

2-1-2012

Selective fluoride removal by aluminum precipitation & membrane filtration

Emily Kowalchuk

Follow this and additional works at: https://digitalrepository.unm.edu/ce_etds

Recommended Citation

Kowalchuk, Emily. "Selective fluoride removal by aluminum precipitation & membrane filtration." (2012).
https://digitalrepository.unm.edu/ce_etds/58

This Thesis is brought to you for free and open access by the Engineering ETDs at UNM Digital Repository. It has been accepted for inclusion in Civil Engineering ETDs by an authorized administrator of UNM Digital Repository. For more information, please contact disc@unm.edu.

Emily Kowalchuk

Candidate

Civil Engineering

Department

This thesis is approved, and it is acceptable in quality and form for publication:

Approved by the Thesis Committee:

Dr. Bruce M. Thomson, Chairperson

Dr. Kerry J. Howe

Joseph D. Chwirka

**SELECTIVE FLUORIDE REMOVAL BY ALUMINUM
PRECIPITATION & MEMBRANE FILTRATION**

by

EMILY EDWINA KOWALCHUK

BACHELOR OF SCIENCE IN CIVIL ENGINEERING

THESIS

Submitted in Partial Fulfillment of the
Requirements for the Degree of

Master of Science in Civil Engineering

The University of New Mexico
Albuquerque, New Mexico

July, 2011

ACKNOWLEDGEMENTS

I want to acknowledge the assistance, guidance, support, and help I received from my advisor Dr. Bruce M. Thomson, my committee members Dr. Kerry J. Howe and Joseph Chwirka, the New Mexico Environment Department, the Albuquerque Bernalillo County Water Utility Authority, the village of San Ysidro, and my husband Scott Kowalchuk.

Thank you to the countless people that made this work possible.

Abstract

Fluoride is an anionic constituent of most natural surface and ground waters. At low concentrations it has the beneficial effect of improving dental health, but at high concentrations it causes skeletal and other problems. The drinking water standard for fluoride is 4.0 mg/L, but even at this level approximately 10% of exposed children will develop dental enamel fluorosis. Several small communities in New Mexico have source waters with fluoride concentrations higher than 4.0 mg/L. No commercial technologies selectively remove fluoride from drinking water in part because it is relatively non-reactive in aqueous solution and also because its chemistry is similar to chloride which is almost always present at much higher concentrations.

The purpose of this project was to evaluate a new technology to selectively remove fluoride from drinking water. This technology is based on precipitation by aluminum hydroxide $\text{Al}(\text{OH})_3$ with subsequent removal of the floc by membrane ultrafiltration. A review of the published literature shows that using aluminum to defluoridate water may rely on aluminum dose, pH, flocculation time and sedimentation time.

Aluminum coagulation and membrane filtration technology (Al-CMF) was shown to selectively remove fluoride from drinking water to concentrations below the drinking water standard. Laboratory experiments were done to characterize fluoride removal regarding pH, aluminum dosage and kinetics; this characterization was used to develop a pilot scale system. Laboratory testing was done using fluoride-spiked tap water in jar tests at pH levels of 5.5, 6.5, 7.5, 8.5, and 9.5 with aluminum doses of 0 to 50 mg/L (0 mmol/L to 1.85 mmol/L). Fluoride removal by the Al-CMF process was found to be independent of pH over the range of 5.5 to 9.5. Mixing intensity was found to be important with the best removal achieved using a blender with a mixing velocity gradient (G) in excess of $9,000 \text{ s}^{-1}$. Laboratory testing found that 1 mmol/L of fluoride was removed for every 4.45 mmol/L aluminum added.

A 0.3 gal/min pilot plant was constructed using the Al-CMF process. The pilot system used a Koch ABCOR[®]-ULTRA-COR[®] ultrafiltration membrane. It was used to treat tap water in the Village of San Ysidro, NM which has a natural fluoride concentration of 5.7 mg/L and arsenic concentration of 85 ug/L. The pilot testing demonstrated fluoride removal to a concentration of 3.5 mg/L at an aluminum dose of 30 mg/L. This produced

a ratio of 1 mmol/L fluoride removed for every 9.53 mmol/L aluminum added. The pilot treatment system was also removed 80% of the arsenic, though the treated water did not meet the arsenic standard of 10 ug/L.

Table of Contents

Title Page	ii
Acknowledgements.....	iii
Abstract.....	iv
Table of Contents.....	vi
List of Figures.....	viii
List of Tables	x
Chapter 1 Introduction	1
Research Objective and Hypothesis	3
Chapter 2 Literature Review.....	4
Aqueous Fluoride and Aluminum Chemistry	4
Methods to Remove Fluoride from Water	8
Precipitation.....	8
Adsorption/Ion Exchange.....	10
Membrane Processes	12
Electrochemical Method.....	14
Summary	14
Chapter 3 Analytical Methods & Materials	19
Overview	19
Analytical Methods	19
Measurement of Metal Concentrations	20
pH.....	20
Materials.....	21
Tap Water.....	21
Fluoride for Bench Scale Testing.....	21
Aluminum Solutions.....	21
pH Control during Bench Scale Testing.....	21
Alum for Pilot Testing.....	22
Mixing Gradient G-Values.....	22
Pilot Scale System pH, kinetics, dosage, and filtration.....	24
Filtration.....	25

Power Requirements.....	25
Pilot Scale System Revisions	25
Pilot Scale System Components.....	27
Field Testing of the Pilot Treatment Unit	29
Arsenic Removal Demonstration Plant	29
Village of San Ysidro	30
Chapter 4 Bench Scale Tests.....	33
Fluoride Removal as a Function of pH	33
Jar Testing	33
Competing Ions	34
Kinetic Studies	34
Adsorption Testing.....	37
Laboratory Test Results.....	38
Jar Testing	38
Kinetic Testing	41
Absorption Testing.....	43
Aluminum Residual Testing.....	43
Ferric Chloride Testing	45
Pilot Scale System Results	46
Pilot Scale System Behavior Over Time.....	47
Chapter 5 Summary and Conclusions.....	53
References.....	55

List of Figures

Figure 1. pH vs. log Concentration of F and Al.....	6
Figure 2. Ion chromatograph showing location of peaks corresponding to F ⁻ , Cl ⁻ , NO ₃ ⁻ , and SO ₄ ²⁻	20
Figure 3. Mixing gradient G values for Phipps & Bird jar testers.	23
Figure 4. Diagram of Koch Abcor®-Ultracor® 5-HFM-251-UVP ultrafiltration module.	26
Figure 5. Flow diagram of the Al-CMF fluoride removal pilot treatment system.	28
Figure 6. Photograph of Al-CMF pilot treatment unit installed in the San Ysidro water treatment facility.	32
Figure 7. Summary of jar tests showing final fluoride concentration and aluminum dose as a function of pH.	38
Figure 8. Kinetic Tests performed in 60 mL syringe, Fluoride Removal by Aluminum Sulfate, Final Fluoride Concentration (mg/L) versus Time (sec) at five pH levels with an Al dose of 30 mg/L	41
Figure 9. Results of F removal by violent mixing in blender Tests at an Al dose of 30 mg/L.....	42
Figure 10. Aluminum Residual from Jar Tests, Fluoride Removal by Aluminum Sulfate, Aluminum Dose (mg/L) vs. Final Aluminum Concentration (mg/L) at five pH levels.	44
Figure 11. Selected Aluminum Residual results from Jar Tests, Aluminum Dose (mg/L) vs. Final Aluminum Concentration (mg/L) at five pH levels.	45
Figure 12. Results of jar test experiments to measure F removal by Fe(OH) ₃ precipitation	46
Figure 13. Selected Permeate Stream Results from Pilot Unit Operation June 2 through June 6, 2011 at San Ysidro (New Mexico) Water Treatment Facility, specifically the grab samples that occurred the latest in the duration of that specific concentration dosage.	47
Figure 14. PLC Pre- and Post-Filter pressure (psi) and Recycle Stream Temperature plotted over time on June 15, 2011 at the Pilot Scale System at San Ysidro (New Mexico) Water Treatment Facility	48
Figure 15. Recovery from Pilot Scale System Operation June 15, 2011 at San Ysidro (New Mexico) Water Treatment Facility.....	50

Figure 16. F reduction over time in the Pilot Scale System on June 15, 2011 at San Ysidro (New Mexico) Water Treatment Facility51

Figure 17. Reduction of TCSF over time in the Pilot Scale System on June 15, 2011 at San Ysidro (New Mexico) Water Treatment Facility52

List of Tables

Table 1. Aluminum Reactions (McEwen, 1997)	5
Table 2. Aluminum Reaction Equilibrium Constants (Bodor, 2000).....	5
Table 3. Defluoridation Techniques	15
Table 4. Summary of parameters to be measured and analytical methods.	19
Table 5. Mixing velocity G values determined for blender tests.	24
Table 6. Chemistry of waters used in pilot testing of the Al-CMF fluoride treatment process.	29
Table 7. Linear Regression of F Removal	39
Table 8. Comparison of laboratory and pilot treatment system fluoride removal at an Al dose of 30 mg/L	54

Chapter 1 Introduction

Fluoride (F) is a naturally occurring anionic constituent of most natural surface and ground waters. It is one of the most prominent components in the class of drinking water constituents that are beneficial to human health at moderate concentrations but hazardous to human health at high concentrations. At low concentrations it has the beneficial effect of strengthening teeth and reducing dental caries, but at high concentrations it is related to a host of skeletal and other problems. This is because in humans F may replace some of the phosphate in bones and teeth forming the mineral fluorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$).

In many water systems in the United States (U.S.) F is added to drinking water to improve dental health. Conversely, there are communities throughout the world with drinking water sources that have higher than safe levels of F. Driscoll et al. (1983) estimates that more than 700 communities in the United States have water supplies with 2.4 mg/L F concentration or higher. At least 31 separate wells, springs, and infiltration galleries in New Mexico have fluoride concentrations of 4.0 mg/L or higher. Some of these provide source water for public water supplies. For example the villages of San Ysidro and Columbus have recorded fluoride levels of approximately 7.0 mg/L.

In January 2011 the United States Department of Health and Human Services proposed a change in the recommended level of F in drinking water to 0.7 ppm. This is the first recommended change for F in 50 years (Rose, 2011); previously the Public Health Service recommended between 0.7 and 1.2 ppm (Public Health Service, 1962). The World Health Organization recommends a F concentration of 1.5 ppm in drinking water (Fawell et al., 2006). These recommended values are based on the desired health benefits of F. The United States Environmental Protection Agency has set a maximum contaminant level of 4.0 ppm (United States, 2009) and a secondary standard of 2.0 ppm to mitigate the negative effects of F.

The negative effects of F include dental enamel fluorosis, a brown staining or pitting of the teeth (USEPA, 2009), and crippling skeletal fluorosis, a significant cause of morbidity that includes limitation of joint movement and crippling deformities of the

spine (Fawell et al., 2006). Dental fluorosis occurs in 10% of children exposed to 4.0 ppm fluoride in their drinking water (United States, 2006), where skeletal fluorosis usually does not occur unless the concentration is greater than 10 mg/L (United States Border Environment Cooperation Commission, 2009).

The chemistry of fluoride [F⁻] and chloride [Cl⁻] is similar; they are both non-reactive in water, present in natural waters at standard temperature and pressures, and do not bond to most other constituents. These negatively charged ions have the same number of valence electrons (7), similar ionic size (1.36 Å for F⁻ and 1.81 Å for Cl⁻), and the same charge (-1). Because the chemistry of F is similar to chloride it is hard to selectively remove F from water.

Conventional water treatment does not remove F. The few available technologies for defluoridation are costly, complicated, and energy intensive. There is a need for cost effective, simple defluoridation processes appropriate for small communities. The most well-known F treatment technologies in the United States are reverse osmosis and activated alumina. Reverse osmosis removes F; however it also removes all other ions thus producing water that is completely demineralized. It also wastes a large fraction of the feed water in the form of brine concentrate that is difficult to dispose of. It is also a costly and complicated process. F adsorption by activated alumina has been studied for over 30 years, and though it is recognized as a best available technology, its utilization for treatment of public water supplies is very limited. No reports could be found that identify public water supply systems that use this technology. Two communities in New Mexico with F levels higher than the EPA MCL include San Ysidro and Columbus. Currently San Ysidro, NM employs point-of-use reverse osmosis technology to remove F and meet EPA MCL levels of other constituents such as arsenic while Columbus, NM uses RO.

The selective removal of F using a coagulant and membrane filtration is similar to the successful ferric hydroxide-coagulation microfiltration (Fe-CMF) process used to remove arsenic (As) (Chwirka, 2004 and Chwirka, 2000). The Fe-CMF process uses an iron

coagulant followed by membrane filtration to remove arsenic from drinking water. Ferric hydroxide ($\text{Fe}(\text{OH})_3$) has a strong affinity for dissolved arsenic (Johnston, 2001), so the Fe-CMF process relies on the “coprecipitation or sorption of As(V) onto freshly precipitated $\text{Fe}(\text{OH})_3$ solids” (Chwirka, 2000). Similarly, aluminum has an affinity for F, so a similar process relying on adsorption of F to an aluminum floc, with removal by filtration, is proposed as a method for achieving selective removal of F from drinking water. This technology relies on the formation of an aluminum hydroxide $\text{Al}(\text{OH})_3$ floc which is subsequently removed by membrane filtration. This process is referred to as Al-CMF.

Research Objective and Hypothesis

This research project was designed to test the hypothesis that the Al-CMF process can selectively remove F from drinking water.

The hypothesis was tested by laboratory testing including jar tests and blender tests. It was then demonstrated at a water utility in NM that has high F concentration to determine its suitability for application to small NM communities.

Chapter 2 Literature Review

Aqueous Fluoride and Aluminum Chemistry

Fluoride exists naturally in surface and groundwater. Most of the F found in groundwater is from the breakdown of rocks such as Fluorite (CaF_2), and soils or weathering and deposition of atmospheric volcanic particles. Other common minerals that contain F are cryolite Na_3AlF_6 (sodium hexafluoroaluminate), fluorspar, which is a halide mineral composed of calcium fluoride CaF_2 and apatite, which is a group of calcium-phosphate minerals (South Africa 2003). The concentration of F found in water depends on concentration of fluoride in the rock or mineral adjacent to the water, other chemical species in the water, and how long the water is adjacent to the rock or mineral. The main processes involved in the shift of the fluoride from the rock to the water are decomposition, dissociation and dissolution (Saxena, 2003). Contrary to Saxena, Corbillon states that the main source of fluoride in water is from industrial activities, not natural sources (Corbillon, 2008). F found in the source water of communities in New Mexico with F levels higher than the EPA MCL are typically naturally occurring. Fluorine is the 13th most abundant element and is released into the environment naturally in both water and air. Fluorine is the most electronegative element in the periodic table and in the environment only occurs in its reduced form as fluoride (F^-). “The range of fluorine-containing compounds is considerable as fluorine is capable of forming compounds with all the elements except helium and neon.” (Miller, 2009)

Fluoride will form complexes and precipitates with aluminum ions which will affect its behavior in solution. Aqueous aluminum solubility varies with pH, as shown by the aluminum hydroxide equilibria reactions in the table below. As shown in table 1, when aluminum reacts with water a hydroxide is formed. The predominant species of aluminum hydroxide present depends on pH. Al^{3+} , $\text{Al}(\text{OH})_2^+$ and AlOH^{2+} are the predominant species at a pH lower than 6. $\text{Al}(\text{OH})_4^-$ is the predominant species at a pH higher than 8 as shown on the dashed line on figure 1.

Table 1. Aluminum Reactions (McEwen, 1997)

	Reaction	log K (25°C)
I.	$\text{Al}^{3+} + \text{H}_2\text{O} = \text{AlOH}^{2+} + \text{H}^+$	-4.97
II.	$\text{AlOH}^{2+} + \text{H}_2\text{O} = \text{Al(OH)}_2 + \text{H}^+$	-4.3
III.	$\text{Al(OH)}_2 + \text{H}_2\text{O} = \text{Al(OH)}_3 + \text{H}^+$	-5.7
IV.	$\text{Al(OH)}_3 + \text{H}_2\text{O} = \text{Al(OH)}_4 + \text{H}^+$	-8.0
V.	$2\text{Al}^{3+} + 2\text{H}_2\text{O} = \text{Al}_2(\text{OH})_2 + 2\text{H}^+$	-7.7
VI.	$3\text{Al}^{3+} + 4\text{H}_2\text{O} = \text{Al}_3(\text{OH})_4 + 4\text{H}^+$	-13.94
VII.	$13\text{Al}^{3+} + 28\text{H}_2\text{O} = \text{Al}_{13}\text{O}_4(\text{OH})_{24} + 32\text{H}^+$	-98.73
VIII.	$\text{Al(OH)}_3(\text{am}) = \text{Al}^{3+} + 3\text{OH}^-$	-31.5

Al(OH)_3 exhibits minimum solubility near a pH of 7 and increases in solubility as Al^{3+} , Al(OH)^{2+} , and Al(OH)_2^+ ions at $4 < \text{pH} < 5$; and as aluminate ion Al(OH)_4^- at $\text{pH} > 9$ (Gensemer and Playle, 1999). The solubility of Al(OH)_3 also changes with the addition of F as shown in figure 1.

Aluminum reacts with fluoride to form various Al-F complexes (Shuping, 1997 and Corbillon, 2007). The theoretical and experiment-based equilibrium constants of different fluoro-aluminum complexes are shown below.

Table 2. Aluminum Reaction Equilibrium Constants (Bodor, 2000)

Reaction	Equilibrium Constant
$\text{Al}^{3+} + \text{F}^- \rightarrow \text{AlF}^{2+}$	7.02
$\text{Al}^{3+} + 2\text{F}^- \rightarrow \text{AlF}_2^+$	12.76
$\text{Al}^{3+} + 3\text{F}^- \rightarrow \text{AlF}_3$	17.03 (could not be identified)
$\text{Al}^{3+} + 4\text{F}^- \rightarrow \text{AlF}_4^-$	19.73
$\text{Al}^{3+} + 5\text{F}^- \rightarrow \text{AlF}_5^{2-}$	20.92 (forms rapidly-octahedral)
$\text{Al}^{3+} + 6\text{F}^- \rightarrow \text{AlF}_6^{2-}$	21.69 (existence unproven)

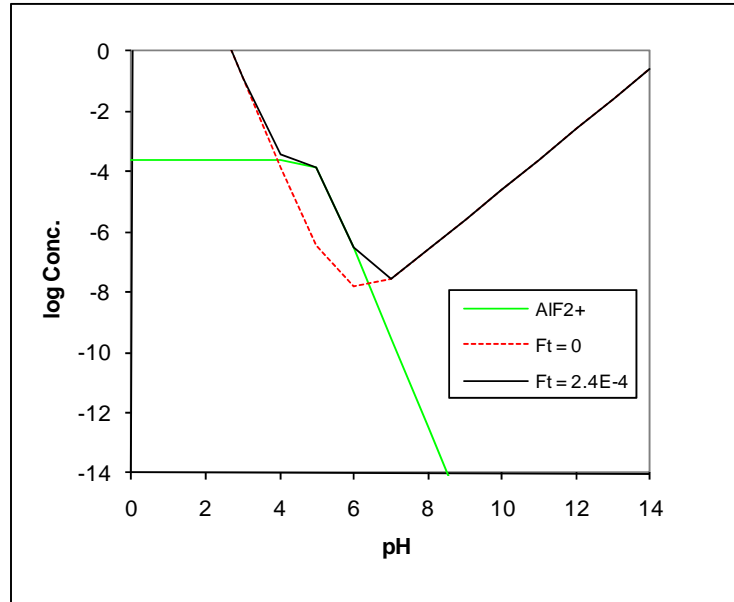
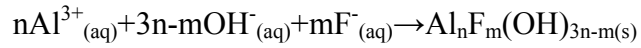


Figure 1. Solubility of $\text{Al}(\text{OH})_3$ as a function of pH in the absence and presence of F^- . F^- concentration corresponds to 4 mg/L (Thomson, 2010).

Several mechanisms might play a role in the removal of fluoride: (1) surface adsorption, (2) coprecipitation (occlusion and adsorption), and (3) precipitation. Among these mechanisms, coprecipitation appears to be the main mechanism. (Randtke et al., 1985 and Lawler, 2004) Because of the relationship between pH and solubility, aluminum's optimal solubility is shifted to a slightly higher pH when fluoride is added, but even more evident is the dramatic increases in the solubility of $\text{Al}(\text{OH})_3$ below pH 7 as shown in figure 1.

An inclusion occurs when the impurity occupies a lattice site in the crystal structure of the carrier, resulting in a crystallographic defect; this can happen when the ionic radius and charge of the impurity are similar to those of the carrier. An adsorbate is an impurity that is weakly bound (adsorbed) to the surface of the precipitate. An adsorbed impurity physically trapped inside a growing crystal is an occlusion.

The overall reaction for F and aluminum is described thusly as (Hu et al., 2005):



Coprecipitation is defined as the contamination of a precipitate by an impurity that is otherwise soluble under the conditions of precipitation (Randtke 1988). Coprecipitation can occur in four different ways: occlusion, surface adsorption, isomorphous inclusion, and nonisomorphous inclusion. Occlusion and surface adsorption, which occur at lattice sites as the crystals are growing, play the major roles in coprecipitation. Coprecipitation by occlusion is especially effective in the early stage of rapid mixing, with precipitates are amorphous.

Much research has been conducted on the factors which control floc size and the rate of floc growth in the coagulation-flocculation process. Related topics include floc breakage and regrowth, shear force/paddle shape and aluminum speciation. No articles surveyed looked at the size of floc and removal of constituents (turbidity, humic acid, phosphates, or fluoride) with rapid mixing over time, thereby tying floc size to constituent removal (Wang, 2009, Spicer, 1996, Hu, 2006, Zouboulis, 2009, Zouboulis, 2010, Shen, 1999, Chu, 2008 and McCurdy, 2004), although one article (Banu, 2008) does tie longer slow mixing to additional removal of TSS and COD. This article shows no additional removal of three phosphorus constituents after 15 minutes, but additional removal of TSS and COD are shown through 30 minutes. Although many journal articles characterize floc size, rarely do they actually measure the floc. In these cases longer or larger floc is indicated by a higher fluorescence intensity. One article (Spicer, 1996) does measure floc length at 100X and 400X magnification at 15, 30, 60 and 90 minutes.

One article ties removal of fluoride to rapid mixing over time, but does not link this to floc growth rate (Hua, 2007). In this article the reaction rate for formation of hydro-fluoro-aluminum precipitate is instantaneous. First order and variable order kinetic models confirm that 99.90% of fluoride is removed before the first sample could be collected (at one minute) and a small additional amount of fluoride is removed by 9 minutes (99.99%) (Hua, 2007). This research suggests that a flocculation step, a pre-flocculation step, and retention time may not be necessary for formation of a filtration

removable precipitate of F. It is difficult to tie this article to previously discussed articles characterizing floc size over time because the previous articles either did not measure floc size at such short time intervals or did not actually measure floc size, using fluorescence intensity instead.

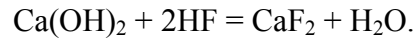
Methods to Remove Fluoride from Water

Because it is costly and difficult to remove, most communities faced with high F concentrations in their source water first seek an alternate source of supply before considering treatment. If an alternate source is not available, many different methods of defluoridation are available. Several processes have been proposed for removing F from drinking water including: 1) precipitation or coprecipitation by metal hydroxides, especially $\text{Al}(\text{OH})_3$, 2) selective adsorption and ion exchange including adsorption onto activated alumina, 3) membrane processes including reverse osmosis and electrodialysis reversal and 4) electrochemical methods.

Precipitation

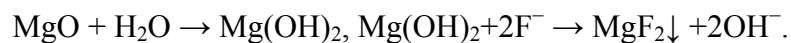
Precipitation or coprecipitation has been studied or practiced using calcium oxide, magnesium oxide, calcium chloride, monosodium phosphate, alum, and an alum + lime mixture. Precipitation is shown to be the cheapest and most established worldwide method of F removal (Ayoob et al., 2008 and Steenbergen et al., 2011). The method involves stirring or mixing in one of the constituents listed above, allowing the precipitate time to settle, and decanting. Although some of these processes are established for household and small community scale operation and the chemicals are typically easily available, there are several limitations. Some of the limitations of precipitation technologies include large quantity of sludge produced, uncontrolled finish water pH, difficulty in establishing dose requirement, and high dose requirements for higher F concentrations (Ayoob et al., 2008). In electrocoagulation coagulant is generated in situ by electrolytic oxidation of an aluminum anode, creating floc. The process then relies on traditional water treatment techniques to settle and waste the floc.

Addition of calcium oxide (CaO), hydrated lime (Ca(OH)₂) or calcium salts (CaSO₄, CaCl₂) will precipitate with fluoride to form insoluble CaF₂. This precipitate is relatively soluble hence the process requires high doses of Ca which leads to increased hardness. This technique does not remove enough F to meet the SDWA MCL (Ayoob, 2008). The chemistry is suggested to be:



The solubility of CaF₂ in water is 0.0016 g/100 mL. Some research indicates that due to slow reaction kinetics the process is not practical (Ayoob et al., 2008), while others indicate that the process is best suited for industrial applications (Islama, 2008).

"Magnesium oxide (MgO) can be used in a precipitation-sedimentation-filtration technique to reduce fluoride." The mechanism for removal of fluoride ions is suggested as chemisorptions or adsorption. Magnesium oxide (MgO) added to water forms magnesium hydroxide (Mg(OH)₂), which then combines with fluoride to produce insoluble magnesium fluoride (MgF₂). The insoluble MgF₂ settles out. Typically other compounds are added to the water to reduce the pH (the magnesium raises pH) and to aid sedimentation. The fluoride-magnesium chemistry is suggested as (Ayoob, 2008):



The solubility product constant K_{sp} for MgF₂ is 7.4×10^{-11} . The solubility for MgF₂ in pure water is 2.64×10^{-4} M.

Aluminum sulfate (alum), Al₂(SO₄)₃, is a common coagulant added to remove dissolved species by chemical precipitation in water treatment. Alum added to water forms aluminum hydroxide Al(OH)₃. This precipitate will selectively remove F. A high dose of alum is required to reduce F concentration levels below the MCL, therefore a large amount of alum sludge is created. Solids handling must be given careful consideration when this technology is used (Ayoob, 2008 and Fawell et al., 2006). Although studies

have shown that alum will selectively remove F little fundamental investigation has been done on the process. Hua's (2007) kinetic study shows that when alum is added to water an $\text{Al}(\text{OH})_3$ precipitate occurs almost instantly. After the precipitate (floc) has been created it grows with time and may take up to 20 minutes of gentle mixing to reach full size.

Electrocoagulation is a method of fluoride removal where an aluminum (or iron) anode in the water stream is subjected to an electric current that produces Al^{3+} , which then hydrolyses to form a hydroxide precipitate with fluoride. Electrocoagulation is similar to Al coagulation-flocculation. Instead of adding an Al salt, the Al^{3+} ions are generated by electrolytic oxidation at the anode. The generation of the Al^{3+} is described thusly: $\text{Al}_{(s)} \rightarrow \text{Al}^{3+}_{(aq)} + 3e^-$. The floc is removed by precipitation or filtration. Various combinations, such as Electrodialysis + Ion-exchange membranes have been evaluated, but not many are being used currently (Ayoob, 2008).

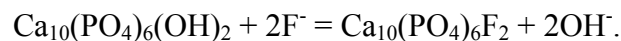
The Nalgonda technique is a coagulation-flocculation-sorption-sedimentation water treatment process that removes fluoride through addition of a high dose of aluminum salts. The process rapidly mixes the aluminum salts (aluminum sulfate or aluminum chloride) and lime followed by flocculation, sedimentation, filtration and disinfection. The addition of lime is added to ensure neutral pH of the final product and to facilitate forming dense flocculent for rapid settling. It is touted as the most economical, simplest, efficient method for fluoride removal in rural India for point-of-use or village-sized water treatment facilities (George, 2009). A drawback to the technique is potential residual aluminum concentration in the finished water above the USEPA's secondary MCL for Aluminum of .2 mg/L. The precipitated sludge product must be disposed of away from wells and gardens.

Adsorption/Ion Exchange

Several F treatment processes which rely upon adsorption or ion exchange have been investigated including bone char, clays and activated alumina. F removal has been studied with these constituents as column sorption media, bed media (Ayoob et al.,

2008), or in batch studies where the adsorptive media and pretreated water with added F are continuously agitated (Abdel-Fattah, 2000 and Chol, 1979). The time required for F removal is different in different studies. Adsorption technology has been used in full scale plants including Bartlett, Texas beginning in 1952. Limitations include limited social acceptance of the bone and bone char medias and low efficiency of the clays (Ayoob et al., 2008). Although considered a “Best Available Technology” (Angers, 2001), activated alumina is expensive, requires a long retention time, and requires regeneration (Agarwal, 2003).

Bone Charcoal (bone char) removes F from drinking water by adsorption. It is a blackish granular material made from charred (heated) animal bones. To get optimum water treatment the bone char must be heated enough to remove organics, but must not be heated at too high of a temperature because the F adsorption is reduced; ‘high quality’ bone char is required for optimum treatment. (Kaseva, 2006) Bone Char removes F by adsorption. Regeneration of the media is possible by reheating or by leaching with sodium hydroxide. Bone char has been proposed for use in a treatment works, or in a point-of-use capacity. When regeneration becomes less cost-effective, the final product can be applied as fertilizer to household gardens. Bone and enamel are essentially hydroxyapatite (HAP) $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ so the reaction between bone char and soluble F create fluorapatite (FAP) $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$. The chemical reaction can be written:



Clay powder, activated clay, and fired clay technologies adsorb or flocculate F as a filter or additive. Double layer clays (e.g. smectites) have high cation exchange capacity, which is not conducive to F removal which is negatively charged (anionic). Literature reports of F removal by clay are not consistent. Some clays used in defluoridation research include ground and fired clay pot, brick chips, calcined clay, palygorskite clay + calcite, and kaolin (Hamdi, et al., 2009 and Bårdsen et al., 1995). Removal is highly dependent on the type of clay used. H_2SO_4 -dosed “activated clay” is clay is better at removing F than clay not dosed (Fawell, et al., 2006). Point-of-use treatment may be

clay's best application even though the clay has a low capacity for F and it is difficult to pass water through a clay adsorptive media. It is not cost effective to regenerate this media. Further, because a column of clay has such low hydraulic conductivity, it is not conducive to use in column applications.

Activated Alumina (AA) is an adsorption process where fixed bed sorption filters with aluminum oxide Al_2O_3 grains are used to adsorb F. AA is manufactured from aluminum hydroxide by dehydroxylating it in a way that produces a highly porous material. When the AA medium is saturated, it is backwashed, regenerated with a concentrated sodium hydroxide, NaOH, solution. The regenerated AA is then neutralized with sulfuric acid H_2SO_4 or alum $KAl(SO_4)_2$, rinsed, neutralized with an acid solution, and rinsed again. In less than 4 hours of contact time more than 90% of the expected F removal can be achieved (Chol, 1979).

Activated carbon and activated bauxite are other adsorbents that can remove F. Neither is as effective as activated alumina, but activated bauxite is an excellent adsorbent and is attractive because it costs less than activated alumina (Chol, 1979). The presence of other chemical species does not significantly reduce F removal.

Membrane Processes

Membrane processes studied in the context of F removal include reverse osmosis (Sehn, 2007), nanofiltration (Elazhar et al., 2009), electrodialysis (Amor et al., 2000), and Donnan dialysis (Hichour et al., 2000). Membrane processes remove more F than other technologies (Ayoob et al., 2008).

Reverse Osmosis (RO) is a technique that forces a solvent through a semipermeable membrane by applying a pressure greater than the osmotic pressure of the solution. Membrane filtration processes remove particulate constituents based on size exclusion, but reverse osmosis does not. Reverse osmosis is able to reject constituents due to electrostatic repulsion at the membrane surface, chemical solubility, diffusivity and straining of solutes (Boysen, 2008). The EPA lists RO as a BAT for F removal (Angers,

2001). Drawbacks to RO include a high-energy requirement associated with operation of high pressure pumps, the complexity of the process, the fact that all dissolved constituents are removed which creates a waste management challenge, and the loss of water associated with the disposal of the high solute concentrate. However, these processes may still be used for the final polishing of the treated effluent (Tetra Chemicals Europe, 2010).

Nanofiltration (NF) is a low-pressure (compared to RO) membrane separation process that removes constituents by size exclusion and ion rejection. A large percent of feed volume, nearly 20%, is wasted. Elazhar (2009) indicate that rejection of F is high (97.8% for a F concentration of 2.32 ppm) and costs are comparable between existing NF drinking water facilities and a NF facility designed for selective F removal.

Distillation is a physical process that removes the water from the high salinity feed water by evaporating it and then condensing the water. Distillation, like RO, will remove F and almost every other constituent in water. Household-sized systems are available. However, like RO and other desalination processes it is expensive and complicated, has very high energy costs, removes all dissolved constituents, not just F, and wastes a large fraction of the feed water.

Electrodialysis is similar to RO but uses an electrical gradient to pass ions through semi-permeable membranes rather than pressure. Negatively charged ions (such as F) migrate towards positively charged anodes, and are prevented from further migration due to a negatively charged cation exchange. Thus, the main stream going through the exchange loses its contaminants. Electrodialysis requires pretreatment to reduce fouling on the anodes. Waterworks in the U.S. use this technology. (Amor et al.,1998)

Donnan dialysis is an irreversible ion-exchange equilibrium non-porous membrane separation process. This technology is not presently in use, but if put into use experiments have shown it to be highly efficient and very expensive (Ayoob, 2008).

Electrochemical Method

Electrosorption, an electrochemical method, is absorption (of F) on the surface of an electrode. In defluoridation techniques the “electrode” is a column of activated alumina (Lounici, 2004). The technique is costly due to high consumption of electric power and has not been studied in full scale water treatment plants or pilot scale systems.

Summary

Table 3 “Defluoridation Techniques” summarizes most of the techniques studied or used to remove fluoride and their strengths and limitations.

For small communities in New Mexico and throughout the world with elevated F concentrations there is a need for simple, effective, inexpensive technology to remove F. After reviewing the available literature there are many techniques available, utilizing different chemical, electrical, and physical mechanics to remove F throughout the world. In the U.S., the methods being used are in-situ electrocoagulation, RO, and activated alumina beds. Further research combining aluminum sulfate or alum as a coagulant and filtration is warranted.

Table 3 Defluoridation Techniques				
Defluoridation technique	Defluoridation capacity/dose	State of development/strengths	Limitations	References
Coagulation				
Precipitation by calcium oxide	~ 30 mg/mg F	Coagulation: Cheapest, established, and most commonly used Technology.	Quantity of sludge production and pH of treated water are high. Poor settling characteristics of the precipitate. High effluent fluoride concentration.	Ayoob, 2008
Precipitation by magnesium oxide	0.8 g/L (for fluoride concentrations of 1.8–3.5 mg/L)	Established technology. Affordable cost.	Quantity of sludge production and pH of treated water are high	Ayoob, 2008
Precipitation by calcium chloride and monosodium phosphate	0.28 g/L and 0.17g/L for domestic use	Emerging technology at reliable operating cost. No health risk in the case of misuse or overdosage of chemicals as in conventional precipitation techniques.	Too short contact times increase the escape of chemicals in the treated water. Long contact time may result in precipitation of calcium phosphates in the upper parts of the filter bed. Both these actions will reduce the removal efficiency	Ayoob, 2008
Coprecipitation by alum	~ 0.15 g/mg F	Well-known and established technique. Widely practiced in fluoride-endemic areas.	Low pH of treated water. High dose requirements for higher fluoride concentrations. Expected presence of sulfate and aluminum concentrations in treated water especially at high pHs.	Fawell et al. 2006

Table 3 continued				
Defluoridation technique	Defluoridation capacity/dose	State of development/strengths	Limitations	References
Coprecipitation by alum and lime (Nalgonda)	12.8 g alum and 6.4 g lime reduces F from 8.8–12.5 mg/L to 2.1±0.7mg/L.	Well known, widely practiced and established technology for individual household, and community level pilot scale applications. Chemicals readily available. Easy operation and maintenance	Difficult to control dosages for different sources of raw water with varying alkalinity and fluoride concentration. Hardness, pH, and residual aluminum of the treated water are high.	Fawell et al. 2006
Adsorption/ion exchange				
Bone	~ 0.9mg F/g	Long established technique for local applications	Impart taste to water. Limited social acceptance.	Fawell et al. 2006
Bone char	2–4 mg F/g	Well known and established technique. Good potential. Local availability and processing facilities aids local applications. Ability to remove fluoride to very low levels	Capacity reduces drastically after successive regenerations. More expensive than coagulation techniques. The use is constrained by the religious beliefs in many societies and communities. Limited social acceptance.	Kaseva, 2006
Clays	0.03–0.35 mg F/g	Economical. Very limited local applications.	Defluoridation potential is generally low. Regeneration is very difficult.	Hamdi, et al 2009 and Bardsen et al
Activated alumina	1.0 mg/g	Very well established technique. Regarded as one of the best available technologies world wide. Best performance at pH ~5. Minimum interference from counter-ions with consistent potential. Versatile applications.	Costly compared to coagulation processes and bone char. High pH reduces potential. Regeneration result in a reduction of about 5–10% in material, and 30–40% in capacity with increased presence of aluminum (>0.2 mg/L).	Angers 2001, Chol 1979

Table 3 continued				
Defluoridation technique	Defluoridation capacity/dose	State of development/strengths	Limitations	References
Electrochemical methods				
Electrocoagulation	Efficiency ~100%	Emerging technique. Efficiency of EC system is very high compared to the traditional coagulation process.	Interference from other anions like sulfate. Need for regular replacement of sacrificial electrodes. Costly due to high consumption of electric power.	Fawell et al. 2006
Electrosorption	Highly efficient	Emerging technique. Capacity of adsorbent enhanced by more than 50%. Excellent regeneration potential.	Costly due to high consumption of electric power.	Ayoob, 2008
Membrane processes				
Reverse osmosis	Highly efficient	Well-studied and established technology. Immense commercial applications. Dominant in many developed countries. Small foot print. Organics and salts are also removed.	Sensitive to polarization phenomenon. Chances of biological and mineral fouling. Treated water may lack the right balance of minerals. Poor water recoveries. High cost.	Ayoob, 2008
Nanofiltration	Highly efficient	Well-accepted membrane separation process. Handles higher water fluxes at lower transmembrane pressures than RO.	More sensitive than RO to pH and ionic strength. Leaves large concentrations of retentate fraction. Expensive technique. Skilled operators required.	Ayoob, 2008
Electrodialysis	Highly efficient	Excellent technique for simultaneous defluoridation and desalination. Commercially established. More economical than RO. More resistant to fouling.	Require high degree of pretreatment. Ineffective in removing low-molecular-mass noncharged compounds. Membrane scaling. Treated water quality is inferior to that of RO.	Ayoob, 2008

Table 3 continued				
Defluoridation technique	Defluoridation capacity/dose	State of development/strengths	Limitations	References
Donnan dialysis	Highly efficient	Recently, received attention in treating fluoride. Electro-membrane processes but with concentration gradient as driving force. A permanent separation between solutions which is not reversed even if the system is closed to the surroundings.	Operation requires addition of a so-called driving counter-ion to stripping solution. Reduced efficiency in high-saline waters. Expensive technique.	Ayoob, 2008

Chapter 3 Analytical Methods & Materials

Overview

This project consisted of two phases. The first phase consisted of bench testing to evaluate the fundamental chemistry and kinetics of F removal by $\text{Al}(\text{OH})_3$ precipitation. The second phase consisted of field testing using a pilot scale membrane filtration unit. Bench scale testing was done first to determine the dependence of F removal on pH, investigate F removal kinetics, determine initial alum dose, and determine if common constituents in water interfere with the process. The initial testing also determined what drinking water treatment processes are required for the pilot testing. Pilot scale testing will be done to compare to the laboratory results and to check the feasibility of the technology.

Analytical Methods

The analytical methods used to measure the parameters in this study are listed in Table 4.

Table 4. Summary of parameters to be measured and analytical methods.

Parameter	Method	Standard Method No.
pH	Glass electrode	4500 H^+
Alkalinity	Titration	2320
F	Ion chromatography	4110
Turbidity	Turbidimeter	2130
Metals (Na, K, Ca, Mg, Al, Fe, etc.)	Atomic Abs. spectroscopy	3111
	ICP spectroscopy	3120
Non-Metals (F, Cl, NO_3 , SO_4 , etc.)	Ion chromatography	4110

Aluminum residuals were measured at the Analytical Chemistry Laboratory in Department of Earth and Planetary Sciences at the University of New Mexico. All other analyses were conducted in the Environmental Engineering laboratories in the Department of Civil Engineering at the University of New Mexico.

Measurement of Anion Concentrations

The concentrations of anions except alkalinity were determined using a Dionex Ion Chromatograph using PeakNet software and an AS14 Column. A 3.5 mM Sodium Carbonate and 1.0mM Sodium Bicarbonate eluent was used as the eluent. A calibration curve for fluoride was prepared using laboratory grade sodium fluoride. A typical chromatograph is shown in figure 2.

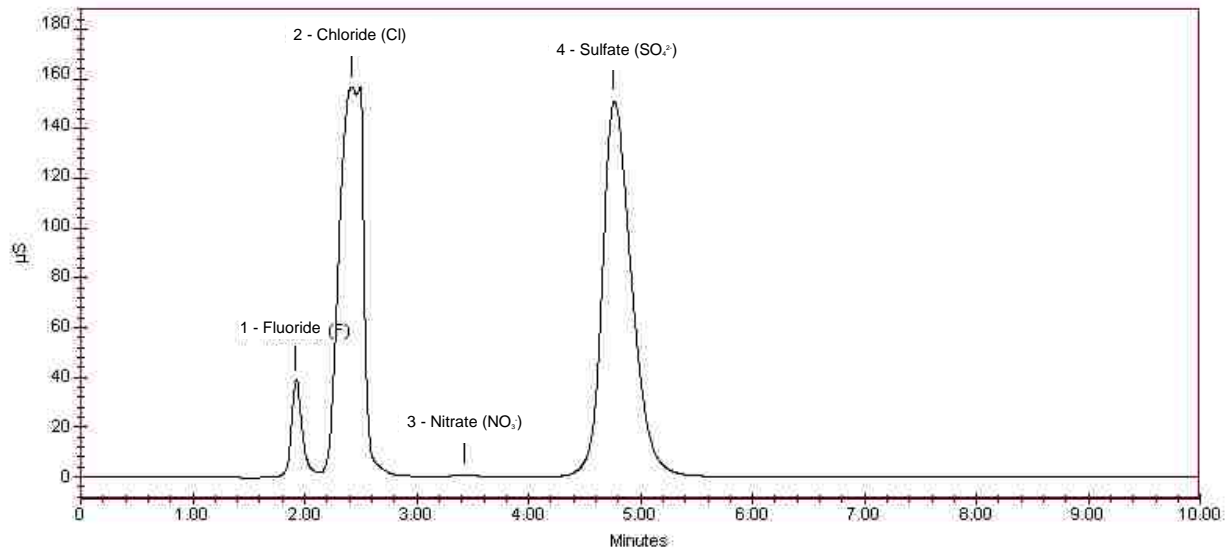


Figure 2. Ion chromatogram showing location of peaks corresponding to F⁻, Cl⁻, NO₃⁻, and SO₄²⁻

Measurement of Metal Concentrations

The United States Environmental Protection Agency Secondary Drinking Water Standard for Aluminum is between 0.05 and 0.2 mg/L. The solubility of Al depends on pH and is also influenced by the F concentration. Figure 1 shows a minimum solubility of Al(OH)_{3(s)} near pH 6.9 and increases as pH increases and decreases.

Samples were analyzed by ICP OES (Inductively coupled plasma optical emission spectrometry) in the Chemistry Laboratory in the Department of Earth and Planetary Sciences at the University of New Mexico to determine metal concentrations.

pH

pH was determined using the Standard Method 4500-H+ B. Electrometric Method with a pH meter (Orion) with a glass electrode (Thermo Fisher Scientific 910001) with a plastic body. The

pH meter is calibrated at least once each day. pH is measured prior to the addition of aluminum in the laboratory testing and after the samples at timed intervals are taken.

Materials

Tap Water

Tap water from the environmental engineering laboratories in Centennial Engineering Center at the University of New Mexico in Albuquerque, New Mexico was used to prepare solutions for laboratory tests.

Fluoride for Bench Scale Testing

A F stock solution containing 1000 mg/L F was prepared using laboratory grade sodium fluoride, NaF. This F was used to spike UNM tap water used in the lab experiments so that the lab experiment water has a F content closer to the values found in the source waters at San Ysidro, NM. Lab testing was conducted using UNM tap water spiked with this stock solution.

Aluminum Solutions

Various concentrations including 1000 mg/L and 3000 mg/L as aluminum (Al) stock solution was created in the laboratory with laboratory grade aluminum sulfate $Al_2(SO_4)_3$.

pH Control during Bench Scale Testing

pH was controlled with solutions made from laboratory grade sodium hydroxide, NaOH, pellets (at 1g/L) and hydrochloric acid, HCl, 36% liquid (at .10 and .02 N). pH was controlled so that the removal of F pH dependence can be determined. pH is controlled in two ways. Initially, the test solution was prepared at a specific pH to within 0.1 pH unit using NaOH and HCl. Because $Al_2(SO_4)_3$ is a weak acid, the initial pH of each solution needed to be adjusted prior to addition of the Al stock to achieve the desired final pH. This was accomplished by adding NaOH at time zero of the experiments. The pH range used for the testing is selected because it evenly brackets the typical pH of natural waters and also brackets the point of least solubility of aluminum.

Testing is done at pH levels of 5.5, 6.5, 7.5, 8.5, and 9.5.

Pilot testing was done at the Arsenic Treatment Plant in Albuquerque, NM which has a F level of .9 mg/L and at the San Ysidro Treatment Plant in the Village of San Ysidro, NM which has a F level of 6.4 mg/L. Hence pilot testing was conducted with a range of F concentrations up to 10 mg/L.

Alum for Pilot Testing

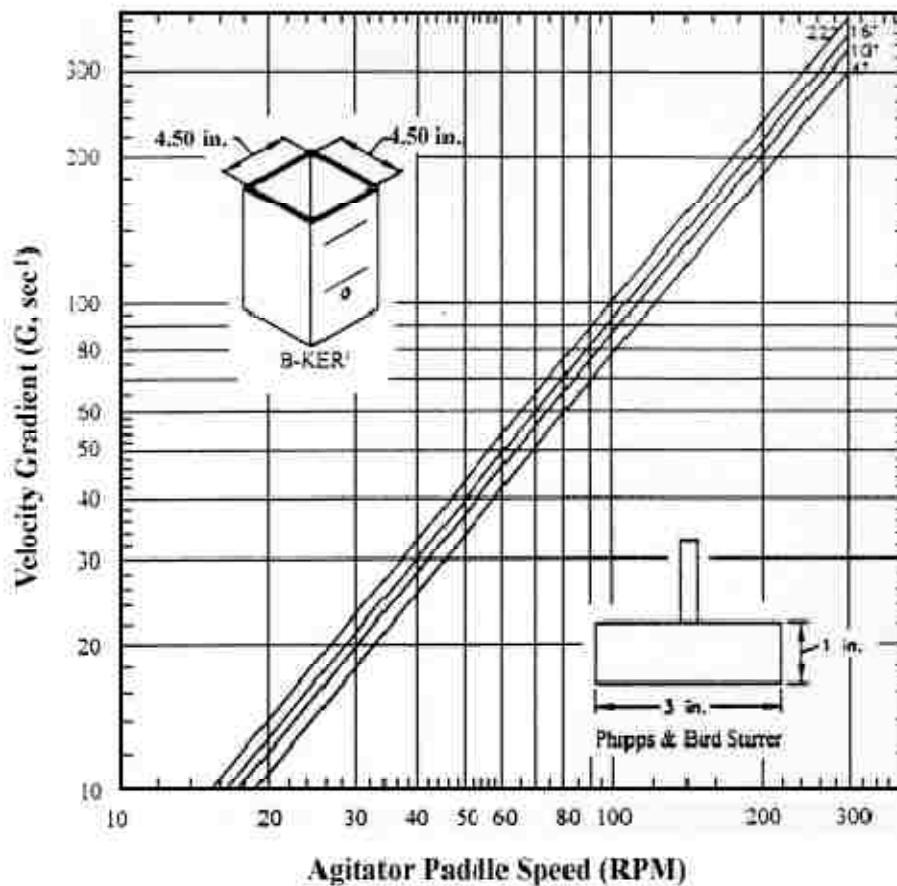
Liquid alum obtained from General Chemical was used for field scale testing of the pilot unit. It was equivalent to 48.5% dry alum $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$.

Mixing Gradient G-Values

The Camp-Stein mixing velocity gradient (G) was used to quantify the mixing intensity. It is calculated as:

$$G = \sqrt{\frac{P}{\mu V}}$$

The G-value is a parameter that assists in scaling between jar tests and plant operation. Jar tests assist in determining the optimal coagulant dose in rapid mix, flocculation time in the flocculation basin, and settling time in the settler. G has units of s^{-1} . It is a mathematical representation of the power put into ‘stirring’ a liquid, the viscosity of the liquid, and volume of the basin or jar. The G-value for the Phipps and Bird jar tester can be obtained via a chart from Phipps and Bird (figure 3) or by calculation using the digital read out of the rotational speed of the stirring blades.



Velocity Gradient vs. Agitator Speed for a 2-liter Square Beaker (B-KER²), Using a Phipps & Bird Stirrer. Water samples are at various temperatures (C°).

Figure 3. Mixing gradient G values for Phipps & Bird jar testers.

To determine if mixing intensity had any effect on F removal, a Waring blender was used to provide a very high degree of mixing. Power for the blender was determined using a Kill-a-watt electric power meter. The amount of power transferred to the water was determined by measuring the difference in power consumed by the mixer motor when the blender was empty and full. Dynamic viscosity of water at 20 deg C is 0.001002 N-s/m². The volume used for the jar tests is 12 liters (.012 m³) since there are six two liter beakers. The volume used for the blender tests is .5 L (.0005 m³). Power changes based on the rpm of the jar tester or the setting chosen on the blender. Mixing velocity gradient G values for different blender settings are tabulated in Table 5.

Table 5. Mixing velocity G values determined for blender tests.

Blender Tests				
Settings	No Water Power (Watts=N-m/s)	.5L Tap Water Power (Watts=N-m/s)	Difference in Wattage	Calculated G Value
high-Grate	169	190	21	6474
blend	182.5	208	25.5	7134
shred	198.5	231.5	33	8116
grind	212.5	251.5	39	8823
liquefy	231	276	45	9477
ice crush	254.5	300	45.5	9530
low-easy clean	108	122	14	5286
puree	125	144.5	19.5	6239
cream	151	173	22	6627
chop	171.5	197.5	26	7204
whip	198	232	34	8238
mix	236.5	278.5	42	9156

Pilot Scale System pH, kinetics, dosage, and filtration

Laboratory results determined pilot plant setup, including if addition of sodium hydroxide to increase influent water pH was required (it was not), where to add alum to the system (at the suction side of the pump for mixing with the greatest G value), if a flocculation step is required (no), and initial dose of alum (40 mg/L).

It was expected that F would be removed at approximately the same rate as blender bench scale testing since the alum was added at the at the recycle pump inlet which provides a large amount of power (P) to the solution. The mixing velocity G for the pump was calculated as the hydraulic power of the pump.

$$P = \gamma Q h_p$$

where:

P = power (kW)

γ = specific weight of water (kN/m³)

Q = flow (m³/s)

h_p = pump head (m)

Pump head was determined as the difference between inlet and outlet pressures. The volume term (V) in the Camp-Stein equation is the volume of the pump and was determined by measuring the volume of water it took to fill the pump housing.

Filtration

The $\text{Al}(\text{OH})_3$ precipitate was removed by membrane filtration. Further, lab testing showed that F removal by $\text{Al}(\text{OH})_3$ precipitation occurred virtually instantly. Thus, a flocculation step in the treatment process to produce formation of a large floc as needed for granular media filtration was not needed. In order to remove floc, filtration in the form of a Koch ultrafiltration membrane module was used. A diagram of the pilot treatment system is presented in figure 6.

Power Requirements

The pilot treatment system requires one 115 V power source. The programmable logic controller requires this power. The PLC powers (and controls) the chemical feed pump and the booster pump.

Pilot Scale System Revisions

The pilot scale system went through three major revisions. Version 1 started as a modification of a GE-Osmonics-E4 RO unit in which the RO membrane was replaced by a Koch Abcor®-Ultracor® 5-HFM-251-UVP ultra filter. This membrane is a PVDF membrane with neutral surface charge contained a PVC housing. A diagram of the membrane is shown in figure 4. Inside the 1.25-inch inside diameter housing there are seven .5-inch tubes. Process water flows from the bottom to the top, with the majority of the water exiting the module at the top as part of the recycle, and the permeate exiting through the tubes, out through the side port.

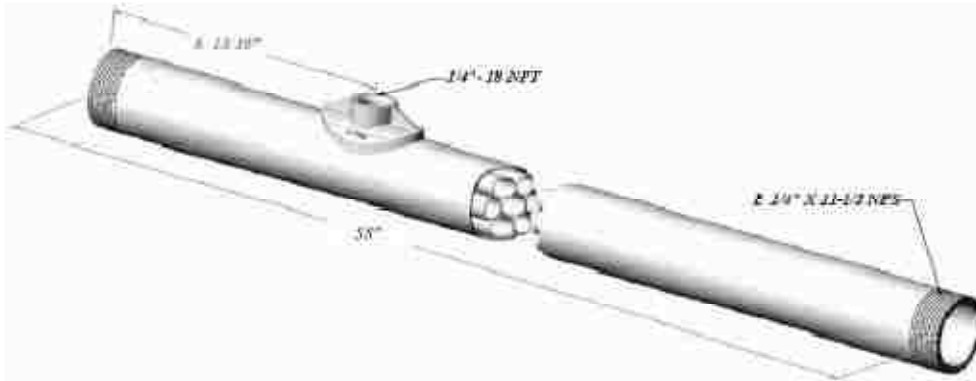


Figure 4. Diagram of Koch Abcor® Ultracor® 5-HFM 251 UVP ultrafiltration module.

Version 1 of the pilot treatment unit utilized the existing Tonkaflo pump on the E4 unit, however this pump was designed for very high pressures (>250 psi) and low flows (~5 gal/min) that were not consistent with the operating parameters for the membrane filter ($P_{\max} < 75$ psi).

Furthermore, it required 480 V power which was difficult to obtain at field testing sites..

Pressures were higher than the maximum allowable for the ultrafiltration module, so version 2 was created.

Version 2 substituted a 1/3 hp centrifugal pump in place of the RO pump, dead-end filtering instead of a recycle, and included operating controls and data collection using a programmable logic controller (PLC). Version 2 was tested at the Albuquerque Bernalillo County Water Utility Authority Arsenic Treatment Demonstration Plant and at the University of New Mexico.

Pressures were still higher than the maximum allowable for the ultrafiltration module due to high line pressures at the treatment plant which were in turn boosted by the centrifugal pump.

Version 3 of the pilot treatment unit used line pressure to provide transmembrane pressure for the membrane filtration process and used the centrifugal pump to create a high volume recycle flow (figure 5). Version 3 stays within allowable pressures for the ultrafiltration module by utilizing a high recycle flow in order to produce the permeate instead of pressure.

Pilot Scale System Components

The Grainger booster pump used in versions 2 and 3 has 1/3 hp, 90 psi max, and 9.5 gpm at 10 psi. A masterflex peristaltic pump (with L/S 24 norprene tubing) is plumbed into the Grainger pump influent in order to deliver alum to the system. The autoflush timer is not used because the Koch membrane does not require flushing. The Koch ultrafiltration membrane is an ABCOR-ULTRA-COR 5 foot module: 5-HFM-251-UVP with multiple 1/2" diameter tubes inside the module (ABCOR, 2009). The module is designed for the efficient removal of solids. The pilot unit is controlled and monitored with an HE-XL102 Programmable Logic Controller from Omega Engineering with two OmegaDyne PX309-300 (0-300 psi range) pressure transducers with 4-20 mA signal, one Omega Engineering SPRTX-M1 temperature sensor (-99 to 208 deg C range) with 4-20 mA signal, and three GF Signet 2100 turbine flow sensors with digital pulse signals. The flow sensors at the permeate effluent and system recycle are in the high range of 0.8 to 10 gpm and the concentrate effluent is monitored with a low range sensor (0.1 to 1 gpm). Figure 5 diagrams the flow through the pilot scale system.

The calculated G value of the Grainger booster pump during typical operation at San Ysidro is $11,110 \text{ s}^{-1}$. The volume of the pump is 238 mL, the power through the pump is 21.3 Watts (calculated based on a differential pressure of 25 psi to 18 psi), and the dynamic viscosity was chosen based on a recycle temperature of 35 degrees.

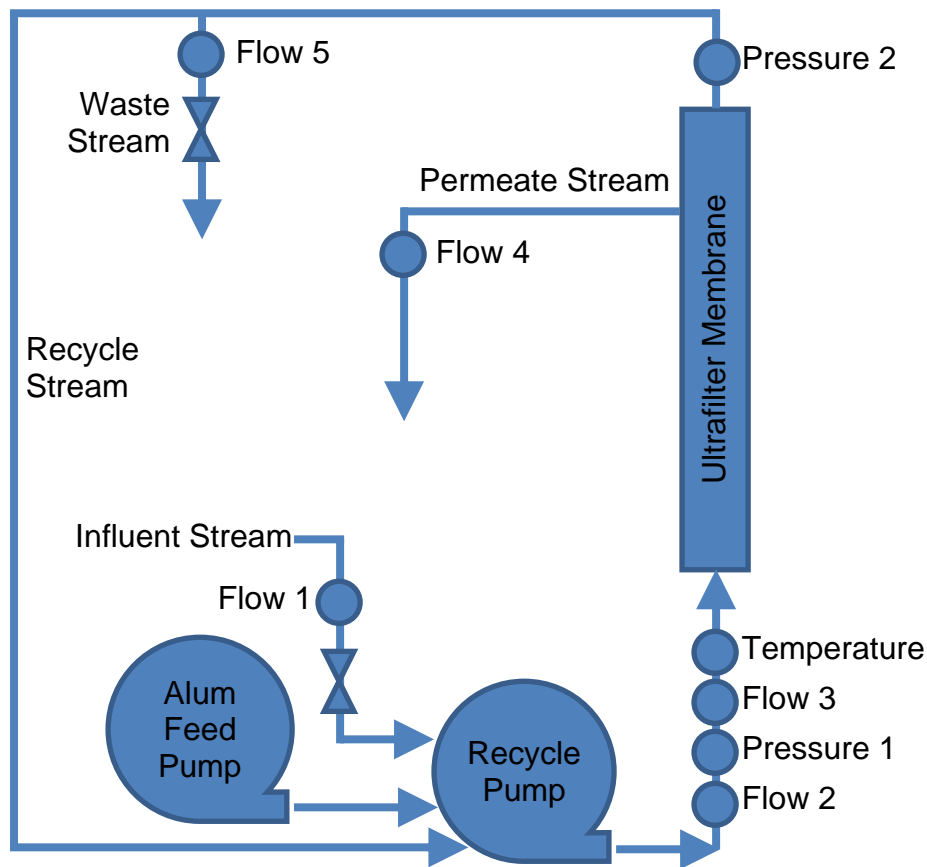


Figure 5. Flow diagram of the Al-CMF fluoride removal pilot treatment system.

Figure 5 Legend:

Temperature: Recycle Water Temperature Electronic Sensor (Analog)

Pressure 1: Pre-Ultrafilter Electronic Pressure Transducer (range 0-300 psi)

Pressure 2: Post-Ultrafilter Electronic Pressure Transducer (range 0-300 psi)

Flow 1: Influent Rotameter Flow Meter (range 0-12 gph)

Flow 2: Recycle Rotameter Flow Meter (range 0-10 gpm)

Flow 3: Recycle Electronic Flow Sensor (range .1 to 10 gpm)

Flow 4: Permeate Electronic Flow Sensor (range .1 to 10 gpm)

Flow 5: Waste Electronic Flow Sensor (range .1 to 10 gpm)

Recycle Pump: Dayton Booster Pump 1/3 HP Multi-stage

Alum Feed Pump: Masterflex Peristaltic Pump

Ultrafilter Membrane: Koch Ultrafiltration Membrane ABCOR ULTRA-COR MODULE 5-HFM-251-UVP

The E4 system has been modified so that a minimum of plumbing and the frame are all that are used of the initial product.

Field Testing of the Pilot Treatment Unit

Arsenic Removal Demonstration Plant

The Al-CMF pilot scale treatment system was set up at the Albuquerque Bernalillo County Water Utility Authority's Arsenic Removal Demonstration Plant in Albuquerque, New Mexico. The experiences gained in operating the system here resulted in redesign of the system which is referred to in this thesis as version 3. Version 2 operated the Koch Ultrafiltration membrane as a dead-end filter; version 3 operated it with a recycle.

Table 6. Chemistry of waters used in pilot testing of the Al-CMF fluoride treatment process.

	Units	Albuquerque, NM	San Ysidro, NM
Metals/Minerals/Nutrients			
Arsenic	µg/L	6	0.2
Barium	mg/L	0.04	0.1
Boron	mg/L	0.16	NF
Chromium	µg/L	5	ND
Iron	mg/L	0.198	0.06
Manganese	mg/L	0.006	0.05
Selenium	µg/L	ND	0.0024
Zinc	mg/L	0.011	ND
Fluoride	mg/L	0.9	6.4
Nitrate	mg/L as N	1.6	0.1
General Chemistry			
Alkalinity	mg/L as CaCO ₃	117	447
Bicarbonate	mg/L as CaCO ₃	115	NF
Calcium	mg/L	24	86.4

Chloride	mg/L	21	88
Hardness	grains/gallon	4.2	272
Magnesium	mg/L	2.9	13.6
Potassium	mg/L	2	NF
Silica	mg/L as SiO ₂	28	NF
Sodium	mg/L	74	480
Sulfate	mg/L	72	30
Total Dissolved Solids	mg/L	298	914
Free Chlorine Residual	mg/L	0.8	NF
Conductance	microOhms/cm	476	NF
pH	Standard Units	8.2	7.78
Temperature	Fahrenheit	70	NF

Table 6 Sources:

- 1 San Ysidro Treatment Plant #1 09-09-2009 New Mexico Environment Department (NMED) "Water Watch" database
- 2 United States Environmental Protection Agency 1990

The pilot unit was hooked up to the Albuquerque Bernalillo County Water Utility Authority water system, not the raw influent water, because the raw influent water did not have adequate line pressure. Version 3 of the pilot scale system would have been able to handle the low inline pressure, but versions 1 and 2 required feed pressures of 50 psi or higher.

The feed water quality at the Arsenic Removal Demonstration Plant is summarized in table 8.

Village of San Ysidro

After the pilot treatment unit was tested at the ABCWUA Arsenic Removal Demonstration Plant it was brought back to UNM and modified. The primary modification was to replumb the system to incorporate a high flow recycle line. The Koch membrane filter used in the system requires a recycle to produce crossflow velocities that provide shear stresses to prevent accumulation of solids on membrane surface. Recommended crossflow velocities ranged from

6.4 ft/s at 23 gal/min to 11.7 ft/s at 42 gal/min. The pump available for this project was a 1/3 hp centrifugal pump that produced a flow of about 8 gal/min at a head loss of 7 psi resulting in a crossflow velocity of about 2.3 ft/s. The principal cause of the high head loss and thus the reduced recycle flow was the large number of fittings, rotameter, and flow control valves in the system. These could be reduced in a more carefully designed system. Though the crossflow velocity was less than recommended by Koch, it was felt that it would be adequate for the purposes of a short term demonstration of the effectiveness of the Al-CMF system for F removal.

Version 3 of the pilot system was operated at the San Ysidro Water Treatment Facility at the approximate address of 389 New Mexico 4, San Ysidro, NM 87053 in June 2011. San Ysidro's water system obtains water from a shallow well and an infiltration gallery near the Jemez River. Treatment train consists of polymer addition, settling in a Lamella Plate settler, sand filtration, and hypochlorite chlorination. The pilot system received settled water prior to filtration at an influent pressure of approximately 15 psi. Figure 6 shows the left side of the pilot system installed at San Ysidro including the ultrafiltration membrane (the 5-foot long, 1.25 inch diameter white PVC pipe) on the left side of the picture. On the top right side of the picture the small box houses the programmable logic controller. The pump and motor in the middle of the picture are not used in version 3. The two tubes at the bottom of the picture are the permeate and concentrate.

The process steps used in the pilot system were based on the UNM lab studies and experience reported in the literature.

The pilot treatment unit was tested by measuring initial and final F concentrations to determine F removal by Al(OH)₃. Initial F levels in the bench scale tests were 7 mg/L to simulate the source water in San Ysidro, NM. Table 6 shows not only recent F levels at proposed pilot plant sites, it also shows additional water chemistry parameters.

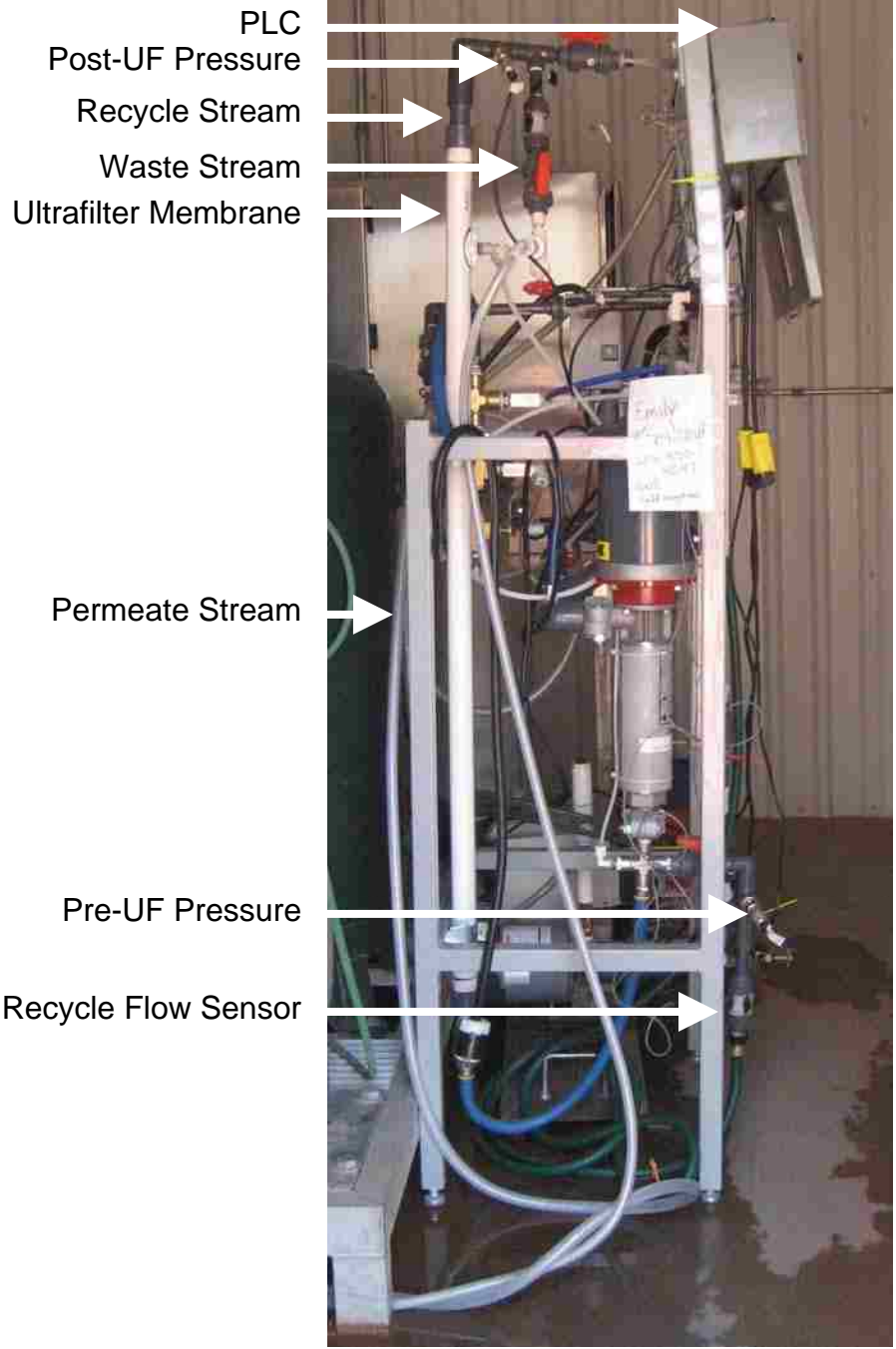


Figure 6. Photograph of AI-CMF pilot treatment unit installed in the San Ysidro water treatment facility.

Chapter 4 Bench Scale Tests

The purpose of the bench scale testing was to investigate F removal by $\text{Al}(\text{OH})_{3(s)}$ precipitation at varying pH levels and to determine the kinetics of the reaction. Final F concentration data from the jar testing and kinetic testing were evaluated by pH, aluminum dose, and time interval to maximum removal. Since every water is unique, and rules do not hold fast between sources, empirical approaches to coagulation such as the jar test and the pilot plant are the only feasible ways to approach water treatment operation and design (Hendricks, 2006).

Fluoride Removal as a Function of pH

The minimum floc solubility of aluminum sulfate ($\text{Al}(\text{OH})_3$) occurs near pH 7.0. Laboratory testing was done at pH levels of 5.5, 6.5, 7.5, 8.5, and 9.5. Since optimum coagulation efficiency occurs at minimum floc solubility it was expected that F removal would be greatest at pH 6.5 and be less at other pHs (Chapter 05 Clarification, 2011). If F removal was pH dependent, the pilot plant would be designed so that the influent water pH is adjusted to optimum, but the jar tests indicated that there was no pH dependence for F removal.

Jar Testing

Jar testing is a typical way to determine coagulant dose in water treatment since the variability of constituents in source water may impact results. Jar testing is done at pH levels of 5.5, 6.5, 7.5, 8.5, and 9.5 and at aluminum doses of 0, 1, 3, 5, 7, 10, 20, 30, 40, and 50 mg/L. All Al concentrations are reported as mg Aluminum per liter. All jar tests are done with F-charged tap water, where 7 mg/L is added to tap water that has an approximate F concentration of .8 mg/L (this is from a combination of F added at the Water Treatment Plant and natural F in the source water). The F concentration is determined at the beginning of each experiment by taking and analyzing a sample prior to time zero. In order to compensate for the drop in pH from the addition of aluminum sulfate, NaOH is added at the beginning of the jar tests, but after pH is adjusted, directly prior to time zero. The amount of NaOH used changes based on aluminum dose.

In addition to aluminum sulfate, the coagulant Ferric Chloride (FeCl_3) was tested at Fe doses of 0, 10, 20, 30, 40, and 50 mg/L.

Maximum stirring was applied for 30 sec followed by slow mix (~1 rev/sec) for 30 minutes. Samples were taken at 1, 5, 30 and 60 minutes, and 24 hours. They were passed through 0.45 μm membrane filters to stop the adsorption reaction. Analyses were performed for F and Al. Testing done for As removal by the Fe-CMF process found that, in contrast to conventional coagulation-flocculation treatment, only a very short flocculation period (< 30 sec) was needed to achieve good As removal. In order to determine whether a flocculation step is needed to remove F, samples are prepared as for the jar testing but placed in 60 mL syringes. A filter disk containing a 0.45 μm membrane is attached to the syringe. An Al dose is added to the syringe after NaOH is added to compensate for the aluminum sulfate and the syringe is shaken rapidly to achieve coagulation. Samples are forced through the membrane filter at 0, 10, 20, 30, 40, 50 and 60 sec and subjected to Al and F analyses.

Rapid mixing of coagulant is key to achieving maximum constituent removal. Although the maximum stirring of the jar test apparatus is used and the syringe tests have vigorous shaking, a household blender can achieve a higher G value than either of these methods. In order to determine if mixing more rapidly than the jar test allows can remove additional F, blender testing is done in 500 mL batches prepared as for the jar testing at pHs of 5.5 and 7.5 with an Al dose of 30 mg/L. Samples are taken at 0 sec, 30 sec, and 5 minutes and subjected to F analysis.

Competing Ions

It is possible that ions may compete against F for available “spots” on the floc created by the coagulant. If the coagulant is “used up” by ions other than F, then less F may be removed from the water. To determine if specific ions compete against F for the floc “spots”, kinetic tests were done with chloride, arsenic, selenium, and a control, all at pH levels of 5.5, 7.5, and 9.5 and an initial F concentration of 7 mg/L.

Kinetic Studies

A series of kinetic studies were done to determine the rate of removal by the Al-CMF process. Initial studies were done using a Phipps & Bird jar tester. The normal coagulation-flocculation jar test procedure consists of a brief rapid mix period followed by a longer flocculation period at

slow mixing speeds. However, since membrane filtration was to be used to achieve removal of the $\text{Al}(\text{OH})_3$ floc instead of sedimentation or granular media filtration, the flocculation period was not important. However, as described below, process performance was found to depend on the mixing power. This was estimated using the Camp-Stein mixing velocity gradient “G” value.

Using a jar test to determine alum dosage for F removal presumptively assumes that a flocculation step is required. Because 1) Ching-Yao Hua’s kinetic study (Hua, 2007) shows that formation of an $\text{Al}(\text{OH})_3$ precipitate occurs almost instantly, 2) coagulation is most efficient when the coagulant is dispersed rapidly (i.e. a high G value), and 3) the laboratory process will involve filtration of the solution through a $.45\mu\text{m}$ filter, kinetic testing beyond jar testing was done to determine the rate of F removal.

Early in the project a conversation with a chemical engineer suggested that mixing intensity might affect F removal because the $\text{Al}(\text{OH})_3$ precipitation kinetics are so rapid. Thus, a series of experiments was conducted to determine if this was in fact the case. As described previously, the first experiments were conducted using a Phipps & Bird jar tester which produced a maximum G value of 300 s^{-1} . The minimum time needed to add reagents, achieve complete mixing, collect a sample and filter it was about 10 seconds. A second procedure was devised in which reagents were added to a large (60 mL) syringe that had a membrane filter cartridge attached. Reagents were added, the syringe shaken vigorously, and then a sample aliquot forced through the filter. This procedure allowed reaction times as short as about 5 seconds to be performed, however, mixing could not be quantified. The final series of kinetic tests used a Waring Blender, which at maximum setting produce G values greater than $9,000\text{ s}^{-1}$.

Kinetic testing using a syringe was performed using an initial dose of 7 mg/L of F added to tap water in a 60 mL syringe. Buffer (NaOH) and a dose of 30 mg/L Al were added at time zero. The syringe was then shaken; samples were filtered upon exiting the syringe using a $.45\mu\text{m}$ filter held in a millipore filter holder at 10 second time intervals up to one minute to see if additional F is removed over time. The results as shown on figure 8 indicate that no additional F is removed after approximately 20 s.

Aluminum doses ranged from 0 mg/L and 50 mg/L and were measured as aluminum, not alum.

Initial bench scale tests used a Phipps and Bird six-paddle stirrer for jar tests with 2 L square jars. However, with this method the minimum reaction time was approximately 30 sec and the maximum G value calculated was 180 (the Phipps & Bird Chart indicate the maximum G value is 380). The F removal reaction was found to be faster than this. Thus, in order to reduce the time for the kinetic experiments a 50mL syringe with a 0.45 μm membrane filter attached was used. These tests were conducted as follows:

- 30 mL of solution was added to the syringe containing F and adjusted to the desired pH.
- An aliquot of stock Al solution was added to the syringe to achieve the desired dose.
- The plunger was placed in the syringe creating a syringe with 30 mL of solution and 20 mL of air. The syringe was violently shaken by hand for the prescribed period.
- At intervals ranging from 2 to 5 seconds aliquots of solution were expelled from the syringe through the 0.45 μm filter into test tubes for F analysis.

This procedure allowed determination of F removal at intervals as short as 2 seconds.

A conversation with a visiting engineer suggested the $\text{Al}(\text{OH})_3$ precipitation reaction was even more rapid than could be measured by the syringe method. It was suggested that a more rapid mixing procedure might thus improve F removal. Accordingly, a procedure was utilized in which mixing was achieved in a Waring Blender. This procedure consisted of:

- 500 mL of solution was added to the blender containing F and adjusted to the desired pH and the blender was turned on.
- An aliquot of stock Al solution was added to the syringe to achieve the desired dose.
- Samples were taken from the blender by syringe and passed through 0.45 μm filters to stop the reaction.

The G value was calculated using the Camp Stein equation. Power was determined by measuring the electric power of the blender with water and without water; the difference in wattage represented the additional energy required to mix the solution.

In the first blender test, the blender was filled with 500 mL tap water with F added to it. The pH was adjusted to the desired pH, It is then buffered with NaOH to counteract the acidifying effect of the aluminum. The blender is turned on and time is started at 0 when the aluminum sulfate is added. Samples are taken at the timed intervals and filtered as indicated above.

The removal mechanism hypothesized in this study was that F was removed by coprecipitation during formation of the $\text{Al}(\text{OH})_3$ precipitate. An F alternative mechanism was considered which consisted of F removal by adsorption onto pre-formed $\text{Al}(\text{OH})_3$ flocs. In the second blender test the sample water containing $\text{Al}(\text{OH})_3$ floc was prepared. Aliquots of F were added and samples were withdrawn by syringe and passed through 0.45 μm filters to stop the adsorption reaction.. These tests were performed at a pH of 7.5 and an aluminum dose of 30 mg/L.

Adsorption Testing

Using aluminum to remove F in drinking water has been studied since 1934 (Boruff, 1934). Since 1934 various studies on F removal from drinking water using aluminum describe the complexation between aluminum and F both as adsorption and as coprecipitation. In addition to using a blender to identify a potential relationship between F removal and G value, the blender was also used to further understand the reaction between aluminum and F regarding F removal. 30 mg/L aluminum (and 28 mL of 1 mg/L NaOH stock to correct pH to initial pH) was added to 500 mL tap water (total) adjusted to a pH of 7.5. The aluminum, NaOH, and tap water was then mixed in the blender on “Ice Crush” mode (the highest speed) for 30 seconds. Aluminum floc were then allowed to grow without mixing for five minutes prior to the introduction of F into the system. Three tests were done in this manner and varied in the amount of time the aluminum floc were allowed to grow; the floc were allowed to grow for 5 minutes, 10 minutes, and 15 minutes respectively before F was added. At the 5, 10, and 15 minute interval 7 mg/L F was added and the constituents mixed for a short period of time. Filtered decant samples were taken at two five-minute intervals following the introduction of F.

Laboratory Test Results

Jar Testing

The purpose of the first round of jar tests was to determine the Al dose range needed to reduce F concentrations. Aluminum doses of 0, 1, 3, 5, 7, and 10 mg/L were used at pH values of 5.5, 7.5, and 9.5. The most significant finding was that this range of Al dose was not enough to reduce natural F levels of 7 mg/L down to the MCL of 4 mg/L. The highest amount of F reduced was 1.36 mg/L with 10 mg/L aluminum at a pH of 7.5. Since the goal was to reduce F by 3 mg/L the dose range needed to change. The second round of jar tests was done with Al doses of 0, 10, 20, 30, 40, and 50 mg/L at pH values of 5.5, 6.5, 7.5, 8.5, and 9.5.

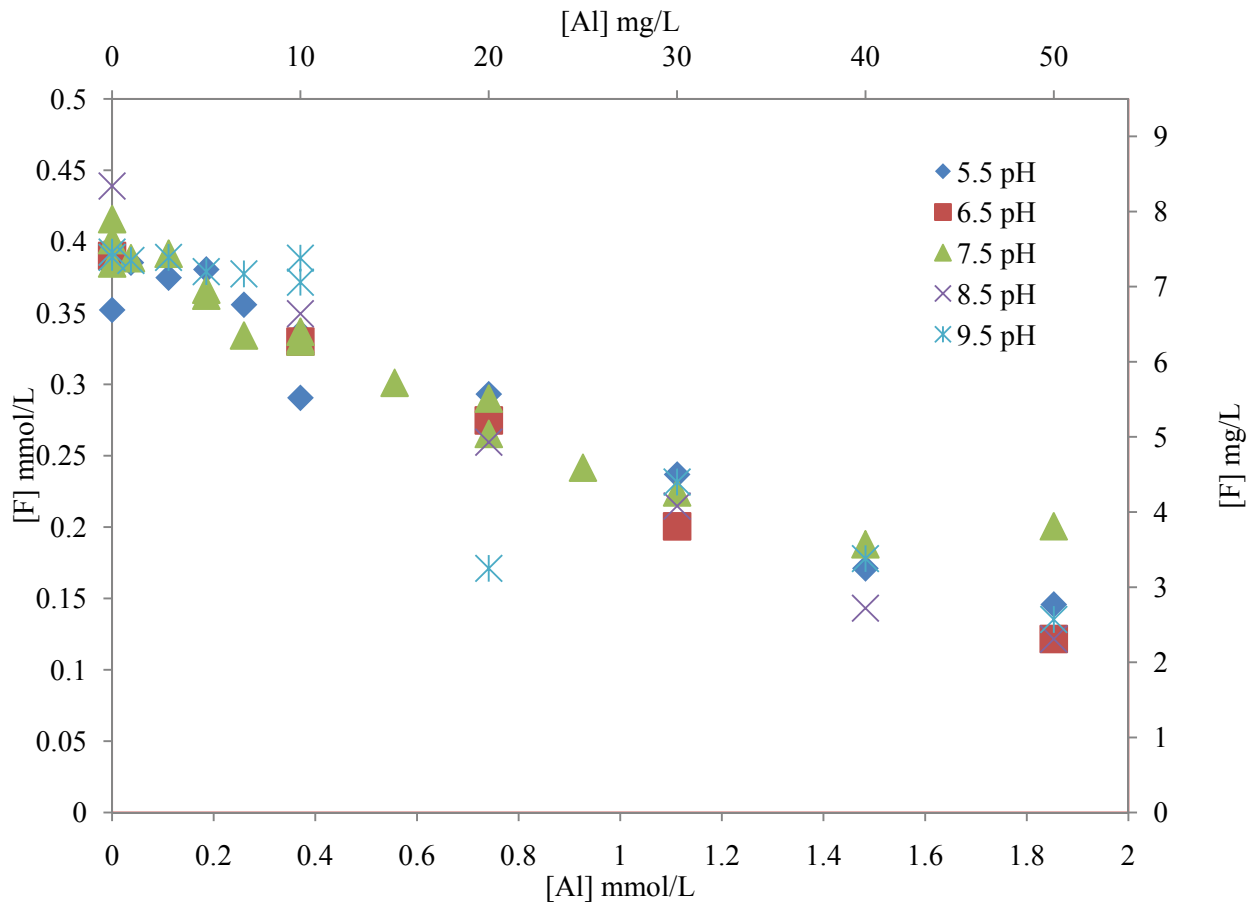


Figure 7. Summary of jar tests showing final F concentration and aluminum dose as a function of pH.

The second round of jar tests showed that the Al dose range could reduce F from approximately 7 mg/L to 4 mg/L. This reduction level was accomplished with the 30 mg/L Aluminum dose at pHs from 6.5 to 9.5. 40 mg/L of Aluminum was required to bring all final F levels below the MCL of 4 mg/L. Original F level varies significantly as shown in figure 7 because of dilution due to pH adjustment was done after F addition. With no pH adjustment original F level for all tests would be approximately .8 ppm from the tap water + 7 mg/L added = 7.8 mg/L.

The second round of jar tests found a linear relationship between aluminum dose and F removal. Between all pH levels, there is an average reduction in F of 1 mg/L for every 10 mg/L Aluminum added. In mol/L this relationship is .15 mol/L F reduction for 1 mol/L aluminum added. A linear relationship is a good fit—the r-squared value for all pH levels combined is .92.

The second round of jar tests also showed that F removal using alum is not pH dependent. This was a surprising finding since F removal by adsorption on Al solids such as activated alumina ($\alpha\text{-Al}_2\text{O}_3$) is strongly pH dependent (Ghorai, 2004). Further, the solubility of $\text{Al}(\text{OH})_3$ is pH dependent and this dependence was expected to influence F removal. The lack of dependence of F removal on pH was determined to be statistically significant testing the slopes of linear regression using a t-test. It was determined with a 90% confidence that the slopes are not significantly different using the student's t-test. The data used for the student's t-test is shown below in table 7. The equation and parameters used for the student's t-test is shown below the table.

Table 7. Linear Regression of F Removal (mg/L)

pH	Linear Regression Equation	R ² Value	Slope
5.5	-.0117x+.9973=y	0.972	-0.0117
6.5	-.014x+.9833=y	0.988	-0.0140
7.5	-.0122x+.9695=y	0.939	-0.0122
8.5	-.0146x+.9462=y	0.9685	-0.0146
9.5	-.0147x+1.024=y	0.8546	-0.0147

$$t = \frac{\bar{x} - \mu_0}{\frac{s}{\sqrt{n}}}$$

t is the t-value required to get the p-value

\bar{x} is the mean

μ_0 is the specified value (will use the range)

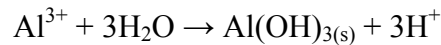
\sqrt{n} is the sample size

s is the sample standard deviation

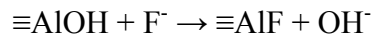
In order to determine the confidence interval a t-distribution table was viewed with 4 degrees of freedom ($v=n-1$) for a one-sided distribution. A t-value for both sides of the distribution (or range) were calculated using the equation above and analyzed using the t-distribution table and the more conservative one (90%) was used as the confidence interval.

The r-squared values for each linear regression line are high, further verifying that there is a linear correlation between F removal and Al dose.

Since more aluminum was required to remove F than originally estimated, the chemical mechanism of F removal may not be the original assumption that an aluminum hydroxide floc is formed:



and then adsorption of the F onto the floc occurs:



Because if this were the only chemical or mechanical mechanism going on then 1 mol of aluminum should remove 1 mol of F. With this first and second round of jar tests complete 1 mol of Al removes approximately 0.15 mol F. In solution each Al^{3+} atom is nominally surrounded by 6 waters of hydration. If one water of hydration is replaced by a F^- atom this would correspond to an F:Al ratio of 0.16 mol F/mol Al. While this research did not rigorously investigate the mechanism of F removal by $\text{Al}(\text{OH})_3$ precipitation, the similarity of the observed the F:Al ratio to substitution of 1 molecule of hydration and the lack of pH dependence may explain the removal mechanism.

Kinetic Testing

In the first series of kinetic tests conducted with the Phipps & Bird jar tester samples were taken at intervals of 0, 1, 5, 30, and 1440 minutes. The results of these tests showed that no additional F after the first minute. This finding led to additional kinetic tests. Figure 8 shows the results of additional kinetic tests. These tests were performed using an initial dose of 7 mg/L of F added to tap water in a 60 mL syringe and buffer (NaOH) and a dose of 30 mg/L Aluminum added at time zero. The syringe was then shaken and filtered at time intervals up to one minute to see if additional F is removed over time. The results indicate that no additional F is removed after approximately 20 s.

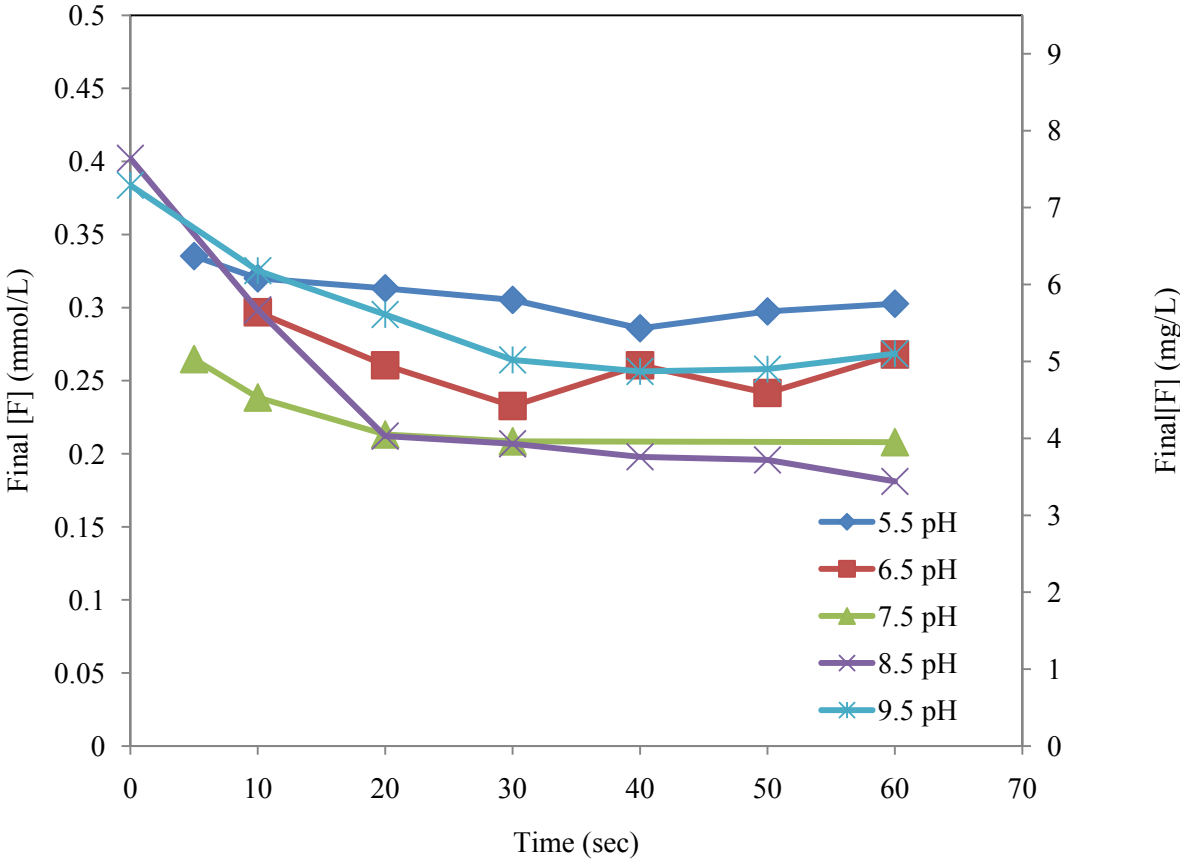


Figure 8. Kinetic Tests performed in 60 mL syringe, Fluoride Removal by Aluminum Sulfate, Final Fluoride Concentration (mg/L) versus Time (sec) at five pH levels with an Al dose of 30 mg/L

Syringe tests in which Al was added to an F-containing solution and immediately filtered through a 0.45 μm filter were used to investigate F removal over shorter times. While the syringe kinetic tests were done to see if any additional F is removed over time, blender tests were done primarily to see if additional F is removed with the same Al dosage used in the jar tests because of the higher G value of the blender. Blender tests performed even better than the jar tests, with a 1.5 mg/L reduction in F for every 10 mg/L Al added (the jar tests had a 1 mg/L F reduction for every 10 mg/L Al added). Figure 8 shows the final F concentration over time. The blender tests shown in figure 9 were only performed with an Al dose of 30 mg/L, but samples were collected at time intervals of 0 seconds, 30 seconds, and 5 minutes.

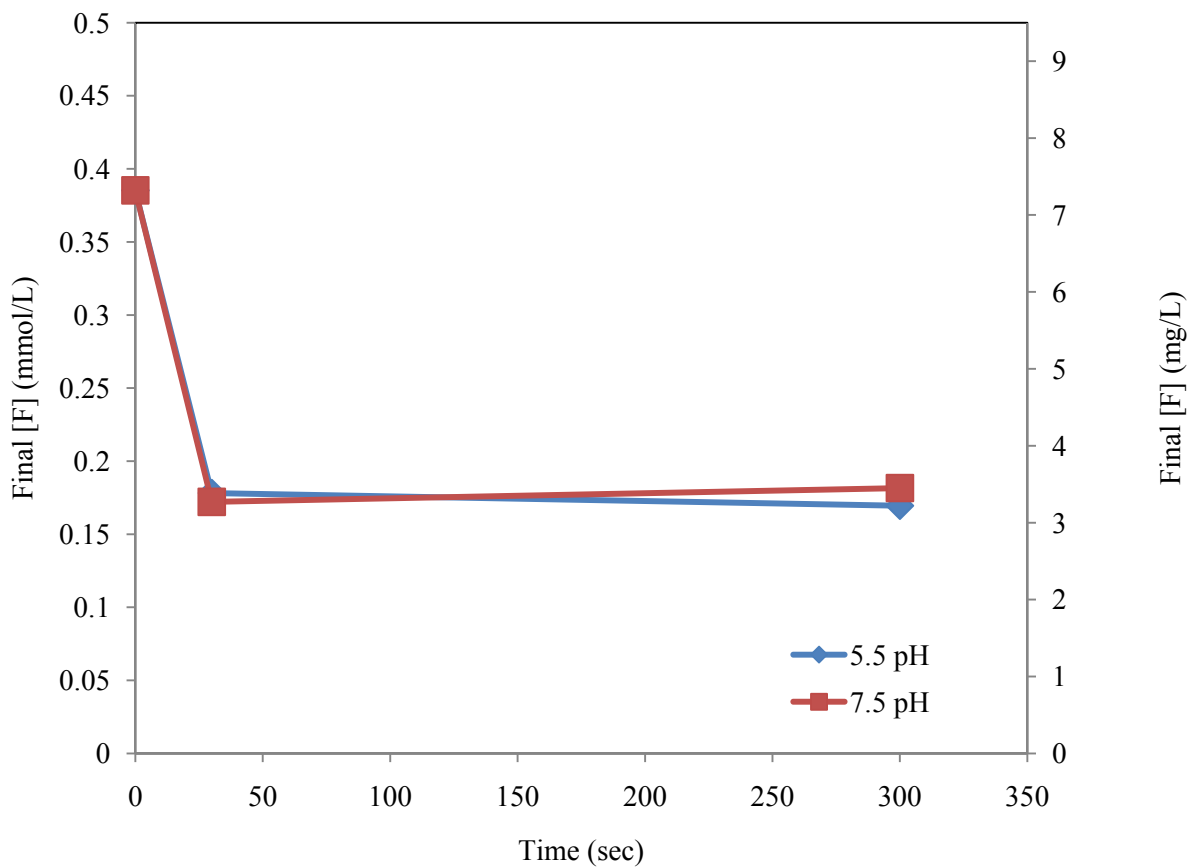


Figure 9. Results of F removal by violent mixing in blender Tests at an Al dose of 30 mg/L. Mixing intensity, or G value, has been shown to effect floc growth, size, and shape (Šulc, 2010). The work done for this research shows that mixing intensity also effects percent removal of F. The higher the mixing intensity the more F is removed.

Adsorption Testing

At time zero the tap water had 0.27 mg/L F and after five minutes of floc growth and five minutes with the 7 mg/L added fluoride the F level was 5.32 mg/L, therefore 1.95 mg/L F was removed. The tests allowing 10 minutes and 15 minutes of floc growth had similar removal (1.94 mg/L removal with floc allowed to grow for 10 minutes and 1.09 mg/L F removal with floc allowed to grow for 15 minutes) Typical jar tests at all pH levels yielded 3 mg/L F removal using 30 mg/L aluminum. Typical “high-G-value” blender tests at a pH of 7.0 yielded 4.1 mg/L F removal using 30 mg/L aluminum. These results show that F removal can be achieved by adsorption onto aluminum hydroxide floc, but that the removal is much less than introducing aluminum while mixing high-F-laden tap water at a high G value. This leads to understanding the complexation between F and aluminum as coprecipitation although there is a lack of a simple stoichiometric correlation between the added aluminum and the obtained fluoride removal (Dahi, 1995).

Aluminum Residuals

After coagulation and filtration was achieved aluminum residual at aluminum doses of 0, 1, 3, 5, 7, 10, 20, 30, 40, 50 mg/L at pH levels of 5.5, 6.5, 7.5, 8.5, and 9.5 was determined. Aluminum residual is important because the National Secondary Drinking Water Regulations have set a secondary standard (upper limit) of .2 mg/L due to potential neurological problems. Since there was no pH dependence for F removal it was expected that there would be no pH dependence for the residual, but some pH dependence was shown. The results are shown in figures 10 and 11.

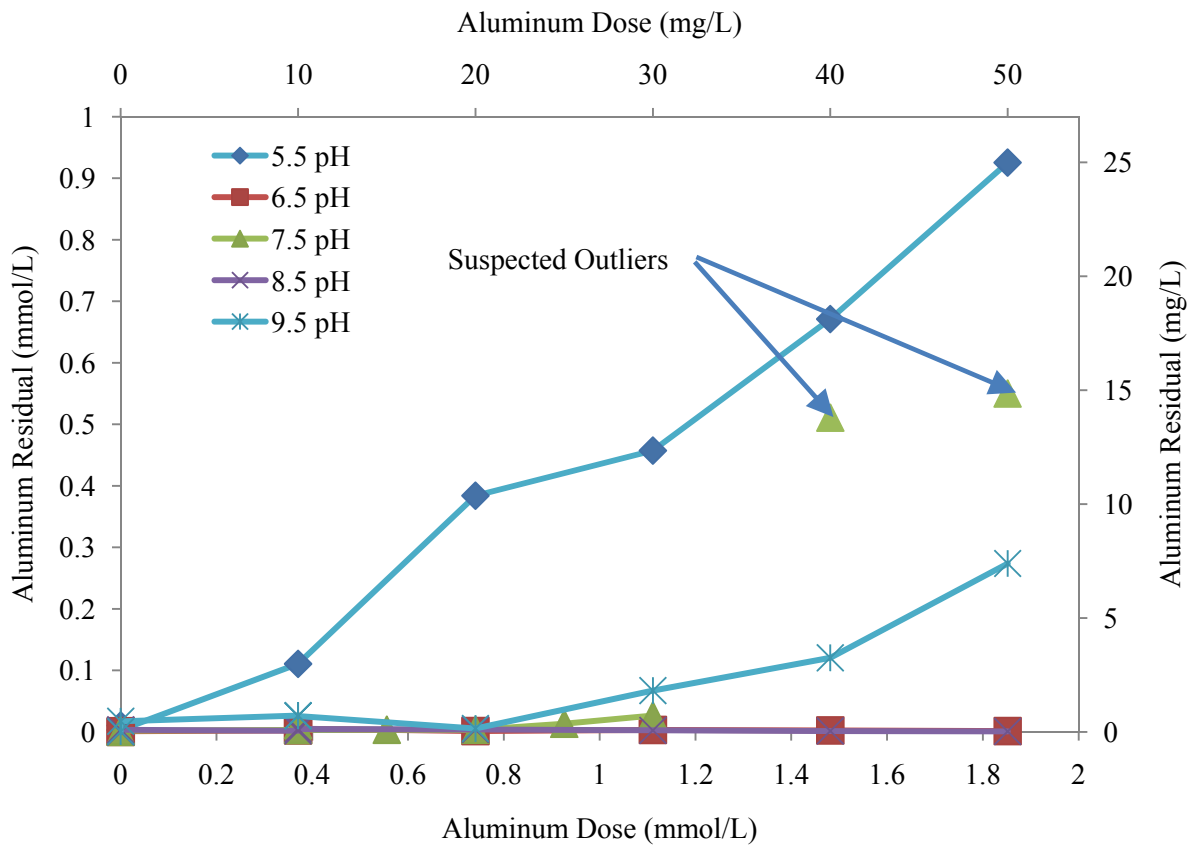


Figure 10. Aluminum Residual from Jar Tests, Fluoride Removal by Aluminum Sulfate, Aluminum Dose (mg/L) vs. Final Aluminum Concentration (mg/L) at five pH levels.

At the aluminum dose desired for removal (30 mg/L) the aluminum residual at both pH 5.5 and pH 9.5 are significantly higher than the secondary standard. At a pH of 9.5 the Al residual is 1.8 mg/L and at a pH of 5.5 aluminum residual is 12.4 mg/L. These individual points are part of a trend where aluminum residual increases as aluminum dose increased for pHs 5.5 and 9.5. They are consistent with the predicted increases in $Al(OH)_3$ solubility below pH 6 and above pH 9 (Table 1). Only pH 6.5 and pH 8.5 meet the secondary standard for aluminum at aluminum doses of 10, 20, 30, 40, and 50 mg/L. This data indicates that this technology may be feasible without an additional step for aluminum removal in the treated water stream at natural water pHs between 6.5 and 8.5. Future work should include aluminum residual monitoring.

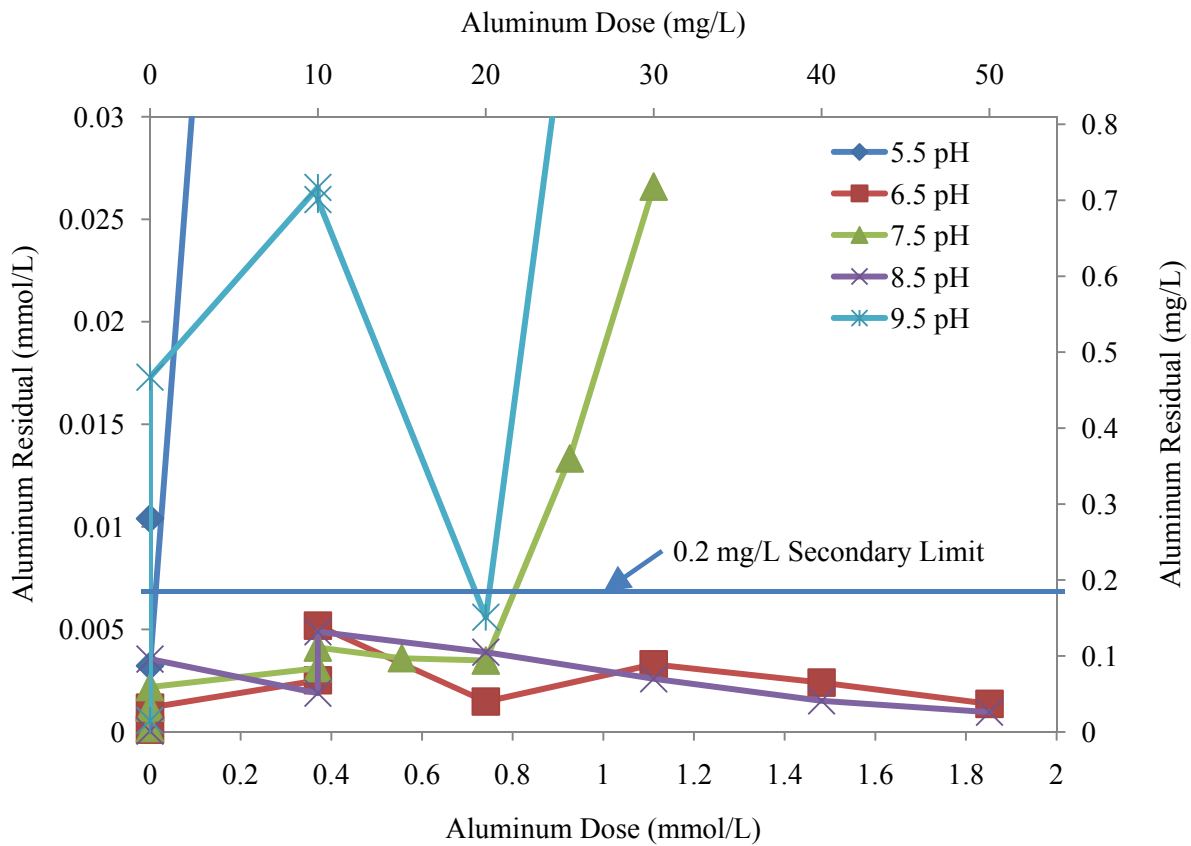


Figure 11. Selected Aluminum Residual results from Jar Tests, Aluminum Dose (mg/L) vs. Final Aluminum Concentration (mg/L) at five pH levels.

Ferric Chloride Testing

There have been reports which suggest that $\text{Fe}(\text{OH})_3$ may remove F (Tang, 2009). Jar tests were done to test F removal by $\text{Fe}(\text{OH})_3$ at Fe^{3+} concentrations of 0, 10, and 50 mg/L iron (using Ferric Chloride) at pH levels of 5.5, 7.5, and 9.5. At each of these pH levels and dosages F removal was found, but less so than with $\text{Al}(\text{OH})_3$. For each 1 mol of Fe added .08 mol of F was removed (.15 mol of F is removed with each 1 mol of Al added).

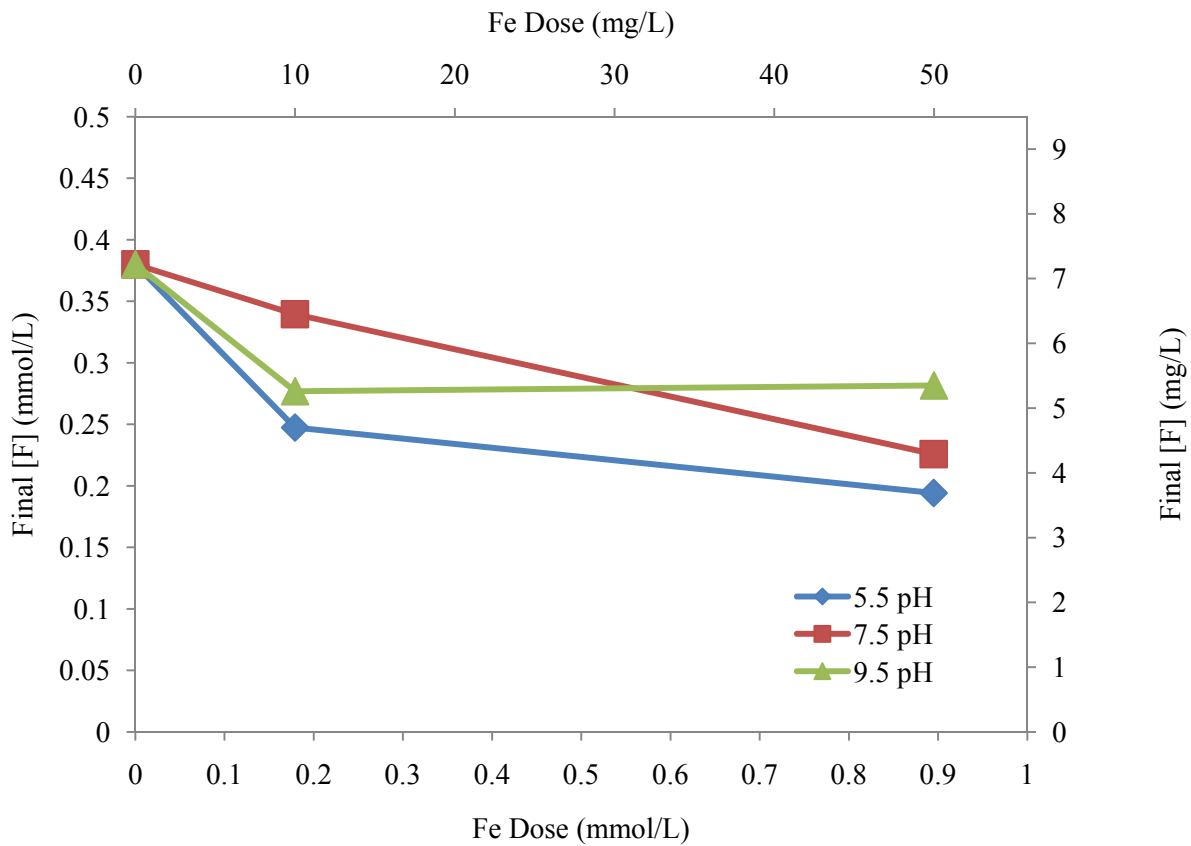


Figure 12. Results of jar test experiments to measure F removal by Fe(OH)₃ precipitation.

Pilot Scale System Results

The regression analyses shown in figure 13 approximately .78 mg/L F is reduced by every 10 mg/L Al added. Jar Tests showed a relationship of 1 mg/L F reduced by every 10 mg/L Al added and blender tests showed a relationship of 1.5 mg/L F reduced by every 10 mg/L Al added. Therefore, addition of Al in combination with ultrafiltration is a viable technology for the removal of F.

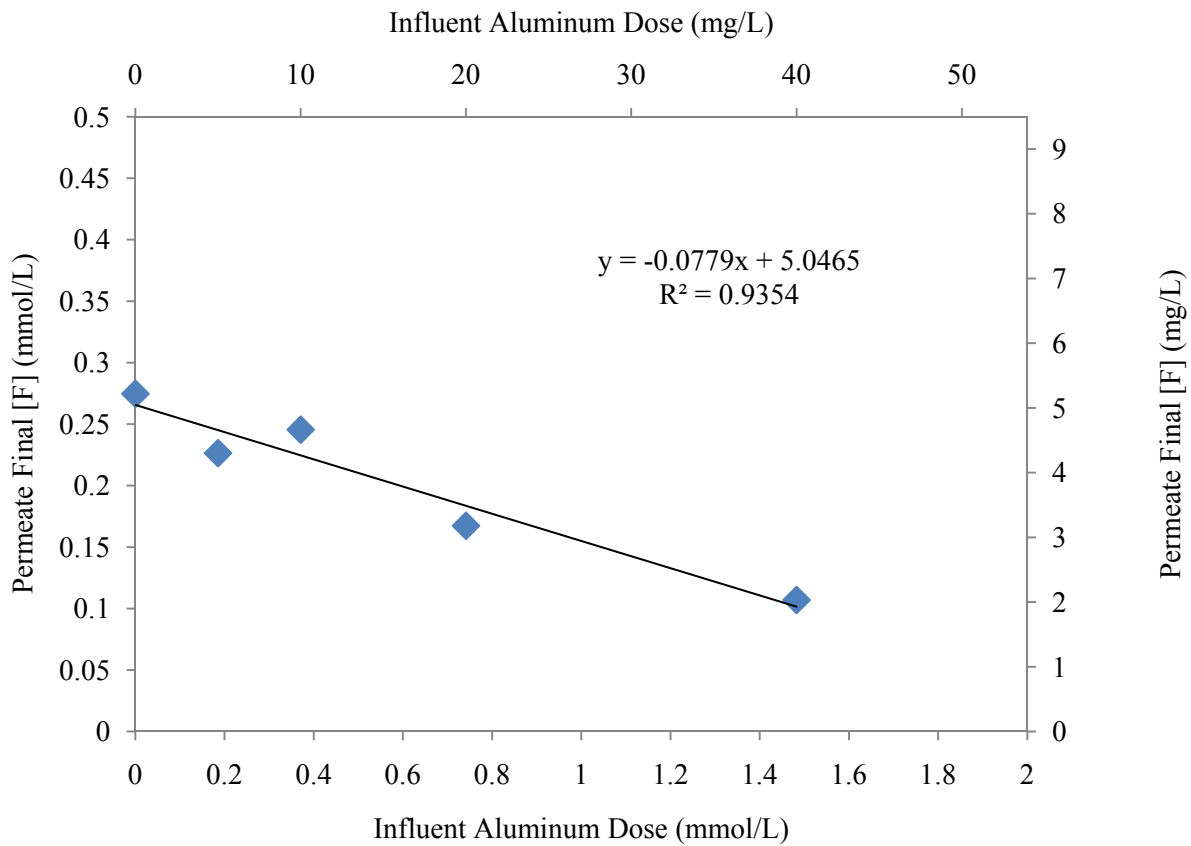


Figure 13. Selected Permeate Stream Results from Pilot Unit Operation June 2 through June 6, 2011 at San Ysidro (New Mexico) Water Treatment Facility, specifically the grab samples that occurred the latest in the duration of that specific concentration dosage.

Pilot Scale System Behavior Over Time

The Al-CMF pilot treatment system was tested at the Village of San Ysidro, NM over a period of two weeks. (Summarize what was tested). Several time dependent parameters were observed in the pilot scale system:

- The recycle flow heats up over time due to the heat of the pump motor,
- Aluminum accumulates in the recycle,
- The concentrate flowrate is reduced over time,
- The system removes more F until steady state is reached, and
- Temperature Compensated Specific Flux decreases over time.

Figure 14 shows the temperature increasing over time. A “steady-state” condition for temperature was not reached on June 15, 2011. This day had the longest uninterrupted run of the system.

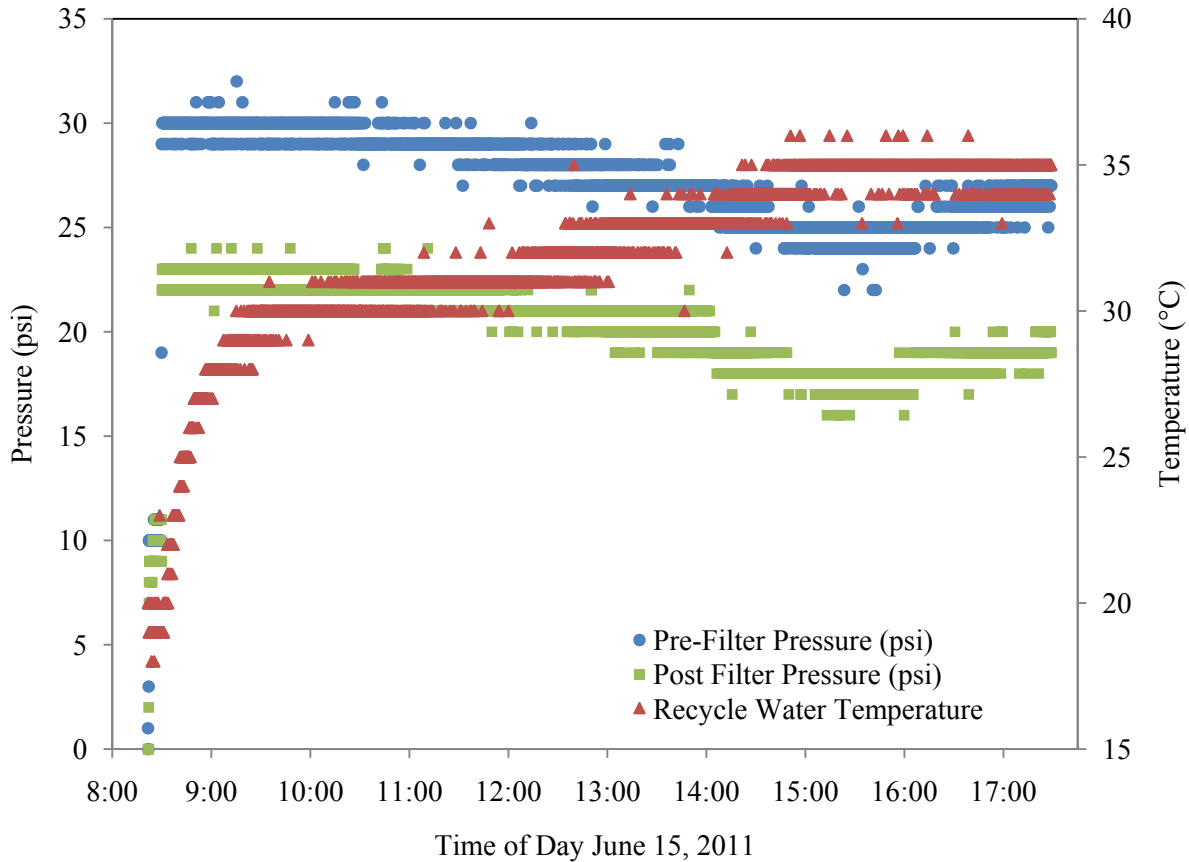


Figure 14. PLC Pre- and Post-Filter pressure (psi) and Recycle Stream Temperature plotted over time on June 15, 2011 at the Pilot Scale System at San Ysidro (New Mexico) Water Treatment Facility

$\text{Al}(\text{OH})_3$ accumulates in the recycle of the unit. At 12:30 PM on June 15, 2011 the pilot unit was operating with an aluminum dose of 40 mg/L, a total influent flow rate of 5.0 mL/s, permeate flow rate of 4.8 mL/s and concentrate flow rate of 0.2 mL/s. These are typical operational values for June 15, 2011. The Al in the recycle was calculated by performing a mass balance, assuming there is no residual aluminum in the permeate. The concentration of Al in the recycle is slightly greater than 1000 mg/L at 95% feed water recovery.

Al waste sludge from the concentrate will require proper disposal in a full scale facility. At San Ysidro the $\text{Al}(\text{OH})_3$ sludge was disposed of in a lined lagoon which receives sludge from the Village's water treatment plant. This sludge consists of $\text{Al}(\text{OH})_3$ precipitate and sediment.

In the pilot testing the concentrate flowrate decreases with time because of solids accumulation near the concentrate stream valve. In a full scale plant an automatic valve might be opened periodically to flush accumulated solids from the system to prevent plugging of the valve. . As the concentrate flow rate decreases, the recovery increases. Recovery on June 15, 2011 is shown in figure 15. By the end of the day the waste flow was immeasurable with the field tools on hand, therefore the last point shows 100% recovery.

It takes a short period of time for the pilot treatment system to approach steady state operation. After a certain time interval F removal is approximately constant as shown in figure 16. This figure indicates F removal lacks dependence on temperature, pressures, recovery, or TCSF.

Koch Membrane Systems recommends that the membrane be cleaned when the specific flux decreases to 70% of design flux. The Temperature Compensated Specific Flux (TCSF) was calculated based on data gathered during a clean membrane run. Figure 17 shows a reduction in TCSF over the course of one day. Al was dosed at 40 mg/L from 9:30 AM to 5:30 PM. It is believed that the first measurement of specific flux may not be valid as the system was just started and pressures and flows were becoming stabilized. If this point is omitted, the specific flux decreased by about 30% over a period of nearly eight hours. The specific flux appears to have stabilized in the last two hours, perhaps as a result of equilibration of a filter cake on the membrane surface that is continuously removed by fluid shear stresses from the cross flow velocities.

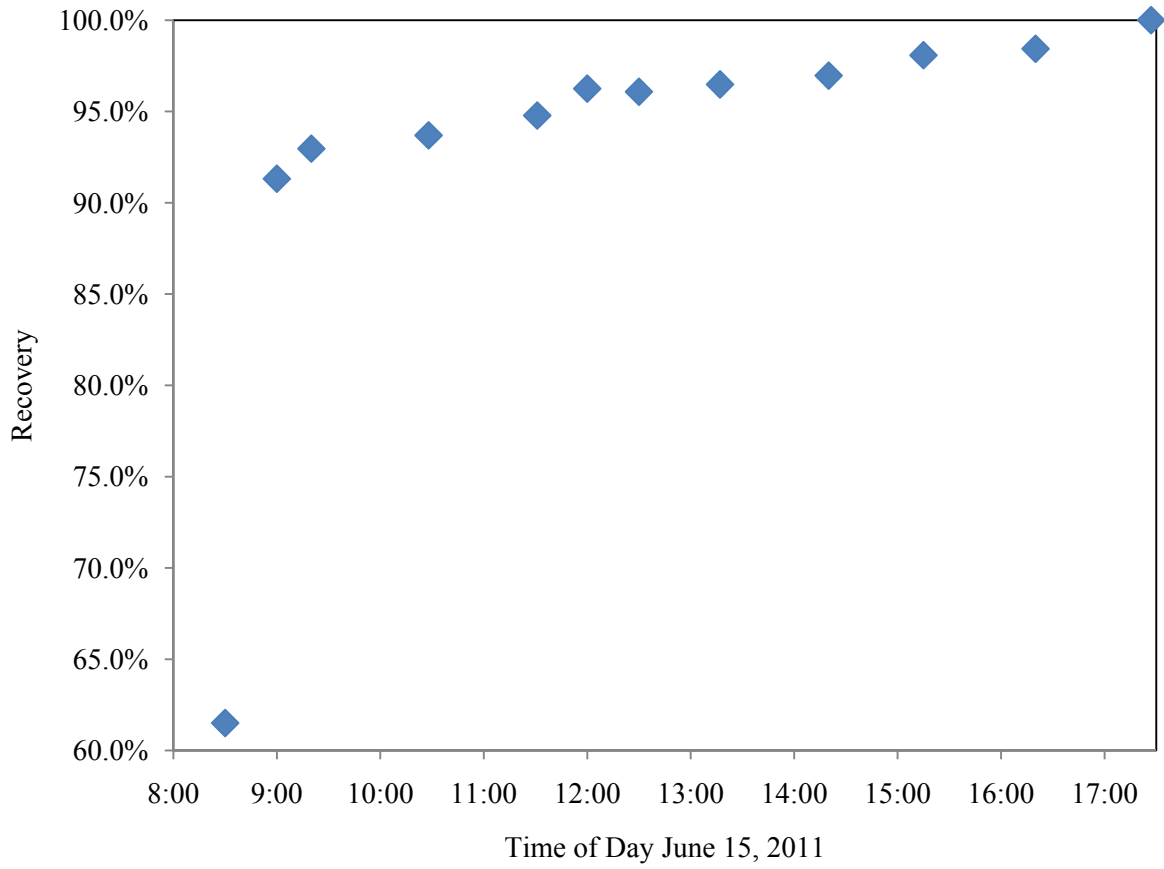


Figure 15. Recovery from Pilot Scale System Operation June 15, 2011 at San Ysidro (New Mexico) Water Treatment Facility

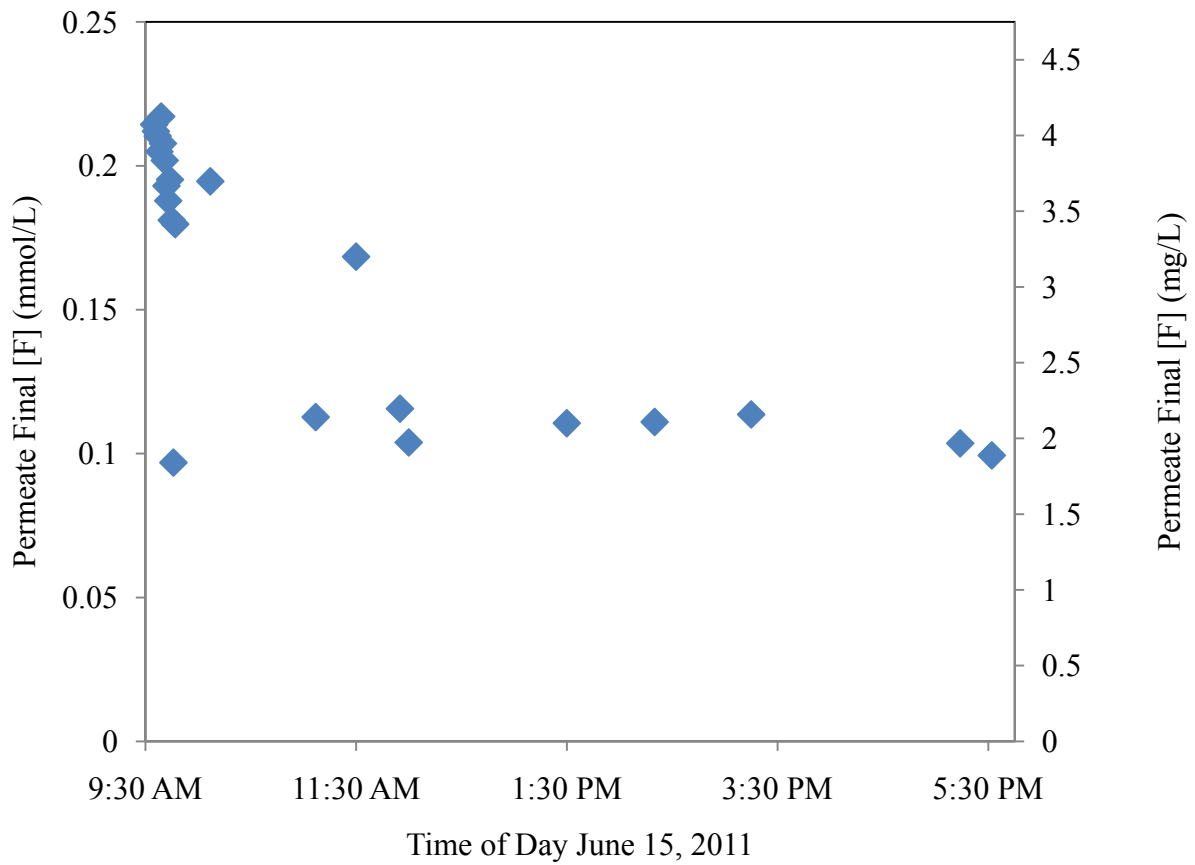


Figure 16. F reduction over time in the Pilot Scale System on June 15, 2011 at San Ysidro (New Mexico) Water Treatment Facility with an Al dose of 40 mg/L

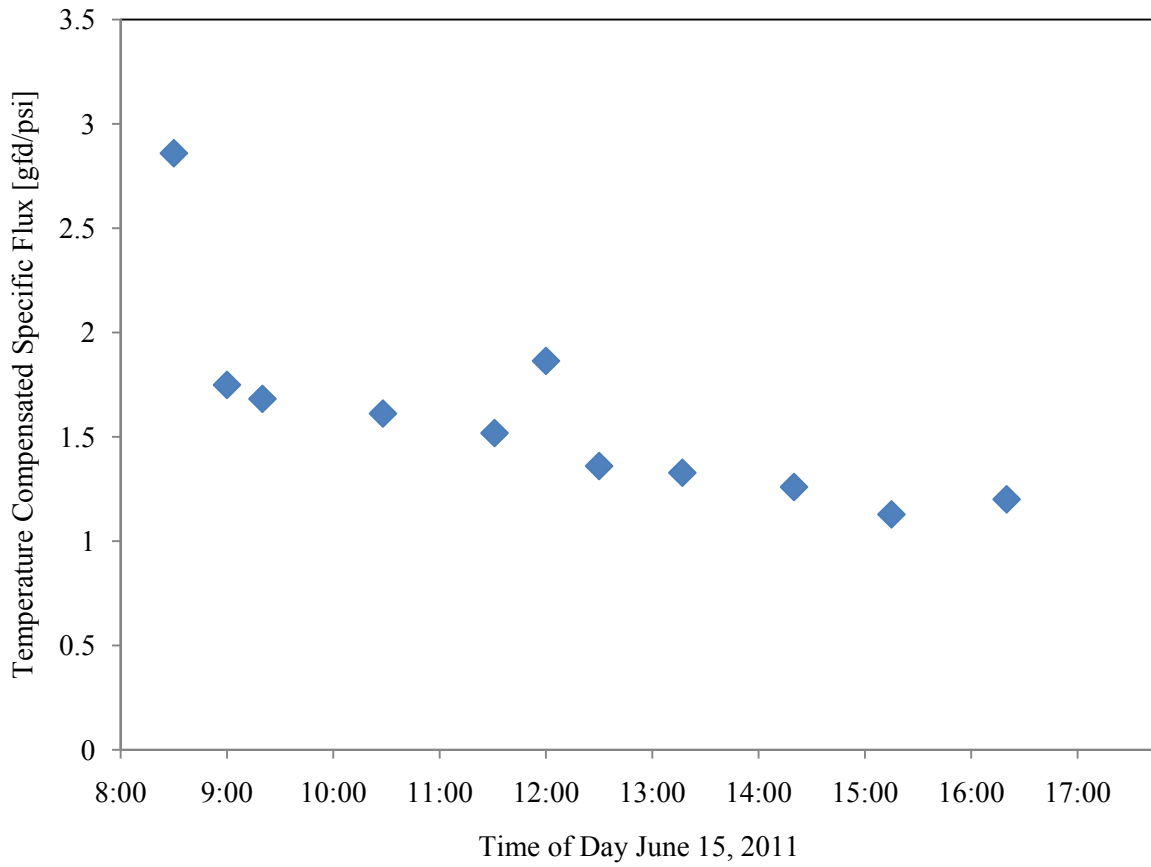


Figure 17. Reduction of temperature compensated specific flux over time in the Pilot Scale System on June 15, 2011 at San Ysidro (New Mexico) Water Treatment Facility

Chapter 5 Summary and Conclusions

The concept of F removal by $\text{Al}(\text{OH})_3$ precipitation is not new, however, combining this precipitation with membrane filtration for the specific purpose of achieving selective F removal has not been previously studied. This study found that this process, referred to as Aluminum Coagulation and Membrane Filtration (Al-CMF) can effectively remove F from drinking water.

A series of laboratory studies found that F removal by the Al-CMF process was independent of pH over the range of 5.5 to 9.5. This is in notable contrast to F removal by activated alumina (Al_2O_3) which is only effective below about pH 7. Further, the lab studies found that F removal predominantly occurs through a co-precipitation process not adsorption. Because the Al precipitation reaction is very rapid, F removal was found to depend on mixing; very high mixing intensities improved removal presumably by increasing dispersal of the Al^{3+} ions through the solution before the precipitation reaction occurred. The lab studies found that approximately 1 mg/L of F was removed for every 10 mg/L of Al added.

A 0.3 gal/min pilot plant was built and operated to test the Al-CMF process. A Koch blah-blah-blah ultrafiltration membrane was used. Mixing was provided by introducing alum and feed water immediately upstream from a recirculation pump. The pilot plant was tested over a period of two weeks. Fluoride removal was measured as a function of feed water recovery and Al dose. Feed water recoveries ranged from 50% to greater than 98%. Fluoride removal was not found to depend on recovery. The field testing found that 0.8 mg/L of F was removed for every 10 mg/L of Al, slightly less than found in the laboratory experiments. The results are summarized in table 8.

Fouling of the membrane was noted in the pilot testing. It was possibly due to inadequate flowrate across the membrane. Future work should include a recycle pump that can produce a higher flowrate.

Table 8. Comparison of laboratory and pilot treatment system fluoride removal at an Al dose of 30 mg/L.

Method	Initial [F]		Final[F]		Amount of F Removed		% F Removed
	mg/L	mmol/L	mg/L	mmol/L	mg/L	mmol/L	
Jar	7.90	0.44	4.26	0.24	3.64	0.20	46%
Blender ¹	7.32	0.41	3.27	0.18	4.05	0.23	55%
Syringe	7.64	0.42	3.95	0.22	3.69	0.21	48%
Pilot ²	5.22	0.29	2.60	0.14	2.61	0.15	50%

1. Average final [F] between two results
2. Final [F] interpolated between 20 mg/L and 40 mg/L

Since the technology is feasible, additional work should include scaling the system up and seeing how low the recovery can be adjusted while still getting optimal F removal and an acceptable decrease in flux over time. The system should also be tested in different source waters, with a full suite of water analysis done so that one can see if additional constituents hinder or aid in F removal and/or are also removed by the system. The system should also be tested at different points within a treatment train answering the question: “Is this a polishing process or can it be used as a stand-alone treatment process?”

For public water systems and small communities in New Mexico struggling to meet the MCL of F this technology should be considered.

References

- Albertus, J., H. Bregnhøj, and M. Kongpun. 3rd International Workshop on Fluorosis Prevention and Defluoridation of Water. "Bone Char Quality and Defluoridation Capacity in Contact Precipitation" 1999 61-72. DUCED-I&UA
- Agarwal, M., K. Rai, R. Shrivastav and S. Dass "Defluoridation of water using amended clay." *Journal of Cleaner Production* 11, 4, Jun 2003: 439-444
- Amor, Zakia, Suad Malki, Mohamed Taky, Bernard Bariou, Nabil Mameri, and Azzeddine Elmidaoui, Optimization of fluoride removal from brackish water by electrodialysis, *Desalination*, Volume 120, Issue 3, 22 Dec 1998, Pages 263-271.
- Angers, Jim. "What are the Best Methods for Fluoride Removal?" *Opflow*. 27:10 (2001) 6-7.
- ASTM Standard D2035-08, "Standard Practice for Coagulation-Flocculation Jar Test of Water," ASTM International, 2008.
- AWWA, APHA, and WEF. 1992. *Standard Methods for the Examination of Water and Wastewater*, 18th ed.
- Ayoob, S., A.K. Gupta, and Venugopal T. Bhat. "A Conceptual Overview on Sustainable Technologies for the Defluoridation of Drinking Water." *Critical Reviews in Environmental Science and Technology*. 38.6 (2008): 401-70.
- Baffrey, Robert. "Development of program implementation, evaluation, and selection tools for household water treatment and safe storage systems in developing countries." MA thesis. Massachusetts Institute of Technology, 2005.
- Banu, R.J., K.U. Do, and I.T. Yeom. "Phosphorus removal in low alkalinity secondary effluent using alum." *International Journal of Environmental Science and Technology*. 5.1 (2008): 93-98.
- Bårdsen, A. and K. Bjorvatn. "Fluoride Sorption Isotherm on Fired Clay." *1st International Workshop on Fluorosis Prevention and Defluoridation of Water. Int. Soc. Fluoride Res.* (1995): 56-59.
- Baruth, E., Edward et.al. *Water Treatment Plant Design*. New York: McGraw-Hill, 2005.
- Bishop, P. L. and G. Sansoucy. "Fluoride Removal from Drinking Water by Fluidized Activated Alumina Adsorption." *Journal American Waterworks Association*. 70 (1978) 554-559.

- Biswas, Krishna, Sanat Kumar Saha and Uday Chand Ghosh. "Adsorption of Fluoride from Aqueous Solution by a Synthetic Iron(III)–Aluminum(III) Mixed Oxide." Industrial & Engineering Chemistry Research 46:16 (2007): 5346-5356.
- Bitner, Kelly, Bruce Thomson, and Joe Chwirka. "The Cost of Compliance with a New Drinking Water Standard for Arsenic in New Mexico." *New Mexico Geology* Feb (2001): 10-12.
- Boysen, Robert E., and Richard C. Chmielewski. Fouling Control for Polymeric Membrane Processes: Proceedings of the 2008 Integrated Petroleum Environmental Consortium at the University of Tulsa
- "Chapter 05 Clarification." *Water & Process Technologies: Water, Wastewater and Process Systems Solutions*. Web. 16 Mar. 2011.
<http://www.gewater.com/handbook/ext_treatment/ch_5_clarification.jsp>.
- Chol, Won-Wook and Kenneth Y. Chen. "The Removal of Fluoride from Waters by Adsorption." Journal American Water Works Association. 71:10 (1979) 562-570.
- Chu, YongBao, BaoYu Gao, QinYan Yue, and Yan Wang. "Investigation of dynamic processing on aluminum floc aggregation: Cyclic shearing recovery and effect of sulfate ion." *Science in China Series B: Chemistry*. 51.4 (2008): 386-392.
- Chwirka, Joseph D., Bruce Thomson, and John M., III Stomp. "Removing Arsenic from Groundwater." *Journal of the American Water Works Association* 92.3 (2000): 79-88.
- Chwirka, Joseph D., Christian Colvin, Juan D. Gomez, and Paul A. Mueller. "Arsenic Removal from Drinking Water Using the Coagulation/microfiltration Process." *Journal of the American Water Works Association* 96.3 (2004): 106-14. American Water Works Association. Web. 11 Mar. 2011.
- Corbillon, M.S., M.A. Olazabal, and J.M. Madariaga. "Potentiometric Study of Aluminum-Fluoride Complexation Equilibria and Definition of the Thermodynamic Model." *Journal of Solution Chemistry*. 37:4 (2008) 567-579.
- Dahi, E., H. Bregnhøj, and L. Orío. "Sorption Isotherms of Fluoride on Flocculated Alumina." *Proceedings of The 1st International Workshop on Fluorosis Prevention and Defluoridation of Water*. Tanzania, Ngurdoto. Dunedin: International Society for Fluoride Research, 1995. 44-48.

- David, W. et.al. *Water Treatment Principles and Design*. New York: John Wiley, 2005.
- Driscoll, W.S., Horowitz, H.S., Meyers, R.J., Heifetz, S.B., Kingman, A. and Zimmerman, E.R. 1983 Prevalence of dental caries and dental fluorosis in areas with optimal and above-optimal water fluoride concentrations. *Journal of the American Dental Association*, 107, 42–47.
- Eaton, Andrew D., Lenore S. Clesceri, Arnold E. Greenberg, and Mary Ann H. Franson. *Standard Methods for the Examination of Water and Wastewater*. Washington, DC: American Public Health Association, 1998.
- Elazhar, F., M. Tahaikt, A. Achatei, F. Elmidaouia, M. Taky, F. El Hannouni, I. Laaziz, S.Jariri, M. El Amrani and A. Elmidaoui. “Economical evaluation of the fluoride removal by nanofiltration.” *Desalination* 249, 1, Nov. 2009: 154-157.
- Engineering & contracting, Publisher Engineering and Contracting Pub. Co., 1920, Original from Princeton University
- Fawell, J., K. Bailey, J. Chilton, E. Dahi, L. Fewtrell, and Y. Magara. "Fluoride in Drinking-water." *World Health Organization*. 2006.
- Feld, Christina M., Darren A. Lytle, and Michael R. Schock. “The Effect of Fluoride on Conventional Drinking Water Treatment using Aluminum Sulfate.” American Water Works Association, Water Quality Technology Conference Proceedings. (2000)
- Frost, Floyd J., Kristine Tollestrup, Gunther F. Craun, Joseph Chwirka, John Stomp, and Robert Raucher. "Evaluation of Costs and Benefits of a Lower Arsenic MCL." *Journal of the American Water Works Association* 94.3 (2002): 71-80.
- Gensemer and Playle, 1999 R.W. Gensemer and R.C. Playle, The bioavailability and toxicity of aluminum in aquatic environments, *Crit. Rev. Environ. Sci. Technol.* 29 (1999), pp. 315–450.
- George, Suja, Prabhat Pandit, Akhilendra Bhushan Gupta, Madhu Agarwal. “Modeling and Simulation studies for Aluminum-Fluoride Interactions in Nalgonda Defluoridation Process.” *Chemical Product and Process Modeling* 2009: Vol. 4, Issue 1, Article 27.
- Guidelines for Drinking-water Quality*. 1st ed. 1. Geneva: WHO Press, 2008.

- Hamdi, Noureddine, and Ezzeddine Srasra. "Retention of Fluoride from Industrial Acidic wastewater and NaF solution by three Tunisian Clayey soils." *Fluoride*. 42.1 (2009): 39-45.
- Harvey, D. *Modern Analytical Chemistry*. McGraw-Hill, 2000.
- Hendricks, David W. *Water Treatment Unit Processes: Physical and Chemical*. Boca Raton, FL: CRC/Taylor & Francis, 2006.
- Hichour, Mustapha, Françoise Persin, Jacqueline Sandeaux. "Fluoride removal from waters by Donnan dialysis." *Separation and Purification Technology* 18, 1, Jan 2000: 1-11
- Hu, Chengzhi, Huijuan Liu, Jiuhui Qu, Dongsheng Wang, and Jia Ru. "Coagulation Behavior of Aluminum Salts in Eutrophic Water: Significance of Al₁₃ Species and pH Control." *Environmental Science Technology*. 40. (2006): 325-331.
- Hu, C.Y., S.L. Lo, and W.H. Kuan. "Effects of the molar ratio of hydroxide and fluoride to Al(III) on fluoride removal by coagulation and electrocoagulation." *Journal of Colloid and Interface Science*. 283:2 (2005): 472-476.
- Hua, Ching-Yao, Shang-Lien Loa, and Wen-Hui Kuan. "Simulation the kinetics of fluoride removal by electrocoagulation (EC) process using aluminum electrodes." *Journal of Hazardous Materials*. 145 (2007): 180–185.
- Islama, M., and R.K. Patel. "Evaluation of removal efficiency of fluoride from aqueous solution using quick lime." *Journal of Hazardous Materials* 143, 1-2, (2007): 303-310.
- Johnston, Richard, Han Heijnen, and Peter Wurzel. "Chapter 6: Safe Water Technology." World Health Organization. 31 Jan 2001. Web. 24 Sep 2010.
- Johnson, Sissy. "Concentrations levels of fluoride in bottled drinking water and filtered water using home filtration systems." MA thesis. West Virginia University, 2000.
- Kadlec, Robert and Scott Wallace. *Treatment Wetlands*. Chelsea: Lewis Publishers, 2009.
- Kaseva, M. E. "Optimization of regenerated bone char for fluoride removal in drinking water: a case study in Tanzania." *Journal of Water and Health* 1 Apr. 2006: 136-146.

- Ku, Young, and Hwei-Mei Chiou. "The Adsorption of Fluoride Ion from Aqueous Solution by Activated Alumina." Water, Air, and Soil Pollution. 133 (2002) 349-360.
- Lai, Y.D. and J.C. Liu. "Fluoride Removal from Water with Spent Catalyst." Separation Science and Technology. 31:20 (1996): 2791-2803.
- Lawler, D., J Kweon. *Integrated Water Treatment: Softening and Ultrafiltration*. IWA Publishing, 2004.
- Lestari, R.B., R. Herzog, A. Nahrstedt, T.C. Schmidt. "Insight in the coagulation and precipitation process in the Nalgonda technique for drinking water defluoridation." Instrumental Analytical Chemistry, Department of Chemistry University of Duisburg – Essen.
- Leyva, Ramos R., J. Ovalle-Turrubiartes, and M.A. Sanchez-Castillo. "Adsorption of fluoride from aqueous solution on aluminum-impregnated carbon" Carbon. 37:4 (1999): 609-617.
- Lounici, H., Addour, L., Belhocine, D., Grib, H., Nicolas, S., Bariou, B., Mameri, N. (1997) Study of a new Technique for Fluoride Removal from Water; Desalination vol.114 241-251.
- McCurdy, Kevin, Kenneth Carlson, and Dean Gregory. "Floc morphology and cyclic shearing recovery: comparison of alum and polyaluminum chloride coagulants." Water Research. 38. (2004): 486-494.
- McEwen, J. Brock. *Treatment process selection for particle removal*. Denver, CO: American Water Works Association, 1997.
- Miller, Frederic, Agnes Vandome, and John McBrewster. *Fluoride*. 2009-12, 2009.
- Montgomery, James M. *Water Treatment Principles and Design Book*. Wiley-Interscience, 1985.
- Murray, J.J. Appropriate Use of Fluorides for Human Health, World Health Organization, Geneva, 1986.
- Mustapha, Hichour, Françoise Persin, Jacqueline Sandeaux, Claude Cavach. "Fluoride removal from waters by Donnan dialysis." Separation and Purification Technology 18.1 (1999): 1-11.

- New Mexico Administrative Code Title 20 Chapter 7 Part 10 Environmental Protection, Wastewater and Water Supply Facilities, Drinking Water. New Mexico Statutes Annotated. 2002.
- Parthasarathy, N., J. Buffle and W. Haerdi. "Combined Use of Calcium Salts and Polymeric Aluminum Hydroxide for Defluoridation of Waste Waters" Water Research 20:4 (1986): 443-448.
- Piñón-Miramontes, Manuel, Raul G Bautista-Margulis, and Antonino Perez-Hernandez. "REMOVAL OF ARSENIC AND FLUORIDE FROM DRINKING WATER WITH CAKE ALUM AND A POLYMERIC ANIONIC FLOCCULENT." *Fluoride*. 36.2 (2003): 122-128.
- Public Health Service 1962 *Public Health Service drinking water standards – revised 1962*. Washington, DC. US Department of Health, Education and Welfare. PHS publication no. 956.
- Randtke, S.J., Frank DeNoyelles, Jr., David P. Young, Phillip E. Heck, Rowley R. Tedlock. A Critical Assessment of the Influence of Management Practices on Water Quality, Water Treatment, and Sport Fishing in Multipurpose Reservoirs in Kansas (1985)
- Randtke, S.J., Organic contaminant removal by coagulation and related process combinations, Journal American Waterworks Association. 80 (1988) (5), pp. 40–56.
- Rose, Maria. "Facts About Fluoride." Denver Water. Web. 14 Mar. 2011.
<<http://www.denverwater.org/WaterQuality/WaterSafety/Fluoride/>>.
- Rubel, Jr., Frederick and R. Dale Woosley. "The Removal of Excess Fluoride From Drinking Water by Activated Alumina." Journal American Water Works Association. 71 (1979): 45–49.
- Saxena, V.K., and Ahmed Shakeel. "Inferring the chemical parameters for the dissolution of fluoride in groundwater." *Environmental Geology* 43.6 (2003): 731-36.
- Sehn, Peter. "Fluoride removal with extra low energy reverse osmosis membranes: three years of large scale field experience in Finland." Desalination, 223, 1-3, Mar 2008: 73-84.

- Shen, Yun-Hwei. "Size distribution of aluminum hydroxide flocs in dilute aluminum (III) solutions." *Toxicological & Environmental Chemistry*. 69. (1999): 363-371.
- Sorg, Thomas J. and Gary S. Logsdon. "Treatment Technology to Meet the Interim Primary Drinking Water Regulations for Inorganics: Part 5." *Journal American Water Works Association*. 72:7 (1980): 411–420.
- South Africa. Department of Health. "Water Fluoridation-A Manual for water plant Operators" 2003. <http://www.doh.gov.za/docs/misc/fluoridation/chapter2.pdf>
- Spicer, Patrick T., Wolfgang Keller, and Sotiris E. Pratsinis. "The Effect of Impeller Type on Floc Size and Structure during Shear-Induced Flocculation." *Journal of Colloid and Interface Science*. 184. (1996):112–122.
- Steenbergen, Frank van, Redda Tekle Haimant, Aschalew Sidelil. "High Fluoride, Modest Fluorosis: Investigation in Drinking Water Supply in Halaba (SNPR, Ethiopia)." *Journal of Water Resource and Protection*, 2011, 3, 120-126.
- Sulc, Radek and Svacina, Ondrej. "Effect of Mixing Intensity onto Kinetics of Flock Growth in an Agitated Tank." *Journal of Chemical and Process Engineering* 31 (2010): 261-271.
- Tang Yulin, Xiaohong Guan, Jianmin Wang, Naiyun Gao, Martin R. McPhail and Charles C. Chusuei. "Fluoride adsorption onto granular ferric hydroxide: Effects of ionic strength, pH, surface loading, and major co-existing anions." *Journal of Hazardous Materials* 171,1-3, (2009): 774-779.
- Thomson, Bruce, Kerry Howe, and Joseph D. Chwirka. Development of A Fluoride Treatment Process for Small Communities in NM Scope of Work and Quality Assurance/Quality Control Plan. (2009).
- "Treatment of Aqueous Effluents for Fluoride Removal." *Tetra Chemicals Europe*. 2005. Tetra Technologies, Inc., Web. 10 Feb 2010.
- United States. Border Environment Cooperation Commission. *Water Treatment Improvements in Lordsburg, New Mexico*. 28 Oct. 2009
<<http://www.cocef.org/aproyectos/LordsburgPCDFINAL.pdf>>
- United States. Environmental Protection Agency. *Drinking Water Contaminants*. EPA 816-F-09-0004, National Service Center for Environmental Publications, 2009.
<<http://www.epa.gov/safewater/contaminants/index.html>>

- United States. Environmental Protection Agency. Point-of-Use Treatment of Drinking Water in San Ysidro, NM, Springfield: National Technical Information Service, 1990.
- United States. National Research Council Committee on Fluoride in Drinking Water. Fluoride in Drinking Water. Washington: National Academies Press, 2006.
- United States. Environmental Protection Agency. National Primary Drinking Water Regulations. Doc. No. 816-F-09-004. May 2009.
- United States. Environmental Protection Agency. Office of Water. National Primary Drinking Water Standards. Doc. No. 816-F-03-016. June 2003.
- Urbansky, Edward, Thomas G. Reeves, Darren A. Lytle, Christina M. Feld, and Michael R. Schock. "Fluoridation Chemistry: Equilibria and Kinetics of Fluoride and Fluoro-complexes." American Chemical Society. 41:2 (2001)
- Wang, Yan, Bao-Yu Gao, Xiu-Ming Zu, Wei-Ying Xu, and Gui-Ying Xu
"Characterization of floc size, strength and structure in various aluminum coagulants treatment." Journal of Colloid and Interface Science. 332. (2009): 354-359.
- "Water Quality Association." *Fluoride Recognized Treatment Techniques For Meeting Drinking Water Regulations For The Reduction Of Fluoride From Drinking Water Supplies Using Point-of-Use/Point-of-Entry Devices And Systems*. Mar 2005. Water Quality Association National Headquarters & Laboratory, Web. 07 Dec 2009. <<http://www.wqa.org/pdf/TechBulletins/TB-Fluoride.pdf>>.
- Zouboulis, A.I., and N.D. Tzoupanos. "Polyaluminum silicate chloride-A systematic study for the preparation and application of an efficient coagulant for water or wastewater treatment." Journal of Hazardous Materials. 162. (2009): 1379-89.
- Zouboulis, A.I., and N. Tzoupanos. "Alternative cost-effective preparation method of polyaluminum chloride (PAC) coagulant agent: Characterization and comparative application for water/wastewater treatment." Desalination. 250. (2010): 339-344.