aromatic	Good DOC removal NOM controls coagulant dosages

*Table derived from Edzwald and Van Benschoten 1990 and Pernitsky and Edzwald 2006.

2.6.2 NOM Removal Requirement

Through the Safe Drinking Water Act of 1974 and subsequent amendments, the USEPA requires water systems to remove a set amount of TOC to prevent the formation of disinfection byproducts (DBPs) and their precursors. DBPs are known to cause adverse health effects and can form as NOM is oxidized by different disinfectants such as chlorine and ozone during the disinfection process. Therefore, removal of NOM prior to disinfection is critical and one option to reduce DBP formation. The USEPA has established a rule for TOC removal when using coagulation processes to lower TOC (Table 2.3). The rule takes into account the source water TOC and alkalinity to determine removal needed, because the removal of TOC is known to become more difficult as alkalinity increases or when the initial TOC is initially low. For blended water systems, the final TOC removal conditions are determined by summing together the proportional contributions of each water's original TOC and alkalinity using the blending ratio.

Table 2.3: Required TOC removal by enhanced coagulation for plants using conventional (USEPA, 1999).

Source Water TOC (mg/L)	Source Water Alkalinity (mg/L as $CaCO_3$)		
	0 – 60	60 - 120	> 120
> 2.0 - 4.0	35.0%	25.0%	15.0%
> 4.0 - 8.0	45.0%	35.0%	25.0%
> 8.0	50.0%	40.0%	30.0%

The procedure accompanying the USEPA's TOC removal rule involves incrementally increasing the coagulant dosage by 10 mg/L until the required TOC removal percent is met. Typically, the required TOC removals are achievable; however, the rule has a provision for water systems that struggle to meet their percent TOC removal. If a water system struggling to remove TOC finds that, at some point during the coagulation process, they cannot remove 0.3 mg/L TOC per additional 10 mg/L coagulant dose, they are exempt from further coagulant dosage increases normally required by the rubric. The water system may operate at the last coagulant dosage that accomplished greater than 0.3 mg/L TOC removal per additional 10 mg/L coagulant dosage increase. This exemption from the required percentage of TOC removal by the rule is known as the "point of diminishing returns" (PODR) and recognizes the inherent complexity of NOM in different water sources and NOM's variable proclivity towards removal by coagulation. In a study comprised of thirty-one natural waters, White et al. (1997) found that the PODR exemption prevented excessive dosages of alum applied at water systems where only modest gains in additional TOC removal could be achieved by the excessive dosages. A pH requirement accompanies the required TOC removal rule before the PODR can be declared (Table 2.4Table 2.4). The intent of the pH requirement is to ensure that coagulation is occurring under the most favorable conditions for removing TOC by coagulation given the source water's alkalinity.

Table 2.4: Target pH required for PODR (USEPA, 1999).

Alkalinity (mg/L as $CaCO_3$)	Target pH
0 – 60	5.5 +/- 0.2
> 60 – 120	6.3 +/- 0.2
> 120 – 240	7.0 +/- 0.2
> 240	7.5 +/- 0.2

Based on the solubility of aluminum with respect to an amorphous gibbsite ($Al_2(OH)_{3(s)}$) precipitate, NOM removal by adsorption onto $Al(OH)_3$ precipitates during alum coagulation should best occur at approximately pH 6.5 (Table 2.e 2.5 and Figure 2.2). This optimum occurs because the surface charge of the amorphous gibbsite precipitate is positive at this pH value and the least amount of aluminum is required for oversaturation. For pH values greater than 6.5, the surface charge of the amorphous gibbsite precipitate is negative which is repulsive to NOM molecules that are also negatively charged in solution. Less NOM removal would occur at higher pH values and more alum coagulant would be needed for precipitation of the aluminum hydroxide.

Table 2.5: Hydrolytic reactions for formation of an aluminum hydroxide precipitate (Stability constants for aluminum hydroxide precipitates taken from Morel and Hering 1993).

Reaction	Log K
$Al^{3+} + H_2O \leftrightarrow AlOH^{2+} + H^+$	-5.0
$Al^{3+} + 2\ H_2O \leftrightarrow Al(OH)_2^+ + 2\ H^+$	-9.3
$Al^{3+} + 3\ H_2O \leftrightarrow Al(OH)_3 + 3\ H^+$	-15.0
$Al^{3+} + 3\ H_2O \leftrightarrow Al(OH)_{3\,(s)} + 3\ H^+$	-8.5
$Al^{3+} + 4\ H_2O \leftrightarrow Al(OH)_4^- + 4\ H^+$	-23

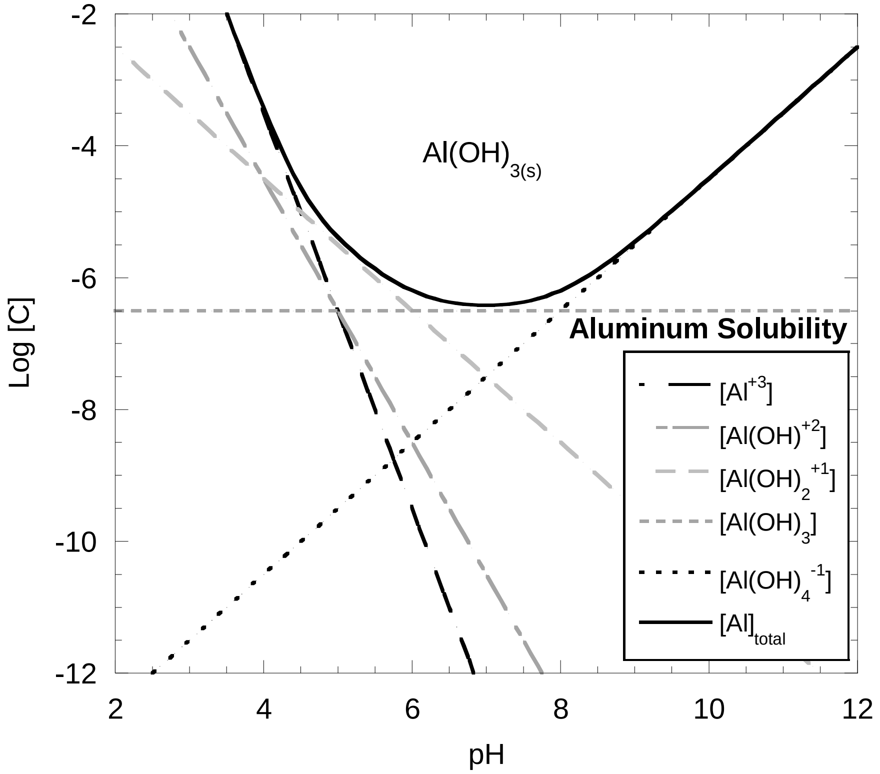

Figure 2.2: Aluminum solubility and speciation.

2.7 COAGULATION AS A DRINKING WATER TREATMENT STRATEGY – FLUORIDE REMOVAL

2.7.1 Defluoridation Mechanisms

Various defluoridation treatment processes have been developed since the discovery of the health effects of high concentrations of fluoride and the detection of high concentrations of fluoride in certain drinking water sources. Two primary removal methods are employed by defluoridation treatment processes. The first method involves precipitation where chemical addition results in the formation of fluoride precipitates or co-precipitates (Figure 2.3A). Chemicals added for precipitation may include aluminum, calcium, or magnesium based compounds (Choi and Chen, 1979; Brindha and Elango, 2011). The second method for defluoridation involves adsorption of fluoride through ion exchange or surface reactions with an adsorbent such as alumina, clays, bioadsorbents, etc (Figure 2.3B). Fluoride is often capable of competing with and replacing surficial hydroxyl groups on adsorbents because they have similar valence and molecular radius (Choi and Chen, 1979; Deshmukh and Attar, 2008). Adsorption can also occur in concert with precipitation methods as fluoride ions adsorb to a freshly precipitated amorphous solid such as aluminum hydroxide.

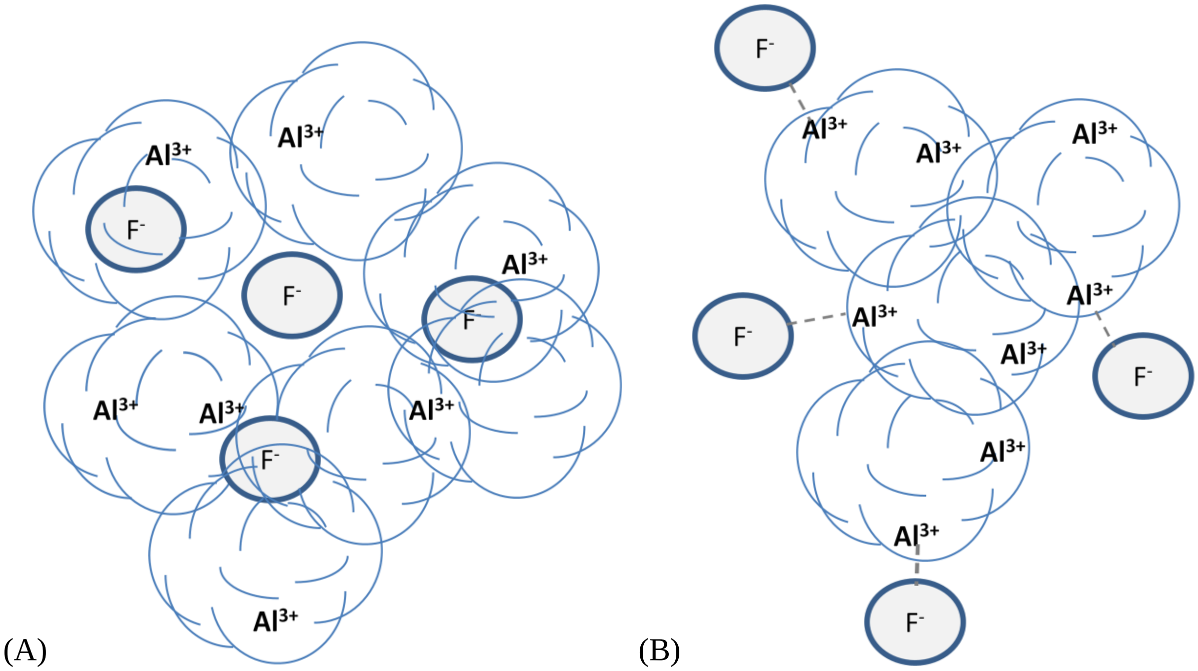

Figure 2.3: Schematic representation of fluoride removal by (A) precipitation and (B) adsorption to amorphous aluminum oxide.

For both precipitation and adsorption defluoridation processes, the optimal pH range for fluoride removal is generally agreed to be within pH 6-7 (Boruff, 1934; Culp and Stoltenberg, 1958; Sollo et al., 1978; Choi and Chen, 1979; Schoeman and MacLeod, 1987; Sujana et al., 1998; Tang et al., 2009; Gong et al., 2012). Outside of this range, fluoride removal diminishes, especially as pH values above 9 and below 5 are reached. Choi and Chen (1979) discuss lower fluoride removals at different pH ranges with respect to aluminum sulfate and alumina. As pH drops below 4.5, the aluminum oxide (Al_2O_3) solid begins to dissolve due to its solubility, increasing the concentration of free Al^{+3} species. The high affinity of fluoride ions to form fluoro-aluminum complexes with aluminum accelerates the dissolution of the aluminum oxide at low pH values. The positive surface charge of the aluminum oxide solid at low pH values further facilitates interaction between and complexation with negatively charged fluoride ions. In systems with high pH values (approximately 8.5 or greater), the removal of fluoride by adsorption is significantly decreased. Under these conditions, the hydroxide ion concentration in solution increases, thereby competing with fluoride ions for remaining adsorption sites; also the surface of the aluminum oxide becomes negatively charged when hydroxo groups deprotonate, thereby repelling like-charged fluoride ions.

2.7.2 Alum Coagulation

Alum coagulation is capable of removing excessive fluoride from drinking waters. Fluoride as a soluble contaminant can be removed by two mechanisms during the alum coagulation process. The first mechanism involves co-precipitation of aluminum and fluoride. Fluoride anions as well as hydroxyl ions are attracted to free aluminum cations in solution following addition of the alum coagulant. Co-precipitation of fluoride and hydroxide aluminum complexes can occur, which results in a mixed aluminum hydroxide precipitate. Fluoride can be incorporated into the structure of the predominant aluminum hydroxide precipitate by substituting in for hydroxide molecules. Hu et al. (2005) and Ayoob et al. (2008) proposed a general formula for the mixed precipitate that can form: $Al_nF_m(OH)_{3n-m}$. Fluoride can also form inner complexes with the surface of the aluminum hydroxide precipitate during co-precipitation. Individual and proposed reactions are shown in Table 2.52.6. Sujana et al. (1998) found with alum sludge that optimum fluoride removal by coagulation occurs within the pH range of 5.5-6.5. This pH range corresponds with the lower half of the pH range for aluminum solubility that permits the best coagulation results.

Table 2.5: Hydrolytic reactions for the formation of an aluminum hydroxide and mixed precipitate incorporating fluoride (Adapted from Pommerenk and Schafran 2002 and Gong et al. 2012).

Reaction
$Al^{3+} + 3\ H_2O \leftrightarrow Al(OH)_{3\,(s)} + 3\ H^+$
$Al^{3+} + 3\ OH^- \leftrightarrow Al(OH)_{3\,(s)}$
$AlF^{2+} + OH^- \leftrightarrow AlF_2(OH)_{(s)}$
$AlF(OH)^+ + OH^- \leftrightarrow AlF(OH)_{2\,(s)}$
$AlF^{2+} + 2OH^- \leftrightarrow AlF(OH)_{2\,(s)}$

Adsorption of fluoride is the second removal mechanism ensuing addition of a coagulant such as alum to a water (Mekonen et al., 2001). Choi and Chen (1979) and Deshmukh and Attar (2008) determined that fluoride can replace surficial hydroxyl groups present on activated alumina (Al_2O_3). Replacement of hydroxyl groups most likely occurs between fluoride and an amorphous aluminum hydroxide precipitate such as that resulting from alum coagulation as well. Replacement occurs because less energy is required to replace atoms or groups in a poorly-defined solid than a solid with a more crystalline structure like activated alumina.

2.7.3 Defluoridation Studies Involving Alum Coagulation

Numerous defluoridation studies were conducted upon the discovery of fluoride as a potential drinking water contaminant. Groundwater was the primary contaminated water source considered. Boruff (1934) and Boruff et al. (1937) conducted a series of adsorption tests using tap water spiked with fluoride and incremental dosages of aluminum sulfate ($Al_2(SO_4)_3$) and alum ($Al_2(SO_4)_3{\bullet}18(H_2O)$), respectively. Initial fluoride concentrations ranged from 4 to 5 mg/L and coagulant dosages up to 333 mg/L as alum were applied to achieve fluoride concentrations under 1 mg/L at system pH values of 7.2. Scott et al. (1937) studied three Ohio well waters with high fluoride (≥1.7

mg/L), high alkalinity (≥290 mg/L $CaCO_3$), and moderate pH (7.2-7.8). Alum dosages of 195, 340, and 905 mg/L were required to reduce initial fluoride concentrations of 1.7, 3.0, and 6.0 mg/L, respectively, down to 1.0 mg/L. Culp and Stoltenberg (1958) reported that alum dosages of 250 mg/L and 350 mg/L were required to reduce fluoride concentrations from 3.6 mg/L in highly mineralized Kansas well water down to fluoride concentrations of 1.5 and 1.0 mg/L. During experimentation, Culp and Stoltenberg used lime to maintain a pH suitable for flocculation.

Later research efforts by Sollo et al. (1978) utilized jar tests to study defluoridation through alum coagulation in synthetic waters with initial fluoride concentrations of approximately 5.0 mg/L. The jar tests included a rapid mix period of 1-5 min, followed by slow mix for 30-60 min, and ending with a settling period of 30 min before sampling. Results from experimentation were similar to those obtained by Culp and Stoltenberg, concluding that high alum dosages were required to remove fluoride to acceptable levels (Sorg 1978). Sollo et al. found that alum doses of 200 mg/L and 300 mg/L were required to lower initial fluoride concentrations from approximately 5 mg/L to 2.09 mg/L and 1.20 mg/L, respectively, at a system pH of 6.1-6.5. Additional experiments considering a lower initial fluoride concentration of 2.86 mg/L and system pH of 6.2-6.4 resulted in alum doses of 75 mg/L and 200 mg/L being necessary for fluoride concentrations to be reduced to 2.0 mg/L and 1.0 mg/L, respectively. Zhang et al. (2005) conducted a similar series of jar tests to Sollo et al. for investigating defluoridation by alum coagulation. System pH values in tests by Zhang et al. were controlled between 6 and 7 such that optimal fluoride removal occurred. An alum dose of 390 mg/L was required to lower fluoride concentrations from 4.0 mg/L to 1.0 mg/L. Gong et al. (2012) also studied the defluoridation by coagulation in jar tests using an aluminum salt ($AlCl_3 \cdot 6H_2O$). At pH 6 and 7, approximately 500 mg/L alum dose equivalent was required to lower fluoride concentrations from 5 mg/L to below 1.0 mg/L, which agrees with defluoridation trends established by previous studies.

The effect of molar ratios of hydroxide and fluoride ions relative to free aluminum cations on coagulation was investigated by Hu et al. (2005). Hu et al. confirmed that both co-precipitation and adsorption can occur when aluminum ions are added to water with high fluoride concentrations. A molar ratio of hydroxide to fluoride ($[OH^-]/[F^-]$) greater than 2.4 was necessary for adequate defluoridation in a coagulation process; otherwise the relative abundance of fluoride prevented the formation of aluminum hydroxide precipitates. Gong et al. (2012) investigated the speciation of fluoride during coagulation with an aluminum salt. At pH values below 5, almost all fluoride in solution existed as fluoro-aluminum complexes and subsequently inhibited overall fluoride removal by alum coagulation (Table 2.62.7). Low pH and high fluoride concentrations were found to favor complexation. As pH increased from 5 to 8, the ratio of free fluoride to total fluoride changed from 0.2% to 98.7% suggesting the absence of fluoro-aluminum complexes at high pH values above 7. Gong et al. (2012) also confirmed through Fourier transform infrared spectroscopy and x-ray photoelectron spectroscopy that during alum coagulation, a mixed aluminum hydroxide precipitate incorporating fluoride was formed. Farrah et al. (1987) had made similar conclusions to those made by Gong et al. concerning the interaction of fluoride with an amorphous aluminum hydroxide. Farrah et al. found that fluoride promoted dissolution of the aluminum hydroxide solid at low pH (<4) through formation of fluoro-aluminum complexes, but sorbed to the solid when pH was in the 4-7 range. At higher pH values (>7), fluoride that had sorbed to the solid was displaced by hydroxyl groups and converted to free fluoride ions.

Table 2.6: Potential fluoro-aluminum complexes formed at low pH values (stability constants taken from Pommerenk and Schafran 2002).

Reaction	**Log K**
$Al^{3+} + F^{-} \leftrightarrow AlF^{2+}$	7.01
$Al^{3+} + 2\ F^{-} \leftrightarrow AlF_2^{+}$	12.75
$Al^{3+} + 3\ F^{-} \leftrightarrow AlF_3$	17.02
$Al^{3+} + 4\ F^{-} \leftrightarrow AlF_4^{-}$	19.72

A number of other studies have investigated defluoridation through adsorption tests with freshly precipitated aluminum hydroxide, gibbsite, and various other aluminum based compounds. Bower and Hatcher (1967) found that fluoride adsorption to freshly precipitated aluminum hydroxide occurred primarily through the exchange of fluoride ions with hydroxyl groups from the surface of the aluminum hydroxide precipitate, rather than by substitution of fluoride into the lattice structure. Karthikeyan et al. (1994) confirmed that adsorption of fluoride to aluminum compounds such as aluminum titanate and bismuth aluminate occurred through the formation of fluoro-aluminum complexes.

2.7.4 Obstacles associated with Alum Coagulation

Most previous research confirms that alum coagulation can successfully be employed for defluoridation purposes. However, a number of potential barriers exist that must be considered or addressed before implementation of an alum coagulation defluoridation process. Table 2.72.8 contains a list of these concerns. The critical message communicated through these potential concerns is that alum coagulation may be suitable for some water systems, but not others. Additional research that builds on prior studies is necessary to better understand defluoridation by alum coagulation and address the validity and extent of concerns.

Table 2.7: Potential obstacles to alum coagulation.

Concern	**Source**
Performance dependence on water quality parameters (pH, alkalinity, fluoride level, NOM, co-existing anions, etc.)	Mekonen et al., 2001; Pommerenk and Schafran, 2002; Hu et al., 2005; Nigussie et al., 2007
Acidity of aluminum ions, alkalinity consumption, and pH reduction	Ayoob et al., 2008
Defluoridation efficiency and high alum consumption	Sorg, 1978; Choi and Chen, 1979; Ayoob et al., 2008
Residual aluminum and sulfate above MCL	Culp and Stoltenberg, 1958; Ayoob et al., 2008
Toxic sludge disposal (high fluoride content)	Fawell, 2006; Ayoob et al., 2008; Bhatnagar et al., 2001; Brindha and Elango, 2011
Economic feasibility	Bhatnagar et al., 2001; Sorg, 1978; Choi and Chen, 1979
Space requirements	Meenakshi and Maheshwari, 2006
Health impacts	Nayak, 2002; Meenakshi and Maheshwari, 2006; Ayoob et al., 2008
Improved defluoridation using alumina	Deshmukh and Attar, 2008

Water systems that struggle with high fluoride levels generally have groundwater sources; however, surface waters with high fluoride levels do exist. Blending with low-fluoride surface water is a practical solution for ground water systems struggling with high fluoride levels. Blending allows the water system an economic alternative to provide potable water without abandoning their current wells or fully switching to a surface water source. Water quality become a concern with blending because the surface water source can contribute additional contaminants such as NOM to the water system that were not present when only groundwater sources were used. Surface water systems with elevated fluoride levels experience these additional contaminant concerns as well. Coagulation or filtration is necessary to remove surface water contaminants, namely NOM and turbidity. If defluoridation of the water is desired, than alum coagulation should especially be considered.

The presence of NOM in the surface water or blended water is likely to lower the defluoridation efficacy of alum coagulation. In addition, competition between fluoride and NOM for adsorption onto and co-precipitation with the aluminum hydroxide solid that forms will inhibit NOM removal. Therefore, the PODR associated with NOM removal is likely to be reached sooner than expected. Pommerenk and Schafran (2002) examined prefluoridation of drinking water systems which provides a comparable treatment situation as blending because both fluoride and NOM are present during alum coagulation. The presence of fluoride at 1.5 mg/L was found to increase the alum dose required for required NOM and turbidity removal, especially for waters with pH values in the range of 5-7. This pH range corresponds with the pH range suitable for fluoride co-precipitation and adsorption to the aluminum hydroxide precipitate. Consequently, some of the fluoride added for beneficial water fluoridation was removed from solution during alum coagulation. NOM competition with fluoride can result in lower overall removals of fluoride and NOM. The interactions of fluoride and NOM during alum coagulation need to be better understood.

Results of this research will have implications for current NOM removal requirements of different waters and decisions regarding when the PODR has been reached. In addition, water systems forced to use water sources with high fluoride content need relevant treatment guidelines so that they can ensure the delivery of safe water to their customers. Review and potential revision of the current fluoride MCL makes this need all the more pertinent as water systems anticipate what treatment their water will require in the near future.

Chapter 3: Methods and Materials

To accomplish the objectives outlined in this study, a series of experiments using jar tests was conducted. Jar tests simulate a full-scale coagulation drinking water treatment process at the bench-scale level. The three conventional phases (rapid mixing, slow mixing, and settling) of a coagulation treatment process were preserved in the jar tests. A number of different conditions were used throughout the jar tests to better understand the removal of fluoride and NOM during the coagulation process in both single and dual ligand systems. These conditions involved varying the following parameters:

- pH
- Alum dose
- Ligand concentration
- Ionic strength
- Source water
- Timing of ligand dosing with respect to floc formation

The removal of fluoride and NOM was first investigated using synthetic waters that were made in the laboratory from de-ionized water and chemical reagents. Natural waters obtained from drinking water systems in the states of Colorado and Texas were used in later jar tests.

3.1 CHEMICALS AND REAGENTS

All chemical reagents used were of analytical grade or higher. The synthetic water solution used in the jar tests was made from a recipe of de-ionized water, calcium chloride dihydrate (Calcium Chloride Dihydrate, $CaCl_2(H_2O)_2$, ACS Powder , Fisher Scientific), and sodium bicarbonate (Sodium Bicarbonate, $NaHCO_3$, Certified ACS, Fisher Scientific) such that a hardness of 2.3 meq/L and alkalinity of 3 meq/L resulted. The alkalinity provided buffering when the alum coagulant was dosed during jar tests. Sodium chloride (Sodium Chloride, NaCl, ACS, EMD) was added to adjust ionic strength in the synthetic waters. Ionic strength usually varied between 0.01 and 0.017 M due to pH adjustment of waters during jar tests with hydrochloric acid or sodium hydroxide. Synthetic water solutions were made in 2 L batches and acidified with 6 mL of 1 N hydrochloric acid that was previously made from concentrated hydrochloric acid (Hydrochloric Acid 50% V/V, HCl, ACS, BDH). Acidification prevented nucleation of aluminum precipitates when jars were dosed with the alum coagulant. A fluoride stock of 1000 mg/L fluoride was used to dose jars to an initial concentration of 5 mg/L fluoride occurred. The fluoride stock was made in 100 mL batches from de-ionized water and sodium fluoride (Sodium Fluoride, NaF, Certified ACS, Fisher Scientific). Alum (Aluminum Sulfate Hydrate, $Al_2(SO_4)_3 \bullet (H_2O)_{14-18}$, 98%, Aldrich Chemical Company) was used as the coagulant in the jar tests and dosed from a stock solution of 13.32 mg/L alum acidified with 4 mL of 1N hydrochloric acid. Alum stock solutions were made in 200 mL batches. Sodium hydroxide (1N) was used to adjust pH during coagulant dosing and was made from concentrated sodium hydroxide (Sodium Hydroxide, NaOH, 10.0N, BDH) in 100 mL batches.

Three low molecular weight organic acids were used as surrogates for natural organic matter (NOM) during jar tests. Stock solutions of 1000 mg/L carbon in 100 mL batches were made for each organic acid from reagents (Salicylic Acid, $C_7H_6O_3$, AR, Mallinckrodt; Pyromellitic Acid, $C_{10}H_6O_8$, 96%, Alfa Aesar; and Phthalic acid, $C_8H_6O_4$, 99.5% ACS, Alfa Aesar) and used to dose organics in jars at 5 mg/L carbon and to make standards. Sonication was initially applied to stocks to dissolve the organic acids.

Aluminum residual samples coming from jar test experiments and analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) were acidified with 100 µL concentrated nitric acid (Nitric Acid, HNO3, ACS, BDH) per 10 mL sample volume. Aluminum standards for ICP-AES analysis were made from a 10 mg/L aluminum stock solution. The aluminum stock solution was made in 100 mL batches by dilution using de-ionized water and a certified ICP aluminum 1000 µg/mL standard solution purchased from Ultra Scientific (ICP-013-5). Fluoride residual samples from jar test experiments were adjusted using TISAB II with CDTA (TISAB II, Orion 940909, Thermo Scientific) at a volumetric ratio of 1:1 to prevent background aluminum interference with fluoride measurements.

3.2 JAR TESTS

Jar tests were used to investigate the efficacy of the coagulation process in removing fluoride and NOM. Experiments were performed using a Phipps and Bird PB-700 Jartester with custom-made, rectangular, polycarbonate jars. The jartester was able to accommodate stirring for six jars. For each run, the jars were filled with 200 mL of solution (synthetic water or natural water). The starting time for each jar in a run was staggered to allow for alum dosing, pH adjustment, and subsequent sampling. Staggering jars also helped maintain consistency for rapid mixing, slow mixing, and settling times. Two different systems and two different removal mechanisms were employed during jar testing involving synthetic waters. Single ligand systems had only fluoride or a single low molecular weight organic dosed into the jar. Dual ligand systems had both fluoride and one of the low molecular weight organics. Jar tests with synthetic waters were classified as single or dual ligand systems and co-precipitated or preformed jar tests. Co-precipitation and preformed jar tests are explained in detail in the next sections. All experiments performed with natural waters followed the co-precipitation jar test procedure.

3.2.1 Co-precipitation Jar Tests

Co-precipitation jar tests were conducted such that co-precipitation of ligand(s) and amorphous aluminum hydroxide precipitates occurred in concert. In co-precipitation jar tests, ligand(s) were initially dosed into each jar containing 200 mL of synthetic or natural water. The desired alum dose was then added to each jar and rapid mixing occurred for 3 min to allow for dispersal of alum throughout the solution. Sodium hydroxide (1N) or hydrochloric acid (1N) was added as needed during rapid mixing to adjust the solution to the desired pH. Following rapid mixing, a 30 min period of slow mixing occurred at a stirring speed of 18-20 rpm (estimated to yield a mean velocity gradient, G, value of 12-15 s^{-1}) (Cornwell and Bishop, 1983). During the slow mixing period, ligand(s) co-precipitated with the amorphous aluminum hydroxide flocs that were forming. The jars were allowed to settle for 40 min after the slow mixing period. Samples from each jar were taken immediately after 40 min of settling and analyzed for turbidity, pH, ligand residual, and aluminum residual.

3.2.2 Preformed Jar Tests

Preformed jar tests were conducted such that an amorphous aluminum hydroxide precipitate was allowed to form prior to dosing the solution with a ligand. Preformed tests were used specifically to investigate differences between the adsorption and co-precipitation removal mechanisms of fluoride with amorphous aluminum hydroxide precipitates formed during alum coagulation. For each preformed jar test, jars were prepared with 200 mL of synthetic water solution. Ligands (e.g., fluoride) were not added during jar preparation. The desired alum dose was added and rapid mixing occurred for 3 min to allow for physical dispersal of alum throughout the solution. Sodium hydroxide (1N) or hydrochloric acid (1N) was added as needed during rapid mixing to adjust the solution to the desired pH. Following rapid mixing, a 30 min period of slow mixing at 18-20 rpm occurred with a mean velocity gradient of 12-15 s^{-1} (Cornwell and Bishop, 1983). During the slow mixing period, flocs comprised of an amorphous aluminum hydroxide formed. After 30 min of slow mixing, ligands were dosed into each jar solution. Mixing velocity was increased slightly during ligand dosing to aid in dispersal, but maintained at low enough velocities to prevent floc breakage. A second 30 min slow mixing period occurred following ligand dosing. The jars were allowed to settle for 40 min after the second slow mixing period and sampled subsequently afterwards for turbidity, pH, ligand residual, and aluminum residual.

3.3 EXPERIMENTAL SYSTEMS

3.3.1 Single Ligand Systems

Synthetic water solutions containing either fluoride or a low molecular weight organic acid anion were classified as single ligand systems. Single ligand jar tests allowed for either co-precipitation of the ligand or adsorption of the ligand onto preformed amorphous aluminum hydroxide flocs. Results from single ligand jar tests established baseline maximum removals for ligands.

3.3.2 Dual Ligand Systems

Synthetic water solutions containing both fluoride and a low molecular weight organic acid anions were classified as dual ligand systems. Dual ligand systems allowed for co-precipitation and adsorption of the ligands to occur. Competition between ligands for removal was expected and results were expected to show overall decreased removals for ligands when compared to ligand removals in single ligand systems.

3.4 EXPERIMENTAL WATERS

3.4.1 Synthetic Waters

Synthetic waters were made in 2 L batches in the laboratory using reagents and de-ionized water. Table 3.13.1 contains the exact recipe for synthetic water experiments. The recipe was intended to be a simplified, controlled version of a natural water.

Table 3.1: Synthetic water recipe (2 L batch).

Reagent	Quantity	Unit	Contribution
$CaCl_2$	336	mg	Hardness
$NaHCO_3$	504	mg	Alkalinity
NaCl	x (varies)	mg	Ionic strength adjustment
HCl (1N)	6	mL	Acidification
H_2O	1.994	L	Background solute

3.4.2 Natural Waters

Natural waters suitable for this project were identified on the basis of two main criteria, fluoride concentration and water source. The primary focus was directed at finding drinking water systems using surface water as their water source because these water systems were likely to have a significant NOM content. The second criterion was that the natural waters have fluoride concentrations greater than 2 mg/L. When fluoride is present in drinking water at concentrations greater than 2 mg/L, it can cause mild cases of dental fluorosis. In addition, the USEPA may lower the fluoride MCL to 2 mg/L or slightly lower in the near future and so these water systems may need to consider defluoridation of their drinking water in the future. Public records (consumer confidence reports and annual water quality reports) available online from state and municipal websites were used to develop a database of potential water systems with natural water suited to this project. Information concerning plant identification, plant contact, water source, population served, system connections, fluoride concentrations, TOC concentrations, and the overall treatment process was collected for the database. Fluoride and NOM content were expected to impact the alum coagulation process. Water quality characteristics for the three natural waters that have been utilized for experimentation are contained in Table 3.23.2.

Table 3.2: Water quality characteristics of natural waters.

Parameter	**Natural Water**				
	Water 1 - TX	Water 2 - TX	Water 3 - CO	Water 4a - TX[a]	Water 4b - TX[a]
Water Source	SW	Blend	SW	GW	SW
pH	8.60	7.77	7.58	7.80	7.97
[F] (mg/L)	3.04	2.09	3.15	3.96	0.29
DOC (mg/L Carbon)	9.20	2.35	1.18	0.63	3.83
UV-254 (absorbance)	0.080	0.034	0.021	0.001	0.067
SUVA (L/mg-m)	0.87	1.46	1.76	0.22	1.74
Alkalinity (mg/L $CaCO_3$)	294.6	219.5	16.8	308.0	137.2
Turbidity (NTU)	15.64	28.93	1.04	19.08	28.93

[a] Water 4 was blended at a 1:1 ratio of groundwater (GW) and surface water (SW) to form Water 2 – TX

To obtain natural waters, contact was made with the water systems prior to requesting natural water samples. Early communication allowed for a relationship to develop between the water system and laboratory as well as further collection of information about the water system. The reception of personnel at each water system to the project and to water sample requests was generally positive. Insulated coolers containing a 20 L Nalgene carboy, ice packs, and filling instructions were shipped via ground courier to each water system. Attendants at the water system rinsed each carboy three times with raw water before filling the carboy with raw water. Carboys were filled to the top to eliminate headspace and placed inside the insulated coolers. The ice packs provided were regenerated and used as packing material for around the filled carboy. The water system shipped the insulated coolers with the filled carboys and ice packs to the laboratory via ground courier. Upon receiving the return shipment, the carboys were taken out of the coolers, sampled, and stored in a 4^{o} C cold room until experimentation.

3.5 SAMPLING PROCEDURES AND ANALYSIS

Water samples were taken at the end of each jar test experiment. Samples were also collected upon receiving natural waters. Depending on the parameter of interest, different methods and materials were used for analysis.

3.5.1 pH Sampling and Analysis

Measurements of pH were taken throughout jar tests and upon receiving natural waters. During jar tests, pH was measured for each jar before alum dosing, during pH adjustment, and at the end of each experiment. An Orion 8175BNWP Ross Sure-Flow Semi Micro pH probe (Thermo Scientific) was used for pH measurements. Hach pH 4, 7, and 10 buffer solutions were used to calibrate the probe daily. Buffer solutions were replaced every three to four weeks and the probe was maintained using Ross storage and filling solutions.

3.5.2 Turbidity Sampling and Analysis

Turbidity measurements were taken directly after completion of jar tests and upon receiving natural waters. Following 40 min of settling, turbidity samples were collected from each jar’s supernatant, avoiding disturbance of settled floc. Received natural waters were mixed in their carboy containers to create a homogenous suspension before taking a turbidity sample. Turbidity was measured using a Hach Turbidimeter with Gelex standards (0-1, 0-10, 0-100, and 0-1000).

3.5.3 Fluoride Sampling and Analysis

Fluoride samples were collected upon receiving natural waters and at the end of each jar test experiment. Fluoride measurement occurred directly after sample collection. All fluoride samples were handled using plastic labware. Fluoride samples contained 10 mL of solution and were filtered through a 47 mm diameter, 0.45 µm pore membrane filter (Pall Corporation) prior to analysis. From the filtrate, 8 mL of sample were extracted and placed in a clean plastic beaker. This extracted filtrate was mixed with 8 mL of TISAB II with CDTA buffer. The TISAB II with CDTA provided pH adjustment and ionic strength consistency, and prevented background aluminum interference with the sample during analysis. An Orion Ionplus Fluoride electrode (single reference and half-cell) purchased from Thermo Fischer Scientific was used for fluoride measurements. Measurements were read as relative milli-volts and converted into mg/L using a fluoride standard calibration curve. A calibration curve for fluoride, similar to the example shown in Figure 3.1, was made after each jar test and before measuring. Because of the tendency for the fluoride probe readings to slowly drift over time, the meter was re-zeroed after every two samples to prevent any misreading. In addition, a fluoride standard was measured after every seven samples.

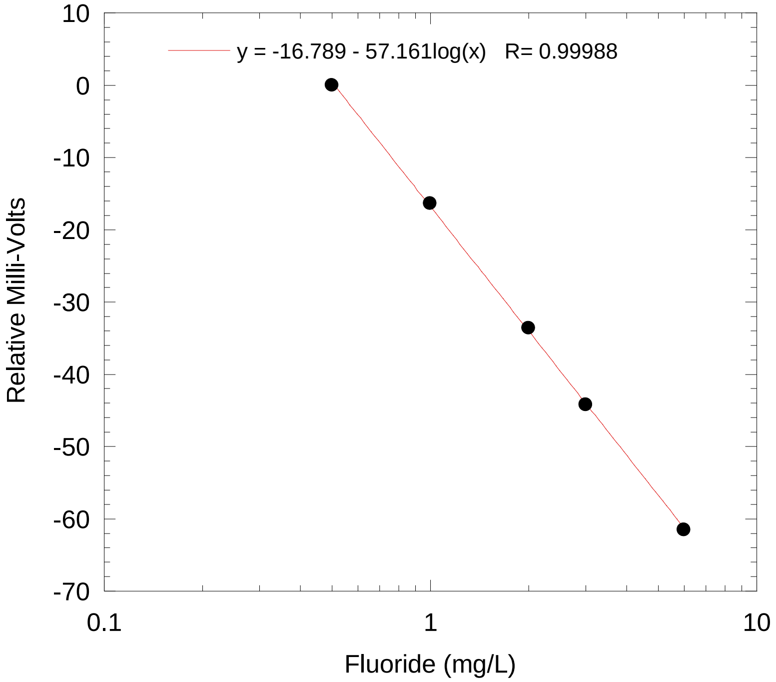

Figure 3.1: Fluoride standard curve.

3.5.4 RESIDUAL ALUMINUM SAMPLING AND ANALYSIS

Samples to measure aluminum residual were collected at the end of each jar test experiment. Samples volumes of 10 mL were collected and filtered through a 47 mm diameter, 0.45 μm membrane filter (Pall Corporation). Concentrated nitric acid at a ratio of 100 μL nitric acid to 10 mL filtered sample was used to acidify and preserve each sample. A Varian 710-ES ICP Optical Emission Spectrometer and Autosampler with 2% concentrated nitric acid mobile phase was used to measure residual aluminum concentrations. Aluminum standards were made from an aluminum ICP stock solution. A sample calibration curve is presented in Figure 3.2. To ensure quality, a standard was measured after every eight to ten samples. Residual aluminum samples were stored in a 4^{o} C cold room following acidification if they were not analyzed right away. Samples were not held for more than two weeks before analysis.

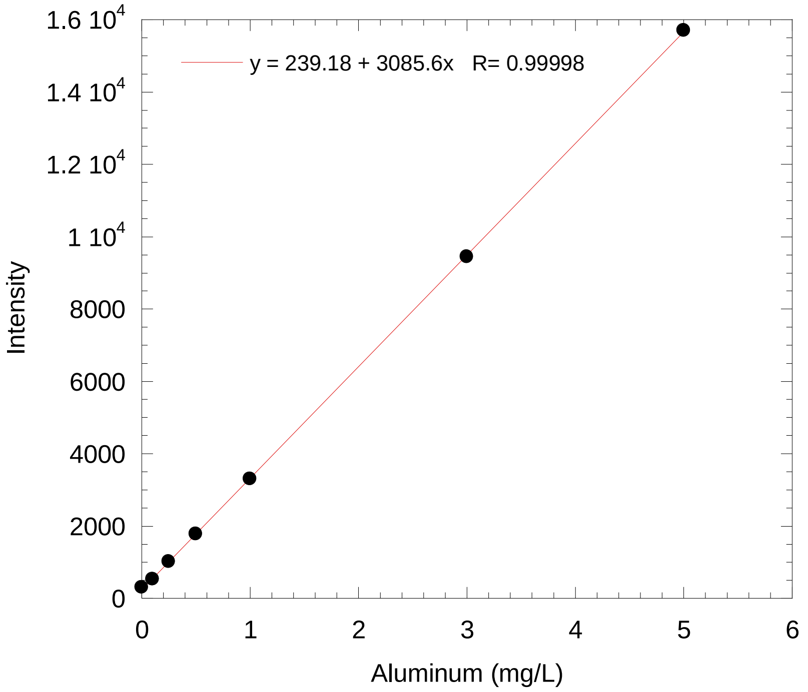

Figure 3.2: Aluminum standard curve.

3.5.5 Organic Sampling and Analysis

Samples for organic analysis were collected upon receipt of natural waters and at the end of each jar test experiment. All samples were filtered using 47 mm diameter, 0.45 μm membrane filters (Pall corporation) before undertaking any organic analysis. An Agilent 8453 spectrophotometer was used to measure organic content by measuring absorbance of samples at various wavelengths through a quartz cell with a 1 cm path length. Table 3.33.3 shows the wavelengths measured for each sample. UV-254 is a common water parameter used to describe the amount of organic material in natural waters. Specific wavelengths were selected for each organic acid of interest by scanning at all wavelengths and identifying the approximate wavelength(s) where the highest absorbance occurred. Calibration curves for each organic were made using a seven-point curve after each jar test (Figure 3.3, Figure 3.4, and Figure 3.5). After every seven samples, a total organic carbon standard was run to ensure quality measurements.

Table 3.3: Wavelengths used to measure organic content in samples.

Organic	**Water Type**	**Wavelength (nm)**
Natural Organic Matter	Natural	254
Phthalic Acid	Synthetic	240, 277
Salicylic Acid	Synthetic	296
Pyromellitic Acid	Synthetic	294, 296

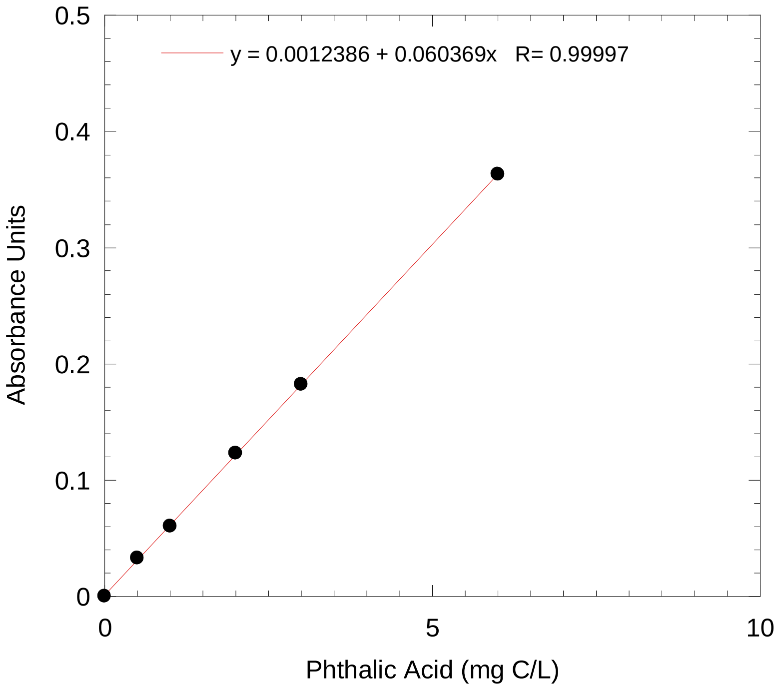

Figure 3.3: Phthalic acid standard curve (absorbance measured at 240 nm).

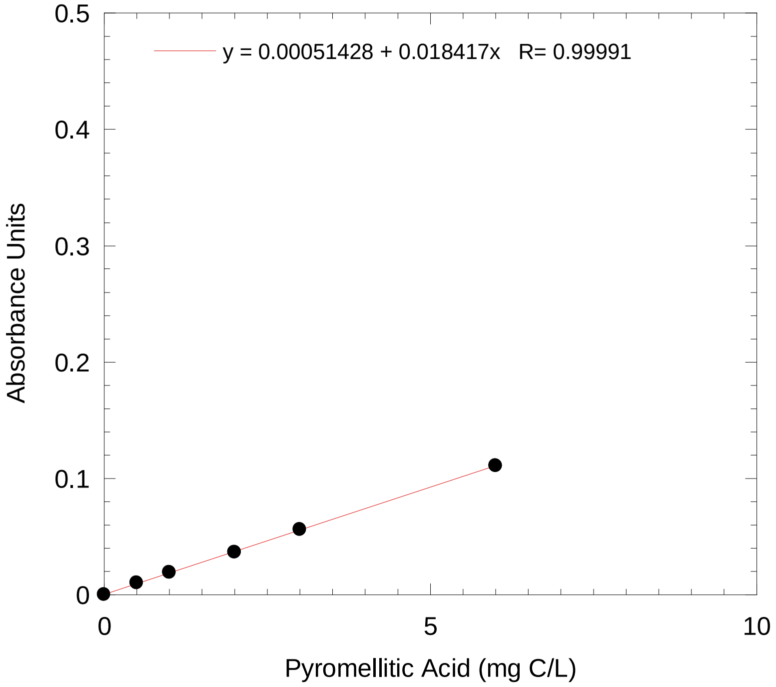

Figure 3.4: Pyromellitic acid standard curve (absorbance measured at 296 nm).

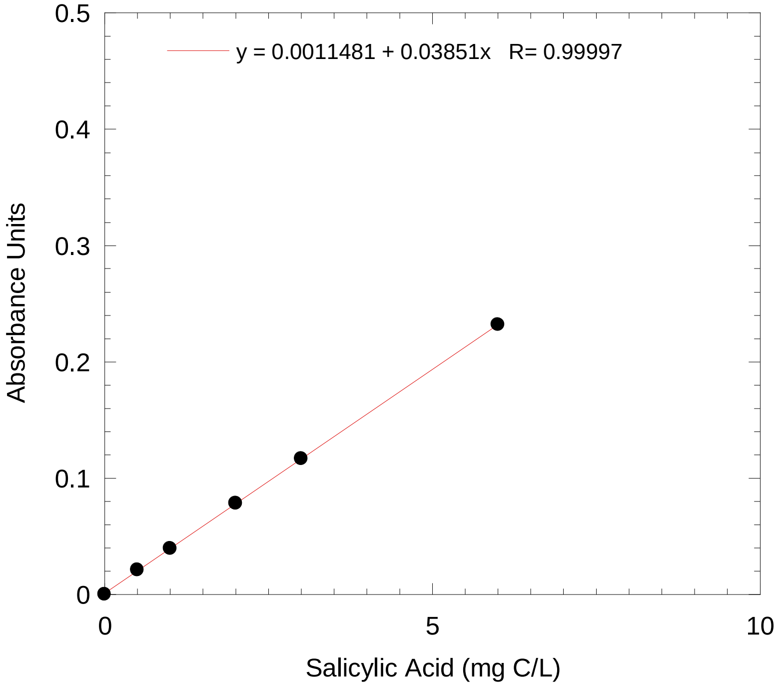

Figure 3.5: Salicylic acid standard curve (absorbance measured at 296 nm).

Select samples for total organic carbon (TOC) analysis were filtered (0.45 µm membrane filter) and preserved with concentrated phosphoric acid according to Standards Methods 5310 (TOC – Wet/Oxidation Method). These samples were stored in the dark in a 4^{o} C cold room until analysis. The TOC samples were not analyzed by in our laboratory, but contracted out to the Environmental Laboratory Services (ESL) of the Lower Colorado River Authority located in Austin, Texas. Sample chains of custody were completed to ensure quality control. Results from ESL were either emailed or received in person.

3.5.6 Alkalinity

The alkalinity of natural waters was measured upon receiving them and before any jar test experiments occurred. Method 2320 (Alkalinity – Titration Method) in Standard Methods was used to measure alkalinity in the natural waters (Eaton and Franson, 2005).

Chapter 4: Experimental Results and Discussion

Experimental results from jar tests are presented in this section of the report and have been divided into three main sections. The first section involves single ligand jar tests conducted using synthetic water that contained either fluoride or a LMW organic acid. Within the first section, optimum pH conditions for defluoridation by alum coagulation are established and removal mechanisms of fluoride and LMW organics by alum coagulation are investigated. The second section involves dual ligand jar tests conducted using synthetic waters that contained both fluoride and a LMW organic acid. Within the second section, the interactions of fluoride, LMW organics, and aluminum during alum coagulation are presented and discussed. The third section presents results from jar tests conducted using natural waters from Texas and Colorado. Within the third section, the interactions of fluoride, NOM, and aluminum during alum coagulation are presented and discussed. More experiments have been performed with the Texas waters than the Colorado water at present. Therefore, only a limited number of results from experiments with the Colorado water are presented in the chapter. A final summary of results from all jar tests concludes the chapter.

4.1 SYNTHETIC WATERS – SINGLE LIGAND EXPERIMENTS

4.1.1 Optimum pH for fluoride removal

The first series of jar tests were performed using synthetic waters and single ligand systems to determine the optimum pH for fluoride and organic removal. Based on the solubility of aluminum with respect to an amorphous aluminum hydroxide, optimum removals for fluoride and organics were expected to occur when the system pH was 6.5 because this is where the highest degree of oversaturation occurs regardless of alum dose.

Jar tests were conducted over a range of pH values to identify the optimum conditions for fluoride removal in synthetic waters. The optimum pH for fluoride removal was observed to occur between pH 6 and 7 and this range agreed with the optimal defluourdation range expected due to aluminum solubility (Figure 4.1). At circumneutral pH, the surface charge of the aluminum hydroxide precipitate is positively charged. The negatively charged fluoride ions in solution are attracted to the positive surface charge of the precipitate and therefore adsorb or complex with the surface of the precipitate. At lower pH values, positively charged, soluble fluoro-aluminum complexes form, decrease the amount of fluoride removal, and scavenge available aluminum to form a precipitate. In addition, the solubility of aluminum increases at low pH values, therefore reducing the overall degree of aluminum oversaturation in solution. Under pH conditions greater than pH 7, the concentration of hydroxide ions increases and they begin to compete with fluoride for adsorption on the aluminum precipitate that forms. The surface charge of the aluminum hydroxide precipitate also becomes negatively charged at high pH values, which decreases adsorption of fluoride onto the precipitate.

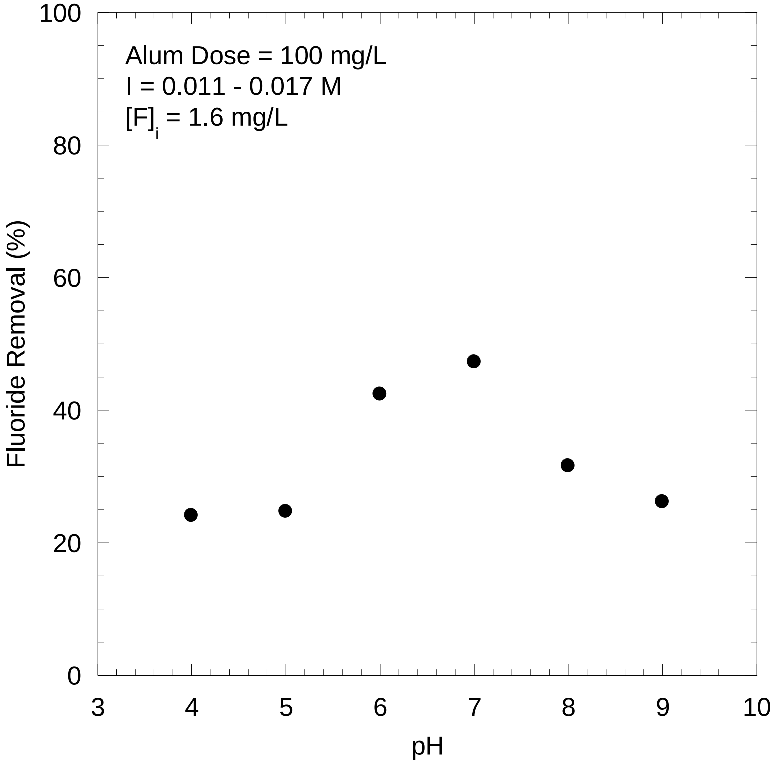

Figure 4.1: Experimental determination of optimum pH for fluoride removal using synthetic waters with no organic matter.

4.1.2 Optimum pH for organic removal

Organic matter exhibited similar removal trends as that of fluoride when the system pH was varied in synthetic waters. Maximum removals for the three LMW organic acids of interest were observed at system pH values slightly below neutral. Salicylic acid was best removed at pH 6. Pyromellitic acid was best removed between pH 5 and 6. Phthalic acid was best removed at approximately pH 5 (Figure 4.2). The differences in optimum pH values for the removal of each organic acid was likely due to differences in the functional groups associated with each organic acid. Functional groups were expected to control the solubility and charge of organic matter in solution. Such groups therefore dictated the charge interactions with and subsequent removal of organic matter by the aluminum hydroxide precipitate formed during alum coagulation.

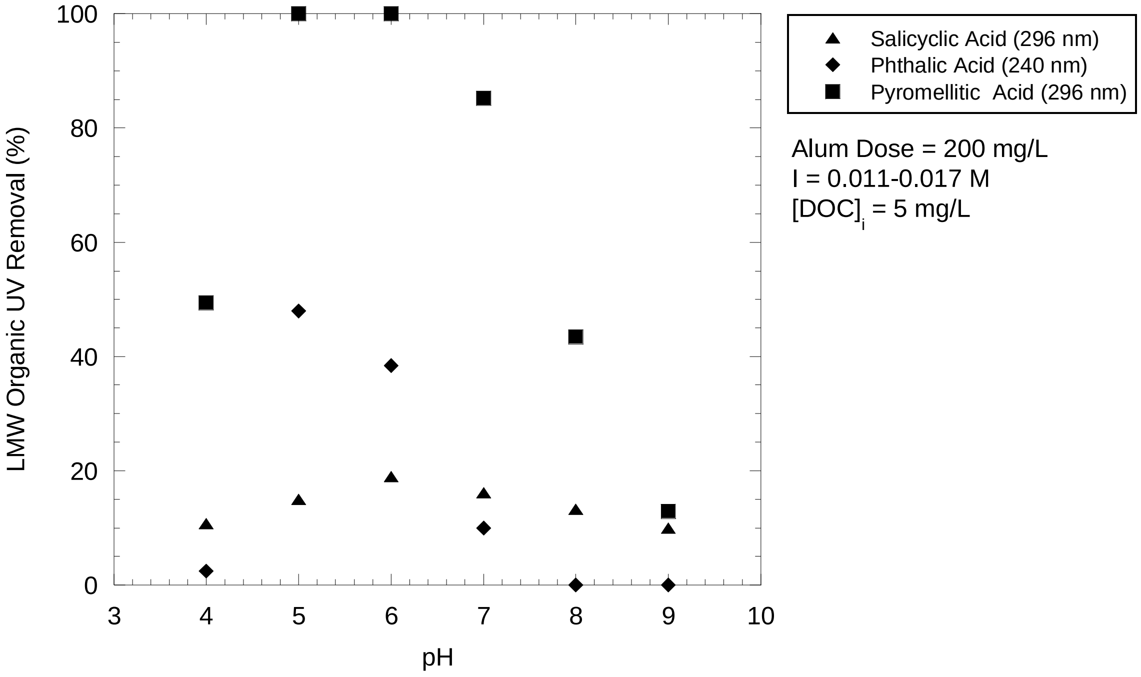

Figure 4.2: Experimental determination of optimum pH for organic removal using synthetic waters.

4.1.3 Fluoride removal by alum coagulation

Defluoridation of synthetic drinking water by alum coagulation was confirmed by single ligand experiments involving a range of alum doses. Preformed experiments isolated the removal of fluoride by adsorption to an amorphous aluminum precipitate because fluoride was introduced to the system after precipitation had already occurred. Co-precipitation experiments showed the combined effects of adsorption and co-precipitation on fluoride removal because fluoride was present during precipitate formation. A maximum fluoride removal of 80-85% was achieved with an alum dose of 500 mg/L in both systems (Figure 4.3). Interpolation of fluoride removals for a co-precipitated and preformed system suggest that approximately 50% fluoride removal can be expected at alum doses of approximately 120 mg/L and 220 mg/L, respectively. Results from preformed experiments demonstrated the importance of the adsorption mechanism for fluoride removal over all alum doses from 20-500 mg/L. At an alum dose of 20 mg/L, little difference (<2%) was observed in fluoride removal between preformed and co-precipitation systems. At that low alum dose, adsorption was the predominant removal mechanism and accounted for almost all fluoride removal. Fluoride removal is enhanced by co-precipitation at higher alum dosages (>20 mg/L) as seen by the higher fluoride removals in the co-precipitated system. Removal of fluoride in a co-precipitated system was nearly double the removal in a preformed system at an alum dose of 100 mg/L. The results from the co-precipitation experiments bode well for defluoridation by alum coagulation in drinking water systems because treatment systems operate under co-precipitation conditions in cases where fluoride is already present in the raw water and aluminum hydroxide precipitate forms during alum coagulation.

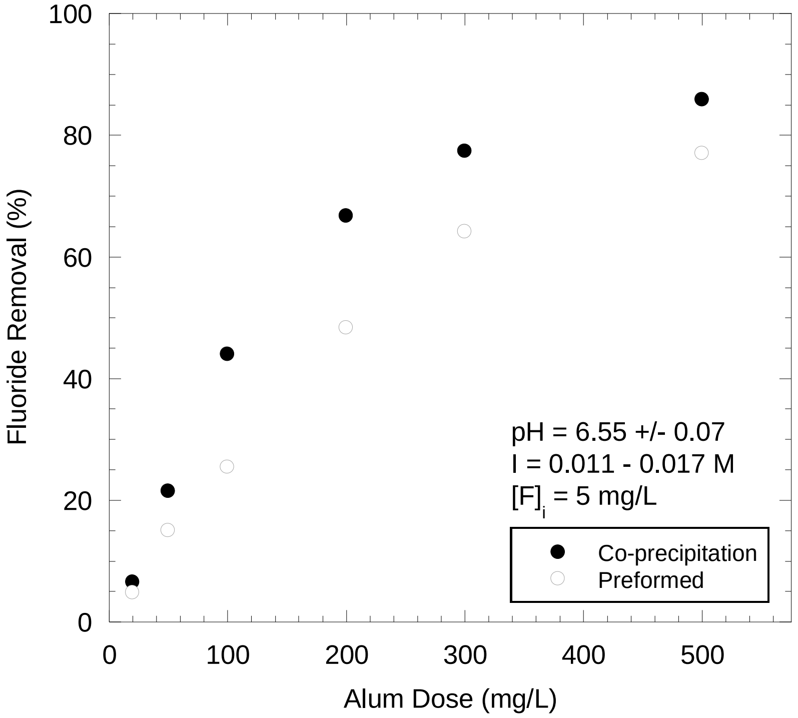

Figure 4.3: Fluoride removal in single ligand systems by co-precipitation and adsorption to aluminum hydroxide in synthetic waters using alum coagulation.

4.1.4 Organic removal by alum coagulation

Alum coagulation is conventionally used to remove particles and natural organic matter. Therefore, removal of low molecular weight organics by alum coagulation was expected in single ligand experiments involving synthetic waters. Significant variation occurred in the relative removals of the three LMW organics of interest as shown in Figure 4.4A. Salicylic and phthalic acid were only removed up to 20-30% after applying an alum dose of 500 mg/L. At 100 mg/L, removals of salicylic and phthalic acid were approximately 7-10%. Pyromellitic acid was most easily removed considering both alum dose and the maximum removal possible. At an alum dose of 100 mg/L, approximately

85% of pyromelltic acid was removed. The number and type of functional groups present on an organic compound influence the removal of that compound by alum coagulation.

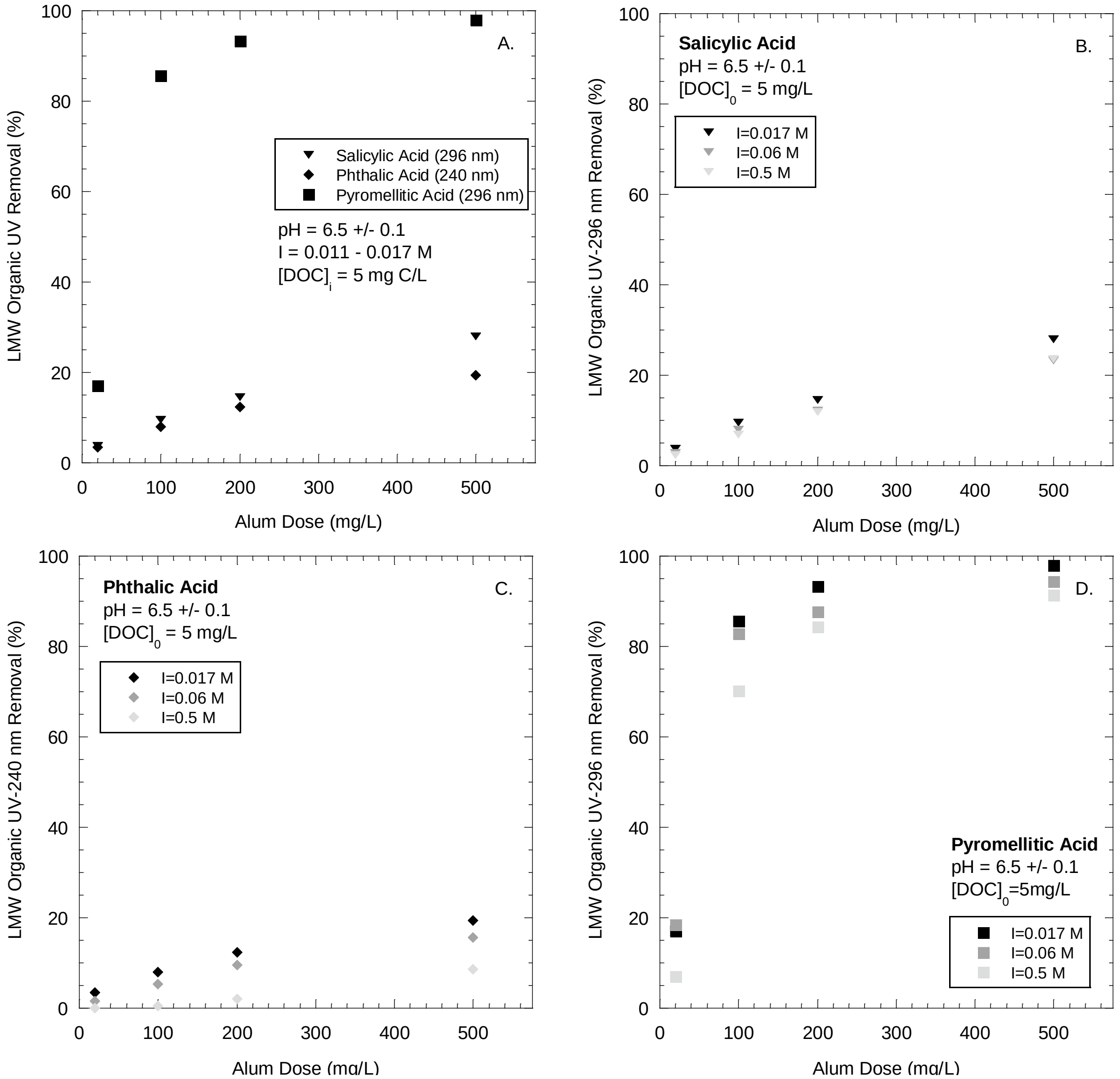

Figure 4.4: Low molecular weight organic removal by co-precipitation in single ligand, synthetic water systems using alum coagulation at low and varying ionic strengths.

The four carboxylic groups on pyromellitic acid promoted its greater removal than salicylic and phthalic acid which only have one and two carboxylic groups, respectively. Other researchers have observed similar trends whereby increased functionality, especially considering the presence of carboxylic groups, improves adsorption of a LMW organic compound onto a metal hydroxide or (oxy)hydroxide mineral surface (Nordin et al., 1998; Evanko and Dzombak, 1998; Boily et al., 2000).

Complexation behavior of each LMW organic acid was expected to influence their interactions with fluoride during alum coagulation. Through ionic strength jar tests in single ligand, synthetic water systems, the complexation behavior of each organic was investigated at pH 6.5. A lack of impact of ionic strength on removal of a sorbing metal ion or anion has often been used as evidence for adsorption via inner sphere complexes. (Stumm and Morgan, 1996). The removal of both phthalic acid and pyromellitic acid decreased as ionic strength increased during alum coagulation, as shown in Figure 4.4 C and D. Such trends suggest that phthalic acid and pyromellitic acid participate in outer sphere complexes with the surface of the aluminum precipitate formed at pH 6.5.In contrast, for salicylic acid shown in Figure 4.4B, there was little effect of ionic strength on removal. Thus, it is likely that salicylic acid sorbs as an inner sphere complex on amorphous aluminum hydroxoide. The complexation behavior of a LMW organic acid or NOM may cause it to interfere with fluoride removal during alum coagulation.

4.2 SYNTHETIC WATERS – DUAL LIGAND EXPERIMENTS

4.2.1 Fluoride removal in dual ligand systems

Dual ligand experiments performed using synthetic waters helped reveal interactions that occurred between fluoride, organic matter, and aluminum during alum coagulation. Fluoride removals observed in dual ligand experiments were not significantly different (<7%) from fluoride removal in a single ligand system for alum doses greater than 20 mg/L, and were both higher and lower than in the single ligand system (Figure 4.5). These results mean that fluoride removal was not systematically affected by the presence of LMW organics at this pH and with these high alum doses. At an alum dose of 20 mg/L, fluoride removal in all dual ligand systems was consistently greater than that observed in a single ligand system containing only fluoride. Such a result was surprising and seems to suggest that the presence of organic matter improves fluoride removal when low alum doses are applied. The presence of organic matter during coagulation may promote the formation of an aluminum precipitate with greater surface area that could facilitate more fluoride removal by adsorption. In addition, organic matter may help facilitate greater precipitation at the low alum dose because as the organic matter is incorporated into an $Al(OH)_3$ floc, it prevents further growth of the $Al(OH)_3$ precipitate and forces further precipitation to occur with new nucleation sites. An increase in aluminum precipitate formation promotes greater removal of fluoride via co-precipitation and adsorption; more bulk precipitate is formed and there is increased surface area for adsorption.

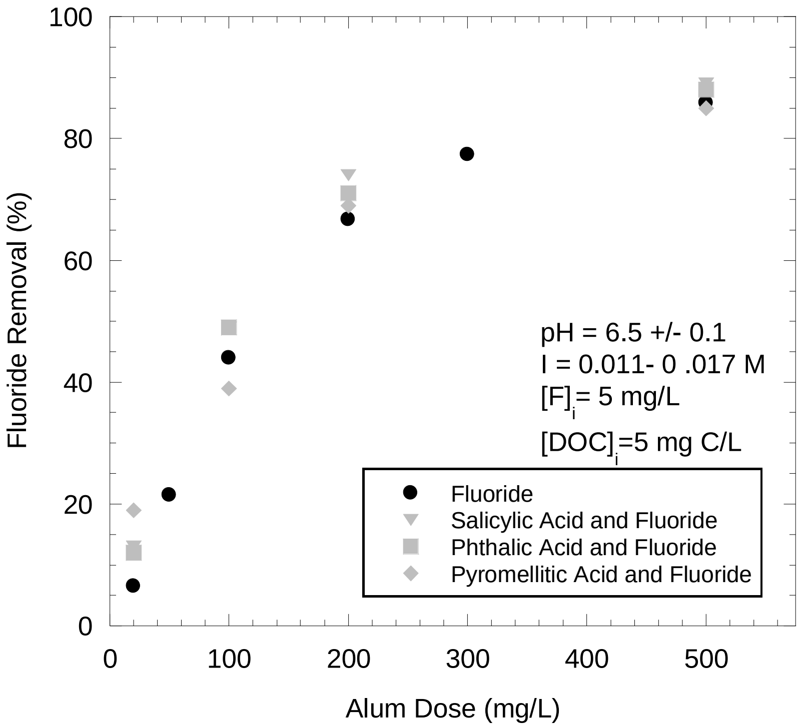

Figure 4.5: Fluoride removal by alum coagulation in dual ligand systems.

Results for aluminum residuals shown in Figure 4.6 confirm that less aluminum residual was observed at the end of dual ligand jar tests than that observed in a single ligand system with only fluoride present when considering an alum dose of 20 mg/L. Therefore, more aluminum was precipitated in the dual ligand systems, which explains the greater removal of fluoride observed in those dual ligand systems at a 20 mg/L alum dose. Aluminum precipitation was greatest in jar tests that contained no ligands; aluminum residual concentrations were below detection in these systems. Differences in aluminum residuals between single and dual ligand systems were minimal for alum doses greater than 20 mg/L which suggests that a similar amount of aluminum precipitate had formed in both systems. Such a result corroborates the conclusion that differences in fluoride removals between single and dual ligand systems at alum doses greater than 20 mg/L were insignificant. Aluminum residuals were highest for a single ligand system with fluoride alone because fluoride disrupts hydroxide bonding during precipitate formation.

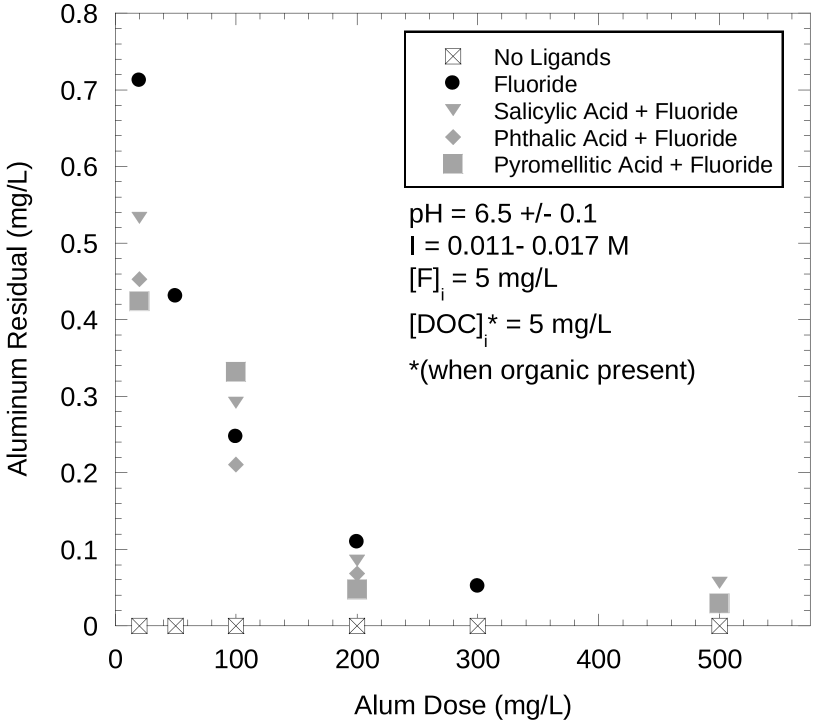

Figure 4.6: Aluminum residuals in dual ligand systems following alum coagulation.

4.2.2 Organic removal in dual ligand systems

The presence of fluoride was expected to negatively impact the removal of LMW organics during alum coagulation in dual ligand systems. Results from dual ligand jar tests shown in Figure 4.7 for each LMW organic of interest confirmed that the removal of each LMW organic was reduced when fluoride was present. Fluoride ions are known to interfere with bridging that occurs between hydroxyl groups in the aluminum precipitate that forms during alum coagulation. Such interference results in less precipitate formed and helps promote fluoride incorporation into the precipitate, thereby altering the structure of the precipitate and its ability to complex with organic matter. As fluoride ions are incorporated into the surface layer of the aluminum precipitate, fewer sites are available for inner sphere complexation of organic matter. At an alum dose of 20 mg/L, the removal of pyromellitic acid with fluoride present was half that of its removal in a single ligand system. Similarly, at the same 20 mg/L alum dose, the removals of salicylic acid and phthalic acid were completely inhibited by the presence of fluoride, representing a 100% decrease in their overall removals compared to those in single ligand systems. Drinking water systems removing fluoride by alum coagulation are likely to exhibit lower organic removal compared to fluoride free systems.

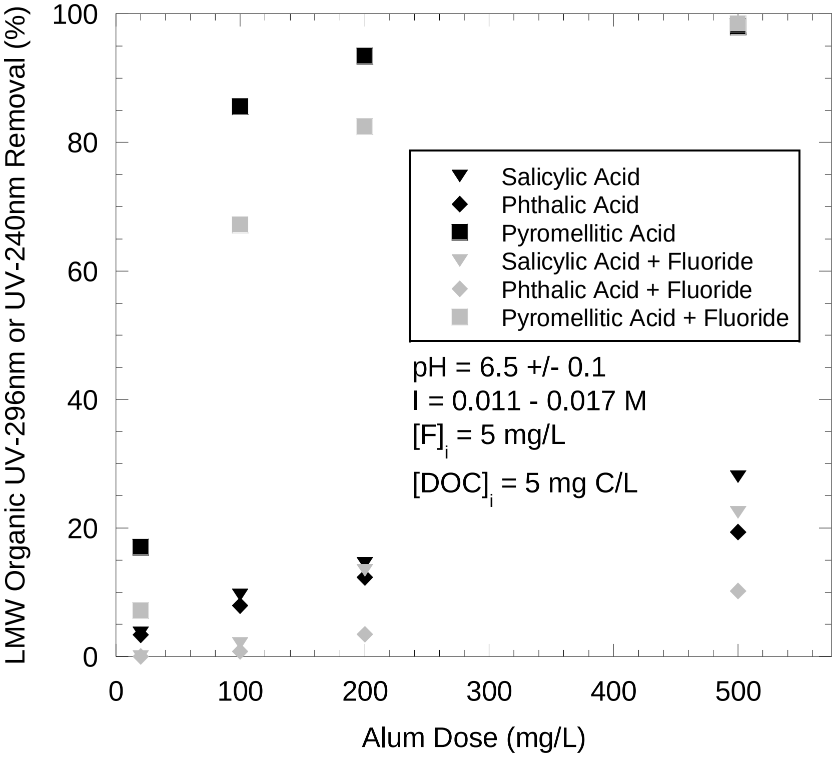

Figure 4.7: Low molecular weight organic removal by alum coagulation in dual ligand systems.

4.3 NATURAL WATERS

4.3.1 Fluoride removal in natural waters

Natural water jar tests served to confirm observations made from synthetic water jar tests and revealed the performance of alum coagulation for defluoridating natural waters. Three natural waters, two from waters systems in Texas and one from Colorado, were used during experimentation. Overall, more results are available for Water 1 –TX and Water 2 – TX than for Water 3 – CO. All natural waters had NOM present and fluoride concentrations greater than 2 mg/L which is the level at which detrimental health effects can occur. The overall composition of the natural waters, shown in Table 3.23.2, was more complex due to NOM, background ions, and particles when compared with synthetic waters. Therefore, less fluoride removal was expected. Results in Figure 4.8 show that the optimum pH for defluoridation of Water 1 – TX and Water 2 – TX occurred between pH 6 and 6.5, slightly below the optimum defluoridation pH observed in synthetic waters.

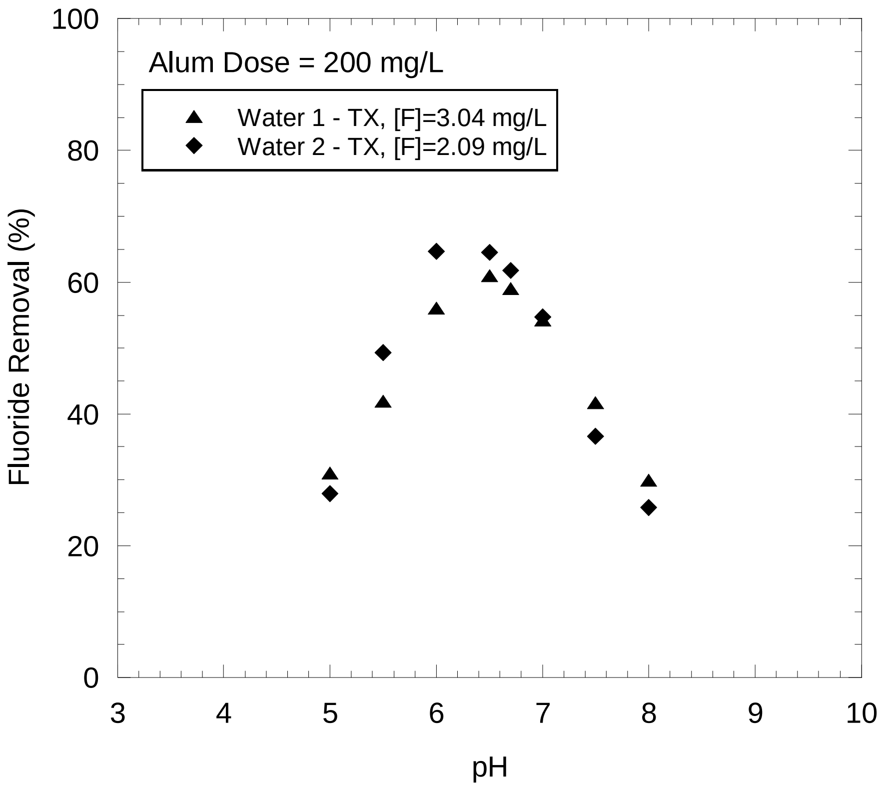

Figure 4.8: Experimental determination of optimum pH for fluoride removal using the Texas natural waters.

Defluoridation by alum coagulation was investigated in natural waters through a series of jar tests conducted at system pH values of 6, 6.5, and 7. For both Texas waters, fluoride removal was best at pH 6.5 and was lower at system pH values of 6 and 7 (Figure 4.9 A and B). Such trends displayed in the Texas waters reflect the importance of pH in controlling defluoridation performance when using alum coagulation. In the Colorado water, no difference between fluoride removals was observed during alum coagulation at pH 6 and 7 (Figure 4.9 C). Fluoride removal in Water 1 – TX was lower than that in a single ligand, synthetic water system at pH 6.5 with an initial fluoride concentration of 5 mg/L (Figure 4.9 A). The NOM concentration (NOM = 9.20 mg C/L) and alkalinity (Alkalinity = 294.6 mg/L as $CaCO_3$) were higher for Water 1 – TX and

NOM and carbonate may have competed for fluoride removal by adsorption onto the aluminum precipitate. Fluoride removal in Water 2 – TX was not significantly different from that seen in a synthetic water system at pH 6.5 where fluoride was the only ligand present (Figure 4.9 B). However, at low alum doses, fluoride removals were greater in Water 2 – TX than in the single ligand, synthetic water system at pH 6.5 containing fluoride. It was hypothesized that the NOM in Water 2 – TX promoted the formation of a finer aluminum precipitate that had greater surface area, allowing for more fluoride adsorption. In addition, increased precipitate formation was hypothesized to account for the greater fluoride removals in Water 2 – TX (Figure 4.9B). Enhanced fluoride removal in comparison to the single ligand synthetic water in Water 3 – CO was observed at low alum doses (≤100 mg/L) which was surprising and is hypothesized to be the result of increased precipitate formation as in Water 2 – TX (Figure 4.9 C).

Because not all fluoride must be removed from a natural water to reach the current or anticipated fluoride MCL, a 50% reduction of fluoride is expected to be sufficient for most natural waters containing high concentrations of fluoride. An alum dose of 150-170 mg/L would achieve 50% fluoride removal in both natural waters based on an alum coagulation process carried out at pH 6.5. Greater than 80% fluoride removal can be attained if necessary by alum coagulation; however, this requires an alum dose of 500 mg/L which is excessive and would generate significant quantities of sludge and increase the sulfate concentration in the finished water. High alum doses would increase chemical and disposal costs for small waters systems, neither of which is desirable.

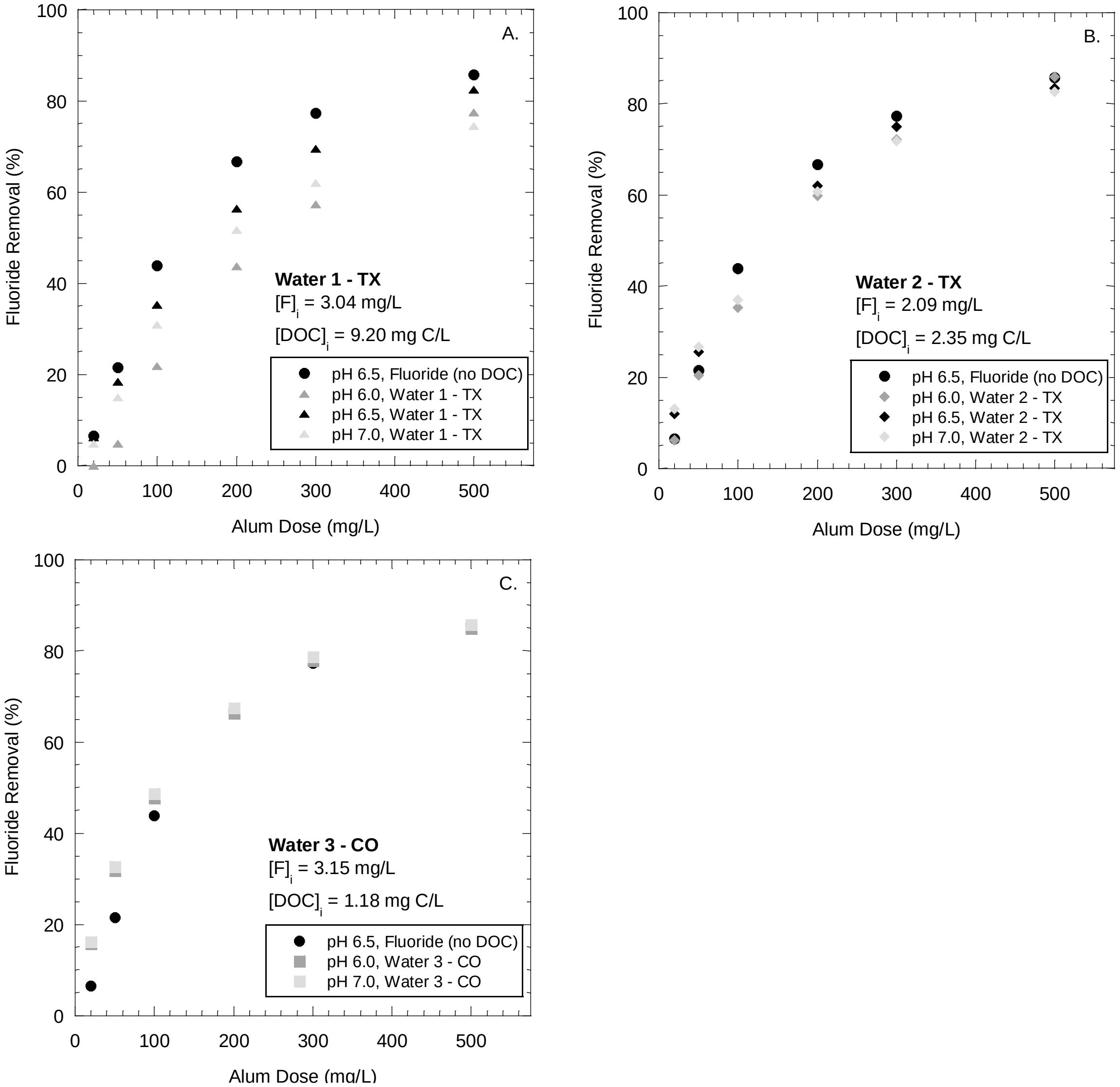

Figure 4.9: Fluoride removal in natural waters at various system pH values using alum coagulation. Fluoride removals in a single ligand, synthetic water system at pH 6.5 with an initial fluoride concentration of 5 mg/L have been included for comparison.

Fluoride removal in Texas natural waters was also investigated using different approaches to alum coagulation. In one case, the pH of the system was adjusted to pH 6.5 and maintained at that pH throughout the jar test, whereas in the other, the system pH was not adjusted and allowed to drop upon addition of the coagulant. It was expected that the high alkalinity of the natural waters would allow for sufficient buffering that a relatively large alum dose could be applied for defluoridation without a concommitant pH drop below the acceptable minimum pH of 6.5 for drinking water. Figure 4.10 shows fluoride removals in the pH 6.5 and pH Natural systems for both Texas natural waters. The results can be interpreted in two ways. First, fluoride removal in a pH Natural system was comparable to that in a pH 6.5 system. Such a conclusion would imply that fluoride removal in these Texas natural waters is best achieved without pH adjustment. Final fluoride removals and system pH values for various alum doses are presented in Table 4.14.1. In a pH Natural system, the final pH did not drop below 6.5 until 300 mg/L and 200 mg/L alum doses were applied to Water 1 – TX and Water 2 – TX, respectively. When the final pH was below 6.5 in pH Natural systems, less fluoride removal was observed compared to pH 6.5 systems; this result was expected considering aluminum solubility and amount of precipitate that could be formed.

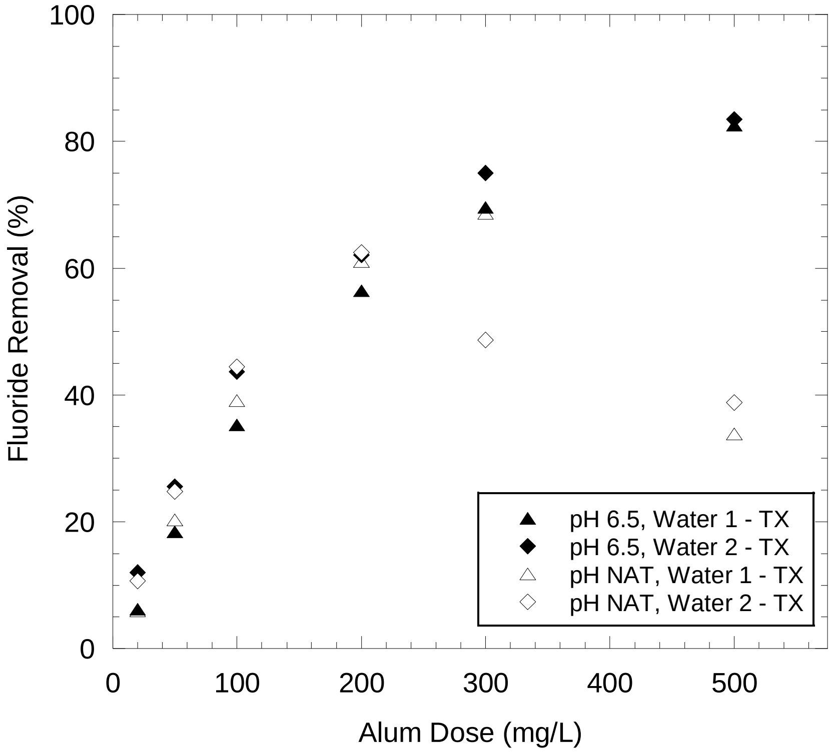

Figure 4.10: Fluoride removal in natural waters using alum coagulation in systems with pH adjustment to 6.5 (pH 6.5 systems) and without pH adjustment (pH Natural systems).

Table 4.1: Fluoride removals and final system pH values from pH 6.5 and pH Natural jar tests using natural waters and alum coagulation.

Alum Dose (mg/L)	Water 1 – TX			Water 2 - TX		
	Final pH in pH NAT system	Fluoride Removal (%)		Final pH in pH NAT system	Fluoride Removal (%)	
		pH NAT	pH 6.5*		pH NAT	pH 6.5*
20	7.94	6%	6%	7.41	11%	12%
50	7.50	20%	18%	7.12	25%	26%
100	7.10	39%	35%	6.77	44%	44%
200	6.60	61%	56%	6.21	63%	62%
300	6.17	69%	70%	5.61	49%	75%
500	5.04	34%	83%	4.60	39%	84%

* Final pH values in the pH 6.5 systems for both natural waters were 6.5 +/- 0.1.

The second interpretation of the comparable fluoride removals between pH 6.5 and pH Natural systems involves an enhanced precipitation effect. The enhanced precipitation effect was observed when considering final pH values of each system and the amount of fluoride removal that is expected. Based on aluminum solubility and prior jar tests in both synthetic and natural waters, greater fluoride removal was expected to be observed in the pH 6.5 system because pH 6.5 was found to be the optimal pH for defluoridation. However, at low alum doses (200 mg/L for Water 1 – TX and 100 mg/L for Water 2 – TX), the final pH values in the pH Natural systems were above pH 6.5. Comparable fluoride removals were seen in the pH Natural systems at low alum doses compared to pH 6.5 systems which were surprising. The amount of aluminum precipitate formed within each system impacted fluoride removal and is discussed subsequently.

4.3.2 Organic removal in natural waters

In the Texas natural waters, the optimum pH for organic removal was not as clearly defined by a single pH range when compared to removal of LMW organics in synthetic waters (Figure 4.11). The maximum organic removal observed for Water 1 – TX occurred at approximately pH 6. The removal of organic matter in Water 2 – TX was quite complex, with approximately 40% removal at pH 5.5 and 6.5 but only approximately 15% at pH 6. Such a rapid drop in removal may potentially represent a significant change in the protonation of the NOM present in Water 2 – TX, a shift in removal mechanism, or an outlying data point. At pH 5.5 and 6.5, a co-precipitation and an adsorption mechanism, respectively, may be removing NOM. However, at pH 6.0 a non-optimal condition may have occurred that did not allow much NOM removal. The difference between the optimum pH for organic removal in synthetic and Texas natural waters was due to differences in the composition of the organic matter present and the respective functional groups of that organic matter. Functional groups are expected to control the solubility and charge of organic matter in solution. Such groups dictate the charge interactions with and subsequent removal of organic matter by the aluminum hydroxide precipitate formed during alum coagulation.

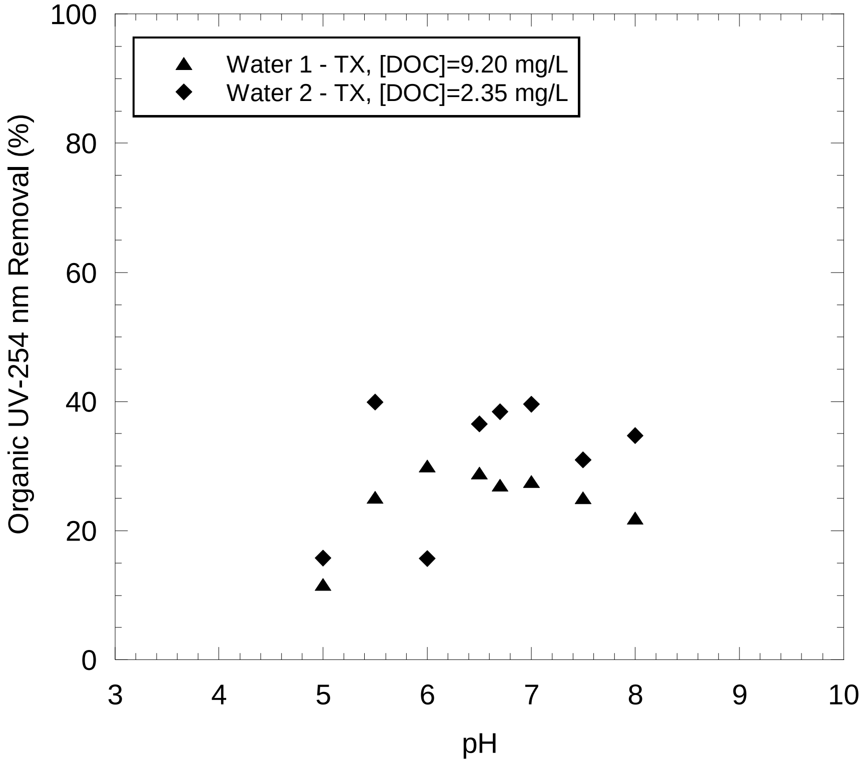

Figure 4.11: Experimental determination of optimum pH for organic removal using natural waters.

As observed in synthetic water systems containing LMW organics, the overall amount of organic removal by alum coagulation in natural waters varied depending on the type of NOM present. Figure 4.12 shows the removal of organic matter from the natural waters which varied significantly depending on the water and system pH. Organic removal in natural water jar tests was measured using both UV-254 and DOC. In general, UV-254 measurements showed organic removals within +/-10% of DOC measurements, suggesting that UV-254 was an appropriate alternative method for measuring organic removal. SUVA calculations did not show significant change as alum dose increased, which provided additional confirmation of UV-254 as a good measure for organic content in natural waters. For Water 2 – TX at pH 6.5, organic removal measured by UV-254 and DOC were significantly different. Such a result likely has to do with the composition, fraction, protonation, and removal potential by alum coagulation of NOM present in Water 2 – TX that can absorb UV light. Based on trends known from the literature, these results suggest that Water 1 – TX was more humic in nature, while Water 2 – TX had more fulvic content.

Trends in organic removals in the natural waters showed that organic removal best occurred at pH 6.5 considering UV-254 measurements. Maximum organic removal measured by UV-254nm for Water 1 –TX and Water 2 – TX appeared to plateau between 35-60% removal at high alum doses (>300 mg/L) depending on the pH of the system. Organic removals in Water 3- CO were rapid and much greater than those observed in Texas waters. At an alum dose of only 20 mg/L, 56% and 78% of NOM was removed from Water 3 – CO in jar tests with system pH values of 6 and 7, respectively. High organic removals observed in Water 3 – CO were attributed to the water having a higher SUVA value, NOM with high aromatic content and an extremely low alkalinity (16.8 mg/L as $CaCO_3$). The stark differences in NOM removal among these three natural waters are an indication of the complexity of the interactions among aluminum, fluoride, and NOM during alum coagulation.

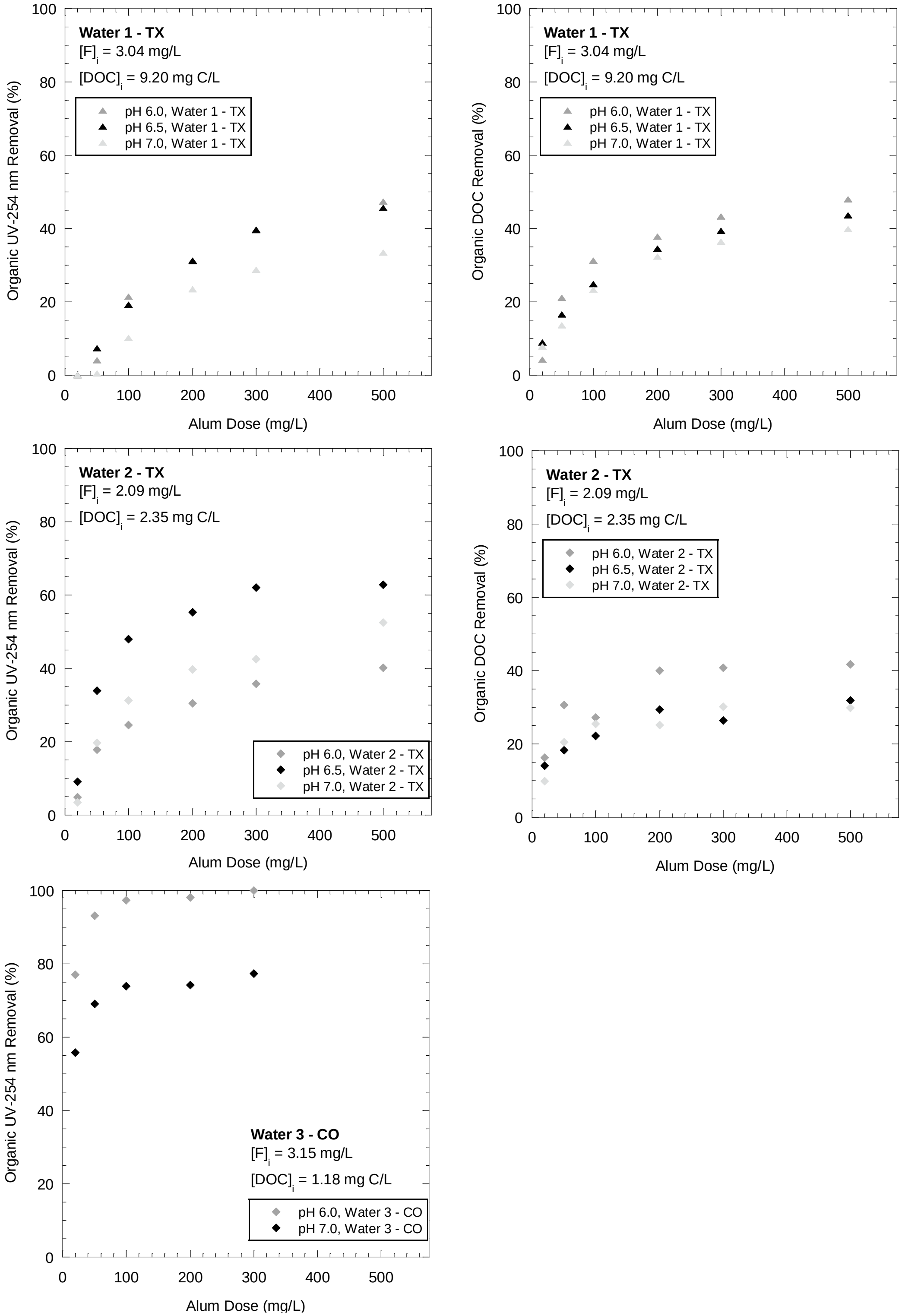

Figure 4.12: Organic removal in natural waters using alum coagulation.

Effects of pH adjustment (pH 6.5 systems) or no adjustment (pH Natural systems) on organic removals in Texas natural waters are shown in Figure 4.13. The organic removal trends for both Texas natural waters were different. In the Water 1 – TX pH Natural system, organic removal was observed to be comparable to or slightly greater than that in a pH 6.5 system, considering alum doses from 20-300 mg/L. At a 500 mg/L alum dose, the final pH of the Water 1 – TX pH natural system drops so far as to inhibit the amount of precipitate formed and organic removal is reduced. On the contrary, organic removals in Water 2 – TX pH Natural system were observed to be below those in the pH 6.5 system for all alum doses applied. Such a result suggests that pH adjustment is necessary for optimal removal of organic matter from Water 2 – TX.

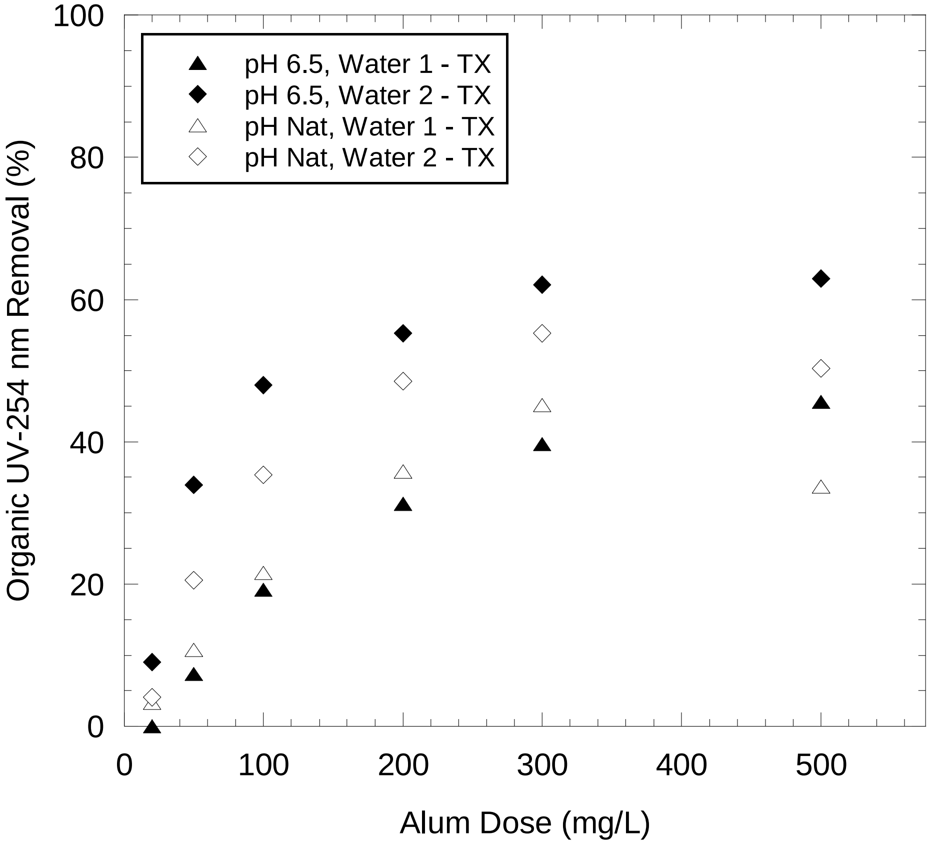

Figure 4.13: Organic removal in Texas natural waters using alum coagulation in systems with pH adjustment to 6.5 (pH 6.5 systems) and without pH adjustment (pH Natural systems).

Concerning the organic removals for Water 1 – TX in pH natural and pH 6.5 systems, two interpretations of the data can be made. The first is that pH adjustment of the water before alum coagulation is unnecessary to achieve the best organic removal provided that the final pH of the water does not drop below a pH value of approximately 6.2. The second possible interpretation is that an enhanced precipitation effect is occurring which is shown more clearly in Table 4.24.2. The enhanced precipitation effect was observed in Water 1 – TX because organic removals were expected to be lower in pH Natural systems when the final system pH was greater than 6.5 due to aluminum solubility and the results from single ligand and natural water jar tests involving organic removal over a range of pH values. However, organic removals were comparable when the final system pH was greater than 6.5 in the Water 1 – TX pH Natural system and such a result was surprising. It is anticipated that aluminum residuals can explain the enhanced precipitation effect and these data are provided subsequently.

Table 4.2: Organic removals and final system pH values from pH 6.5 and pH Natural jar tests using natural waters and alum coagulation.

Alum Dose (mg/L)	Water 1 – TX			Water 2 - TX		
	Final pH in pH NAT system	Organic (UV-254 nm) Removal (%)		Final pH in pH NAT system	Organic (UV-254 nm) Removal (%)	
		pH NAT	pH 6.5*		pH NAT	pH 6.5*
20	7.94	3%	0%	7.41	4%	9%
50	7.50	11%	7%	7.12	21%	34%
100	7.10	22%	19%	6.77	35%	48%
200	6.60	36%	31%	6.21	48%	55%
300	6.17	45%	40%	5.61	55%	62%
500	5.04	34%	46%	4.60	50%	63%

* Final pH values in the pH 6.5 systems for both natural waters were 6.5 +/- 0.1.

4.3.3 Aluminum residuals in natural waters

Aluminum residuals for jar tests using Texas natural waters in pH 6.5 and pH Natural systems are shown in Figure 4.1 and Table 4.34.3. The results show that aluminum residuals in pH Natural systems are lower than those observed in pH 6.5 systems when considering alum doses ≤100 mg/L. Such a result was unexpected at first, but can be explained by aluminum solubility and fluoride interactions with aluminum. Within the pH Natural systems, precipitation begins to occur at a high pH (7.8 and 8.6). At high pH values, there is little interference of aluminum precipitation by fluoride. Fluoro-aluminum complexes are dominant species below approximately pH 6 (Figure 4.15), but not above. Therefore, much more aluminum hydroxide precipitate is able to form when precipitation begins at a high pH. As precipitation occurs, the pH in the pH Natural systems drops. The reduced pH allows for increasing interaction between fluoride and aluminum as fluoride complexation and adsorption increases with decreasing pH in this range. Therefore, greater fluoride removal occurs because much more aluminum hydroxide precipitate and available surface area has formed. and pH conditions in the system have changed to favor fluoride interaction with aluminum. NOM removal may also increase due to the greater surface area that becomes available when the enhanced precipitation effect occurs in pH Natural systems.

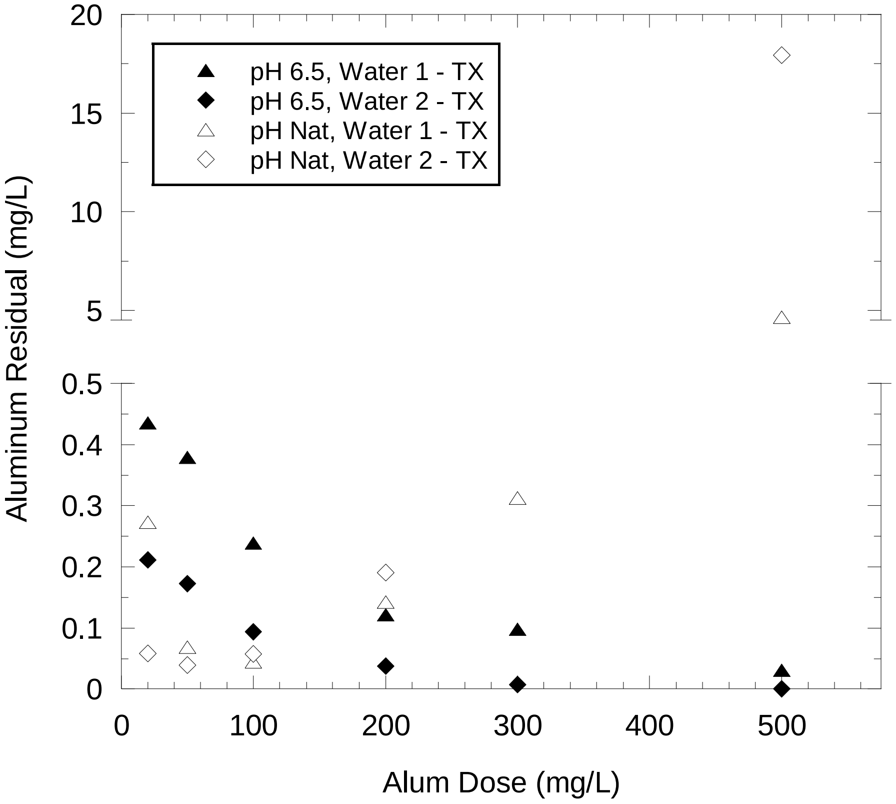

Figure 4.14: Aluminum residuals in Texas natural waters from alum coagulation in systems with pH adjustment to 6.5 (pH 6.5 systems) and without pH adjustment (pH Natural systems).

Table 4.3: Aluminum residuals and final system pH values from pH 6.5 and pH Natural jar tests using Texas natural waters and alum coagulation.

Alum Dose (mg/L)	Water 1 – TX			Water 2 - TX		
	Final pH in pH NAT system	Aluminum Residual (mg/L)		Final pH in pH NAT system	Aluminum Residual (mg/L)	
		pH NAT	pH 6.5*		pH NAT	pH 6.5*
20	7.94	0.27	0.43	7.41	0.06	0.24
50	7.50	0.07	0.38	7.12	0.04	0.23
100	7.10	0.04	0.24	6.77	0.06	0.14
200	6.60	0.14	0.12	6.21	0.19	0.05
300	6.17	0.31	0.10	5.61	0.78	0.01
500	5.04	4.64	0.03	4.60	17.92	0.00

* Final pH values in the pH 6.5 systems for both natural waters were 6.5 +/- 0.1.

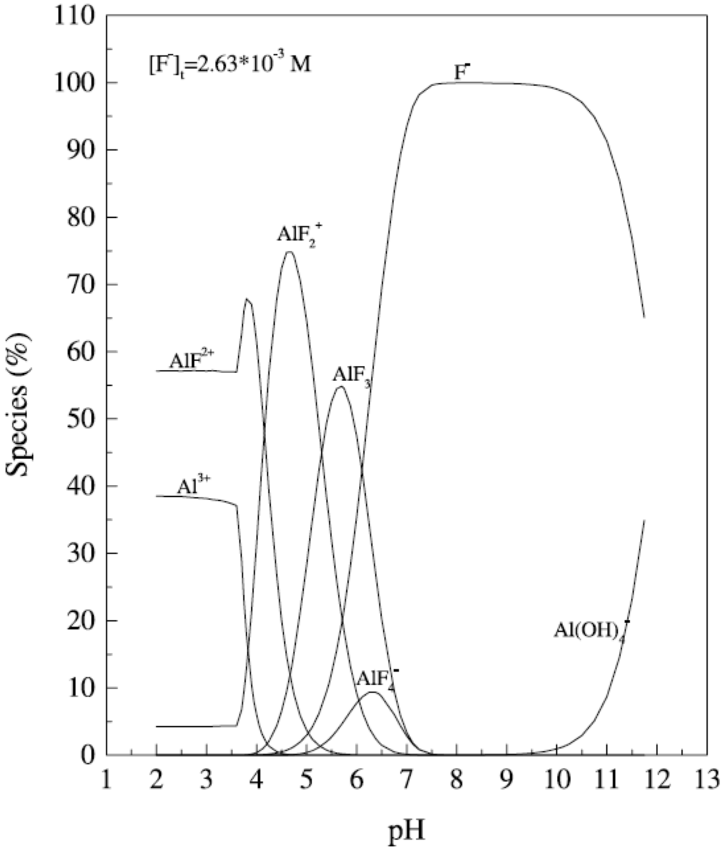

Figure 4.15 Species distribution of fluoride as a function of pH in the presence of 4.0 x 10^{-3} M aluminum (figure taken from Stewart 2009).

In pH 6.5 systems, fluoride interferes with precipitate formation because, at this pH, soluble fluoro-alumino complexes are more likely to form and dominate. Therefore, less precipitate forms and lower fluoride removals are observed. Aluminum residuals were higher in pH Natural systems at high alum doses (≥200 mg/L) when compared to pH 6.5 systems. Such a trend in aluminum residuals at high alum doses was expected and is explained by considering the final pH of the systems, whereby low final pH values (<6.5) observed in the pH Natural systems improved aluminum solubility and increased formation of soluble fluoro-aluminum complexes.

4.4 SUMMARY

Defluoridation by alum coagulation and interactions of fluoride, NOM, and aluminum were investigated through jar tests in both synthetic and natural waters. Experiments with synthetic waters established that fluoride could be removed in single and dual ligand systems that contained organic matter. In addition, the presence of fluoride during alum coagulation reduced organic removal in synthetic water jar tests. Natural waters established that defluoridation was possible in a more complex water matrix containing NOM, and that defluoridation of drinking water sources with high fluoride concentrations was possible. Fluoride removal was relatively unaffected by the presence of LMW organics in synthetic waters. High DOC concentrations may have inhibited fluoride removal in Water 1 – TX. An enhanced precipitation effect was also observed in Texas natural waters which suggested that pH adjustment of waters with high pH and alkalinity may be unnecessary for NOM and fluoride removal by alum coagulation. The enhanced precipitation effect also reveals that interactions of fluoride, NOM, and aluminum during alum coagulation are not yet completely understood.

Chapter 5: Conclusions

Fluoride naturally occurs at elevated concentrations in a small number of ground and surface waters across the United States. Recent health concerns associated with over-exposure to fluoride in drinking water has prompted the USEPA to review its MCL (4 mg/L) and MCLG (4 mg/L) for fluoride. It is possible that the USEPA will consider establishing tighter regulations on fluoride concentrations in drinking waters in the near future, especially because many other countries and the WHO recommend an MCL of 1.5 mg/L for fluoride. The effect of a new MCL for fluoride would place many water systems out of compliance regarding fluoride levels in their drinking water in addition to those water systems already struggling to meet the current fluoride MCL.

Alum coagulation is a potential treatment strategy for defluoridation of drinking waters. Defluoridation by alum coagulation is promising because fluoride can be adsorbed to and co-precipitated with the amorphous aluminum hydroxide solid that is formed. The purpose of this research was to evaluate alum coagulation as a defluoridation treatment strategy for drinking waters and develop an understanding of interactions among NOM, fluoride, and aluminum during the coagulation process. Previous studies are sparse in number and have demonstrated defluoridation of groundwater by alum coagulation, but do not involve blended or surface waters which contain NOM that may interfere or compete with fluoride for removal.

Research experiments for this study involved jar tests to simulate an alum coagulation defluoridation process at the bench-scale level. Both synthetic and natural waters were used throughout the study. Synthetic waters were simplified drinking water matrices made in the laboratory, and natural waters were comprised of two surface waters and a blended water obtained from three small drinking water utilities located in Texas and Colorado. Single and dual ligand experiments elucidated interactions and removal mechanisms of fluoride and NOM surrogates which was the first objective of this study. The second objective of this study was to investigate the removal of fluoride in complex systems and verify results obtained in synthetic water systems. Jar tests with natural waters provided complex water matrices through which the efficacy of alum coagulation as a drinking water defluoridation treatment strategy was confirmed. Treatment guidelines were developed for defluoridation for natural waters used in this study as part of the third objective and are presented in this section of the report.

5.1 CONCLUSIONS

Results from this study confirmed alum coagulation as a treatment option for defluoridation of drinking water. Specific conclusions that can be made concerning the alum coagulation defluoridation process as determined by jar tests are as follows:

1. Fluoride was successfully removed from both synthetic and natural drinking waters. The optimum system pH for removal was approximately pH 6.5 which facilitated 50% fluoride removal with a 150-170 mg/L alum dose. Approximately 80% fluoride removal could be achieved if desired, provided that a very large alum dose (500 mg/L) was applied.
2. Fluoride removal was not significantly impacted by the presence of NOM during alum coagulation in synthetic waters due to its preferential removal and tendency to form strong complexes with soluble and insoluble aluminum. However, in natural waters, increasing concentrations of NOM were expected to compete for adsorption with fluoride onto the aluminum precipitate and resulted in lower fluoride removals.

3. The presence of fluoride during alum coagulation resulted in higher aluminum residuals as observed in synthetic water experiments, because fluoride forms soluble fluoro-aluminum complexes and can interfere with bridging of hydroxide groups in the aluminum hydroxide precipitate that forms.
4. NOM can participate in various surface complexes with the aluminum precipitate that forms during alum coagulation as demonstrated by removal of LMW organic acids in jar tests experiments with varying ionic strength. The functionality of NOM influences the type of surface complex NOM molecules participate in with the aluminum precipitate.
5. NOM removal was negatively impacted by the presence of fluoride during alum coagulation as observed during dual ligand experiments with LMW organic acids acting as NOM surrogates. The PODR from the USEPA's TOC removal requirements for alum coagulation is likely met prematurely when fluoride is present in drinking water. In addition, systems that pre-fluoridate their water before alum coagulation may experience less NOM removal and partial loss of the beneficial fluoride dose applied.
6. Fluoride and organic removals were generally comparable and even enhanced when no pH adjustment was made to the natural water systems used during these jar tests. Therefore, pH adjustment was observed to be unnecessary when using alum coagulation to defluoridate natural waters with high alkalinity, provided that enough buffering capacity is present to maintain a system pH above 6.5.
7. Treatment guidelines for defluoridation of natural waters, Water 1 – TX Water 2 – TX, and Water 3 – CO, are presented in Table 5.15.1.

Table 5.1: Treatment guidelines for defluoridation of natural waters by alum coagulation.

Fluoride Concentration (mg/L)		Water 1 – TX	Water 2 - TX	Water 3 - CO
Initial		3.04	2.09	3.15
Fluoride Concentration (mg/L)		**Alum Dose (mg/L)**		
Target	4.0	-	-	-
	2.0	80	10	70
	1.5	140	60	130
	1.0	280	150	220
	0.5	500	300	500

Note: pH adjustment to 6.5 is not required except for cases where >200 mg/L alum dose is recommended. Water 3 - CO requires pH adjustment to pH 6 or 7 regardless of alum dose based on results obtained so far.

5.2 FUTURE WORK

The interactions of fluoride, NOM, and aluminum during alum coagulation are still not completely understood. Additional studies on the competition among fluoride, NOM, and co-ions for removal during alum coagulation would provide beneficial information regarding what species and NOM concentrations are most important to consider when evaluating alum coagulation as a defluoridation option for drinking waters. Future jar tests involving natural waters are necessary to confirm the fluoride and organic removal trends observed in the three natural waters studied. Future experiments with natural waters could also help confirm the enhanced precipitation effect that was observed during natural water experiments. Because current studies have been conducted in batch systems through jar tests, a continuous flow pilot study using alum coagulation to defluoridate drinking water at a drinking water treatment facility is recommended to confirm results observed in jar tests and demonstrate the potential of alum coagulation as a defluoridation strategy.

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