Fluoride Floc Blanket, Spring 2016

August Longo, Pooja Desai, Katie Dao

May 21, 2016

Abstract

In many developing countries, high levels of fluoride in groundwater have been found to have chronic effects on bone health. Though some countries intentionally add fluoride to water in order to strengthen teeth, overexposure to fluoride has grown as a problem worldwide. The Fluoride team has been working to solve this very issue, by testing and developing a fluoride removal system fit for AguaClara plants in India and Honduras. In spring 2016, the Fluoride team built on the previous work of the Fluoride and Countercurrent Stacked Floc Blanket Reactor team to create a more optimal and efficient fluoride removal system. In the fall, the Fluoride team worked to understand the efficiency of fluoride removal using polyaluminum chloride (PACl) while the CSFBR team developed a reactor system to remove undesirable soluble particles. This semester, a new system was built consisting of a single floc blanket formed using PACl and clay. In the future, this system will be optimized by changing flow rates and dosages to better understand fluoride treatment and optimize AguaClara plants for fluoride removal.

Introduction

With 85% of its drinking water sourced from groundwater, India is the largest user of groundwater in the world. In stark contrast to tap water sources in the United States that are supplemented with fluoride, India's groundwater sources often display excess levels of fluoride - making villagers who rely on these well sources for water at a high risk of overexposure to fluoride (EPA, 2016a). The prevalence of dental fluorosis, an indicator of excessive fluoride concentrations, differs across India, but has been shown to range from 13-91% depending on the age group in question and the water source supplying the state or municipality (Arlappa et al., 2013).

Heavily fluorinated groundwater occurs in many areas of the world. To date, two fluoride belts have been identified with the first extending through parts of Africa, China, the Middle East, India and Sri Lanka, and the other extending from Turkey to Iraq (WHO, 2016).

Teams from previous semesters worked to analyze the efficiency of fluoride removal by using the coagulant polyaluminum chloride (PACl) when a 10 mg/L solution of fluoride was passed through a sand filter. This semester, a similar relationship between PACl and fluoride will be further researched by using a floc blanket reactor instead of the traditional sand filter. The floc blanker reactor forms flocs of PACl and clay that adsorb the fluoride from water, and the excess

flocs overflow into a floc weir as the floc blanket grows while purified water flows out of the top of the reactor. This reactor is modeled after the floc blanket, floc weir, and plate settlers in the sedimentation tank of an AguaClara water treatment plant. This semester, it is expected that the floc blanket reactor will be able to remove fluoride with a significantly higher efficiency than the sand filter from previous semesters and will also be able to run for extended periods of time because there will be no head loss to require backwash.

Literature Review

Fluoride Limitations and Hazards

Over-consumption of fluoride can lead to arthritis, dental fluorosis, crippling fluorosis, bone deformation and ligament calcification (Roholm, 1937). Fluoride can cause irritation through inhalation, digestion, and touch and can cause damage to both eyes and exposed skin (of Health, 2010).

Though there isn't an established "average" level of fluoride in India, the literature suggests that fluoride levels are seldom above 5 mg/L in groundwater. However, in the remote Karbi Anglong district of India, fluoride levels range from 5-23 mg/L causing severe anaemia, stiff joints, painful and restricted movement, mottled teeth and kidney failure (LeChevallier and Au, 2004).

According to the National Research Council (NRC), the maximum contaminant level (MCL) of fluoride in drinking water is 4 mg/L. However, a secondary limit of 2 mg/L has been established by the EPA to avoid potential cosmetic effects such as tooth and skin discoloration. The World Health Organization (WHO) established a safe upper limit of 1.5 mg/L to avoid all potential risks of fluoride consumption, with 0.8-1.2 mg/L providing a beneficial balance of fluoride and water by preventing tooth decay and strengthening the skeleton. The team will be striving towards the WHO guideline of 1.5 mg/L of fluoride this semester.

Polyaluminum Chloride and Fluoride Removal

One common type of water treatment consists of a series of coagulation, flocculation, and clarification. During coagulation, raw water is mixed with a positively charged coagulant (typically an aluminum salt or iron salt), altering or destabilizing any negatively charged particles or dissolved and colloidal contaminants (EPA, 2016b). Depending on the dose of coagulant, there are two methods of particle destabilization. The first, charge neutralization, occurs with a lower coagulant dose and happens as the negative colloids are attracted to the positively charged coagulant particles. The second method, sweep flocculation, requires a very high coagulant dose and transpires when the contaminants are caught by precipitates as they settle in the suspension (EPA, 2016b). The destabilized particles then proceed through flocculation, where additional mixing increase the rate of particle collision, forming larger precipitates. Following the formation of flocs, clarification removes the agglomerated particles through sedimentation or other removal processes (EPA, 2016b).

In recent years, polymerized forms of aluminum salts have been used increasingly to replace standard aluminum salt coagulants (Ingallinella and Pacini, 2001). Polyaluminum chloride, a partially hydrolyzed aluminum salt is one of the most widely used, as it delivers results similar to aluminum sulfate coupled

with a polyelectrolyte (Ingallinella and Pacini, 2001). The main advantages of using polyaluminum chloride instead of alum include a reduction in sulfates added to treated water, lower sludge production, reduced odor problems, and overall higher removal efficiency (Gebbie, 2001). In the Daylesford Water Filtration Plant, a dose of 45 mg/L of alum was required to produce potable water, while only 12 mg/L of PACl was necessary for the equivalent treatment (Gebbie, 2001). Additionally, PACl is advantageous in particulate removal because its hydrolyzed state allows for it to be less affected than typical aluminum salts when temperature conditions are inconsistent (EPA, 2016b).

Several techniques are currently in existence that use PACl to specifically reduce high fluoride levels. The Nalgonda technique is a popular fluoride removal method that involves a combination of rapid mixing, flocculation, sedimentation, filtration and disinfection, although actual fluoride removal is done through co-precipitation (Bailey and Fawell, 2004). The technique has traditionally been done using aluminum sulfate, but more recent experiments have proven that PACl can be an effective substitute (Kumbhar and Salkar, 2014). The Nalgonda technique typically utilizes a "batch filtration" method, where large quantities of water are treated in buckets. This technique does not utilize continuous flow, and requires a series of treatments to obtain decontaminated water for extended periods of time. For this reason, the Nalgonda technique has been largely introduced as a household treatment method, and has been introduced to various Indian villages, including those in Nalgonda and in the state of Telangana. It is also currently being studied at the pilot scale in Kenya, Senegal and Tanzania (Dahi et al., 1996). In addition to the restrictions implied by batch treatment, the Nalgonda method requires a high dosage of aluminum sulfate to aggregate with fluoride and precipitate. A study conducted by (Dahi et al., 1996) suggests that 13 g/L alum (1.2 g/L as Al) is needed for the Nalgonda method to effectively treat fluoride levels between 9 and 13 mg/L. Despite the high concentrations of coagulant, the fluoride residual in the test was still unable to meet the WHO safety guidelines of 1.5 mg/L of fluoride. The high dose of aluminum sulfate also leaves high sulfate residuals in the water, which causes taste and odor issues (Bailey and Fawell, 2004).

In regards to other filtration methods, a study by Inganiella achieved 33.3% removal of fluoride using a combination of a gravel prefilter and a sand rapid filter to capture granules of fluoride, PACl, NaClO and SO4H2 (Ingallinella and Pacini, 2001).

Floc Blankets

Floc blankets develop when vertical flow sedimentation tanks form a fluidized bed of particles that then facilitates particle removal by "increasing particle-particle interactions that lead to flocculation and filtration occurring in the floc blanket" (Hurst, 2010). The process of forming flocs requires both the precipitation of aluminum hydroxide from the coagulant and contact with raw water colloidal particles (Hurst, 2010). Once the combination of precipitation and mixing forms small particles, those new flocs collide to form larger, more porous flocs that can then be used for clarification (Hurst, 2010).

This floc blanket clarification is considered hindered settling, which is a form of sedimentation (Gregory et al., 1996). Sedimentation processes are characterized by the removal of suspended particles, e.g. flocs, sand and clay, from water. Removal is possible due to the differences in density between water and the sus-

pended particles, but is also dependent on the size of the suspended particles, water temperature, turbulence, stability of flow, bottom scour and flocculation (Sun, 2004). Floc blanket clarification, however, is primarily governed by upflow velocity of the water and by floc concentration (Gregory et al., 1996). The relationship between upflow velocity, concentration and water quality can be combined into the mass rate of settling, which is equal to the product of upflow velocity and concentration. This mass flux can then be used to establish proper combinations of velocities and concentrations to produce clear water, as within an appropriate range of mass fluxes, a distinct interface is established between clear water and a suspension of floc particles. At concentrations above that ideal mass flux range, the aggregation of flocs becomes thick enough that compression settling occurs. At concentrations below that appropriate range, flocs are not inhibited by other particles and a suspension with different settling velocities is formed (Gregory et al., 1996).

Floc blanket clarification is used to purify water in many ways around the world. In Taiwan, a process of pre-sedimentation, floc blanket clarification and sand filtration is used to reduce 100 NTU water down to potable levels (Lin et al., 2004). Floc blankets have also been used extensively to purify water of algae, protozoa and specific virus strains (LeChevallier and Au, 2004). Therefore, it is believed that the adaptability of this method in conjunction with the use of PACl will allow for effective fluoride removal.

Previous Work

In the fall of 2015, the main goal of the team was to create a sand filter system that removed fluoride using Polyaluminum Chloride (PACl). First, the team had to work with a fluoride probe in order to make an accurate calibration curve that was able to convert voltage readings from the probe into concentrations. After creating a curve using 9 standards ranging from 0 to 50 mg/L, the team realized that a curve needed to be recreated each day because of the variation produced by the fluoride probe on subsequent days. Standards of 20, 10 and 1 mg/L were used to make a daily calibration curve to calculate concentrations from voltages for that day (Dao et al., 2015).

The system was set up with a dosing system of PACl and fluoride that went into a rapid mix and then a sand filter. In the effluent of the sand filter, the team would take their measurements of concentrations to test the efficiency of the sand filter. For the majority of the semester, the team tested different concentrations of PACl for 10 mg/L of fluoride (which is towards the higher end of fluoride concentrations seen in India). PACl dosages of 20, 40, and 50 mg/L were tested and it was found that 50 mg/L of PACl brought the fluoride concentration down to below 1.5 mg/L; WHO's safety standard (Dao et al., 2015).

However, after looking into other factors of the filter, it was decided that a sand filter would not be efficient enough for the removal of fluoride. A sand filter provided adequate removal of the fluoride, and cheaper removal of fluoride per mg of PACl than any other process in literature. However, a key issue with the sand filter was the system run time. The sand filter became saturated with PACl and fluoride too quickly and the head loss built up very quickly.(Dao et al., 2015). Due to this, the system has to be backwashed too frequently to

be an effective method. Research was previously conducted on the relationship between the amount of coagulant added and head loss accumulation. Since 50 mg/L of PACl was necessary last semester to remove an appropriate amount of fluoride, the head loss accumulation for that dosage of PACl was very high which made the possibility of a fluoride sand filter unreasonable and not feasible (Zhi, 2016). As a result of this realization, this semester the team has decided to look into the floc blanket reactor.

Last semester, the countercurrent stacked floc blanket reactor team built a three part reactor system with the goal of determining whether contaminants such as fluoride and arsenic can be removed through multiple, PACl-loaded floc blanket systems. As a result of the novel nature of the experiment, the CSFBR team spent the majority of the fall semester developing the reactor set-up and the parameters of an efficient floc blanket. With the assistance of previous literature and trial and error, the team determined adequate floc blanket density and upflow velocity. The set up, flow rates and PACl and clay concentrations were adapted from the CSFBR team - but were tested and altered for the team's single reactor system.

Methods and Discussion

Apparatus Design

Design: The goal in the first iteration was to establish an apparatus and a method file that could begin running experiments as soon as possible, due to the time constraints of the EPA competition. Using much of the process that the Countercurrent Stacked Floc Blanket Reactor team developed in the Fall of 2015, a simplified system consisting of only one reactor was built and new flow rates and concentrations were established. These flow rates and concentrations of PACl were chosen based on both the fluoride and CSFBR research done in Fall 2015.

Experimental Apparatus

The apparatus was based on the work of the Countercurrent Stacked Floc Blanket Reactor (CSFBR) team from the Fall 2015 semester, but several significant changes were made. Though the CSFBR team's system consisted of three reactors in a countercurrent series, it was decided that a single reactor that was three times the length of a single CSFBR reactor, would be best for the Fluoride team. This was because the Fluoride team wanted to parallel the design of the CSFBR's team in regards to the floc blanket length. This made it easier to compare results between one reactor vs. three. The reactor design for dye can be used for fluoride because both substances exhibit an electronic charge. Since the PACl has a positive charge, it will attract the dye and clump with the dye to remove it. Similarly, fluoride has a negative charge so it can also be removed by the positively charged PACl. The reactor itself consisted of a vertical 2.54 cm (1 in) diameter clear PVC pipe with a branched floc weir 70 percent up the height of the total reactor for flocs to exit from. After the floc weir, the pipe bent with a PVC elbow at a 45 degree angle connected to another clear PVC pipe to create the tube settler for the clear water to exit from.

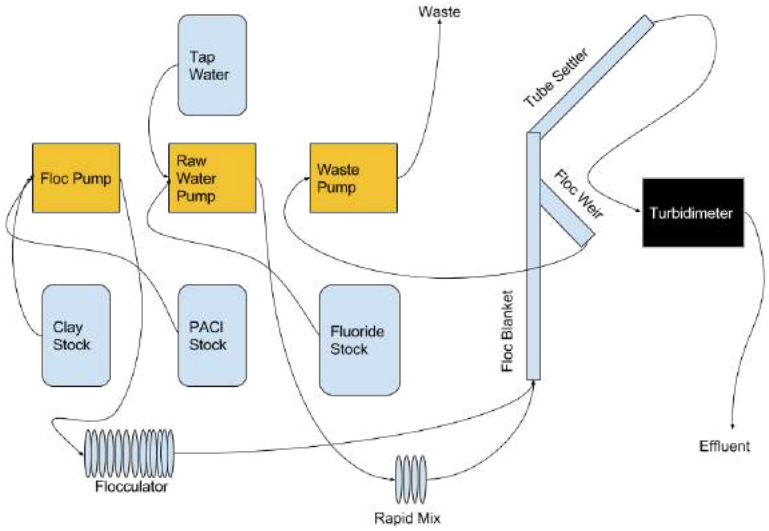


Figure 1: Schematic for the Floc Blanket Reactor. Water flows through sample fitting, and then is collected in a bucket for effluent disposal. The flow exiting the floc weir is pumped out into a red waste line.

The system began with diluted PACl (20 mg/L for the first iteration) and clay (400 mg/L). The PACl concentration of 20 mg/L was determined from last semester, as 50 mg/L was used to remove the appropriate amount of fluoride. Therefore, 20 mg/L seemed reasonable to start for a floc blanket. A concentration of 400 mg/L of clay was determined by a jar test. Using 20 mg/L of coagulant and adding different concentrations of clay from 1:1 to 40:1 clay to PACl ratio found that 20:1 gave the best flocs with the least amount of clay needed. Both substances were pumped with separate pump heads that were attached to the same pump. These two flows met at a t-fitting, before combining and entering a flocculator. In another pump, dilute fluoride and raw water were pumped through separate pump heads fitted to the same pump. The mixture was combined through a tee and then sent through a rapid mix. The PACl/clay mixture and the fluoride/water solution were then combined through a tee right before the flow entered the bottom of the reactor. An upflow velocity was maintained at 1 mm/s through manipulations of the volume of each component being dosed into the system. The upflow velocity of 1 mm/s was determined by using the value of 100 m/day that Matthew Hurst found to be ideal (Hurst, 2010). Hurst determined that 100 m/day was sufficient to produce turbulent flow, which leads to better floc collisions within the reactor (Hurst, 2010). Additionally, flow rates below 100 m/day were not sufficient to offset the particles' settling velocities, while flow rates above 100 m/day caused floc breakup and increased production of flocs that were too small to be settled out (Hurst, 2010). The following are examples of MathCad equations and code that was used to determine the flow rates and stock concentrations.

$$Q = v_{up} * A_{reactor} \tag{1}$$

$D_{reactor} := 1in$ Diameter of the reactor tube

$v_{up} := 1\frac{mm}{s}$ Upflow Velocity

$Q_{reactor} := \pi \cdot \left(\frac{D_{reactor}}{2}\right)^2 \cdot v_{up} = 30.402 \cdot \frac{mL}{min}$ Flow Rate Into Reactor

$Ratio_{water} := .8$ Percent of Flow going to Flocs and Water

$Ratio_{flocs} := 1 - Ratio_{water} = 0.2$

$Q_{water} := Ratio_{water} \cdot Q_{reactor} = 24.322 \cdot \frac{mL}{min}$ Raw Water Pump Flow Rate

$Q_{floc} := Ratio_{flocs} \cdot Q_{reactor} = 6.08 \cdot \frac{mL}{min}$ Total Flocs Pump Flow Rate

$Q_{pacl} := \frac{Q_{floc}}{2} = 3.04 \cdot \frac{mL}{min}$ Flow Rate of PACl pump head

$Q_{clay} := \frac{Q_{floc}}{2} = 3.04 \cdot \frac{mL}{min}$ Flow Rate of Clay pump head

Figure 2: MathCad Calculations for Flow Rates

$C_{reactorpac} := 10\frac{mg}{L}$ Concentration of PACl in the reactor

$C_{stockpacl} := 2Q_{reactor} \cdot \frac{C_{reactorpac}}{Q_{pacl}} = 200 \cdot \frac{mg}{L}$ Cocnentration of Stock PACl

$C_{stockclay} := 20 \cdot \frac{C_{stockpacl}}{2} = 2 \times 10^3 \frac{mg}{L}$ Concentration of Stock Clay

$C_{reactorclay} := C_{stockclay} \cdot \frac{Q_{clay}}{Q_{reactor}} = 200 \cdot \frac{mg}{L}$ Concentration of Clay in the reactor

Figure 3: MathCad Calculations for Concentrations

Using the set of dilution equations below, a clay concentration of 2400 mg/L and a PACl concentration of 200 mg/L were chosen for the stock solutions. The

clay was made by adding 36 grams of clay to 15 liters of water, and the PACl solution was made by adding 10 mL of 69.4 g/L PACl to 3.5 L of water.

$V_{StockPacl} := 3.5L$ Volume of Stock PACl

$C_{Labpacl} := 69400 \frac{mg}{L}$ Concentration of the PACl in the lab

$V_{Pacladded} := C_{stockpacl} \cdot \frac{V_{StockPacl}}{C_{Labpacl}} = 10.086\,mL$ Amount of PACl added to the volume of water

$V_{StockClay} := 15L$ Volume of Stock Clay

$M_{clay} := C_{stockclay} \cdot V_{StockClay} = 30\,gm$ Mass of Clay added to volume of water

Figure 4: MathCad Calculations for Dilutions

The flow then passed through the reactor, where fluoride was adsorbed to the flocs and treated water flowed out of the top of the reactor. The upflow velocity was chosen and maintained such that the flocs would be prevented from flowing out with the clean water and more importantly to maintain the floc blanket. Additionally, the tube settler was installed to catch and remove flocs that were too small to settle in the main column. Clean water exiting the top of the reactor was then passed through a turbidimeter to check the amount clay left in the flow.

Next, the water flowed through sample fitting that was used to check fluoride concentration. This mixture is then collected in a bucket below the apparatus, where it can be disposed of. The flow exiting the floc weir is pumped out into a red waste line.

Table 1: List of important parameters for reactor

Parameter	Symbol	Value
Residence Time	θ	4513 s
Hydraulic Gradient	G	75.2 s^{-1}
Gtheta	$G\theta$	13000
Upflow Velocity	v	1 mm/s
Capture Velocity	v_{cap}	0.12 mm/s
Total Flow Rate	Q	30 mL/min
Floc Flow Rate	Q_{Floc}	6 mL/min
Water Flow Rate	Q_{Water}	24 mL/min
Reactor Floc Blanket Length	L	24 inches
Flocculator tubing length	l	46 feet
Tube settler length	L_{TS}	14.75 inches

Important Apparatus Constraints:
The flocculator and the rapid mix are the only two tubings in the apparatus that use 0.635 cm (1/4") flexible tubing so they can be wrapped around 8.26 cm and 6.03 cm pipes, respectively. 0.635 cm hard tubing was used to connect the stock tanks, pumps, and the reactor. 0.635 diameter tubing was found to provide adequate flow without clogging or settling the clay and PACl inside the tubing.

A single reactor height of 61 cm (24") was used based on the three 20.3 cm (8") reactors created by the CSFBR team. As discussed above, a 61 m reactor will give the same floc blanket length of three 20.3 cm reactors, which was an important design parameter.

The 47 foot flocculator tubing length was found using a MathCad file with constraints of a $G\theta$ as 13000, a 0.635 diameter tubing, and a radius of curvature of 4.25 cm. The $G\theta$ value was set to allow adequate collision potential at each section of the tube over the length of the whole flocculator. Using trial and error, the CSFBR team found that this $G\theta$ value was high enough to create enough collisions for flocs, but not too high to break the flocs as a result of high collision energy.

Flocculator Calculations

Inputs

$Q_{flocculator} := Q_{reactor}$ this is the flow rate of the system

$G\theta_{goal} := 13000$ target G*theta to design flocculator to

$D_{Floctube} := 0.125 \cdot in$ inner diameter of flocculator tubing

$R_c := 4.25 \cdot cm$ radius of curvature (the radius of the tube the flocculator is wrapped around)

Residence time of design flocculator

$$\theta_{flocc} := \theta\left(Q_{flocculator}, D_{Floctube}, L_{Flocc}\right) = 1.663 \cdot min$$

G*theta of design flocculator

$$G_{floc} \cdot \theta_{flocc} = 13000$$

Length of design flocculator

$L_{Flocc} = 20.95 \cdot ft$ This is the length of your flocculator

$2 \cdot \pi R_c = 0.267\,m$

Figure 5: Flocculator Calculations

The total flow rate into the reactor was determined using the upflow velocity, diameter and height of the reactor, and the diameter of the tubing entering the reactor. The team decided to choose a ratio of water flow, which is a combination of tap water and fluoride, to floc flow, which is a combination of PACl and clay, of 8 to 2 based on a previous team's work that found that a 9 to 1 did not provide a dense enough floc blanket in the reactor.

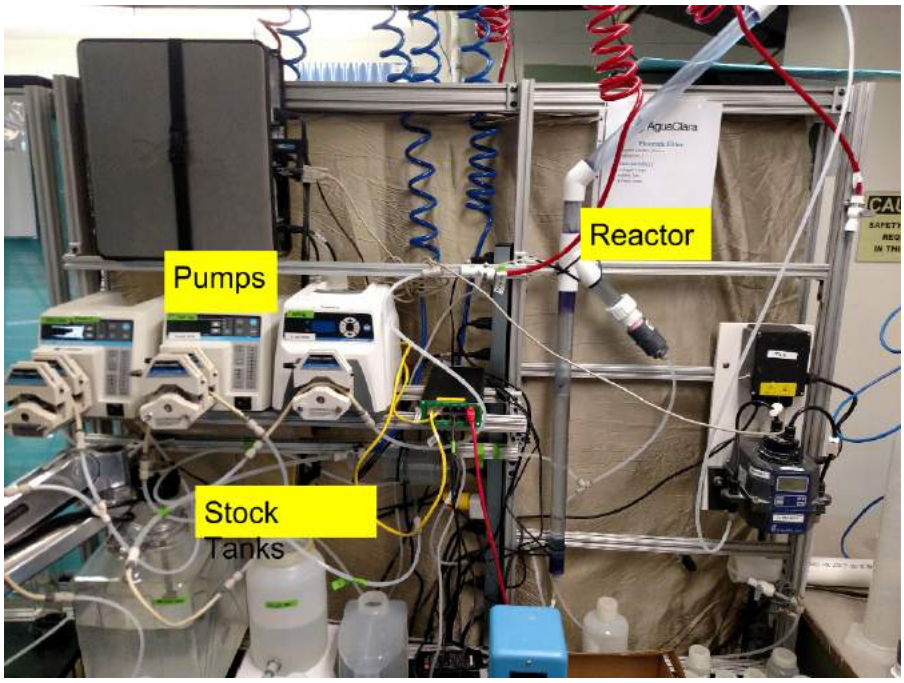


Figure 6: Image of Lab Setup with Labels

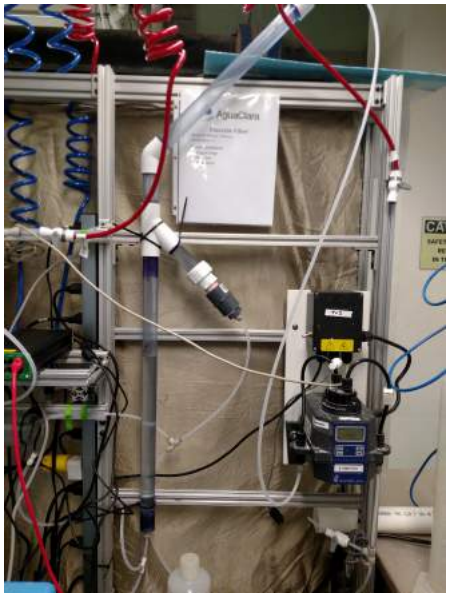


Figure 7: Image of the Reactor with Turbidimeter

Materials:

- Two 600 RPM Pumps and one 100 RPM

- Clear 2.54 cm (1") PVC piping
- White PVC 45 degree Elbow and Wye
- Various White PVC attachment pieces and push-to-connects
- Flexible and Hard 0.635 cm (1/4") tubing
- Turbidimeter
- Polyaluminum Chloride (PACl), Clay, Fluoride Ion Solution
- Various connectors and buckets for stocks
- Mechanical Stir and Stir plate with stir bar

Complications with Construction:

In regards to the setup of the system, there were a lot of problems with the interface between the computer and the pumps. The interface box had several issues that prevented the computer inputs from being properly received by the pumps. However, after much troubleshooting, the problem was found to be faulty digital cords attached to the pumps. Once the cords were fixed, the pumps and system were able to run correctly.

ProCoDA Methods

ProCoDA is a process control system that was developed by Monroe Weber-Shirk in order to set process parameters through a computerized system. It can be set to different system states that control the system pumps depending on what flow rates are desired. Additionally, it collects the data from probes, allowing for data on the fluoride concentrations to be compiled. To begin the ProCoDA method file, two states were made: ON and OFF. In the OFF state, all the valves were closed and no pumps were on. In the ON state, all the pumps were ON and the valves were opened. The pumps controlling the PACl, fluoride, clay and water were connected through the pump ports on the ProCoDA box, but the waste pump was connected to a valve through a variable power source, as there were no more pump ports available. ProCoDa can turn this pump on and off via a normal valve control, as long as the pump was already set to a proper flow rate. The system was set to be run on Manual setting, as a proper run time had not yet been determined.

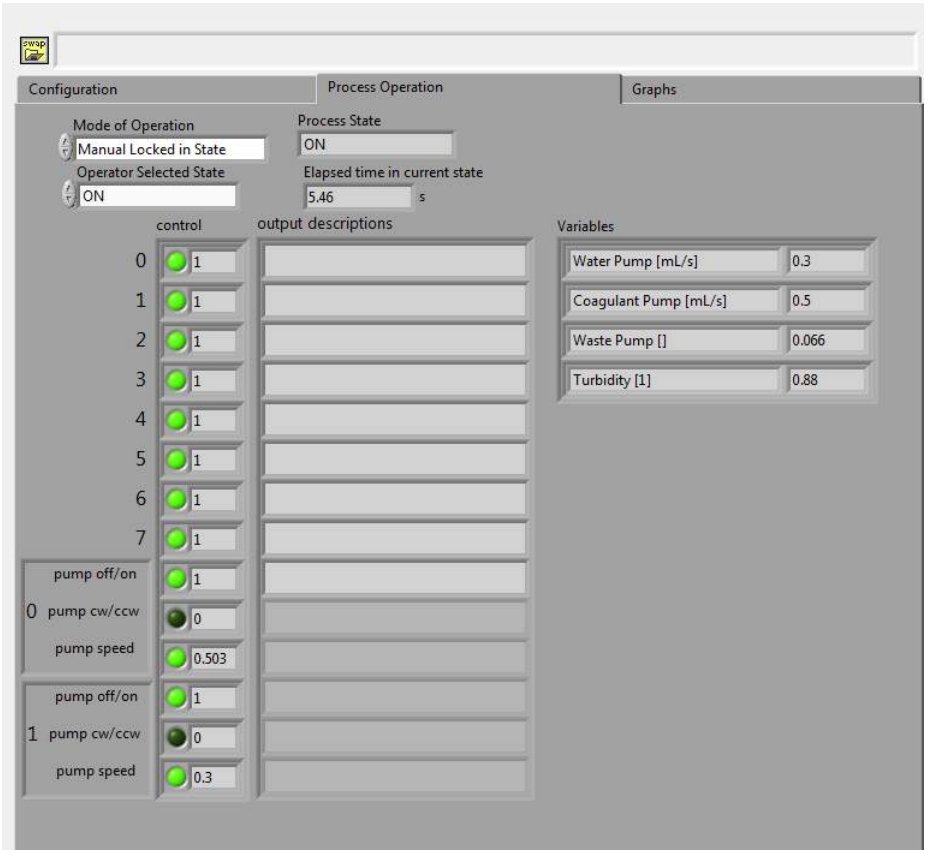


Figure 8: ScreenShot of ProCoDA Panel

For the first iteration, the method file was only set to control the Revolutions per Minute (RPM) of the PACl/Clay pump and the Fluoride/Tap water pumps. This was done using the peristaltic pump ProCoDA file available in the AguaClara server, and using inputs for desired flow rate and tubing size. Since the PACl and clay pump heads were attached to one pump, and the fluoride and tap water pump heads were attached to another, the flow rates, concentrations and tubing size had to be calculated so that the proper dosage of each component was added to the system.

Procedure 1

For this iteration, the team built the reactor. The reactor was set up to handle a floc blanket consisting of Clay and PACl and an upflow of raw water (a combination of fluoride and tap water). The floc weir maintained the height of the floc blanket so that the floc blanket did not go through to the tube settler, and any excess flocs that flowed down the floc weir were pumped out. The tube settler at the top of the reactor was responsible for catching any flocs or particles that were too small to be settled out in the floc blanket and flowed past the floc weir. These particles flow past the floc blanket because they have a capture velocity that is lower than the upflow velocity. This way fluoride can

be removed and clay can settle out to keep the turbidity low. The team worked closely with the CSFBR team to design comparable design parameters for the reactor system.

Results and Analysis 1

During this iteration, the team came across many observations. To begin, the size of the hard tubing connecting the stock clay to the floc pump, was too big and clay was settling out inside the tube. This meant that a much smaller concentration of clay was actually being pumped into the system. To fix this issue, the 1/4" tubing was replaced with microtubing and a different pump head was used with size 13 tubing to pump the clay. The smaller tubing meant that there would be a larger velocity pumping the clay into the system, thus diminishing the issue of clay settlement.

Additionally, the team recently learned that the pump tubing was twisted inside of the pump head. This set back the team's work a few days, since results from trials previous to this observation were not accurate.

Next, the team learned that flocs made with the 12:1 ratio of stock clay to stock PACl (2400 mg/L clay, 200 mg/L PACL) were relatively large - and thus, settled out at the bottom. This settling caused new flocs to remain stagnant at the bottom of the column - thus, clogging the bottom of the system and preventing the jet of flocs to break through. The excessive PACl being pumped into the system caused the extremely large flocs. To solve this issue, a smaller concentration of PACl was needed.

The next PACl concentration tested was 30 mg/L. The flocs at this concentration where much smaller than those observed at 200 mg/L. However, most of the flocs were not big enough to settle out inside the column because their capture velocity was too small. This meant that most of the flocs left out of the top of the column, and were not captured by the tube settler.

Finally, the team tested 100 mg/L of PACl with the same concentration of clay. During the initial creation of the floc blanket, flocs appeared bigger and were settling out into a dense floc blanket in the column. Initially, the flow weir also appropriately maintained the height of the floc blanket. However, after about an hour, flocs began to settle and stay at the bottom of the column. This then caused the density of flocs in the upper part of the floc blanket to decrease significantly, and as a result, flocs started to flow out the top of the column. The team hypothesizes that the flocs may still be too large for the system - and will continue to test varying floc sizes by altering PACl, clay and water's flow rates in order to solve this issue.

Table 2: Parameters for Floc Blanket Testing

Run	Stock Clay Dosage	Stock PACl Dosage	Size of Flocs
1	2400 mg/L	200 mg/L	Huge
2	2400 mg/L	30 mg/L	Small/Tiny

Floc Blanket Creation and Fluoride Testing

The goal of the second iteration was to make a stable floc blanket, and from there to start running fluoride through the system to test out if this idea is a

valid solution for the removal of fluoride.

Experimental Apparatus

Design: The apparatus was very similar to the original, with the exception of two main changes. The first change was the addition of a container where the fluoride probe could be inserted to give a constant reading of fluoride. The water would flow out of the tube settler, then through the turbidimeter, and then through the fluoride probe holder, where it then exited into the effluent. The second change was all the input streams (clay, PACl and fluoride water) were sent into the flocculator where as before only the PACl and clay were sent through the flocculator. This provided more time for the fluoride to interact and adsorb to the PACl in the flocculator before going into the floc blanket to be removed.

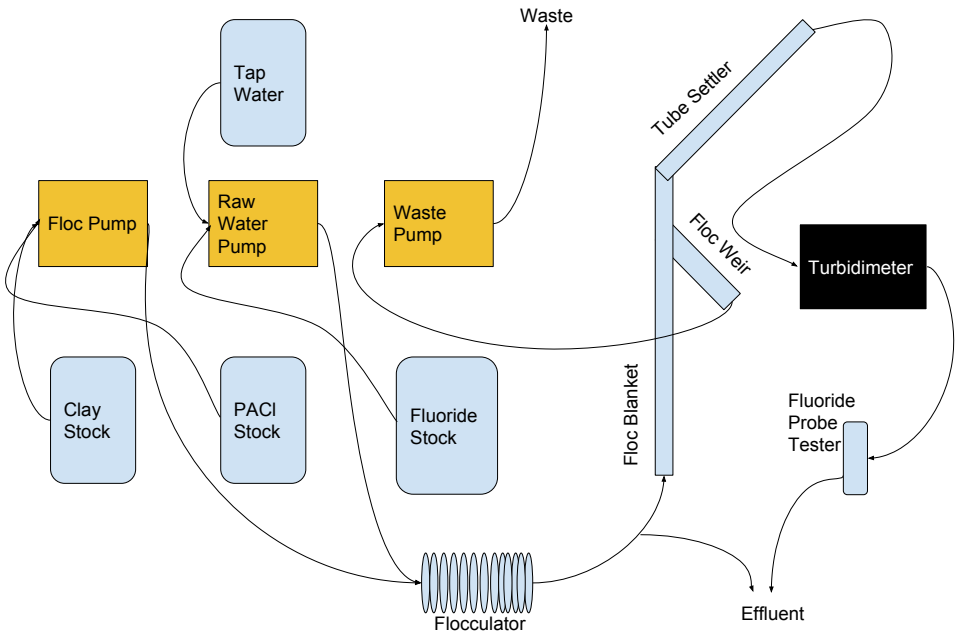


Figure 9: Updated Schematic of System

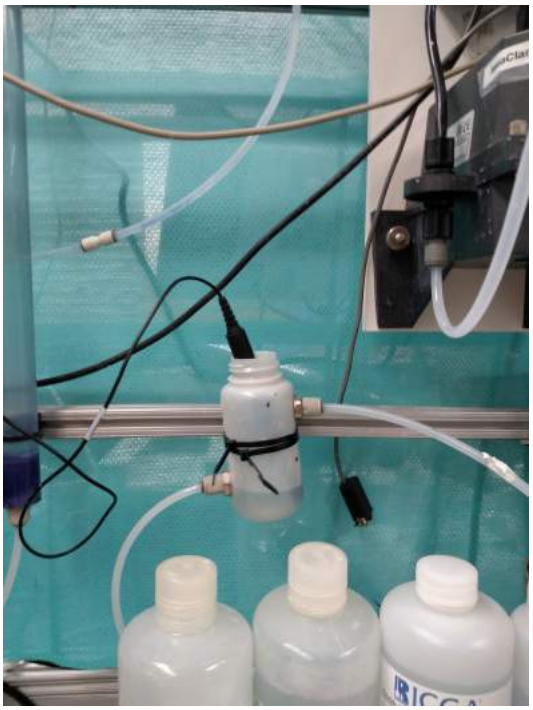


Figure 10: Addition of Constant Fluoride Monitor

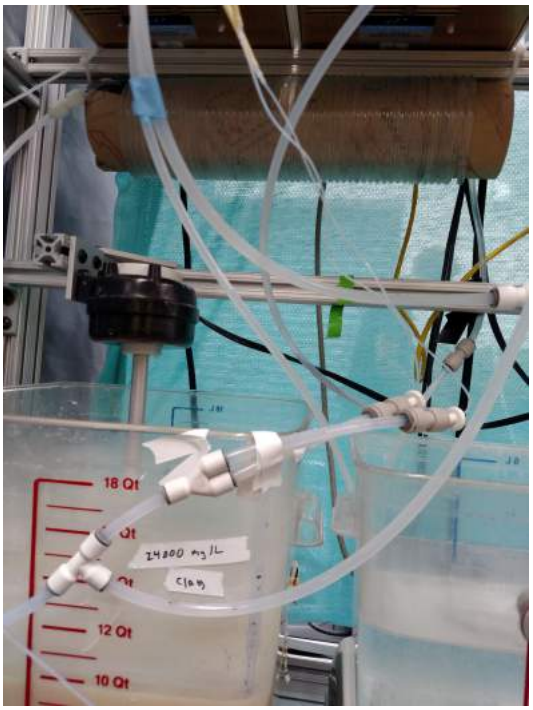


Figure 11: Connections between pumps and flocculator

Additionally, it was noted that with the 6.35 mm (1/4 in) tubing that was pumping clay into the system, the clay was settling within the tubing instead of being pumped properly into the flocculator. This caused there to be less clay flowing into the reactor than expected, which negatively impacted floc formation. To combat this, the 6.35 mm tubing was switched to microtubing, so that the significantly smaller cross sectional area and higher velocity would not allow for settling.

Figure 12: Pump with Microtubing on Pump Heads

Materials:

- 1/4" Hard Tubing
- Small Bottle
- Fluoride Probe

ProCoDA Methods

To simplify experimentation, it was decided that the stock concentrations of PACl and clay should be kept constant and the flow rates in the ProCoDA file instead should be altered whenever the concentration going into the reactor needed to be adjusted. The new flow rates were calculated in the MathCad file so that the overall upflow velocity was constant at 1 mm/s, but clay and PACl would go in at a different ratio to fluoride and water. The MathCad files used to calculate these flow rates to input into ProCoDA are given below. Also, a

set of equations were developed in order to give an estimate of the amount of time to create a full floc blanket.

$C_{stockpacl} := 500\,\frac{mg}{L}$ $C_{StockClay} := 24000\,\frac{mg}{L}$ These are the concentrations of your stocks

$C_{reactorpac} := 25\,\frac{mg}{L}$ This is the Concentration you want in the reactor

$Q_{stockpacl} := Q_{reactor}\cdot\frac{C_{reactorpac}}{C_{stockpacl}} = 0.025\cdot\frac{mL}{s}$ Flow Rate to Input to ProCoDA for Coagulant Flow Rate

$C_{ReactorClay} := \frac{Q_{stockpacl}\cdot C_{StockClay}}{Q_{reactor}} = 1.2\times 10^{3}\cdot\frac{mg}{L}$ Concentration of Clay in the reactor

$Q_{Tap} := Q_{reactor} - 2\cdot Q_{stockpacl} = 0.456\cdot\frac{mL}{s}$ Flow Rate of Raw Water Entering Reactor

$Q_{fluoride} := \left(\frac{1}{2}\right)\cdot Q_{Tap} = 0.228\cdot\frac{mL}{s}$ Flow Rate to Input to ProCoDA for Water Flow Rate

Figure 13: MathCad File for Calculation Flow Rates

$H_{FB} := 24in$

$C_{FBClay} := 3000\,\frac{mg}{L}$ something between 2000 and 6000 mg/L

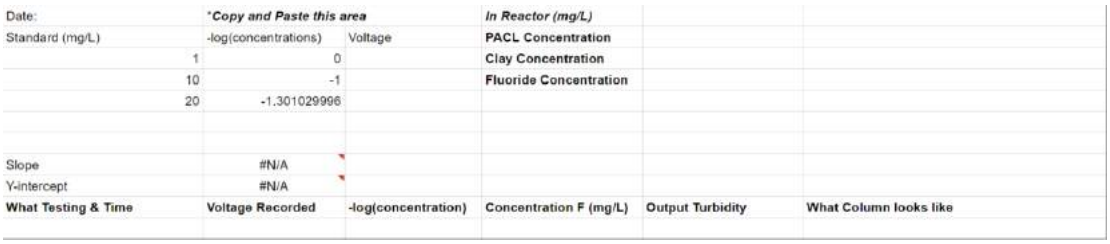
$V_{FB} := v_{up}\cdot\frac{C_{ReactorClay}}{C_{FBClay}} = 0.4\cdot\frac{mm}{s}$

$T_{FB} := \frac{H_{FB}}{V_{FB}} = 0.423\cdot hr$ Time for the Floc Blanket to Form

Figure 14: MathCad File for Floc Blanket Creation

Procedure

The team decided to run PACl, clay and fluoridated water all into the reactor at the same time. After using the MathCad File to determine flow rates to input into ProCoDA, the system was run for around 12 hours to test whether or not the system worked for a long period of time. Since a section of the apparatus was made for the insertion of the fluoride probe, there was a constant recording of fluoride concentration data over the entire experiment. Also, a new excel sheet was made in order to keep updates on the floc blanket during the entire length of the experiment.



Date:	*Copy and Paste this area		In Reactor (mg/L)		
Standard (mg/L)	-log(concentrations)	Voltage	PACL Concentration		
1	0		Clay Concentration		
10	-1		Fluoride Concentration		
20	-1.301029996				
Slope	#N/A				
Y-intercept	#N/A				
What Testing & Time	Voltage Recorded	-log(concentration)	Concentration F (mg/L)	Output Turbidity	What Column looks like

Figure 15: Sample Data Input Analysis for Fluoride Experiment

Results and Analysis

In the first trial, 10 mg/L of PACl was used with 200 mg/L of clay. The initial fluoride concentration measured by the probe was 6 mg/L. After two hours, the fluoride was measured to be 1.76 mg/L yielding 70.7% removal.

In the second trial, 12 mg/L of PACl was used with 200 mg/L of clay. The initial fluoride concentration measured by the probe was 8.8 mg/L. After two hours, the fluoride was measured to be 1.61 mg/L yielding 81.7% removal.

In the third trial, 25 mg/L of PACl was initially used with 1200 mg/L of clay, followed by 50 mg/L of PACl with the same amount of clay. 8.5 mg/L of initial fluoride was measured by the probe. After approximately two hours, the final fluoride concentration was measured to be 1.24 mg/L - yielding 85.4% fluoride removal. The shape of the graph was slightly more irregular with this trial, due to change in PACl concentrations mid-way through the trial. With 25 mg/L of PACl, effluent fluoride concentrations were measured to be approximately 4 mg/L. After 4750 seconds (approximately an hour an a half), the PACl concentration was doubled to 50 mg/L. An hour after the PACl concentration change, at the 2.5 hour mark of the experiment, effluent fluoride was measured to be 1.24 mg/L.

Overall, the team's experiments show that the single reactor system is highly effective at removal fluoride from concentrated raw water. According to our research, the extreme upper end of fluoride in well water is 10 mg/L. 70-85% removal of fluoride in the well water of these areas can drastically improve bone health and dental health in these areas.

Table 3: Floc Blanket with Fluoride Runs

Date	Clay Dosage	PACl Dosage	Initial Fluoride	Final Fluoride	Percent Removal
3/21/16	200 mg/L	10 mg/L	6 mg/L	1.76 mg/L	70.7%
3/22/16	200 mg/L	12 mg/L	8.8 mg/L	1.61 mg/L	81.7%
3/23/16	1200 mg/L	25 mg/L	8.5 mg/L	1.85 mg/L	78.2%
3/23/16	1200 mg/L	50 mg/L	8.5 mg/L	1.24 mg/L	85.4%

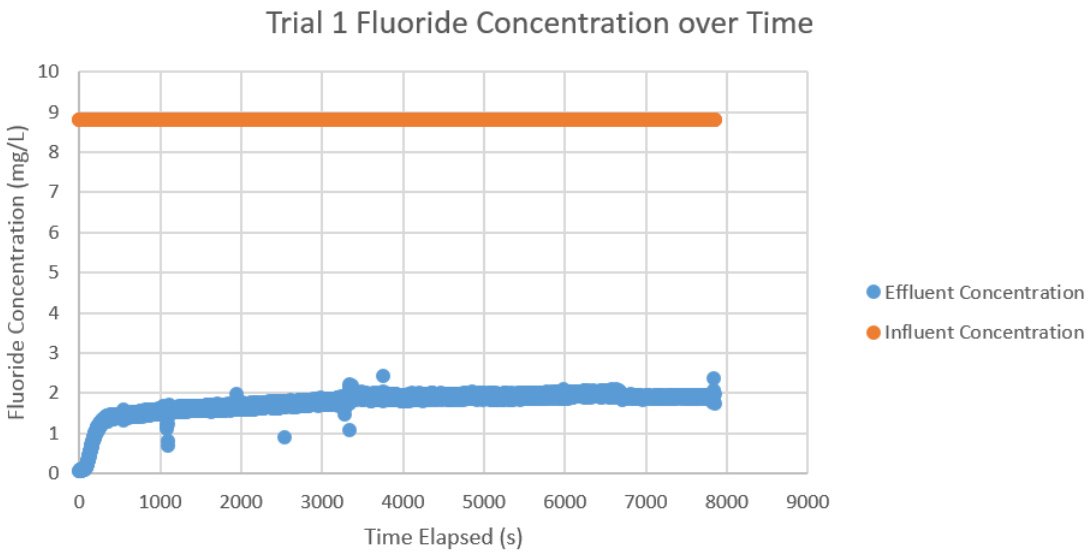


Figure 16: Trial 1 for Fluoride Removal with 12 mg/L PACl Dosage and 200 mg/L clay dosage

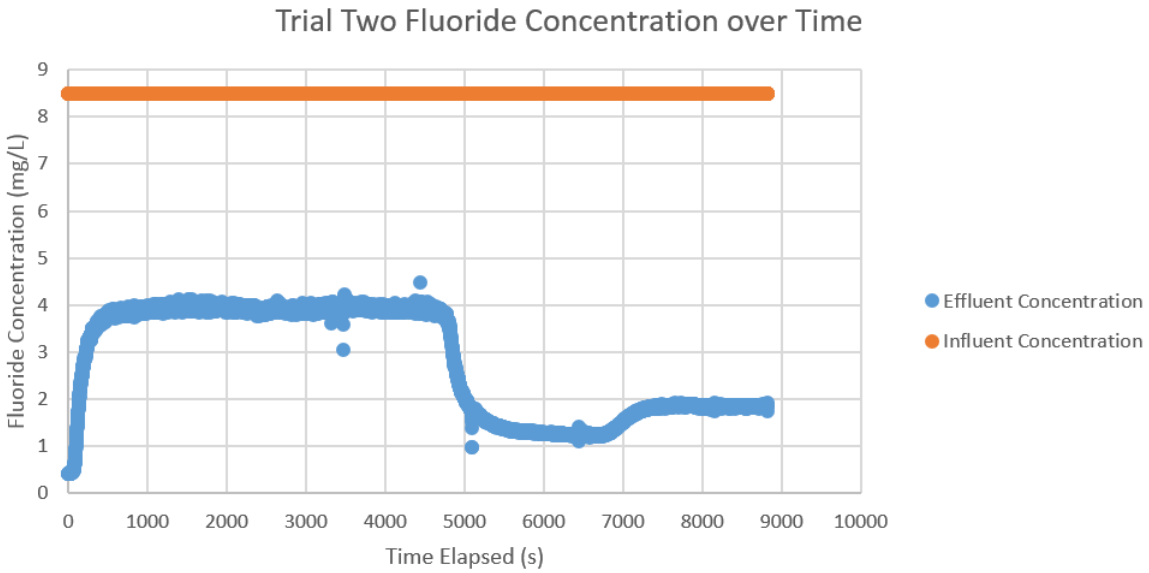


Figure 17: Trial 2 for Fluoride Removal with 25 mg/L then 50 mg/L PACl Dosage and 1200 mgL clay dosage

Figure 18: Thick Floc Blanket

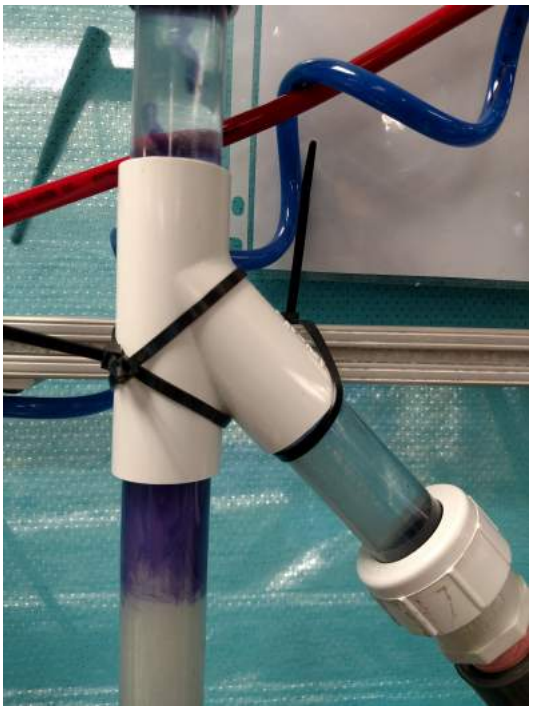


Figure 19: The Floc Blanket with Clear Water Flowing above it

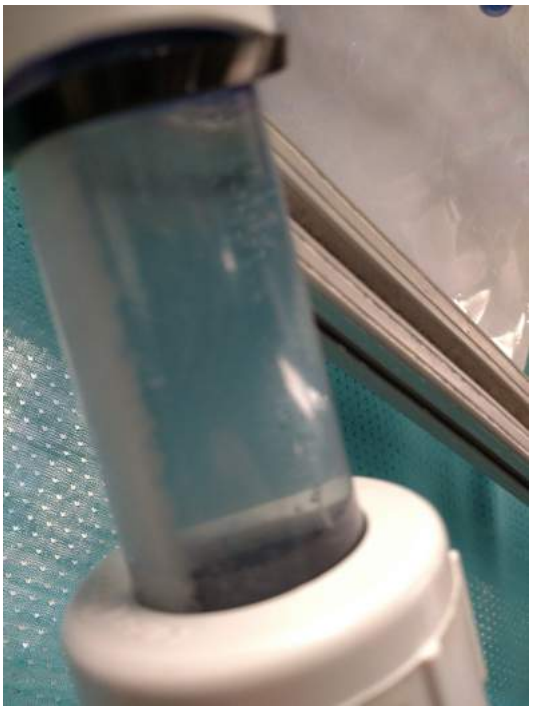


Figure 20: Floc Slide in the Floc Weir

Dye Testing

The goal of the third iteration was to test if dye could be as successfully removed as fluoride, given our design parameters. This research was motivated by the successful removal of dye by the CSFBR team using three reactors in succession.

Experimental Apparatus

Design: No changes were made to the setup of the system, but the design of the reactor was changed. In the previous reactor system, there were some parts of the system including the wye connecting the floc blanket and weir that were white, and inhibited the view of the reactor. A new physical reactor was built to make the system more transparent. In place of the wye, a PVC tube was plastic welded onto the reactor with the same design constraints as the previous system. Additionally, the tube settler was welded using PVC pipe at a 30 degree tilt with respect to the vertical as opposed to a 60 degree tilt, to allow for increased settling for particles that escaped the floc blanket and were not heavy enough to be taken out by the weir.

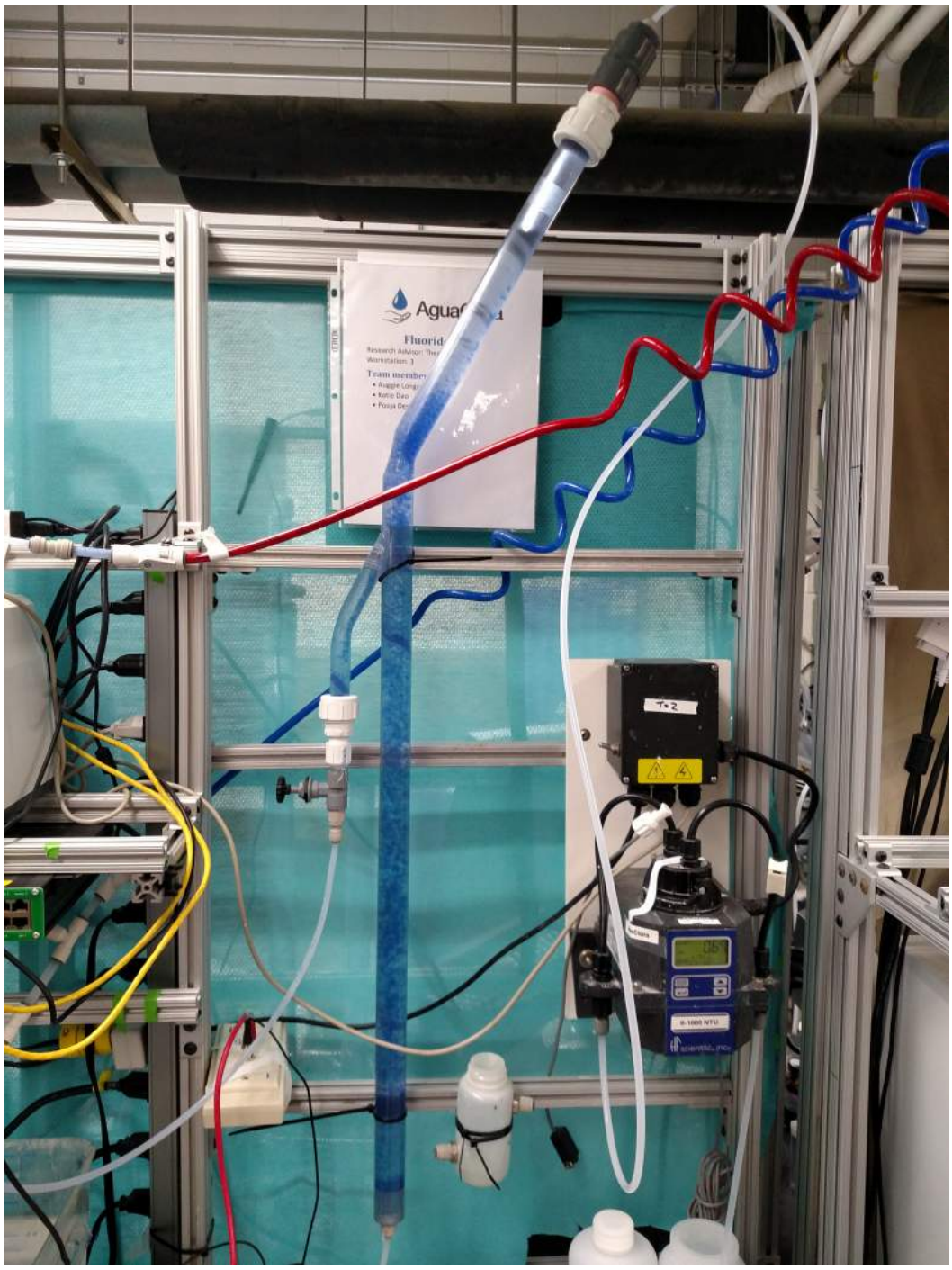


Figure 21: Transparent Floc Blanket Reactor

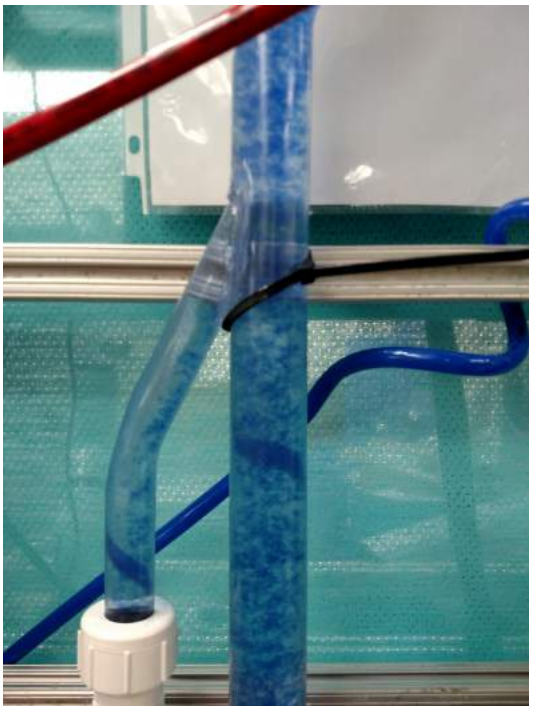


Figure 22: Transparent Weir Connection

Figure 23: Transparent Tube Settler Connection

Few changes were made to auxiliary components to allow for the use of dye as opposed to fluoride. Jar tests allowed the CSFBR team to determine that dye flocculates well with PACl, without the use of clay. In fact, the addition of clay resulted in a relatively high effluent turbidity during CSFBR experimentation. As a result of this insight, the clay stream was removed. The stream of fluoride was removed and substituted with a 500 mg/L stock stream of concentrated dye. Additionally, the fluoride probe was removed as fluoride measurements were not necessary during these experiments. Dye removal was measured through the use of a newly connected photometer.

Materials:

- Remazol Brilliant Blue R Dye

Procedure

Stock concentrations of 500 mg/L of dye and 500 mg/L of PACl were run through the system using the same design parameters as the team's experiments with fluoride. The goal of these experiments was to test if dye would be removed at a similar rate to fluoride removal, and if a floc blanket would successfully form without clay in a single-reactor system, as it did in the triple-reactor system. The system was monitored every hour, and effluent concentrations were measured through the use of the photometer. The concentration of both the PACl and dye in the reactor were 25 mg/L because a 1 to 1 ratio was found to best create flocs in a jar test.

Results and Analysis

Table 4: Dye Floc Blanket Run

PACl Dosage	Initial Dye	Final Dye	Percent Removal
25 mg/L	25 mg/L	4.5 mg/L	82%

The floc blanket formed through the combination of PACl and dye was opaque, dense, and exhibited a deep indigo color. Additionally, the flocs were noted to be slightly larger than what was seen in the fluoride system. Over time, the Dye floc blanket became very sticky and made huge clumps within the reactor causing less of the flocs to settle within the floc blanket. After six hours, using 25 mg/L of PACl, and an influent dye concentration of 25 mg/L - the team observed 82% dye removal, bringing the final dye concentration to 4.5 mg/L.

The high removal rate of dye using design parameters almost identical in nature to those used for fluoride removal, points to distinct parallels between the properties of fluoride and dye. As a result, the team anticipates using the removal of dye, a process that is much easier to visualize compared to the removal of fluoride, during various demonstrations to engagingly exhibit the team's work.

Figure 24: The Reactor with a Dye Floc Blanket

Figure 25: Dye Flocs Sliding Down the Weir

Testing Clay Necessity

The goal of the fourth iteration was to test to see if clay is actually necessary in the apparatus in order to remove fluoride from the water. From observations and data from the dye, it appeared that the dye did not require clay for removal, so the same principle was tested in this iteration.

Experimental Apparatus

Design: The apparatus used in this iteration was a jar test apparatus. There were six spots for six different experiments to be run at the same time.

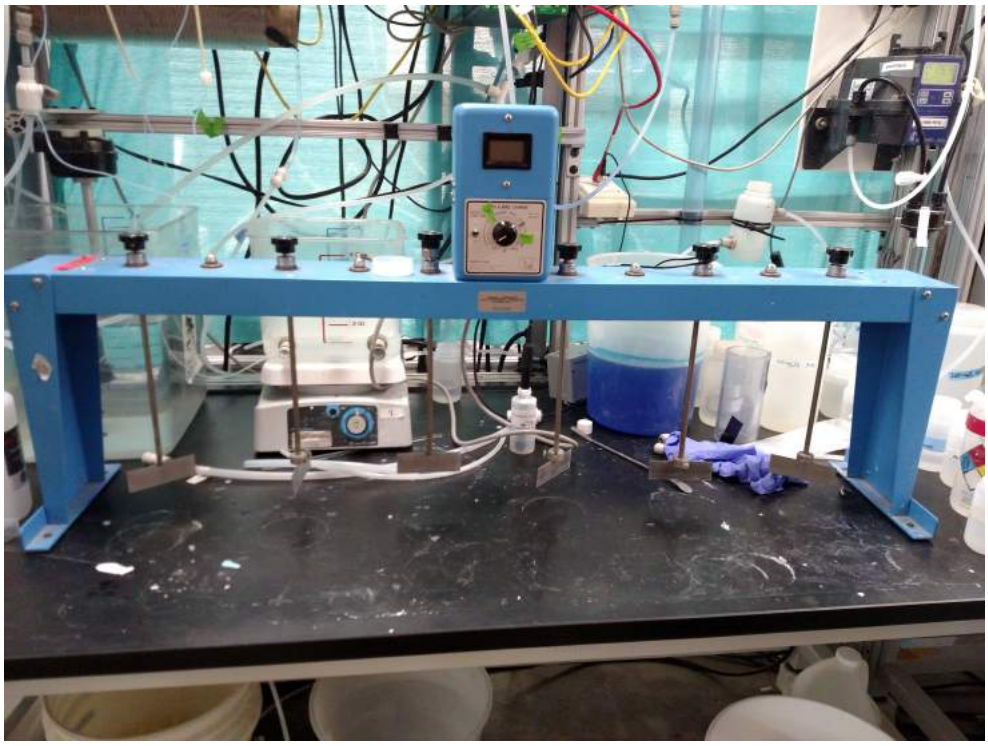


Figure 26: Jar Test Apparatus

Materials:

- Jar Test Apparatus

Procedure

A constant concentration of both fluoride and PACl will be added to six different containers with 0.5 liters of water. Then varying amounts of clay will be added to each of the six containers to test if a certain amount of clay is needed to provide adequate removal. These will all be mixed by the jar test apparatus. For initial flocculation simulation, the speed was set to approximately 100 rpm for one minute, then switched to a lower rpm for five minutes. The speed was then switched back to 100 rpm for one minute, then it was reverted to a lower rpm for 10 minutes. The jar test apparatus was then turned off so that the flocs could settle. For the experiments, the PACl was kept at approximately 25 mg/L and the goal initial fluoride concentration was 10 mg/L.

Results and Analysis

Table 5: Clay Jar Test Results

Clay Concentration	Clay:PACl Ratio	Initial Fluoride	Final Fluoride	% Removal
12000 mg/L	480:1	8.76 mg/L	3.77 mg/L	56.9%
6000 mg/L	240:1	8.87 mg/L	4.127 mg/L	53.5%
4000 mg/L	160:1	10.46 mg/L	5.40 mg/L	48.4%
2000 mg/L	80:1	10.23 mg/L	5.99 mg/L	41.5%
1000 mg/L	40:1	10.097 mg/L	5.28 mg/L	47.7%
0 mg/L Trial 1	0:1	9.92 mg/L	5.07 mg/L	48.9%
0 mg/L Trial 2	0:1	10.052 mg/L	6.46 mg/L	35.7%

From the table of results above, it seems that even with no clay in the solutions, there was still some removal of fluoride, though small. **Therefore, clay may not be necessary in the removal of fluoride, but can significantly help with the removal of it.** This means that fluoride treatment is still feasible for groundwater with low turbidities.

Conclusions

Thus far, the team has learned that the floc blanket reactor system is highly effective in removing fluoride, as results with varying PACl and clay dosages have yielded removal rates ranging from 70-85%. Based on our research, 70% removal of fluoride in villages with heavily concentrated well water would not only allow villages to have safe drinking water, but it would allow them have beneficial drinking water; water with fluoride concentrations that are working to strengthen the bones rather than deteriorate them. Additionally, the team has discovered the parallels between fluoride removal and dye removal - with almost identical design parameters (to the fluoride system) yielding 85% removal of dye. Not only does the reactor system remove both fluoride and dye, but with simple modifications the reactor can be electricity-free and implemented in AguaClara plants in India, as well as in other locations with highly fluoridated water. This reactor works more efficiently than the the currently accepted method of fluoride removal, namely the Nalgonda Method, due to its continuous flow and relatively low coagulant dosage. Overall, the fluoride reactor system is a promising solution to eliminating concerns regarding excessive fluoride in well water in an affordable, efficient, easily operable manner, and the dye reactor system offers an engaging visual to explain the impacts of our research.

The team has embraced the value of collaboration. Working with CSFBR has allowed the fluoride team to not only clarify goals but also advance the design and set up of the reactor system. The Fluoride Team has been able to uniquely synthesize past work from CSFBR and Fluoride to quickly begin work and complete tasks. The teams work not only communicating with CSFBR but learning from and working with CSFBR is a testament to AguaClara's collaborative, hands-on, learning process.

Future Work

Looking forward, the team will primarily work on researching how realistic implementation of this research is in the field. Currently, the system is heavily reliant on electricity through the use of pumps and stirrers. The team will be working with Monroe Weber-Shirk, to determine how to best scale the reactor systems to match the needs of AguaClara facilities, and how to eliminate the system's dependence on electricity. Additionally, jar tests have shown that clay is not a necessity when creating a floc blanket. As a result, it is encouraged that future teams experiment with running the reactor system without clay, when only PACl may be necessary for removal.

More broadly, the development of an optimal floc blanket reactor design is a step forward in creating an affordable and efficient system capable of removing fluoride in rural villages across the world. This work is crucial to improving the safety of well water for villagers in India, who depend on it most.

Semester Schedule

Task Map

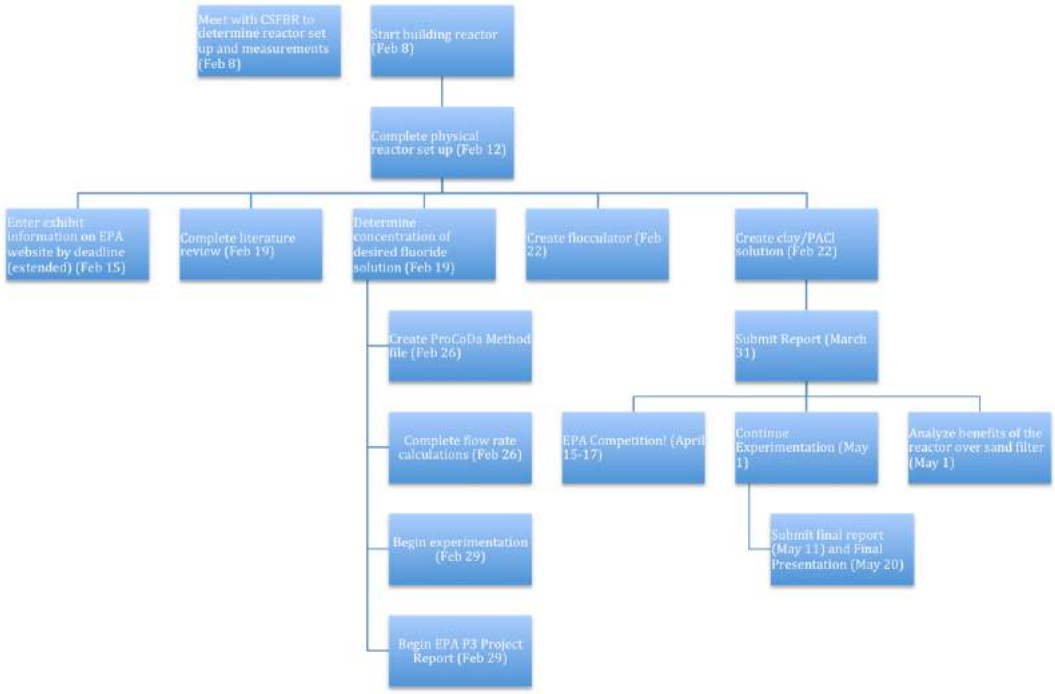


Figure 27: Fluoride Task Map

Task List

*Note: With such a small team, all team members will assist with each task. Names in parenthesis are members who will "spearhead" the task.

February 8, 2015

- Speak with CSFBR to determine reactor set-up and measurements (Team) - Completed
- Start building reactor (Auggie) - Completed

February 12, 2015

- Complete physical reactor set-up (Auggie) - Completed

February 15, 2016

- Enter exhibit information on EPA by deadline (Pooja) - Completed

February 19, 2016

- Complete Literature Review (Katie)- Completed
  - Research floc blankets, fluoride, tube settlers
- Determine concentration of desired fluoride solution (Auggie, Pooja) - Completed

February 22, 2016

- Create Flocculator (Auggie) - Completed
  - Research MathCAD file detailing relationship between tube diameter and 'turns' (Katie)
- Create clay/PACl solution (Pooja) - Completed

February 26, 2016

- Complete method file on ProCoDA (Katie) - Completed
- Complete flow rate calculations with the help of CSFBR's MathCAD file (Katie) - Completed
- Perform jar tests with fluoride and PACl to determine the optimal concentration of PACl needed in the floc blanket of the reactor(Auggie, Team) - Completed

March 7, 2016

- Create an optimal floc blanket with clay and PACl - Completed
- Begin experimentation with 10 mg/L of fluoride to compare reactor results with sand filter results. Vary concentration of coagulant to find optimal dosing for fluoride removal. (Auggie, Team) - Completed

March 14, 2016

- Test varying initial pH's to see which provides optimal fluoride removal. (Katie, Team)

March 31, 2016

- P3 Project Report due at 11:59 (Pooja, Collaboration between Lishan, Fluoride, CSFBR) - Completed
  1. Go to http://www.grants.gov/web/grants/applicants/apply- for-grants.html
  2. Click "Get Application Package" (a red button on the right side of the page).
  3. Enter "EPA-G2015-P3-PHASE2" in the Funding Opportunity Number box and click Submit.

April 15-17, 2016

- P3 Competition (Team) - Completed

May 1, 2016

- Continue experimentation with varying levels of fluoride. With the bulk of our experiments before P3 involving 10 mg/L of fluoride, it will be important to branch out to both higher and lower raw water concentrations. (Team)
- Continue analyzing the differences between the fluoride removal results obtained through the reactor system and the sand filtration system. (Katie, Team)
  - Highlight these differences in the final report.

May 20, 2016

- Submit Final Report and Final Presentation

Report Proofreader: Katie Dao

References

Arlappa, N., Aatif Qureshi, I., and Srinivas, R. (2013). Fluorosis in India: an overview. *Int J Res Dev Health*, 1(2).

Bailey, K. and Fawell, J. (2004). Fluoride in Drinking-water.

Dahi, E., Mtalo, F., Njau, B., and Bregnhj, H. (1996). Defluoridation using the Nalgonda Technique in Tanzania. In *Reaching the Unreached: Challenges for the 21st Century*, New Delhi, India.

Dao, K., Desai, P., and Longo, A. (2015). Fluoride, Fall 2015.

EPA (2016a). Fluoride – Ground Water & Drinking Water.

EPA (2016b). Water Treatability Database.

Gebbie, P. (2001). Using Polyaluminum Coagulants in Water Treatment.

Gregory, R., Head, R. J. M., and Graham, N. J. D. (1996). The Relevance of Blanket Solids Concentration in Understanding the Performance of Floc Blanket Clarifiers in Water Treatment. *Chemical Water and Wastewater Treament*, IV.

Hurst, M. W. (2010). *Evaluation of Parameters Affecting Steady-State Floc Blanket Performance*. Degree of Master of Science, Cornell University, Ithaca, New York.

Ingallinella, A. M. and Pacini, V. A. (2001). Simultaneous removal of arsenic and fluoride from groundwater by coagulation-adsorption with polyaluminum chloride. *Journal of Environmental Science and Health, Part A*.

Kumbhar, V. S. and Salkar, V. D. (2014). Use of PAC as a Substitute for Alum in Nalgonda Technique. *International Journal of Emerging Technology and Advanced Engineering*, 4(10).

LeChevallier, M. W. and Au, K.-K. (2004). Water Treatment and Pathogen Control.

Lin, W., Chen, L. C., Chung, H. Y., Wang, C. C., Wu, R. M., Lee, D. J., Huang, C., Juang, R. S., Peng, X. F., and Chang, H.-L. (2004). Treating High Turbidity Water Using Full-Scale Floc Blanket Clarifiers. *Journal of Environmental Engineering*, 130(12):1481–1487.

of Health, N. D. (2010). Sodium Fluoride.

Roholm, K. (1937). *Fluorine Intoxication: A Clinical-Hygienic Study*. Copenhagen, Denmark.

Sun, S. F. (2004). Sedimentation. In *Physical Chemistry of Macromolecules: Basic Principles and Issues, Second Edition*, pages 243–266. John Wiley & Sons, Inc.

WHO (2016). WHO | Naturally occurring hazards.

Zhi, H. (2016). *Arsenic(V) removal from drinking water by concurrent introduction of As contaminated water and Polyaluminum chloride in a sand filter medium*. PhD thesis, Cornell University.