Evaluating Polyaluminum Chloride Coagulants for a Large Drinking Water Provider Using Benchtop and Pilot Plant Scale Analysis

A Thesis
Presented in Partial Fulfillment of the Requirements of the
Degree of Master of Science
With a
Major in Environmental Science
in the
College of Graduate Studies
University of Idaho
By
Nicole Holloway

Approved by:
Major Professor: Sarah (Xiao) Wu, Ph.D.
Committee Members: James McCarty, Ph.D.; Lide Chen, Ph.D.
Department Administrator: Jaap Vos, Ph.D.
August 2022

ABSTRACT

In this study, polyaluminum chloride (PACl) coagulants were evaluated for use at a surface water treatment facility in that currently uses aluminum sulfate (alum). The coagulants were evaluated using a triple bottom line approach incorporating publich health, fiancial viability, and environmental impact in three phases. In phase 1, jar tests were utilized determine two high performing PACls out of 8 to move forward into phase 2 based on treatment efficiency in comparison each other and to alum. One of the top performing PACl coagulants was evaluated to determine the treatment factors that are significant to turbidity removal via jar testing utilizing a central composite design (CCD). In phase 2, the selected PACl coagulants were evaluated at the pilot plant scale. The data from phase 2 was utilized in the triple bottom line analysis. Finally, in phase 3, financial analysis and sludge production of PACls was conducted and compared with Alum to evaluate the environtmental impact and financial viability. The research concluded the PACl coagulants performed as well or better than alum at meeting clean and safe drinking water treatment criteria. Alum, PACl 1, and PACl 2 had a similar disinfeciton by product formation potential with negligable difference in THM production. Both PACls performed better in removing TOC and DOC consistently above the EPA guideline of 25% through the pilot plant runs with 28-42% and 30-40% for PACl 1 and PACl 2 respectively and 19-42% for alum. PACl coagulants displayed an increased percentage of turbidity removal per mg/L of coagulant added. During the pilot trail, alum exhibited 1.88-2.23% turbidity removal per mg/L coagulant added while PACl 1 and PACl2 exhibited 4.35-5.64% and 3.86-4.85% respectively. The PACl coagulants were not as financially feasible as alum based on the pilot plant data. PACl treatment trains in pilot runs retained alkalinity and thus reduced lime feed and had zero caustic feed. Sludge production was reduced in PACl treatment. These reductions were not enough to offset the increased chemical cost of PACl to alum with PACl 1 being $402,203 and PACl 2 being $652,100 higher than alum annualized and extrapolated based on 2018 production data. The reduction of chemical additions and sludge prodcution made the PACl coagulants more environmental friendly. The CCD examination validated that raw water pH and coagulant dosages are the significant variables to both settled and filtered turbidity removal when using polyaluminum chloride coagulants on water from Beaver Lake. The study produced significant model equations to determine values for these variables to achieve optimal treatment.

ACKNOWLEDGEMENTS

The author of this thesis would like to first thank Beaver Water District for making this study possible. It was a wonderful experience working on such an impactful project, getting to potentially steer major decisions at the treatment facility. I would like to thank Dr. Robert “Bob” Morgan for pushing me to start this degree program and steering my studies to a thesis track. Mindi Dearing, my supervisor provided support and encouragement through the entire lengthy process. Staff at BWD helped a tremendous amount in performing the study; Darryl Fendley, Danny Dearing, and Cody Hudson helped to design the study, run the preliminary jar tests, and complete pilot plant runs. Dr. James McCarty was there to answer any technical questions I had along the way and provided generous guidance. My advisor Dr. Sarah Wu helped me turn this project with a seemingly insurmountable amount of data into a fully formed and meaningful thesis.

DEDICATION

This thesis is dedicated to my family. To my daughter Emily, who's birth was the reason for stalling my project and who's pride in her mother was a reason to finally finish it. I wanted her to know she could always count on me to finish what I started. To my husband John, who challenges me, pushes me to be a better person, and encourages me to keep going. To my mother and father, Rita and Arlie for always being my number one supporters and believing in me no matter what, and to my sisters, Rhonda and Renay who I can count on to lend a listening ear to both triumphs and frustrations along the way.

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CHAPTER 1 INTRODUCTION

1.1 Background

The primary focus of a public drinking water treatment facility is to provide clean and safe drinking water to the public. In order to do this, the raw (untreated) water must run through a series of physiochemical processes designed to remove or inactivate pathogens, remove contaminants, and provide water quality stability from the treatment plant to the customer’s tap.

The conventional treatment method utilized by most water treatment facilities provides a multiple barrier approach to water treatment. The general process is as follows: raw water is piped to the water treatment facility and first enters an area called the rapid mix, in which treatment chemicals called coagulants are introduced as the water is stirred at a high velocity. The coagulant chemicals, through physiochemical processes, cause colloids, stabilized small particles naturally present in the water, to become destabilized. In the next process, called flocculation, these destabilized particles are mixed slowly in order to agglomerate. This coming together of small particles creates larger particles called flocs, which are dense enough to settle out of the water. In the next process, sedimentation, the water moves slowly through a basin and the floc particles are allowed to settle. In filtration, the water passes through a filter apparatus which removes additional particulate matter not removed through the previous processes. Finally, during the disinfeciton process, a physical or chemical oxidant is applied to inactivated most pathogens. There are additional processes that are common but not part of the conventional treatment process including stabilization, in which the water pH, alkalinity, and hardness are adjusted for stability within the distribution piping system.

For an existing drinking water treatment facility, improvements or changes to the treatment process can be costly and must be done cautiously with public safety in mind. One of the easier changes a facility can make is to optimize its coagulation process through coagulant chemical selection and appropriate dosing. This process of optimization will allow the utility to potentially obtain improved water quality by either raising or lowering the current treatment chemical dosages or by selecting different treatment chemicals optimized for the specific raw water quality of the treatment plant. Through coagulant optimization the plant is able to enhance the removal of turbidity, Total Organic Carbon (TOC), Dissolved Organic Carbon (DOC), and color while imparting fewer negative effects on the process such as pH and alkalinity changes.

1.2 Motivation

In this study, Beaver Water District (BWD), a large surface water treatment facility providing drinking water in Northwest Arkansas, was evaluating its treatment process through coagulant selection and optimization. This project will examine the performance and feasibility of switching from alum to polyaluminum chloride coagulants in the treatment process.

1.2.1 Protecting Public Health

The motivation behind this project was threefold and follows the triple bottom line approach of people, profit, and planet. The first and most important factor in this equation is “people”, which, for this study, took the form of public safety. The key objective of any water treatment facility is to provide adequate, clean, and safe water. Population growth, emerging contaminants, and new regulations are increasing the imperative to ensure the treatment process is adequate to keep up with the quality of water needed. In the selection of a coagulant in the jar test stage, this was assessed by filtered turbidity. During the pilot plant stage, this was assessed by analyzing disinfection by-product formation, specifically trihalomethanes and chlorite. Total chlorine and filtered turbidity were also assessed during the pilot plant stage as metrics for public health.

1.2.2 Financial Viability

To remain profitable, the treatment facility must be able to provide affordable water. Keeping production costs low is an important goal of any sustainable facility or business. Polyaluminum chloride (PACl) is a coagulant that has been shown to conserve more alkalinity in the raw water than alum leading to less need for stabilization chemical addition. Although the current coagulant in use is cheaper than the ones being examined, it is reported that PACl requires a lower dosage than alum to produce the same treatment results. Natural organic matter (NOM) removal rates, chemical costs, theoretical sludge production, and cost of disposal will all be assessed to examine the comparative cost of treatment.

1.2.3 Reduction of Environmental Impact

As good stewards of the earth and an industry that benefits from having clean natural water sources, an environmentally friendly treatment process is important. The water treatment process directly impacts the environment through the production and disposal of sludge residuals. Theoretical sludge yield was examined to assess this component of the triple bottom line approach. The actual make-up of the coagulants themselves will also be examined briefly for environmental impact.

1.3 Research Objectives

This research includes the following specific objectives:

1. Examine the performance of aluminum sulfate and eight polyaluminum chloride coagulants at the bench scale utilizing raw water entering BWD and a jar testing procedure set up to mimic the treatment process at the treatment plant. Analyze and rank the PACl coagulants on treatment effectiveness compared to Alum based on turbidity removal rates, required dosage, and alkalinity retention.

2. Determine the optimal operating conditions based on critical factors out of pH, conductivity, temperature, coagulant dosage, and initial settled turbidity to coagulant efficiency using a top performing polyaluminum chloride coagulant and a Central Composite Design (CCD) degian with response surface analysis.

3. Select two polyaluminum chloride coagulants from those examined to move forward into further testing at the pilot plant scale. Use the dual train pilot plant at BWD to test each polyaluminum chloride coagulant against aluminum sulfate. Analyze and rank the PACl coagulants on treatment effectiveness, cost, and envionmental impact compared to alum.

CHAPTER 2 LITERATURE REVIEW

2.1 History of Water Treatment

The history of drinking water treatment has been well documented. Before the discoveries of modern science, including germ theory, the best indicator humans had towards the safety of drinking water was appearance and taste. The earliest known recorded mention of treating water for consumption dates back as early as 4000 BC where Ancient Sanskrit and Greek documents referred to charcoal filtration, exposure to sunlight, boiling, and straining water ("25 Years of the Safe Drinking Water Act: History and Trends" 1999). In 1500 BC, Ancient Egyptians were reportedly using alum to settle out cloudiness in the water, which is now referred to as turbidity ("25 Years of the Safe Drinking Water Act: History and Trends" 1999). Tomb paintings show an apparent sedimentation apparatus made of large jars and siphoning hoses as well as wick siphons (Symons 2006). By the 8th century AD, Arabian scientists had discovered distillation to purify water (Hall and Dietrich 2000). Little progress was made in water treatment until the 17th century when Sir Francis Bacon applied the newly discovered scientific method to conduct water treatment experiments regarding filtration, boiling, distillation, and coagulation (Symons 2006). Within the same century, bacteria within water were identified by Antony van Leeuwenhoek, the inventor of the microscope (Gest 2004). The relation between bacteria, called animacules, and health was not recognized until the 19th century.

The first patented water treatment technology was a water filter by Joseph Amy. Amy proposed a sponge filter in lead or earthen containers to replace sand filters in copper that were sometimes used for household filtration. Although this eliminated copper in water treatment, it introduced lead which is also tied to toxicity in humans. Thankfully, this filter apparatus was not popular and not available after 1760 (Hall and Dietrich 2000). During the 18th century, scientists studied water softening and developed slow sand filters as well as up flow filtration. The 19th century ushered in the modern slow sand filter, modern lime softening, and the first modern water filter plant in Paisley Scotland. In addition, detailed studies using alum as a coagulant came from Algeria, and treatment plants in the US began using chemical coagulation in New Jersey ("25 Years of the Safe Drinking Water Act: History and Trends" 1999). Chlorine was used to purify foul smelling water as early as 1830 but it was not until germ theory and the discovery of tuberculosis bacteria that chlorination for disinfection purposes was used. This addition brings us to the basics of modern conventional water treatment.

2.2 Modern Conventional Surface Water Treatment

Conventional surface water treatment for producing drinking water is generally comprised of 5 main stages: coagulation, flocculation, sedimentation, filtration, and disinfection. First, raw water enters the treatment plant and undergoes the coagulation stage. One of the issues solved in conventional treatment is removal of solids in water. Some solids will settle out on their own over time, but others are held in suspension in the water. These are called colloids and repel each other electrostatically. The process keeping them in suspension is called Brownian motion ("10.27: Colloids" 2016). A positively charged coagulant chemical is added to neutralize the charges on these colloids. The coagulant is added in a process called rapid mix, in which mechanical mixers are used to disperse the coagulant and allow maximum contact in the water body. Once the particle charges have been neutralized, they can now stick together in small particles called micro floc. The table below describes the settling time through one meter of water if no treatment chemicals are added.

Table 1: Settling Time of Particles of Various Diameters (Peterson 2002).

Diameter of Particle	Type of Particle	Settling time through 1 m of water
10 mm	Gravel	1 second
1 mm	Sand	10 seconds
0.1 mm	Fine Sand	2 minutes
10 um	Protozoa, Algae, Clay	2 hours
1 um	Bacteria, Algae	8 days
0.1 um	Viruses, Colloids	2 years
10 nm	Viruses, Colloids	20 years
1 nm	Viruses, Colloids	200 years

After the initial rapid mix stage, the water enters a gentle mixing flocculation step. This step pushes the micro floc together allowing bonding and the formation of larger floc particles that are now visible to the eye. Some treatment facilities add additional coagulants at this stage or organic polymers to enhance the flocculation process. Additionally, coagulant aids and high molecular weight polymers can be added at this point to bridge, bind, and add strength to the newly formed floc (Minnesota Water Works 2009). The mixing speed is often tapered off as the floc size increases to prevent the floc from breaking apart. Once the floc has formed and has enough mass to settle, the water slowly moves through sedimentation tanks and the floc settles out of the water column. The particles that settle to the bottom, called sludge, are collected through the use of mechanical means, such as mechanical rakes. The sludge is transported to a thickening process and the water is moved to another stage of treatment (“Sedimentation Processes | IWA Publishing” n.d.).

At Beaver Water District, the water then moves to an optional stabilization step, where the alkalinity and pH are adjusted through lime and soda ash addition to make up for any alkalinity lost through the addition of coagulant chemicals. This step ensures the water will not be corrosive in the distribution system. Once the water leaves the sedimentation basins, it moves on to filtration where the remaining particulate matter is removed from the water by passing it through a bed of material. This is the final step in removing suspended matter through various mechanisms including straining, adsorption, absorption, sedimentation on the media, and biological action (Pensylvania Department of Environmental Protection 2014). At Beaver Water District, chlorine is added at the top of the filters to help restrict biological growth in the filters.

The most common forms of filtration utilized in water treatment facilities are slow sand and rapid sand filters. Other forms of filtration include reverse osmosis, microfiltration, and ultrafiltration. Beaver Water District utilizes mixed media filters containing anthracite coal, garnet, and sand. There are two separate treatment plants at BWD, the Steele plant utilizes shallow-bed Leopold filters while the Croxton plant utilizes deep-bed filters (Operator 2014). At post filtration, the water is disinfected to treat for parasites, bacteria, and viruses. Common disinfectants include chlorine, UV disinfection, chlorine dioxide, ozone, and chloramines (“Water Disinfection with Chlorine and Chloramine | Public Water Systems | Drinking Water | Healthy Water | CDC” 2020). Beaver Water District uses chlorine dioxide as a pre-oxidant and chlorine as a primary disinfectant.

2.3 Treatment Optimization for Coagulation

Optimizing the coagulation process by studying alternative coagulants and dosages is one of the easiest ways for a water treatment facility to cut costs while maintaining adequate water treatment. While a reduction in turbidity is important, it is also important to look at other factors when optimizing treatment dosages. Gologan & Popescu (2016) found that when they were optimizing dosages at a large multibarrior treatment plant, optimizing for a reduction in settled water turbidity and chlorine demand decreased costs of chemical additions but increased costs in waste disposal as more sludge was created. The researchers concluded that the optimal dose is one that gives you not only the lowest turbidity but one that also considers organic matter reduction, residual aluminum reduction, and a diminished effect on the raw water pH. In a study done at a water treatment plant in Poland, the optimal coagulation process was determined by the least expensive treatment, combined with the most effective coagulant, and lowest coagulant dosage (Wolska et al. 2018). The factors measured by Wolska et al. (2018) included pH, alkalinity, color, turbidity, UV254, DOC, and aluminum residuals.

McKeon and Muldowney (1987) examined the use of alternative coagulants, comparing ferrous sulfate and aluminum sulfate while considering turbidity reduction, chlorine demand, and lime usage. BWD uses aluminum sulfate as the primary coagulant, with ferrous sulfate as a secondary coagulant. The study outlined the different variables that go into making a successful treatment chemical decision. McKeon and Muldowney (1987) first used jar testing to decide whether to move forward with ferrous sulfate or ferrous chloride in the plant tests. They found that while ferrous chloride performed slightly better in the jar testing with turbidity removal, it required a higher lime dosage to stabilize the water, which would render it more expensive than ferrous sulfate (McKeon and Muldowney 1987). These considerations were used in this study at the BWD Drinking Water Facility.

Various researchers have indicated that while the jar testing method is beneficial, it could use some improvements. Alansari (2020) noted that settled water turbidity was used as a measure of optimum coagulation when treated water went through a filtration process. Their research suggests that to find the optimum chemical additions, turbidity should be assessed using jar tests and an additional filtration step (Alansari 2020).

2.4 Coagulant Characterization

There are two main types of coagulants: organic and inorganic compounds. Organic coagulants include polydiallyldimethylammonium chloride (DADMAC), which is a high-density cationic polymer. While organic polymers are far more effective at turbidity and NOM removal, their high cost prohibits their usage for most water treatment applications with the exception of very low turbidity waters where little chemical addition is required (Jin et al. 2006). Inorganic coagulants rely on aluminum or iron as the active ingredient. With aluminum-based coagulants, the aluminum is hydrolyzed to aluminum hydroxide floc as well as hydrogen ions. The hydrogen ions interact with alkalinity in the water and lower the water pH. This hydrolysis reaction takes place at a dosed water pH of 5.8 to 7.5 where colloidal matter is removed with adsorption with the metal hydroxide hydrolysis products that are formed. This is generally referred to as sweep-floc coagulation (Gebbie 2006). The reaction for alum is as follows:

$$Al_2(SO_4)^3{\bullet}18H_2O \rightarrow 2Al^{3+} + 3SO_4{}^{2-} + 18H_2O \rightarrow 2Al(OH)_3 + 6H^+ + 3SO_4{}^{2-} + 12H_2O \qquad (1)$$

While examining enhanced coagulation, Sun et al. (2019) concluded that there are three main flocculation mechanisms; adsorption and bridging, which are carried out by organic flocculants with a high molecular weight, and charge neutralization, which is carried out by high-charge density organic flocculants.

Polyaluminum coagulants are relatively new to the drinking water treatment industry with use beginning in the 1980's. There are three main types: polyaluminum chloride, polyaluminum chlorohydrate, and polyaluminum sulfate. Unlike alum or ferrous which have been used as industry standards, the polyaluminum coagulants can vary in their active ingredient concentration and basicity and can also contain other substances such as silica, sulfate, and calcium. PACl is formed through a partial hydrolysis of acidic aluminum chloride solution in a reaction vessel that controls heat and the addition of calcium carbonate (Zhang Lipeng 2014). During the hydrolysis reaction, the most commonly accepted species produced include Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_{3(am)}$ and $Al(OH)^{4-}$, as well as a dimer ($Al_2(OH)_2{}^{4+}$), trimer ($Al_3(OH)_4{}^{5+}$), and tridecamer ($Al_{13}O_4(OH)_{24}{}^{7+}$, often denoted by Al_{13} (Bertsch and Parker 1996)). Bao-Yu Gao (2005) examined the impact of speciation of hydrolysis. PACl was prepared and then separated and purified to increase the concentration of $Al_{13.}$ The PACl-Al_{13} was then compared against PACl and Aluminum Chloride for treatment efficiency. It was found that the PACl-Al_{13} exhibited the best results for removing turbidity, humic acid, and color. The floc formed by PACl-Al_{13} was larger and had a negative charge. Both PACl-Al_{13} and PACl performed coagulation and flocculation by charge neutralization and bridge-formation mechanism (Gao et al. 2005).

Pernitsky (2001) evaluated polyaluminum coagulants of low, medium, and high basicity with and without sulfate. Basicity is a quantitative measure of the hydroxyl ions in the chemical makeup of the coagulant. The higher the basicity, the lower the impact on dosed water pH (Gebbie 2006). It was discovered that PACls had higher solubility and higher pH of minimum solubility than alum. Also, for PACls, the pH of minimum solubility was positively correlated with basicity (Pernitsky 2001). The aluminum speciation data indicated that high basicity PACls contain the largest fraction of dissolved polymeric species in solution over the broadest pH range when compared to the other aluminum-based coagulants. This can be explained by the fact that the polymeric fraction present, or the pH range over which polymer was present, decreased as basicity was decreased. Pernitsky (2001) found that high basicity PACls were effective for all raw waters tested under a wide variety of treatment conditions. PACls with added sulfate or silica were found to be especially effective for treatment plants utilizing sedimentation applications (Pernitsky 2001).

All aspects of drinking water treatment should be viewed through the lens of human health which BWD first examined in their triple bottom line approach. Aluminum species can have negative impacts on human health. In a study by Krupinska (Krupińska 2020), aluminum species distribution analysis was performed on aluminum coagulants using spectrophotometry to measure the complexation time with Ferron. Three forms of Aluminum were categorized: monomeric Aluminum (Al) species, which had an instantaneous reaction (Al_a), medium-polymerized Al species that reacted within 120 minutes (Al_b), and colloidal Al that did not react within 120 minutes (Al_c) (Table 2). The removal mechanism of Al_a is complexation, Al_b is charge neutralization, and Al_c is adsorption (Krupińska 2020).

Table 2: The degree of polymerization of the aluminum coagulants tested according to conventional ferronometry (Krupińska 2020).

Aluminum Species	Aluminum Sulfate (VI)	Sodium Aluminate	PAX XL10	Flokor 105B
Monomeric Al Species (Al_a)%	91	100	6	3
Polymerized Al Species (Al_b)%	9	0	28	54
Colloidal Al Species (Al_c)%	0	0	66	43

According to Krupinska (2020), PAX XL10 and Flokor 105B, both polyaluminum coagulants, had the highest percentage of polymerized and colloidal Al species. After water treatment, the concentration of aluminum left in the water is determined by the products of the hydrolysis reaction of aluminum coagulants. The dissolved products not used to destabilize colloids remain after the treatment process. The type and concentration are influenced by coagulant type and dosage, and the treated water pH, alkalinity, and temperature. When characterizing dissolved aluminum in treated drinking water, Krupińska (2020) found that the concentration increased with the use of monomer forms (Al_a) and was lower when polymerized coagulants (Al_b) and (Al_c) were used.

2.5 Environmental Impact Including Sludge Production

Sludge production and disposal is a key concern for drinking water treatment facilities. All coagulants produce sludge through the flocculation process in the form of metal hydroxides combined with colloidal matter that has been removed from the raw water (Kumar and Balasundaram 2017). Both alum and PACl coagulants yield sludge that contains aluminum, inorganic and organic matter, and hydroxide precipitates. Other chemicals from the treatment process might also be present such as lime, activated carbon, or clay. The sludge is gelatinous due to its water retention and does not dewater easily (Nansubuga et al. 2013). The water content generally varies between 95 – 99% (Twort, Ratnayaka, and Brandt 2000). The most common sludge disposal methods currently used are landfilling and land application. It was estimated in 1997 that worldwide aluminum water treatment sludge production was 10,000 tons day^{-1} (Dharmappa, Hasia, and Hagare 1997). Neither of these options are beneficial to either the utility or environment. Inorganic aluminum ions can be toxic to certain crops which could complicate land application. Aluminum in soil is well known to by phytotoxic to coniferous trees. Additionally, tomatoes, lettuce, beet, alfalfa, barley, and some grasses are sensitive to aluminum concentrations in the soil. A study by Kluczka (2017) examining the speciation of aluminum ions in land applied sludge found that the form of aluminum predominant in the sludge depends primarily on the pH of the solution. This is meaningful as different forms of aluminum are more bioavailable than others. Kluczka found that the "composition of the aqueous aluminum sulfate (VI) solution, depending on its concentration, is predominated by $AlSO_4$ + (55–60%) and $Al(SO4)_2$ − (30%) ions while the concentration of the hydrated Al^{3+} ions is approximately 10–11%" (Kluczka et al. 2017). Aluminum sulfate was found to be dangerous to the environment as its ionic breakdown yields bioavailable aluminum species.

A more novel approach was studied by Nansubuga (2013), who examined the potential use of polyaluminum coagulant sludge in wastewater treatment. It was found that the application of this sludge as a flocculant aid during primary sedimentation decreased the total suspended solids, chemical oxygen dement, total ammonium nitrogen, and total phosphates in wastewater supernatant (Nansubuga et al. 2013).

Because the aluminum hydroxide present in the sludge is amphoteric, it is highly soluble in acidic or alkaline conditions. This lends the sludge to aluminum recovery through pH adjustment. This recovery process also releases water molecules bound to the floc leading to enhanced dewatering of the sludge (Nair and Ahammed 2017). Between removing the aluminum hydroxide and bulk of the water content, the sludge weight and volume are drastically reduced which lowers both the sludge handling cost as well as the environmental impact. It was discovered that sludges formed from PACl coagulants facilitated a greater aluminum recovery by percentage than sludge formed from alum coagulants. The aluminum recovery efficiency was increased from 62-74.5% with alum sludge to 70.7-84% with PACl sludge (Nair and Ahammed 2017).

BWD currently landfills or land applies its sludge. Aluminum sulfate, the current coagulant, is less desirable due to its increased bioavailability. Aluminum sulfate also requires a greater chemical addition due to its lower aluminum concentration and reaction efficiency, leading to greater sludge production. The use of a polyaluminum coagulant would reduce the potential environmental impact of water treatment at BWD by reducing the total amount of sludge production and producing a sludge with the potential for re-use in other applications.

CHAPTER 3 MATERIALS AND METHODS

3.1 Overview

The proposed research will take place at BWD, a drinking water treatment facility in Northwest Arkansas. To achieve above-mentioned research objectives, the investigation will consist of three research phases. Phase 1 consisted of narrowing down the polyaluminum chloride coagulants from eight to two based on treatment efficiency using jar testing. Phase 1 also comprised a central composite design experiment using jar tests to establish the significant variables in treating with PACls and devloping a treatment model. Phase 2 consisted running a pilot scale analysis of the selected coagulants from Phase 1 to generate data. Phase 3 consisted of a financial and environmetnal impact analysis of PACls vs alum. Raw Water Characterization

3.2 Raw Water Characterization

Untreated water used in this experiment was collected from the influent meter vault at BWD drinking water treatment facility. BWD gets their water from Beaver Lake in Northwest Arkansas. Beaver Lake is a reservoir created by the United States Army Corps of Engineers in the 1960's by damming the White River (Green and USGS 2013). The reservoir is the sole water source for BWD. Figure 1: Beaver Lake Map shows the entirety of Beaver Lake as it begins in the Southwest as the White River and ends in the Northeast at Beaver Dam. BWD has two raw water intakes located on Beaver Lake at the location indicated in the Figure.

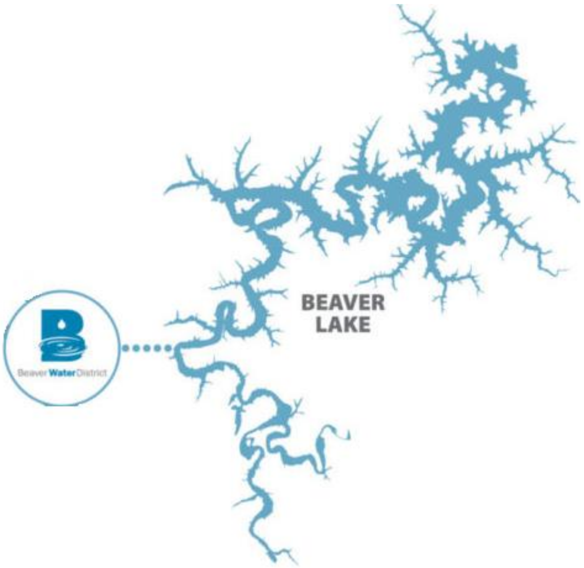


Figure 1: Beaver Lake Map

Beaver Lake is a river fed reservoir in the humid subtropical climate of Northwest Arkansas. The lake has a surface area of 114 km^2 with 722.6 km of shoreline and has a capacity of roughly 635.9 Trillion Gallons. It has an average depth of 18.3 m with a maximum depth of 73 m. It is a multipurpose water storage reservoir that supplies power generation, drinking water, flood control and recreational activities. Beaver Lake is monomictic, meaning it stratifies and mixes once per year with stratification happening in the summer and mixing in fall through early spring. The characteristics of the Lake change throughout the lake from riverine or river like, to a transition zone, to lacustrine or lake like towards the dam. The intakes for BWD are located in the transition zone of the lake.

Water quality from the intake is monitored on a daily basis by operators and laboratory analysts at BWD. Because the lake is monomitic and subject to runoff and rainwater influence, the water quality changes both throughout the seasons and during weather events. Water quality data was pulled from operations laboratory records. The alkalinity, hardness, pH, and temperature measurements were performed and recorded daily. The daily records were then averaged for each month. Each month was then averaged from the year 2016 to 2021 for each parameter. From this data, water quality information was obtained free from the direct influence of weather events. The water quality parameters of alkalinity and total hardness reach their peak during the late fall and early winter months of September through December from 2016 - 2021 as shown in Figure 2. These two factors are correlated and follow the same general trend.

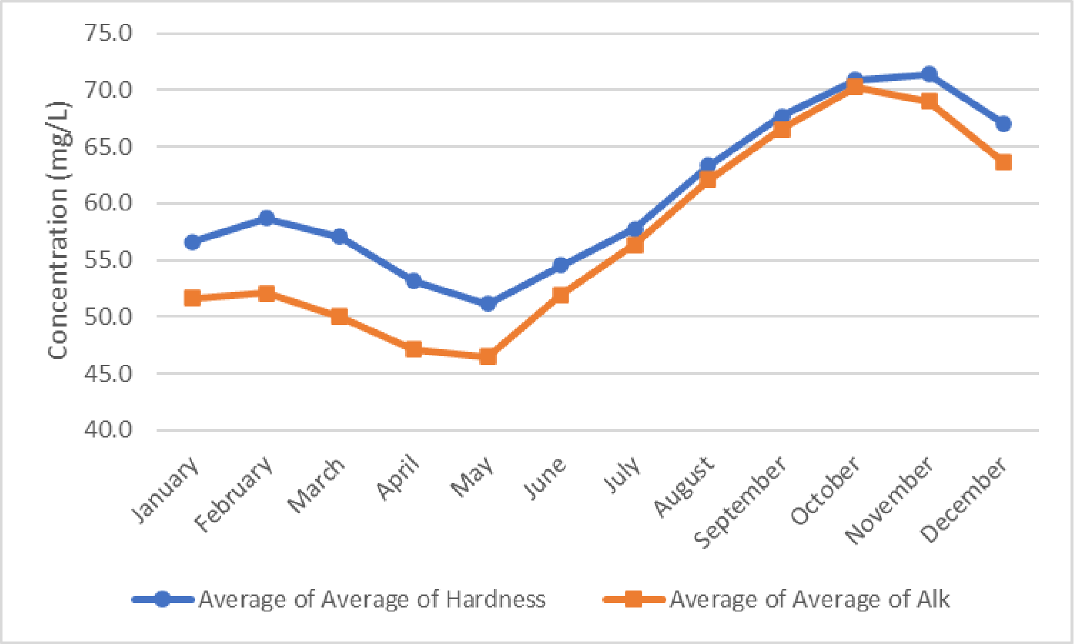


Figure 2: Monthly Average Alkalinity and Hardness at BWD Intake (2016-2021).

Other water quality parameters that appear to be correlated are pH and temperature that reach their highest values in the summer months of June through August. This can be seen in Figure 3: Monthly Average Temperature and pH at BWD Intake (2016-2021). During this time, turbidity ranged from 1 to 270 NTU with an average of 13.7 NTU. All of this data is summarized in The laboratory at BWD measures certain water quality characteristics daily. These include conductivity, iron, and manganese. Other water quality parameters are measured weekly, these include chloride and sulfate. The data was pulled for these parameters through the years 2006 to 2021 from the laboratory information system. The minimum, maximum, and average values are shown in Table 4..

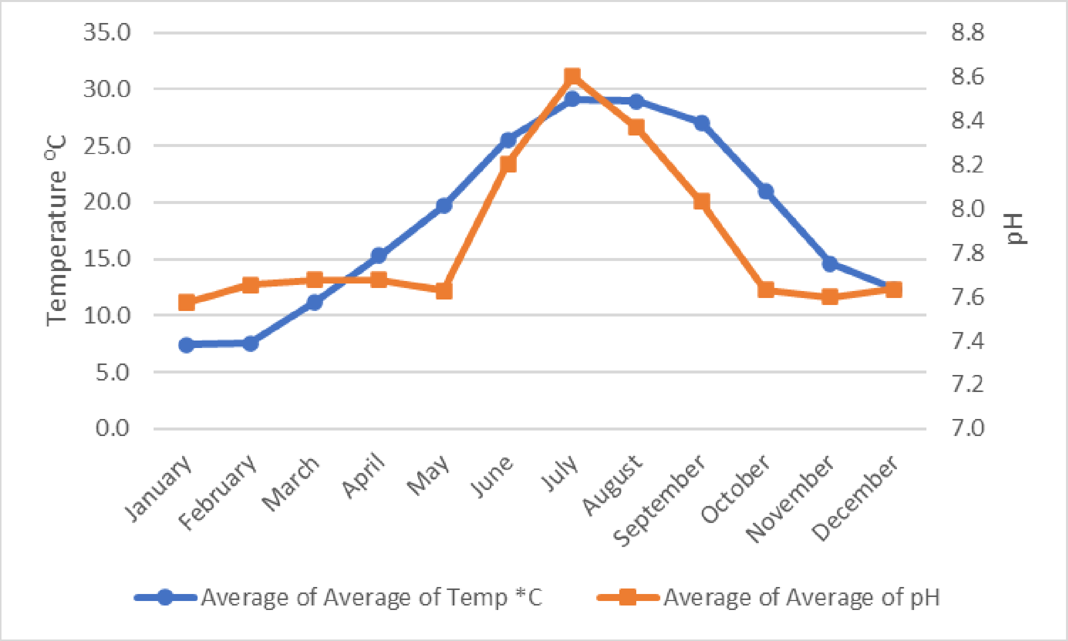


Figure 3: Monthly Average Temperature and pH at BWD Intake (2016-2021).

The laboratory at BWD measures certain water quality characteristics daily. These include conductivity, iron, and manganese. Other water quality parameters are measured weekly, these include chloride and sulfate. The data was pulled for these parameters through the years 2006 to 2021 from the laboratory information system. The minimum, maximum, and average values are shown in Table 4.

Table 3: Raw Water Quality Data from BWD Intake (2016-2021).

Test	Unit	Min	Max	Average	St Dev
Alkalinity	mg/L	18	85	56.8	12.0
Hardness	mg/L	18	89	60.4	10.5
pH	s.u.	6.8	9.4	7.9	0.4
Temperature	ºC	3.3	32.2	18.5	14.3
Turbidity	NTU	1	270	13.7	20.3

Table 4: Raw Water Quality Data from BWD Intake (2006-2021) *Chloride and Sulfate (2012-2021).

Test	Unit	Min	Max	Average	St Dev
Conductivity	uS/cm	60	241	147	25.8
Iron	mg/L	0.00	3.14	0.11	0.20
Manganese	mg/L	0.000	0.675	0.056	0.05
***Chloride**	mg/L	0.76	7.27	3.21	0.88
***Sulfate**	mg/L	0.00	13.55	6.67	1.51

3.3 Coagulant Selection

This experiment was conducted to potentially alter the treatment process at a large municipal water treatment facility, therefore, the chemical selection process needed to consider the reliability of the supplier. Chemicals were sourced from suppliers with a background in the water treatment sector who could provide the chemicals reliably at a high-volume demand. These suppliers were CedarChem, Chemtrade, GEO Specialty Chemicals, and USALCO. Raw water quality parameters were provided to the suppliers prior to their visit so they could recommend coagulant chemicals that would meet the specific needs of BWD. These included pH, turbidity, alkalinity, hardness, and water temperature. Some coagulants were formulated for this specific water quality and some were pre-made by the company. The suppliers ran jar tests at BWD using the jar test apparatus provided by BWD and BWD raw water. They then supplied reports with their findings to BWD. Even though only two treatment chemicals would be tested on a pilot scale, because the chemical suppliers did not use a consistent procedure when performing their jar tests, it was decided that the coagulation chemicals that produced positive results from the suppliers should be tested via a new round of jar testing with a standardized procedure within this experiment. All chemicals used for the experiments were listed in Table 5.

Table 5: Coagulant Comparison.

Coagulant Tradename	Coagulant Code Used	Aluminum %	Basicity %	Specific Gravity	Price per Pound
Alum	A	8.25	--	1.325	$ 0.06
HyperIon 4064 PACl 2	B	10.50	70	1.270	$ 0.35
HyperIon 4393	C	16.80	70	1.310	$ 0.35
1757 X1	D	16.06	Med-High	1.328	$ 0.35
1757 XL8, PACl 1	E	12.14	Med-High	1.292	$ 0.35
Ultrafloc 1406	F	15.69	74.2	1.306	--
Ultrafloc 3759	G	14.48	--	1.296	--
AlcoPAC 6	H	25.00	79	1.390	$ 0.28
AlcoPAC 1010	I	16.70	57	1.325	$ 0.22

3.4 Phase 1: Preliminary Jar Testing

Jar testing is an industry standard practice used to test treatment chemicals and optimize chemical dosages as well as treatment plant processes. The test uses a series of jars, each containing a variable speed mixer, to mimic the treatment process. During jar testing, water (often raw water from the same source as the treatment facility) is added to the series of jars along with treatment chemicals at various times during the process. These jars are set to mix concurrently at set speeds for a set amount of time to mimic the rapid mix, coagulation, and flocculation steps. They are then allowed to rest with no mixing for a set amount of time to mimic the settling phase of treatment.

3.4.1 Preliminary Jar Test Setup and Procedures

The preiliminary jar tests consisted of five total rounds or experiment sets. Rounds 1-3 were used to narrow down the coagulants moving forward with eight used in round 1, four in round 2, and three in round 3. Rounds 4-5 were used to optimize the dosage of the coagulants prior to Phase 2: Pilot Plant. Alum, the current coagulation chemical was also run as a control and baseline to measure against with a full set of alum in each round and a jar of alum in each PACl set.

3.4.1.1 Aluminum Equivalency and Coagulant Dosage

Chemical additions were calculated prior to analysis. All dosages were based on the alum feed concentration equivalency because this experiment was being used to determine the top performing coagulant based on the lowest coagulant dosage required to reach a turbidity as good as or better than alum. Aluminum Oxide, Al_2O_3, was used to compare dosages since alum and each PACl contained a different blend of ingredients and percentatge of Al_2O_3 .

The equation used to calculate feed equivalency is as follows:

$$\boldsymbol{Feed\ mg/L} = (\boldsymbol{Alum}\ \%\ \mathbf{Al_2O_3} \div \boldsymbol{Coagulant}\%\ \mathbf{Al_2O_3}) \times (\boldsymbol{Concentration}\ \frac{\boldsymbol{mg}}{\boldsymbol{L}}) \times (\%\ \boldsymbol{Relative\ Al\ Dose\ Needed})$$

Equation 1: Coagulant feed equivalency

For example: Based on Table 5 , Coagulant B has a Aluminum % of 10.5% and a specific gravity of 1.27 compared to 8.25% and 1.325 in Coagulant A. To deliver a 100% equivalent dosage of Coagulant B to Coagulant A, when coagulant A is being fed at 30 mg/L, you must perform the following calculation.

Feed mg/L = (8.25% / 10.5%) * (30 mg/L) * (100%)

= 23.6 mg/L

In order to take this into a jar testing dose, the specific gravity of each coagulant and total jar volume had to be taken into account. For the above coagulant, the following equation was used to determine the jar dosage.

Dosage uL = Concentration mg/L / specific gravity * final volume

Equation 2: Jar test coagulant dosage.

Dosage uL = 23.6 mg/L / 1.27 mg/L * 2000 mL

= 37.1 uL

Since the plant alum dosage might change for each round of jar testing, this could not be used as a comparison factor. The dosages then needed to be calculated into the Aluminum Oxide dose concentration of each jar. For coagulant B in the above example, this was calculated as:

Al_2O_3 Dose Concentration (mg/L) = concentration mg/L * Coagulant % Al_2O_3

Equation 3: Aluminum dose concentration

Al_2O_3 Dose Conentration (mg/L) = 23.6 * 10.5%= 2.48 mg/L

The dosages for coagulant B in round 2 were set up as follows based on a plant alum feed concentration of 30 mg/L (Table 6)

Table 6: Jar Test Dosage Calculation Example.

Jar	Coagulant	Relative Al Dose	Coagulant Concentration (mg/L)	Coagulant Dose (uL)	Al_2O_3 Dose (mg/L)
1	A	100%	30.0	45.3	2.48
2	B	70%	16.5	26.0	1.73
3	B	80%	18.9	29.7	1.98
4	B	90%	21.2	33.4	2.23
5	B	100%	23.6	37.1	2.48
6	B	110%	25.9	40.8	2.72

3.4.1.2 Raw Water Collection

Raw water was collected from a sample tap coming off the header pipeline in the influent meter vault, where raw water first enters the BWD Treatment Facility. This is water collected from an underwater inlet pipe at Beaver Lake. The water was passed through a large screen and was treated with a pre-oxidant, chlorine dioxide, prior to entering the treatment facility.

The water was collected in large clean 5 gallon buckets and carried to the testing lab. The water was used immediately for the jar test procedure. This water was then stirred to ensure homogeneous consistency and 2000 mL was measured out via graduated cylinder and poured into each of 6 square pre-washed acrylic jars on the jar test apparatus. The water was then run through a jar test procedure designed to mimic the plant processes at BWD.

The jar test stages were as follows:

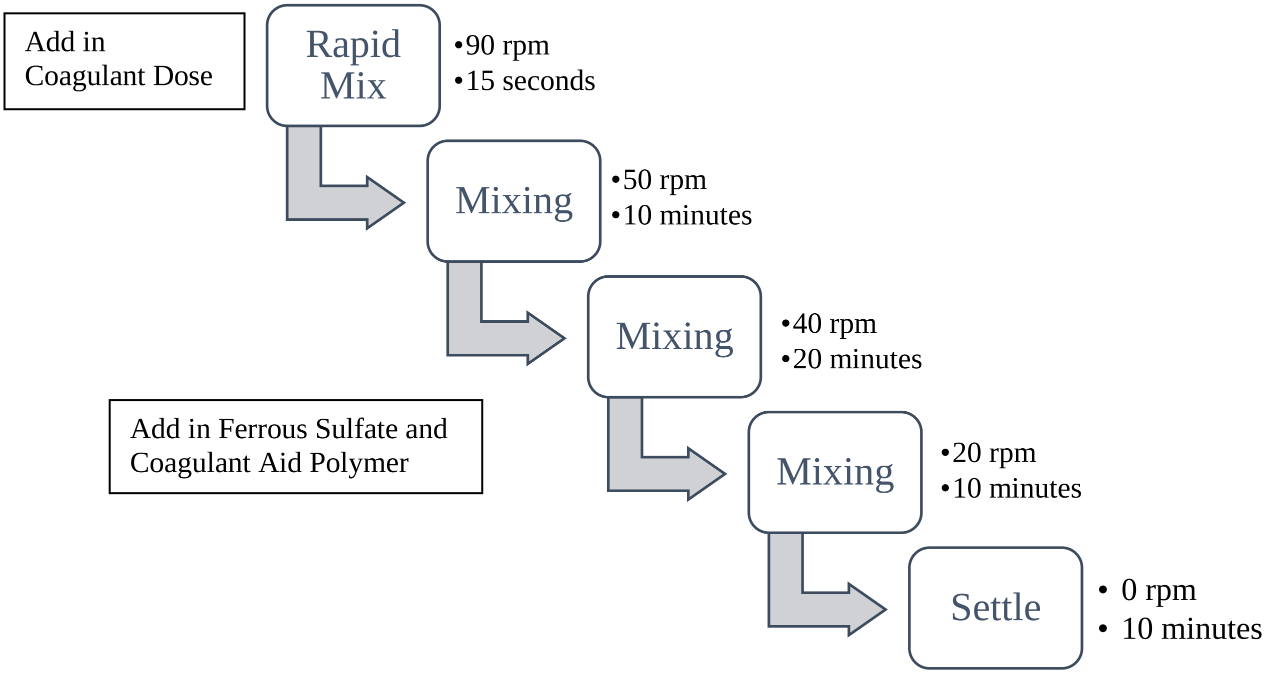


Figure 4: Jar Test Stage Diagram.

3.4.2 Preliminary Jar Test Control Measures

Due to the variable nature of the raw water source, enough water was collected at once to run a complete jar test set so that each jar contained water with the same starting water quality. The starting raw water quality was measured prior to each jar test set so that the final water quality after the jar test procedure could be evaluated relative to the incoming water quality. The jar test apparatus minimizes inconsistencies in the experiment by mixing each jar at the same speed at the same time. This was done with a series of paddles and rotors to control mixing speed and a control panel.

To keep the chemical reaction processes consistent between each jar, the jars were dosed simultaneously. Each coagulant and treatment chemical was measured out prior to the run and pipetted onto non-reactant silicone disks. The disks were then placed on a bar that rested on top of the jars, above the jar designated for each dose that spanned across the entire apparatus. This allowed us to flip the bar and dose each jar simultaneously with each chemical. The disks stayed in the jars for the duration of the set until they were cleaned for the next set. One jar each round was used to run the optimum dosage of alum through the jar test process alongside the alternative coagulants to measure reproducibility in the jar test process, sample collection, and sample analysis.

3.4.3 Preliminary Jar Test Independent Variables

Raw water variability led to having independent variables that could not be controlled and differed between jar test rounds and sets. These uncontrolled indepenent variables were measured and include raw water temperature, alkalinity, and pH. Controlled independent variables were coagulant selection and dosage.

3.4.4 Preliminary Jar Test Responses

Measured dependent variables include settled water pH, settled water alkalinity, settled water hardness, settled water DOC, settled water UV254, settled water turbidity, and filtered water turbidity. Dependent variables that were calculated include estimated sludge production and estimated NaOH dosage requirements.

3.4.5 Preliminary Jar Test Laboratory Analysis

Water was collected prior to testing to set a baseline measurement to compare with the treated water. This was done prior to each jar test due to the varaiblity in raw water quality inbetween jar test runs. After each jar test set was completed, water was taken from each of the treatment jars using a syringe with a tube attached on the end inserted below the water surface and below any floating flocculation matter. The samples were taken at the same depth in each jar, carefully as to not disturb any of the floc that has settled or clung to the side of the jars, and the samples taken were analyzed in the following ways (Table 7):

Table 7: Jar Test Lab Analysis Method Summary.

Metric	Method	Measurement	Instrument
% Settled and Filtered Turbidity Removal	SM2130B	Turbidity	HACH 2100 N Turbidimeter
Relative Change in pH	SM4500HB	pH	HACH HQ11d pH Meter
Relative % Alkalinity Retention	SM2320B	Alkalinity	HACH HQ11d pH Meter
Relative % UV254 Removal	SM5910	UV254	HACH DR6000 Spectrophotometer
Relative % DOC Removal	SM5310B	TOC	Shimadzu TOC-L

3.4.5.1 DOC Removal

Samples were collected from a single jar using the method outlined above. Samples were filtered using a 0.45 um filter screwed onto end of syringe and deposited into a clean 40 mL acidified (2 drops 2 N HCl) vial. The vial was filled taking care to not overfill but with no headspace and closed with screw top cap with silicone septa. The samples were batched and refrigerated until analysis following SM5310B using a Shimadzu TOC-L Analyzer. Analysis was completed by laboratory staff at BWD using a robust QC program including before and after blanks, a calibration standard, independent check standards before and after run, a duplicate sample, and a spike sample.

3.4.5.2 UV 254

Samples were collected using the method outlined above and deposited directly into a clean 10 mL plastic tube and sealed with screw on cap with headspace. Samples were analyzed following Standard Method: SM5910 using a HACH DR6000 Spectrophotometer. The method is checked monthly using a blank and an independent check standard.

3.4.5.3 pH and Alkalinity

Samples were collected from a single jar using the method outlined above excluding filtration. Samples were measured into 100 mL aliquots and poured into clean beakers. Initial pH was measured using a HACH HQ11d pH meter calibrated on a 3-point calibration curve following HACH manufacturer procedures and utilizing an independent check standard. The measurement was taken using Standard Method: SM4500HB. Alkalinity was analyzed using same aliquot following Standard Method: SM2320B. Alkalinity measurements included a standard check and blank once per run.

3.4.5.3 Settled and Filtered Turbidity

Samples for settled turbidity were collected from a single jar using the method outlined above excluding filtraiton using a HACH 2100 N Turbidimeter following Standard Method: SM2130B. The turbidimeter was calibrated following manufacturer procedure and was checked with a blank and independent check standard at least once per day of use. Filtered turbidity samples were collected using the method outlined above including filtration through a 0.45 um filter screwed onto end of syringe and measured identitally to settled turbidity.

3.5 Phase 1: Central Composite Design Jar Test for Significant Variables

In order to determine significant variables to treatment using PACl, three independent variables, coagulant chemical dosage, starting pH, and starting turbidity were tested at five different levels. The independent variables were chosen based on both literature information and the preliminary jar test data as they were found to be the most influential in affecting the settled and filtered turbidity levels.

3.5.1 CCD Jar Test Setup and Procedures

An experimental scheme was developed using Design Expert version 11 in order to optimize the controlling values of the independent variable and minimize the measured responses of settled and filtered turbidity. The coded values within the CCD/RSM analysis were -2, -1, 0, 1, and 2. The central point values for dosage, pH, and turbidity were chosen with the normal operation parameters of drinking water treatment processes in mind. Based on this design, eighteen experiments were conducted for the three independent variables, each at five levels with four replicates of the center values (Table 8).

The independent water quality variables were altered prior to collecting the baseline water quality analysis samples and beginning the jar test procedure. The water was run through a jar test procedure designed to mimic the plant processes at BWD, which was outlined in 3.4.1.

This experiment was performed twice. Initially, the five levels of initial turbidity were set at 0 (since raw water turbidity was not zero, the current raw water turbidity of 4.02 was used), 15, 30, 45, and 55.98 mg/L. The five levels of pH examined were 6.6, 7.2, 8, 8.8, and 9.4 SU. The five levels of coagulant dosage were set at 12.68, 20, 30, 40, and 47.32 mg/L (Table 8).

Table 8: CCD Experiment Design Trial 1.

Jar	Initial Turbidity (NTU)	Coagulant Dose (mg/L)	pH (SU)
1	4.02	30	8
2	15	40	8.8
3	15	40	7.2
4	15	20	8.8
5	15	20	7.2
6	30	30	6.61
7	30	30	8
8	30	12.68	8
9	30	30	8
10	30	30	9.39
11	30	30	8
12	30	47.32	8
13	30	30	8
14	45	40	8.8
15	45	20	7.2
16	45	20	8.8
17	45	40	7.2
18	55.98	30	8

During the second experiment, the five levels of chemical dosage were set at 0, 10, 20, 30, and 40 mg/L. The five levels of pH examined were 6, 7, 8, 9, and 10 SU. The five levels of initial turbidity were 0 (since raw water turbidity was not zero, the current raw water turbidity of 4.77 was used), 15, 30, 45, and 55.23 NTU (Table 9).

Table 9: CCD Experiment Design Trial 2.

Jar	Initial Turbidity (NTU)	Coagulant Dose (mg/L)	pH (SU)
1	15	10	7
2	45	10	7
3	15	30	7
4	45	30	7
5	15	10	9
6	45	10	9
7	15	30	9
8	45	30	9
9	4.77	20	8
10	55.23	20	8
11	30	3.18	8
12	30	36.82	8
13	30	20	6.32
14	30	20	9.68
15	30	20	8
16	30	20	8
17	30	20	8
18	30	20	8

3.5.1.1 Raw Water Collection

Water for this experiment was collected from the same influent water pipe as the Pilot Plant Trial. This water was coming directly from the Steele Influent Header. A large clean container located inside the pilot plant facility was filled with enough water to run all experiments within this design without needing to re-collect any water. This allowed for more control of the raw water quality throughout the experiment. Water from the main container was collected into a clean 5 gallon carboy container and immediately taken to the laboratory to use for the jar test experimental design.For the experimental runs, 2000 mL was measured out via graduated cylinder and poured into each of 6 square pre-washed acrylic jars on the jar test apparatus.

3.5.2 CCD Jar Test Control Measures

To ensure water would be at room temperature it was allowed to sit for 24 hours before any analysis was performed. The container was kept closed and water was collected using an outlet at the bottom. Prior to collecting water from the container, a mixer inside the container was started and ran for approximately 5 minutes. The mixer was kept on during the water collection procedure to make certain the water was homogeneous during each experiment. After bringing the 5 gallon container of raw water into the lab for jar test analysis, it was mixed prior to each jar test run. All jar test apparatus control measures implemented in the preliminary jar tests were used for the CCD jar tests.

3.5.3 CCD Jar Test Independent Variables

Artificial turbidity was created using a mixture of kaolin clay. De-Ionized water was mixed with the clay to create a stock turbidity solution which was used to dose the experimental jars prior to running the jar test procedures. The turbidity level was measured prior to each jar test run in order to calculate the necessary addition. The natural turbidity level in the raw water was taken into account so that the resulting turbidity would be a mixture of natural and artificial turbidity equaling the desired experimental level.

The pH of each jar was checked using a calibrated pH meter and the pH was adjusted using a 5 N Acid solution to equal the desired experimental level. The turbidity and conductivity levels of each jar were measured post pH adjustment to give an accurate baseline level. Prior to running the designed experiment, control experiments were conducted to examine the different variable repsonses.

3.5.3.1 CCD Jar Test Independent Variable Control Experiments

For the initial CCD Design, each of the 5 levels of targeted turbidity were run with no coagulant dosages but with all other standard jar test operating procedures. Settled and Filtered turbidty were analyzed to make sure the turbidity reductions achieved were from the pH adjustment and coagulant dosage and not from the general jar test procedure.

For the second CCD Design, a similar control experiment procedure was followed, but adjusting the pH and coagulant dosage and leaving turbidity to the current raw value, or value coming into the treatment plant at the time. This design was presented in Table 10. The measured parameters were pH adjusted turbidity to ensure that turbidity was not being produced or lost during the pH adjustment procedure, settled and filtered water turbidity.

Table 10: CCD Control Run Parameters.

Control Jar	Turbidity (NTU)	pH (SU)	Coagulant Dose (mg/L)
1	Raw Value	Raw Value	0
2	30	Raw Value	0
3	30	Raw Value -1.7	0
4	30	Raw Value +1.7	0
5	30	Raw Value	8
6	30	Raw Value	22

3.5.4 CCD Jar Test Responses

Dependent variables that were measured included settled water pH, settled water conductivity, settled water turbidity, and filtered water turbidity.

3.5.5 CCD Jar Test Laboratory Analysis

Water was collected and analyzed prior to testing to set a baseline measurement due to the variability of the raw water source. After the jar tests runs were completed, the samples were collected using the method from the preliminary jar tests and analyzed in the following ways (Table 11).

Table 11: CCD Lab Analysis Method Summary.

Metric	Method	Analyte	Instrument
% Settled and Filtered Turbidity Removal	SM2130B	Turbidity	HACH 2100 N Turbidimeter
Relative Change in pH	SM4500HB	pH	HACH HQ11d pH Meter
Conductivity	SM2510B	Conductivity	HACH SensION 5

3.6 Phase 2: Pilot Plant Trial

3.6.1 Overview

The pilot plant at BWD was designed to mimic the processes going on in the treatment facility. Water was plumbed in directly from the raw water intake source coming into the main treatment plant. It had already been dosed with an oxidant, chlorine dioxide, prior to entering the treatment plant. Treatment chemicals were collected directly from the treatment facility to use in the pilot plant. The pilot plant had two side by side treatment trains that were identical and operated independent of each other.

To establish that each treatment train was operating correctly and at the same efficiency, both treatment trains were run using the same treatment process, utilizing Aluminum Sulfate as the coagulant for each. Next, one of the PACl coagulants determined in Phase 1 Preliminary Jar Testing was examined on one of the treatment trains with the other side using aluminum sulfate as a control. This coagulant was examined for a week. Then, the second PACl identified in Phase 1 was ran using the same procedure. This was performed once in the summer and once in the fall.

For both trials, in-line analyzers and process grab samples were utilized to make any necessary treatment changes and to correct for any issues during the treatment process such as pump failure and feed line blockage. These readings were taken and recorded twice a day while the pilot plant was running. Laboratory analysis samples were taken Monday-Friday while the pilot plant was operating to be analyzed at the BWD water quality laboratory. These samples examined the utility and performance of each coagulant.

3.6.2 Treatment Train Set-Up

To reflect a scaled down flow rate from the treatment plant, each treatment train was set at 5 GPM.. This water was piped directly from the head box where the water entered the main treatment plant. The water first entered a rapid mix compartment where coagulation chemicals were added and mixing occured via an inline mixer. The water then flowed through four equally sized flocculation chambers with paddle mixers. Each chamber had a different mixing speed, slowing as the water entered through each chamber from 70, 60, 40, to 30 RPM allowing for floc development. A non-ionic polymer was added as a coagulant aid in the second flocculation basin. After leaving the flocculation basins, the water was then allowed to settle by passing through a sedimentation basin with a plate settler. The sludge was cleared from the sedimentation tank with a chain and flight system. The sludge was allowed to accumulate for 120 seconds and then flushed for 5 seconds from the lowest point on the tank. The water flowed from the top of the sedimentation tank to the lime basins where a lime slurry was added for pH and alkalinity adjustment.

The water was then pumped up to the top of the filter beds where it was split between two distinct filters measuring 3-meter tall and 20.3 cm in diameter. The Croxton filters contained approximately 122 cm of anthracite coal, 31 cm of sand, 10 cm of garnet, and 30 cm of torpedo sand. The Steele filters contained approximately 42 cm of anthracite coal, 23 cm of sand, 11 cm of garnet, and 30 cm of gravel. The filters were set up so that a liquid chlorine solution, for free chlorine disinfection residual, and sodium hydroxide, also known as soda ash for pH adjustment, could be fed at the top and the bottom of the filters.

3.6.3 Control Measures

Control measures utilized in this experiment were the identical treatment trains. Each coagulant was tested using the same treatment procedures, apparatuses, and chemical additions. For additional process control, the treatment trains contained in line analysis meters outlined in section **3.6.6** and operational grab samples were pulled, outlined in section **3.6.7.** These were monitored to ensure the treatment trains were running correctly with the same incoming water pH, turbidity, and flow to each train. These measurements were used to monitor the chemical feed pumps for consistency and to make adjustments as needed, and to troubleshoot any issues in the treatment process. In line meters were read twice daily and operational grab samples were taken once per day.

Chemical delivery pumps were all maintenance and calibrated prior to each pilot trial use to create a pump curve for accurate dosing. The pumps were run at increasing RPM speeds while measuring the volume of liquid chemical pumped through into a graduated cylinder. Each pump was tested using the chemical that would be dosed with that pump to account for changes in viscosity. These results were used to create a pump curve for each pump. The pump curves were then used to select the appropriate RPM needed based on chemical feed needs.

3.6.4 Independent Variables

The only controlled independent variable in this stage of the experiment was the coagulant chemical added to each treatment train. Uncontrolled but measured independent variables included the raw water quality parameters of temperature, pH, and alkalinity.

3.6.5 Responses

Dependent variable that were measured included THM formation and 7 day THM formation, chlorite, chloride, sulfate, alkalinity, pH, hardness, TOC, DOC. Dependent variables that were calculated included estimated sludge production, sludge disposal costs, and treatment costs.

3.6.6 In-Line Meter Analysis

Each train of the pilot plant was equipped with identical in-line meters. The meters were calibrated following manufacturer's instructions prior to the pilot plant run. The following were in-line meters that were utilized.

- Raw Water – pH
- Train 1 and 2 front end - flow rate, turbidity, SCD, settled pH, settled turbidity
- Train 1 and 2 back end - Croxton filter pH, Croxton filter turbidity, Croxton filter flow rate, Steele filter pH, Steele filter turbidity, Steele filter flow rate

3.6.7 Operation Grab Samples

Each treatment train was equipped with identical sample points within the treatment process. Samples were taken from these points and analyzed immediately using benchtop laboratory equipment within the pilot plant following the methods listed in Table 12. The laboratory equipment was calibrated per manufacturer's instructions prior to analysis.

The following were process grab samples that were analyzed.

- Raw water – turbidity, pH
- Train 1 and Train 2 settled water- pH, turbidity
- Train 1 and Train 2 after lime addition – pH
- Train 1 and Train 2 finished water – turbidity, pH, total chlorine

Table 12: Pilot Plant Grab Sample Analysis Method Summary.

Analyte	Method	Instrument
pH	SM4500HB	HACH HQ11d pH Meter
Total Chlorine	HACH8021	HACH Colorimeter II
Turbidity	SM2130B	HACH 2100N Turbidimeter

3.6.8 Laboratory Analysis

Each treatment train was equipped with identical sample points within the treatment process. Samples were taken from these points and analyzed by trained laboratory staff in the BWD

Water Quality Laboratory using methods approved for drinking water analysis. The following were analyses performed by the laboratory using the methods listed Table 13.

- Raw water- alkalinity, total hardness, chlorine dioxide, chloride, sulfate
- Train 1 and Train 2 settled water – alkalinity, total hardness, TOC, DOC
- Train 1 and Train 2 finished water – alkalinity, total hardness, chloride, sulfate, TOC, DOC, total trihalomethane, 7 day total trihalomethanes

Table 13: Pilot Plant Lab Analysis Method Summary.

Metric	Method	Analyte	Instrument
Relative % Alkalinity Retention	SM2320B	Alkalinity	Manual Titration
CSMR	EPA 300.0	Chloride	Metrohm Ion Chromatograph: 930 Compact IC Flex
Chlorine Dioxide	HACH Method 10126	Chlorine Dioxide	HACH DR6000
Relative % DOC Removal	SM5310B	DOC	Shimadzu TOC analyzer- Model TOC-L
CSMR	EPA 300.0	Sulfate	Metrohm Ion Chromatograph: 930 Compact IC Flex
Relative % TOC Removal	SM5310B	TOC	Shimadzu TOC analyzer- Model TOC-L
Total Hardness	SM2340C	Total Hardness	Manual Titration
DBP Formation Potential	Purge and Trap GC	Total THM	Parker THM analyzer
DBP Formation Potential	Purge and Trap GC	7 Day Total THM	Parker THM analyzer

3.6.9 Set-Up and Running Procedure

The treatment trains were cleaned prior to each treatment trial. This included draining out the mixing and settling basins and scrubbing them to remove any biological growth or sediment build up. All water delivery lines were flushed. The filter media was backwashed until effluent backwash water ran clear and showed no added color. Chemical feed pumps were maintenanced as outlined in **Section 3.6.3**. All in-line meters were maintained and calibrated per manufacture instruction. The treatment trains were then allowed to re-fill and run with no chemical feed additions. In-line meters were monitored to ensure that both trains were running the same. This also allowed both sets of inline meters to be compared for continuing calibration performance. Prior to calibrating chemical feed pumps, the stock treatment chemicals were prepared to the same feed concentrations used in the main treatment facility. The chemical batching procedures were carried out initially to fill the tanks and then as needed throughout the pilot plant run as the chemical levels dropped. The batching procedures followed are detailed in Table 14. The pilot plant trials then continued following the schedule outlined in **Section 3.6.1**

Table 14: Pilot Plant Chemical Batch Procedures.

Name	Amount Chemical	Amount Water	Batch Notes	Max Batch Tank Vol
Alum	2 L	to 20 L	1/4 Water then add chemical & shake	100 L
PACl 1& PACl 2	3 L	N/A	Undiluted	5.5 L
Ferrous	3 L	N/A	Undiluted	5.5 L
NonIonic Polymer	5 g	to 20 L	1/4 H_2O then add chemical & shake	40 L
Lime	50 g	to 20 L	1/2 H_2O then add chemical & shake	210 L
Caustic	100 mL	to 20 L	1/4 H_2O then add chemical & shake	90 L
Chlorine	200 mL	to 20 L	From Bleach, 1/4 H_2O then add chemical & shake	35 L

The online meters were checked twice per day. These are outlined in **3.6.6**. Any meter results outside control parameters underwent the following troubleshooting procedure. The treatment chemicals were first checked for volume, if any chemicals had run out or were getting low, they were re-made and added to chemical feed vessels. If that was not the issue, the chemical feed pumps were then checked to make sure they were feeding correctly. This was accomplished by checking the outlet for flow rate. If the flow rate was not correct, the connections and valves were checked for blockages and cleaned, if necessary, the tubing was checked for blocks, crimps, or wear in the peristaltic head that would impede flow. If these did not solve the flow rate, the pump speed would be adjusted accordingly to compensate for under or over feeding.

During each day of the experiment, operational grab samples, outlined in Section 3.6.7, would be collected once per day. These were measured in the pilot plant laboratory and used both as a system control and to collect dependent variable measurements. Once per day, on weekdays only, Lab Analysis Samples, outlined in Section 3.6.8, were collected. These samples were analyzed at the BWD water quality laboratory and used to collect dependent variable measurements. Prior to each coagulant change, the system was allowed to equilibrate again by running the system without any chemical additions and then with chemical additions, but no lab analysis samples.

CHAPTER 4 RESULTS AND DISCUSSION

4.1 Phase 1: Preliminary Jar Results and Discussion

Round 1 of the preliminary jar tests was conducted using Alum, Coagulant A, and all 8 polyaluminum chloride coagulants, Coagulants B-I. During this round, the coagulant dosages were miscalculated, leading to overdosing each jar by 49%. The results were still usable as some of the coagulants required lower dosages to reach a turbidity lower than or equal to the equivalent dosage of alum. Through this test, it was determined that Coagulant B, Coagulant E, Coagulant F, and Coagulant I would continue to Round 2. Figure 5: Round 1 Jar Test Results: Filtered Turbidity vs Al2O3 Dosage presented results from this round.

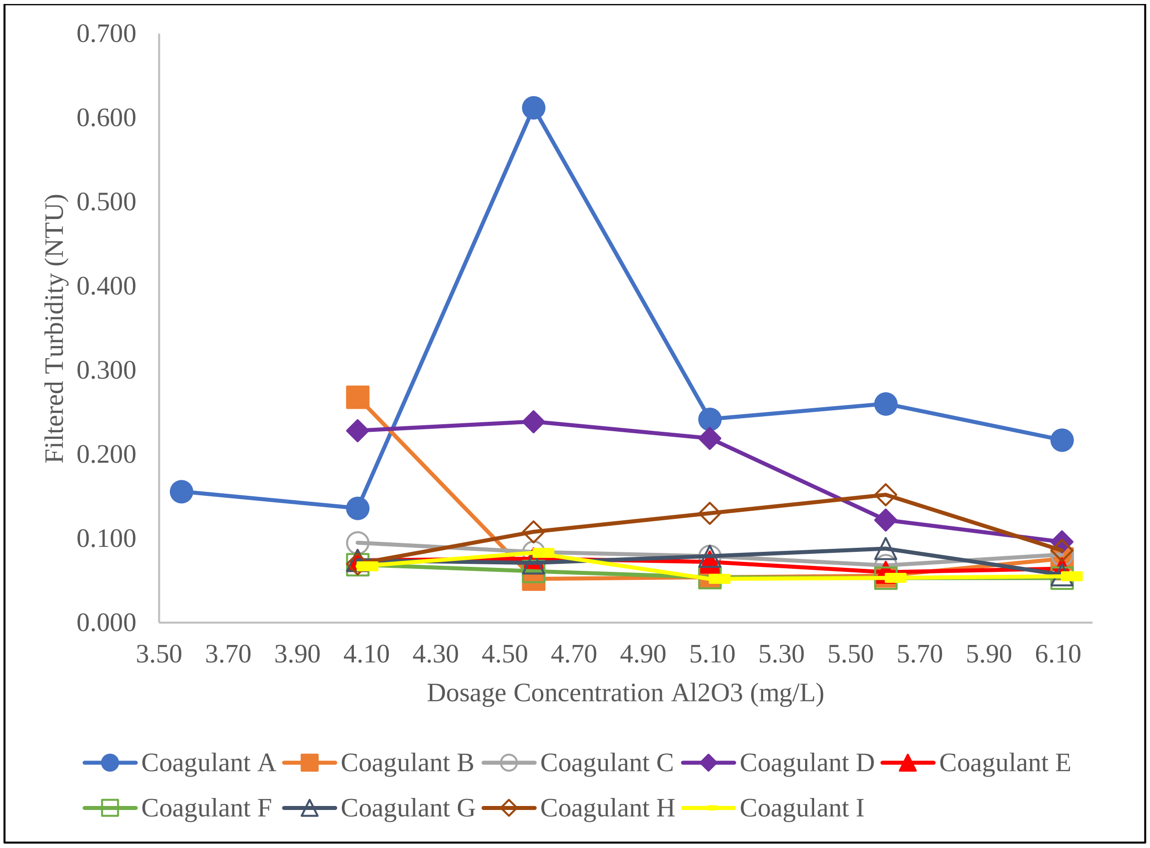


Figure 5: Round 1 Jar Test Results: Filtered Turbidity vs Al_2O_3 Dosage.

In Round 2, Coagulant A, B, E, F, and I were dosed at 70%, 80%, 90%, 100%, and 110% of the plant Alum dose concentration of 30 mg/L. This round was used to determine which two polyaluminum chloride coagulants performed as well as or better than alum and would move onto dose optimization and ultimately to use in the Pilot Plant Trials. Coagulants B and E had the best performance with dosages concentrations of 1.98 mg/L and 1.98 mg/L Al_2O_3 achieving a filtered turbidity of <0.15 NTU. Coagulant F also had similar performance to Coagulant B but exhibited a higher Filtered Turbidity of 0.368 NUT at the 70% dosage of 1.73 mg/L AL_2O_3 compared to Coagulant B's 0.297 NTU at 1.73 mg/L Al2O3. Results are documented below in Figure 6: Round 2 Jar Test Results: Filtered Turbidity vs Al2O3 Dosage.

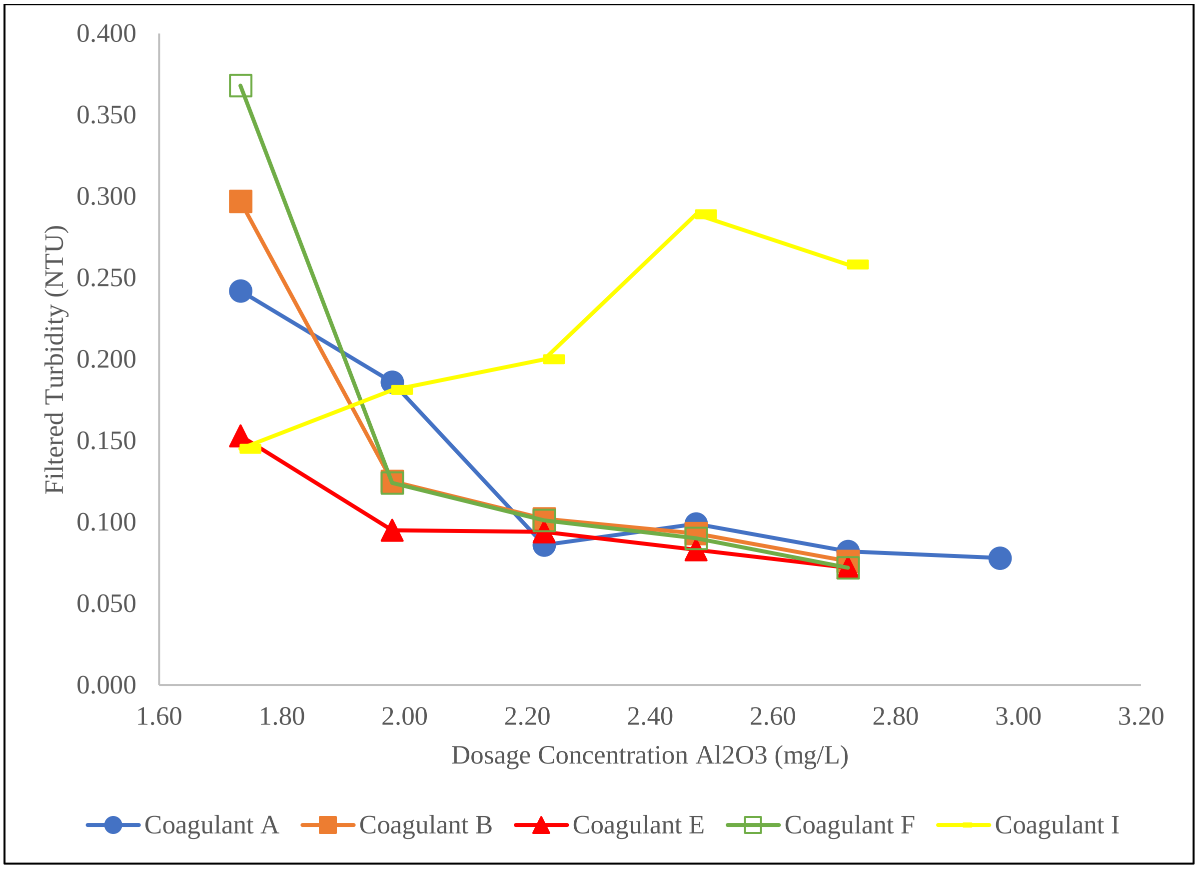


Figure 6: Round 2 Jar Test Results: Filtered Turbidity vs Al2O3 Dosage.

Round 3 tested coagulants A, B, and E. Coagulant E had lower Filtered Turbidity values than either Alum (coagulant A), or the other PACl, Coagulant B. All three coagulants achieved a filtered turbidity of <0.15 NTU at a dosage of 1.98 mg/L Al_2O_3. EPA requirements specify a Turbidity MCL of <0.30 NTU for combined filter effluents in finished waters which all of these coagulants met at their lowest dose. These results, found in Figure 7: Round 3 Jar Test Results: Filtered Turbidity vs Al2O3 Dosage, also showed the importance of dose optimization, as all three coagulants reached their optimized dosages around 1.98 mg/L Al_2O_3. Subsequently higher dosages did yield lower NTU values but only marginally so.

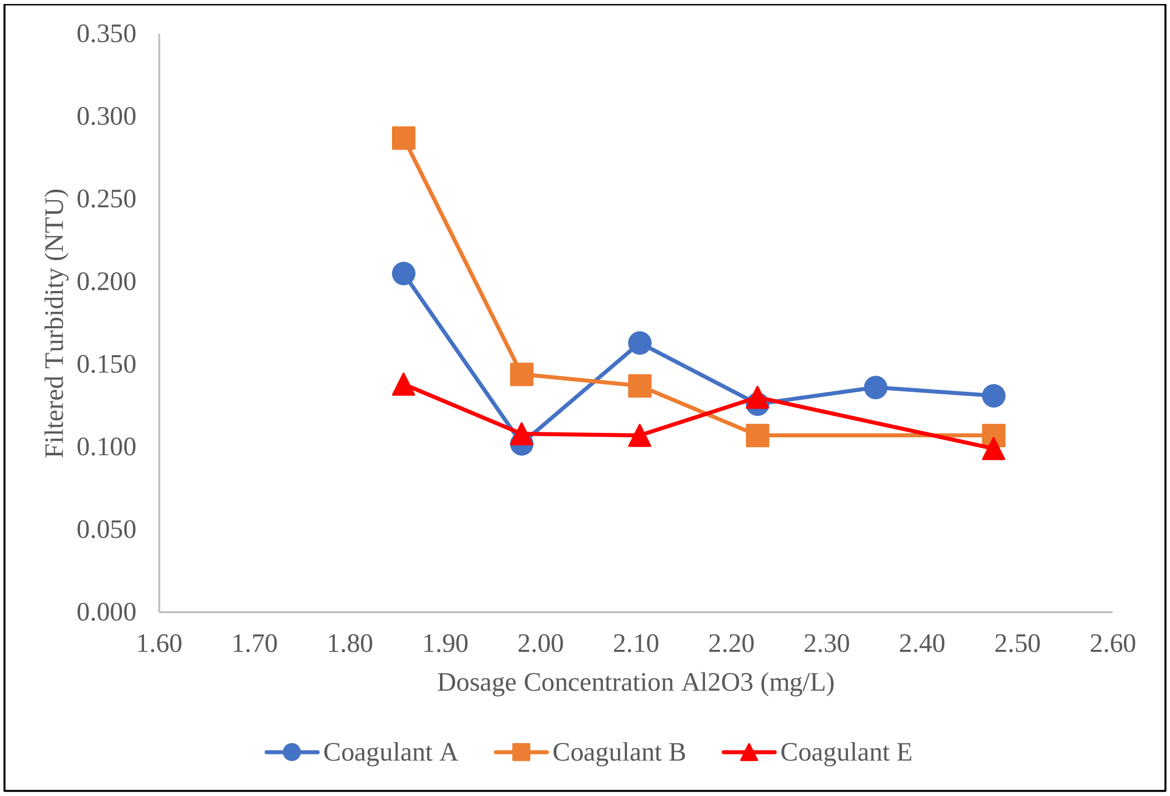


Figure 7: Round 3 Jar Test Results: Filtered Turbidity vs Al_2O_3 Dosage.

Round 4 was preformed directly prior to the summer Pilot Plant procedure to optimize Alum, Coagulant A, and the PACls selected during the preliminary jar tests in rounds 1-3, Coagulants B and E for the raw water quality coming into the pilot plant. In this round, the PACls were tested at 75%, 80%, 85%, 90%, and 100% of the plant alum dosage concentration at the time of 31.5 mg/L (2.6 mg/L Al_2O_3). Coagulants B and E reached optimum dose with a Turbidity of <0.1 NTU at 80% and 85% Alum Plant Dose Concentration respectively.

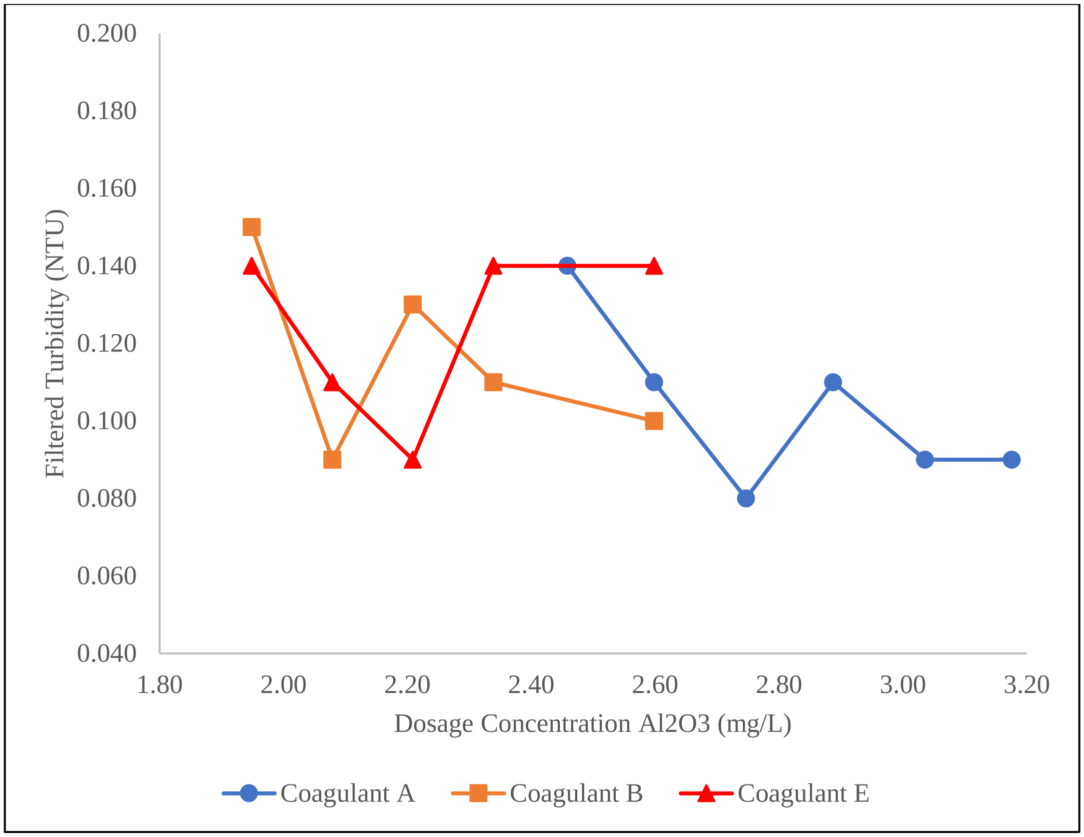


Figure 8: Round 4 Jar Test Results: Filtered Turbidity vs Al2O3 Dosage.

Round 5 was performed just prior to the Fall Pilot Plant run to optimize coagulant dosages and select appropriate dosages to use in the Pilot Plant. Much like Round 4, Coagulant B reached optimum finished water turbidity of <0.1 NTU at the second dosage level of 2.11 mg/L Al2O3 which was 80% of the current water treatment plant alum Al_2O_3 equivalent dosage (Figure 9).

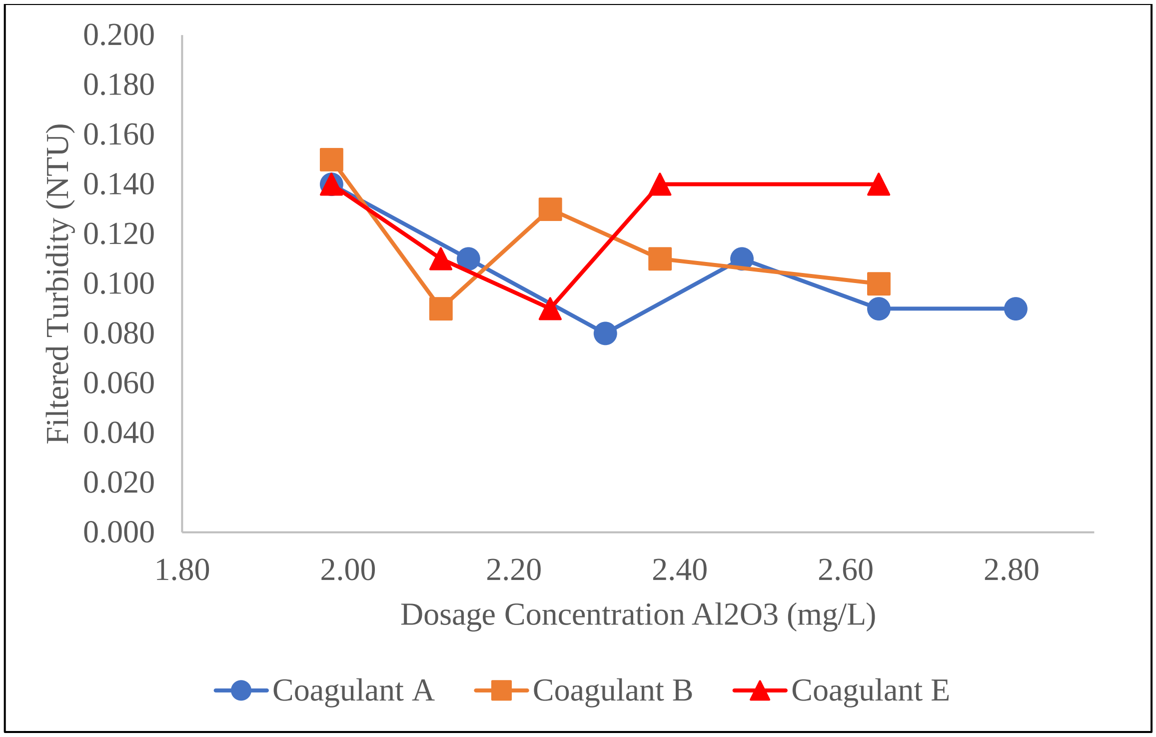


Figure 9: Round 5 Jar Test Results: Filtered Turbidity vs Al_2O_3 Dosage.

Initially, the purpose of Phase 1: preliminary jar tests was to decide what coagulants to move forward with into the pilot plant runs and then to determine the optimal dosages of each coagulant prior to each pilot plant run. This information was discerned from the preliminary test and moved onto the pilot scale runs. After looking at the data, we thought it would be both interesting and helpful to determine the most important water quality or experimental factors in turbidity removal for the polyaluminum chloride coagulants used in the pilot scale testing. Because this experiment was done using a natural system without controlling the input water quality, it was necessary to isolate different analysis parameters in order to see if they had any real effect on the turbidity removal efficiency. We attempted to compare jar test runs that used the same coagulant and dosage and had similar starting pH but differing starting temperature to see if the temperature had an effect on coagulation efficiency. An issue found was that the other input factors also varied. For instance, every run at a low temperature and neutral pH also had a higher starting turbidity due to a turbidity event. Because of this there was no way to be sure if the lower temperature or higher starting turbidity was the significant factor in turbidity removal. We found that this was not possible with the jar test procedure we had used. The jar tests didn’t have enough replicate samples run to statistically prove that the variables significantly impacted the turbidity removal.

Because there were so many factors that could be affecting the coagulation efficiency, using a single variable manipulation design was not ideal as there would be a large number of jar test runs required to test each one in isolation. It was decided that a second part would be added to Phase 1, Central Deposit Design, or CDD experimental design.

4.2 Phase 1: CCD Jar Test Results and Discussion

The first CCD test was performed following the design outlined in Table 8.

During this experiment, the raw water turbidity coming from Beaver Lake was 2.73, so this was the lowest level of turbidity and represented the first level. After looking at the data, it was determined that the dosages were set too high. Almost all filtered turbidity levels, with the exception of Jar 4, were at or below the threshold value of 0.15 NTU (Table 15). It was also proposed that perhaps the filtering would remove turbidity below 0.150 consistently no matter the treatment parameters established.

Table 15: CCD Trial 1 Results.

Jar	Initial Turbidity (NTU)	Coagulant Dose (mg/L)	pH (SU)	Initial Turbidity after pH adjust (NTU)	Final Settled Turbidity (NTU)	Final filtered Turbidity (NTU)
1	Raw	30	8	2.73	0.262	0.077
2	15	40	8.8	15.1	0.374	0.125
3	15	40	7.2	14.9	0.362	0.115
4	15	20	8.8	15.1	0.44	0.202
5	15	20	7.2	15	0.492	0.101
6	30	30	6.61	30.1	0.456	0.043
7	30	30	8	30.5	0.385	0.075
8	30	12.68	8	30.1	0.542	0.098
9	30	30	8	30	0.405	0.062
10	30	30	9.39	30.1	0.64	0.118
11	30	30	8	29.7	0.45	0.068
12	30	47.32	8	29.8	0.394	0.108
13	30	30	8	29.9	0.399	0.072
14	45	40	8.8	44.1	0.368	0.111
15	45	20	7.2	44.1	0.405	0.091
16	45	20	8.8	46.1	0.442	0.151
17	45	40	7.2	44.2	0.365	0.074
18	55.98	30	8	55.9	0.412	0.096

Moving forward, a second CCD design was established with lower dosages. The filtered turbidity would also be examined post pH adjustment and before any treatment had taken place to to ensure the treatment parameters were in fact altering this variable. This design is outlined in Table 9. During this experiment, the raw water turbidity coming from Beaver Lake was 9.05, so this was the lowest level examined and represented the first level of the 5 levels. The results were presented in Table 16.

Table 16: CCD Trial 2 Results.

Jar	Initial Turbidity (NTU)	Coagulant Dose (mg/L)	pH (SU)	Initial Turbidity after pH adjust (NTU)	Initial Filtered Turbidity (NTU)	Final Settled Turbidity (NTU)	Final filtered turbidity (NTU)
1	15	10	7	14.4	1.2	3.99	0.366
2	45	10	7	37.5	0.971	14.8	0.383
3	15	30	7	14.5	1.16	0.587	0.135
4	45	30	7	37.5	1.04	0.66	0.087
5	15	10	9	14.9	1.21	13	0.626
6	45	10	9	37.5	1.02	28.1	0.713
7	15	30	9	14.8	1.18	0.671	0.099
8	45	30	9	38.6	1.02	0.662	0.144
9	Raw	20	8	9.05	0.851	0.181	0.101
10	55.23	20	8	45	2.5	0.856	0.168
11	30	3.18	8	26.1	1.3	23.8	0.187
12	30	36.82	8	26.5	1.27	0.46	0.052
13	30	20	6.32	26.1	0.668	1.92	0.16
14	30	20	9.68	26.5	0.942	9.84	0.32
15	30	20	8	26	1.21	1	0.087
16	30	20	8	26.2	1.18	0.802	0.115
17	30	20	8	26.5	1.04	1.28	0.085
18	30	20	8	26.5	1.35	0.996	0.11

For this experiment set, the initial filtered turbidity was too high to fall within our regulatory operating parameters for turbidity of <0.15 NTU. Also, in a practical sense, with turbidity that high coming into the filters, a treatment facility would need to backwash often to prevent clogging or other compromising issues. Initially, it appeared that the experiment design with lowered dosages had been successful as not all filtered turbidites fell below the threshold of 0.150 NTU. An interesting observation from these experiments was that the starting turbidity did not seem to be a determining factor in the settled or filtered turbidity values. In both experiments, the highest turbidity level of around 55 NTU was brought down to right around or below the 0.150 NTU threshold with the midpoint coagulant dosages and midpoint pH. Using this observation, we were able to remove initial turbidity as a variable critical to the coagulation efficiency in this experimental design in hopes of producing a model to fit the results.

In Design Expert, the experimental design was adjusted to remove initial turbidity as a variable which reduced the number of experiments required to 12. The results from CCD Design Experiment 2 were added into the new experimental design, including only the 12 that fit the new design parameters. The new design parameters and results are seen in Table 17 below.

Table 17: CCD Experiment Refinement Responses.

Jar	Coagulant Dose (mg/L)	pH (SU)	Initial pH	Final Settled Turbidity (NTU)	Final Filtered Turbidity (NTU)
1	10	7	3.99	3.99	0.366
2	34.14	8	0.46	0.46	0.052
3	20	9.41	6.84	6.84	0.32
4	30	7	0.587	0.587	0.093
5	10	9	13	13	0.626
6	20	8	1.28	1.28	0.085
7	20	8	0.996	0.996	0.11
8	30	9	0.671	0.671	0.099
9	20	8	1	1	0.087
10	5.86	8	13.8	13.8	0.65
11	20	8	0.802	0.802	0.115
12	20	6.59	1.92	1.92	0.16

4.2.1 Quadratic models developed using CCD/RSM data

The central composite design (CCD) algorithm in the Design-Expert software produced two quadratic models for the two independent variables (coagulant dosage and adjusted raw water pH) tested in this study. The results showed that the two models were able to fit the two response variables (final settled turbidity and final filtered turbidity) relatively well. In addition to the model fitting results, the ANOVA analysis also revealed the significant relationships between the independent and response variables using the fitted quadratic equations as discussed below.

The quadratic equations of the models for coagulant dosage and operating pH with final settled turbidity and final filtered turbidity as response variables were presented in Equation 4 and 5. All the coefficients (β_is) in the two equations were generated by the regression analysis of the experimental data performed by the Design-Expert software.

$$\textit{Final settled turbidity (NTU)} = 1.02 - 4.7\,D + 1.63\,pH - 1.48\,D*pH + 2.94\,D^2 + 1.57\,pH^2$$

Equation 4

$$\textit{Final filtered turbidity (NTU)} = 0.0992 - 0.2057\,D + 0.0615\,pH - 0.0635\,D*pH + 0.126\,D^2 + 0.0705\,pH^2$$

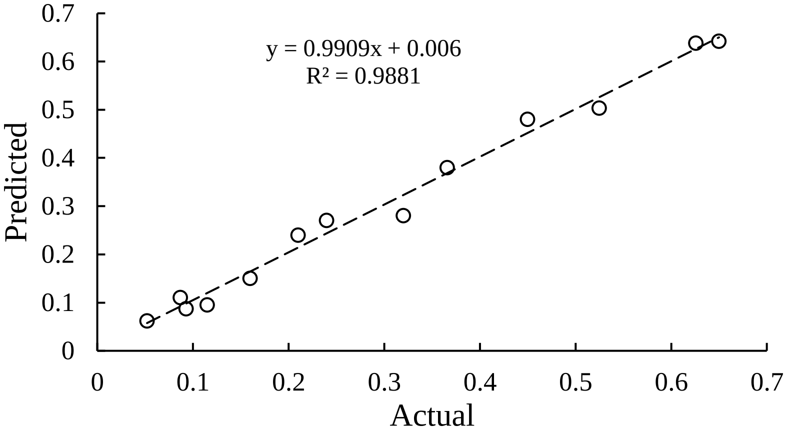
Equation 5

Where: D – coagulant dosage (mg/L); pH – adjusted raw pH

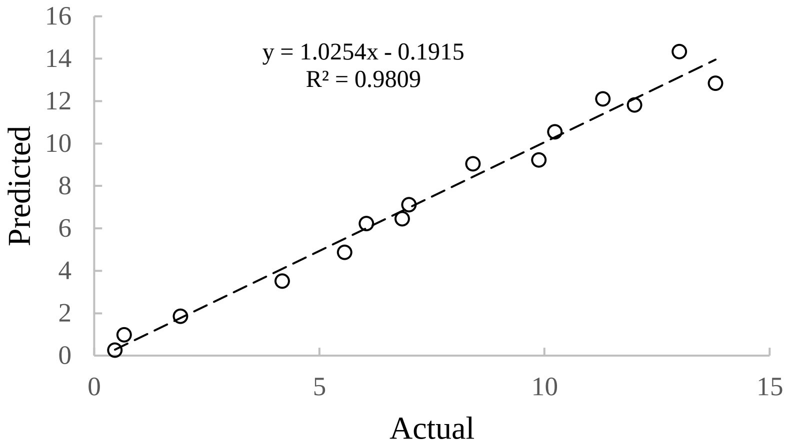
Table 18 presented the results of ANOVA analyses for Equation 4 and 5, which showed that the two models demonstrated a significant goodness-of-fit with *F* values being 533.66 and 510.65, repectively. The corresponding *P* values were all less than 0.0001 (much smaller than 0.05). Generally speaking, the goodness-of-fit of regression models for both final settled turbidity and final filtered turbidity was similar because the *F* values for Equation 4 and 5 were very close to each other (533.66 vs. 510.65). The goodness-of-fit for regression models could also be examined using another important factor, i.e., the “lack of fit” analysis. According to Table 18, both *P* values for the lack of fit analyses were much greater than 0.05 (0.1345 for Equation 4 and 0.6386 for Equation 5), rendering the “lack of fit” insignificant. To further verify the models, additional experiments were conducted to correlate the predicted with the actual responses (Figure 10). The coefficients of determination for the two responses were 0.9881 to 0.9809, respectively. This indicates that both regression models can explain at least 98% of the response variability if these models are used to simulate the experiments. Therefore, it can be concluded based on the data analysis that the two quadratic regression models generated by the CCD/RSM design are able to fit the experimental data adequately. It is thus applicable and feasible to use these models to accurately estimate the effects of the two independent parameters (coagulant dosage and adjusted raw pH) on the water purification process performance evaluated in this study with respect to reductions in final settled turbidity and final filtered turbidity.

Table 18: ANOVA analysis for fitting models for final settled turbidity and final filtered turbidity.

Model ANOVA Analysis	Final settled turbidity (NTU)	Final filtered turbidity (NTU)
Sum of squares	268.67	0.50
Mean squares	53.73	0.10
R square	0.9978	0.9977
Adjusted *R* square	0.9959	0.9957
Mean	4.03	0.23
Std. deviation	0.3173	0.014
C.V. (%)	7.88	6.08
Adeq Precision	59.243	58.786
F value	533.66	510.65
P value	< 0.0001	< 0.0001
Lack of fit		
F value	4.20	0.6401
P value	0.1345	0.6386



(a)



(b)

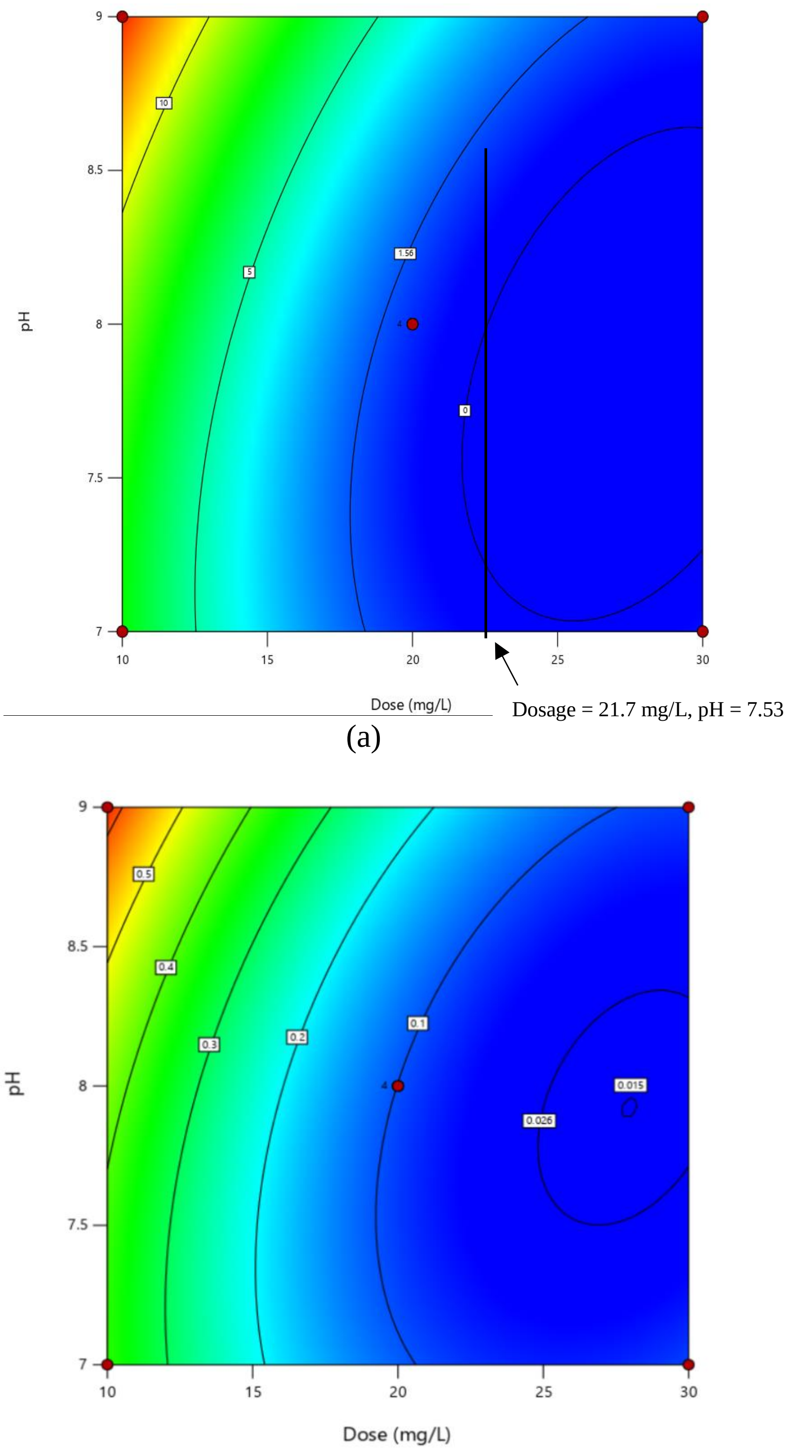
Figure 10: The linear correlations between the actual and predicted data for the two models: (a) final settled turbidity; (b) final filtered turbidity.

To further assess the goodness-of-fit of the regression models, more parameters including adjusted R^2, adequate precision, and coefficient of variation (C.V.) were also investigated in addition to R^2, F, and P values (Table 18). The adjusted R^2 for the two regression models with the independent variables (coagulant dosage and adjusted raw pH) were 0.9959 and 0.9957, respectively, which meant that over 99% of variation for both final settled turbidity and final filtered turbidity in the predicted values could be explained by the variation in coagulant dosage and adjusted raw pH. The very high values of the adjusted R^2 evidenced that the goodness-of-fit of the two models was robust, and they could be used to precisely determine the response variables based on the independent variables in simulation (Lehmann and Romano 2005). Besides these findings, the adequate precision values for the two models were much greater than 4.0 (59.24 for the final settled turbidity model and 58.79 for the final filtered turbidity model), which indicated adequate signals to constitute a narrow spread of data around the means in making predictions. This information clearly infers that use of these models can sufficiently estimate the values of responses within the design space defined in the experimental design in this study (Draper 1998).

The ANOVA analysis of the two variables (coagulant dosage and adjusted raw pH) in the regression equation (4) and (5) as well as their interactions was presented in Table 19. The results showed that for both models, the *P* values for all the coefficients in the regression equations were all equal to or smaller than 0.0001, which indicated that the two variables, their interactions, and their quadratic forms all had a significant impact on the response variables (final settled turbidity and final filtered turbidity). The interacting effect of coagulant dosage and adjusted raw pH could be verified by the contours shown in Fig. 11a and 11b, in which elliptical shapes were demonstrated. The elliptical contour shapes indicated that the interacting effect between the two independent variables was significant for both responses (Fig. 11) (Stagni and Lizzio 1983).

Table 19: ANOVA analysis for model variables and their interactions for final settled turbidity and final filtered turbidity.

Model ANOVA Analysis (Final settled turbidity)	**Response Variables**				
	A (dose)	**B (pH)**	**A x B**	**A^2**	**B^2**
Sum of squares	176.70	21.29	8.78	55.49	15.77
Mean squares	176.70	21.29	8.78	55.49	15.77
F – value	1754.86	211.48	87.19	551.08	156.57
P – value	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
(Final filtered turbidity)					
Sum of squares	0.3385	0.0303	0.0161	0.1016	0.0318
Mean squares	0.3385	0.0303	0.0161	0.1016	0.0318
F – value	1727.89	154.61	82.32	518.59	162.35
P – value	<0.0001	<0.0001	0.0001	<0.0001	<0.0001



Dosage = 21.7 mg/L, pH = 7.53

(a)

(b)

Figure 11: The response surface contours with respect to coagulant dosage and adjusted raw pH, (a) final settled turbidity and (b) final filtered turbidity.

4.3 Phase 2: Pilot Plant Results and Discussion

To analyze the pilot plant experiments performed, Pilot plant process grab samples along with samples collected and run in the BWD laboratory were analyzed. As the primary concern for drinking water is public health, turbidity removal is the first condition looked at when evaluating the coagulants.

Turbidity is regulated at BWD by the USEPA as part of the Long Term 2 Enhanced Surface Water Treatment Rule. Although the rule can be complicated and has a few ways to meet criteria, in general, the water treatment facility must maintain a single fitler turbidity equal to or less than 0.15 NTU in at least 95% of it's turbidity measurement and a combined filter turbidity equal to or less than 0.30 NTU in at least 95% of it's turbidity measurement (US EPA 2015a). The turbidities recorded from grab samples during the pilot plant experiment can be seen in **Error! Reference source not found.** The solid red line indicates the 0.15 N TU limit set by the USEPA. There were only a couple of data points that fell above this limit. In addition to the USEPA guidelines, BWD tries to go above and beyond by following the American Water Works Association Partnership for Safe Water limits, which require a combined filter turbidity level at or below 0.10 NTU in 95% of samples (Cheng et al., n.d.). This can be seen in Figure 12 represented by the dashed red line. PACl 1 is the only coagulant that consistently achieved this lowered turbidity level standard.

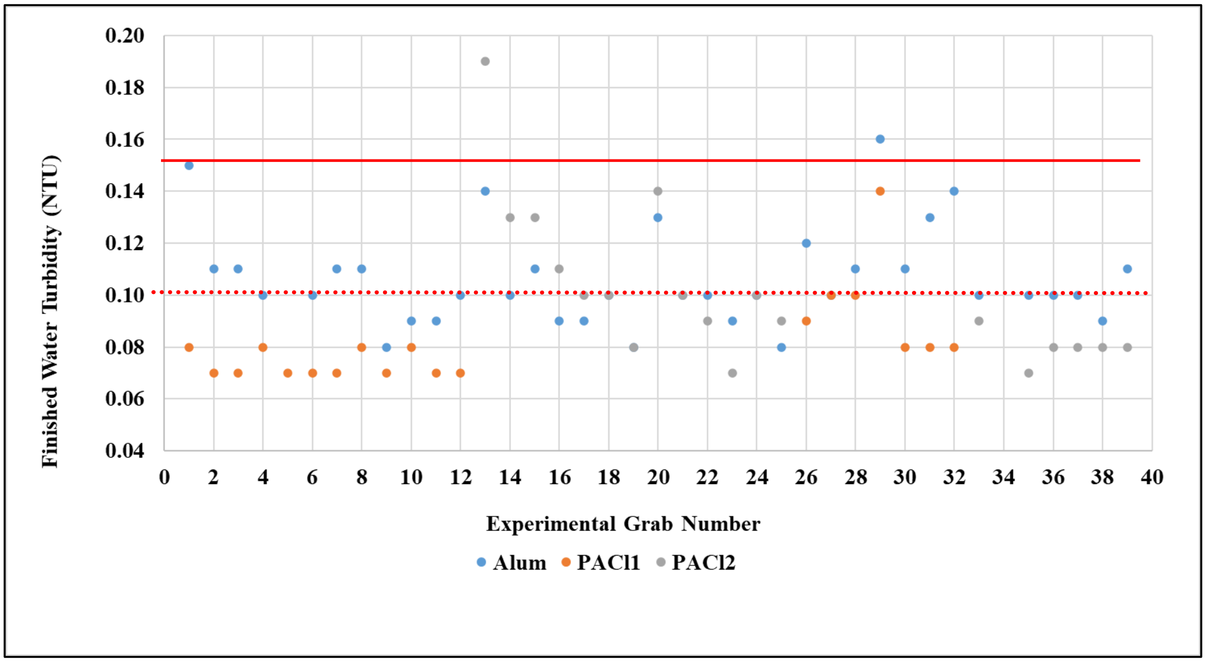


Figure 12: Finished Water Turbidity Results from Pilot Plant Experiment.

Figure 13 and Figure 14 below summarize the % Turbidity Removal Per Coagulant.

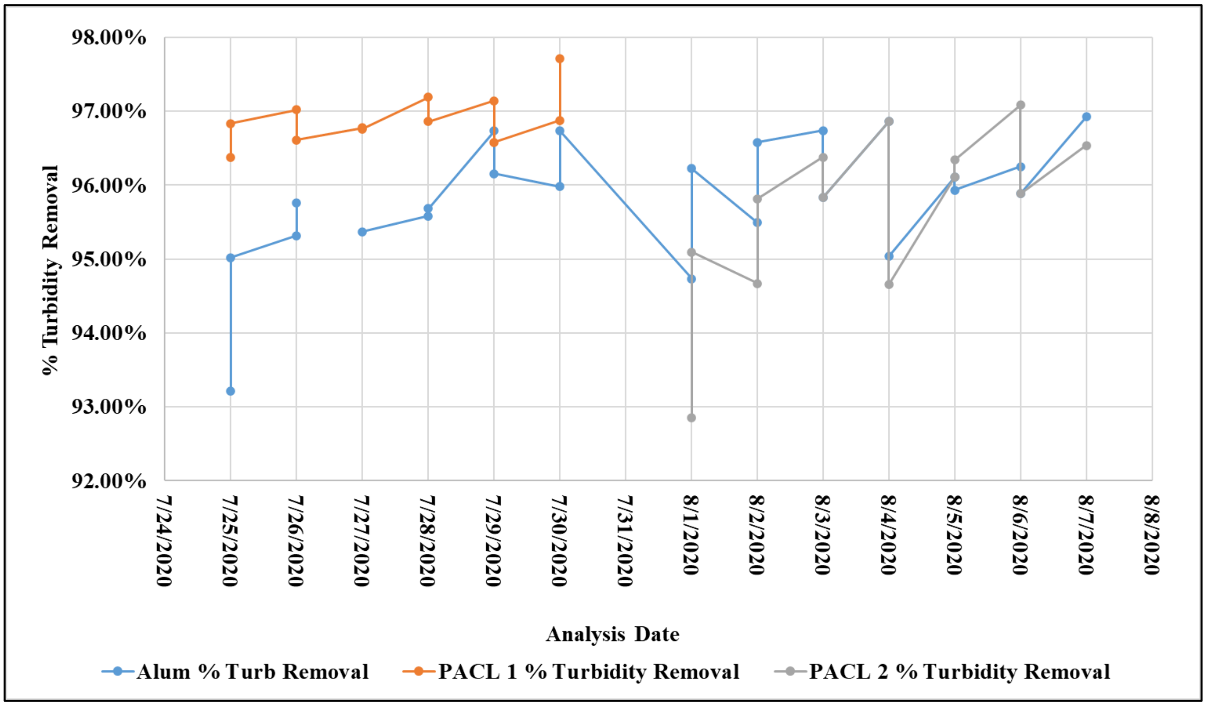


Figure 13: Summer Pilot Plant Run % Turbidity Removal Per Coagulant.

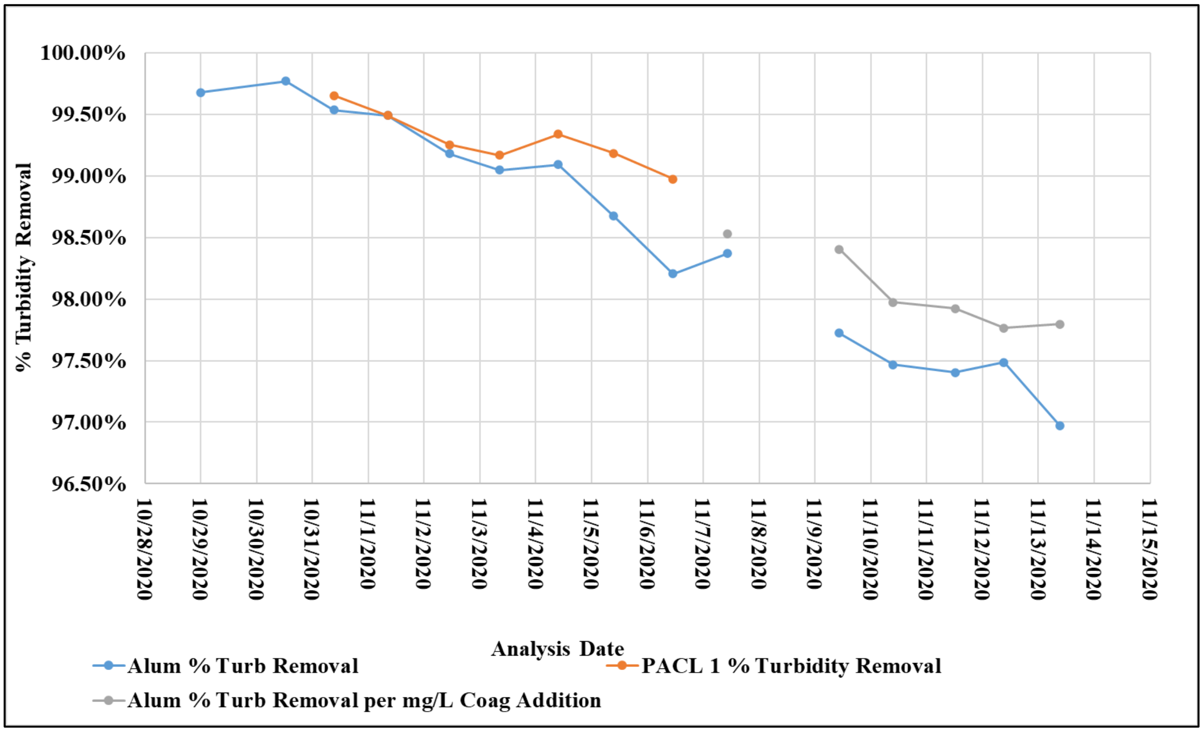


Figure 14: Fall Pilot Plant Run % Turbidity Removal Per Coagulant.

For both the Summer and Fall pilot plant runs, PACl 1 had a higher overall % Turbidity removal rate than either Alum or PACl 2. Looking at the parameters however, the mg/L dosage of each coagulant was standardized based on the jar test results so the coagulants were not being dosed the same. To account for this, the turbidity removal rate was then calculated based on % Turbidity Removal per mg/L coagulant added for each coagulant. These results were summarized in Figure 15 and Figure 16.

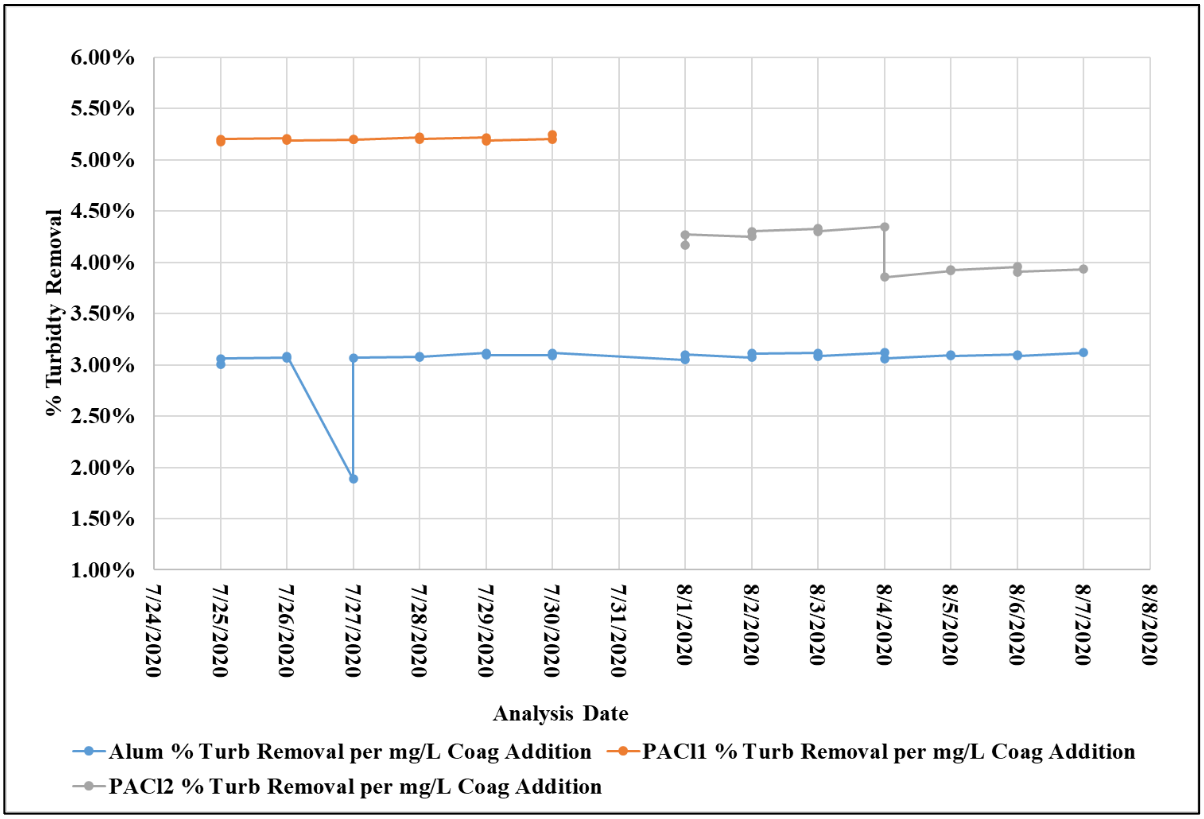


Figure 15: Summer Pilot Plant Run % Turbidity Removal per mg/L Coagulant Addition.

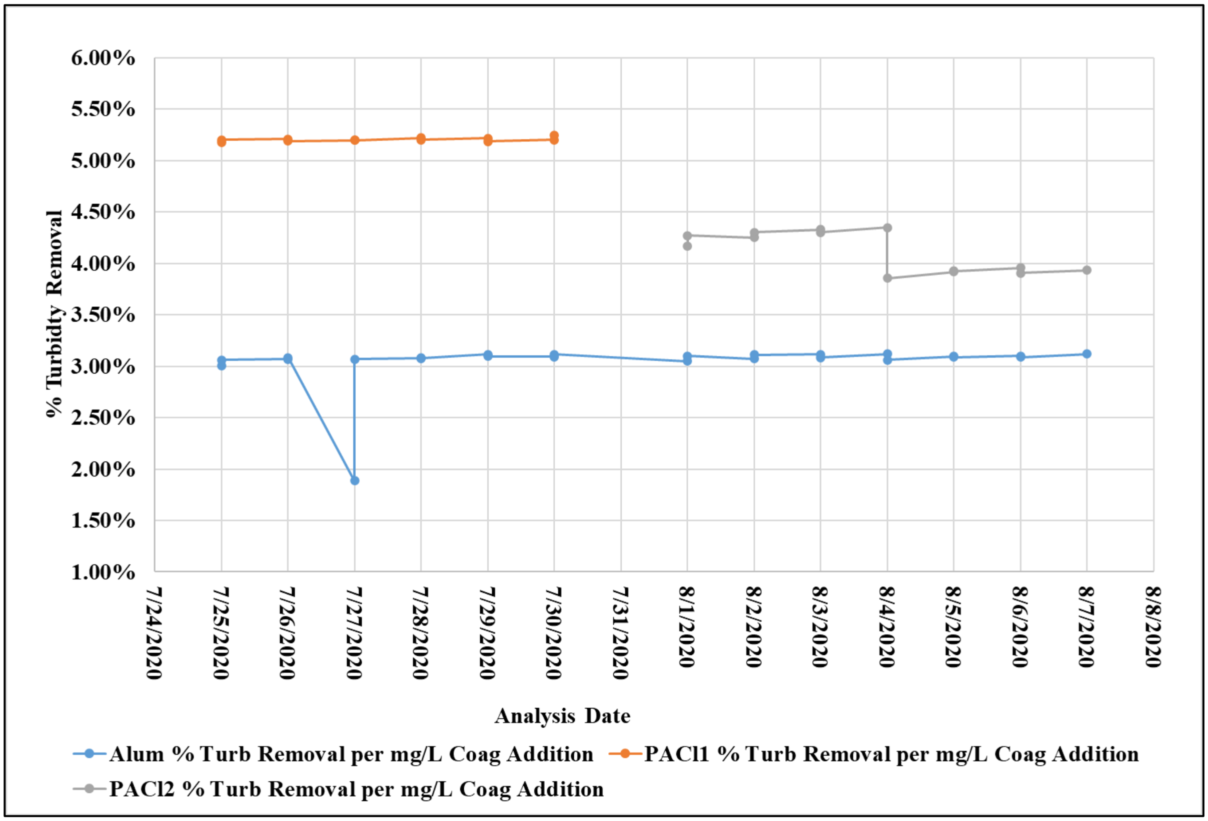


Figure 16: Fall Pilot Plant Run % Turbidity Removal per mg/L Coagulant Addition.

When standardized in this manner, PACl 1 still exhibited higher turbidity removal rates than Alum or PACl 2 for both the Summer and Fall Pilot Plant sessions. Because both PACl 1 and PACl 2 have a higher percentage of the active ingredient, Aluminum Oxide than Alum, they have a higher percentage of turbidity removal per mg/L added. PACl 1 and PACl 2 have a % Aluminum Oxide of 12.14% and 10.50% respectively. This could explain the higher efficiency of PACl 1 to PACl 2. To account for this difference in Aluminum Oxide concentration, the results were then normalized as % Turbidity Removal per mg/L Aluminum Oxide addition. These results can be found in Figure 17 and Figure 18 below.

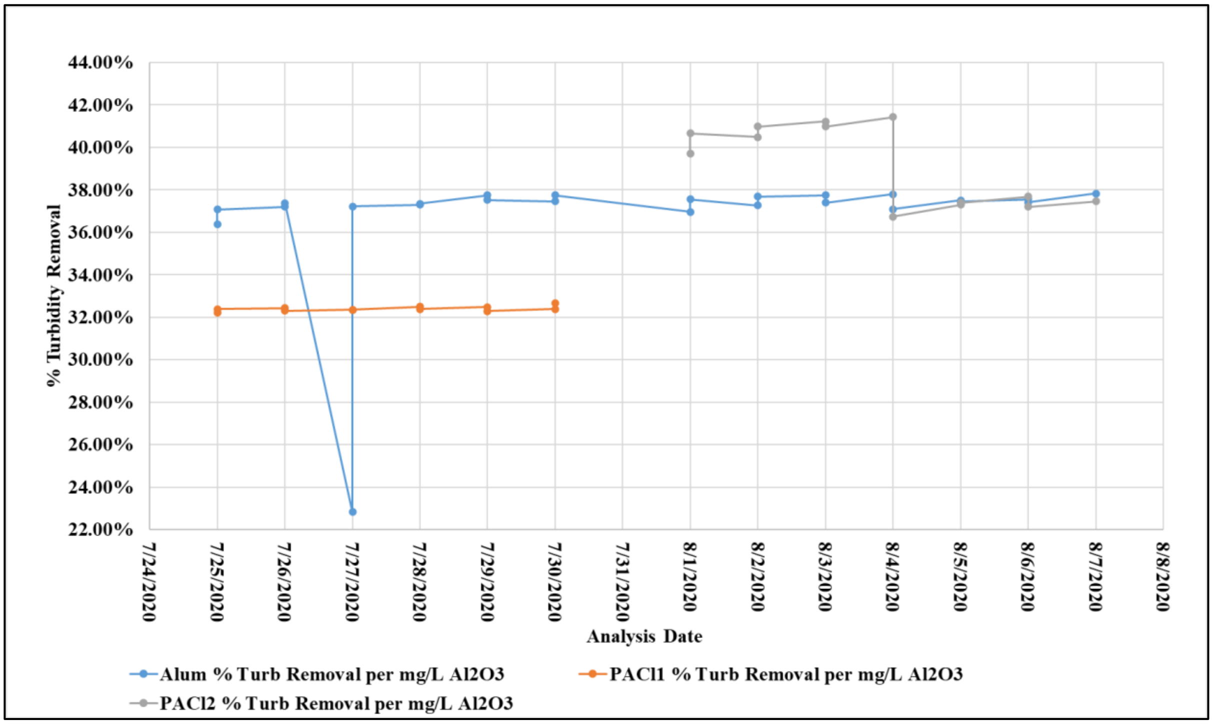


Figure 17: Summer Pilot Plant Run % Turbidity Removal Per mg/L Al2O3 Addition.

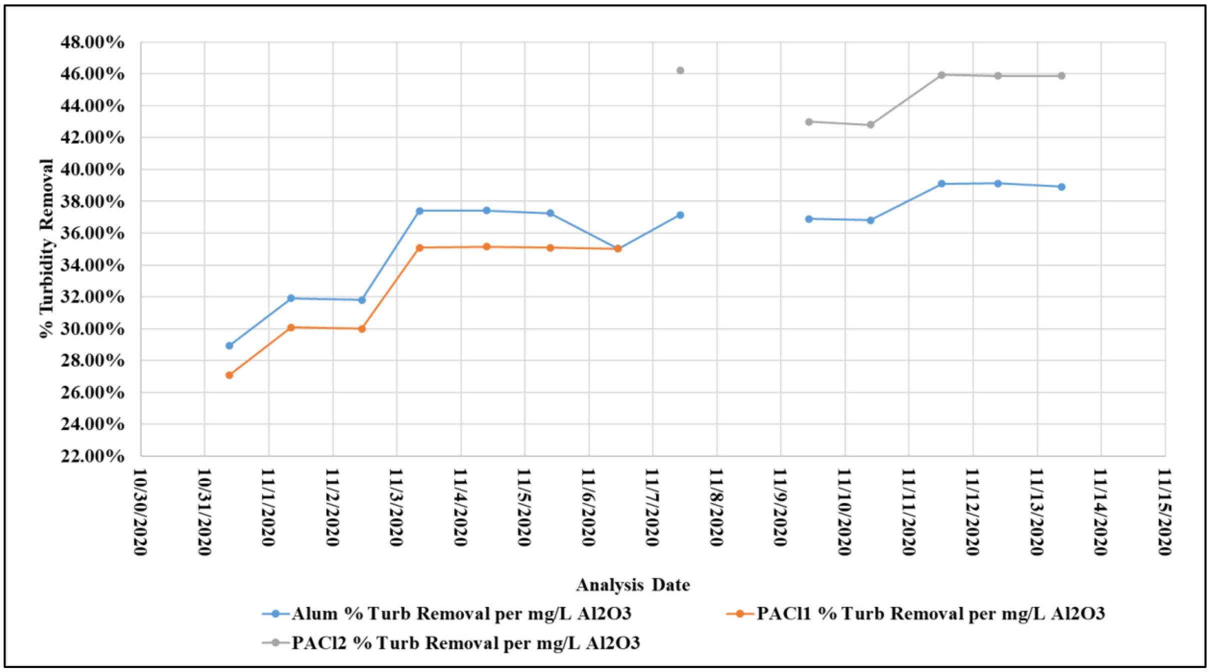


Figure 18: Fall Pilot Plant Run % Turbidity Removal Per mg/L Al2O3 Addition.

Interestingly, when normalized this way, PACl 2 actually became the higher performing coagulant in both the summer and fall Pilot Plant runs with PACl 1 actually underperforming

Alum. Looking at the results this way was important when factoring in the environmental impact of the coagulants. Having less Aluminum in the resulting sludge is beneficial for the environment.

When looking at switching treatment chemicals, it is important to look at the chemicals under a wide range of conditions. Surface water sources especially exhibit continuously changing water quality parameters. Where one coagulant might be highly efficient at turbidity removal at a narrow range of beginning turbidity or pH range, a coagulant that instead offers moderate efficiency at a wide starting turbidity or pH range might be more appropriate for a surface water treatment facility.

In Figure 19 below, the % Turbidity removal per mg/L of coagulant addition is compared to the influent turbidity for each coagulant. This data set contains both the summer and fall pilot plant runs. There were multiple data points for each coagulant as the influent turbidity changed throughout the experiments. All of the coagulants performed well over a range of influent turbidity with PACl 1 and Alum seeing the largest range of turbidity throughout the experiments. PACl 1 did see a drop in %Turbidity removal as the turbidity increased but all % removals were higher than Alum and the lower removals were right in line with PACl 2 removal rates. PACl 2 also had higher removal rates than Alum and the rates increased as turbidity increased. Alum exhibited a fairly steady removal rate through the varying turbidities.

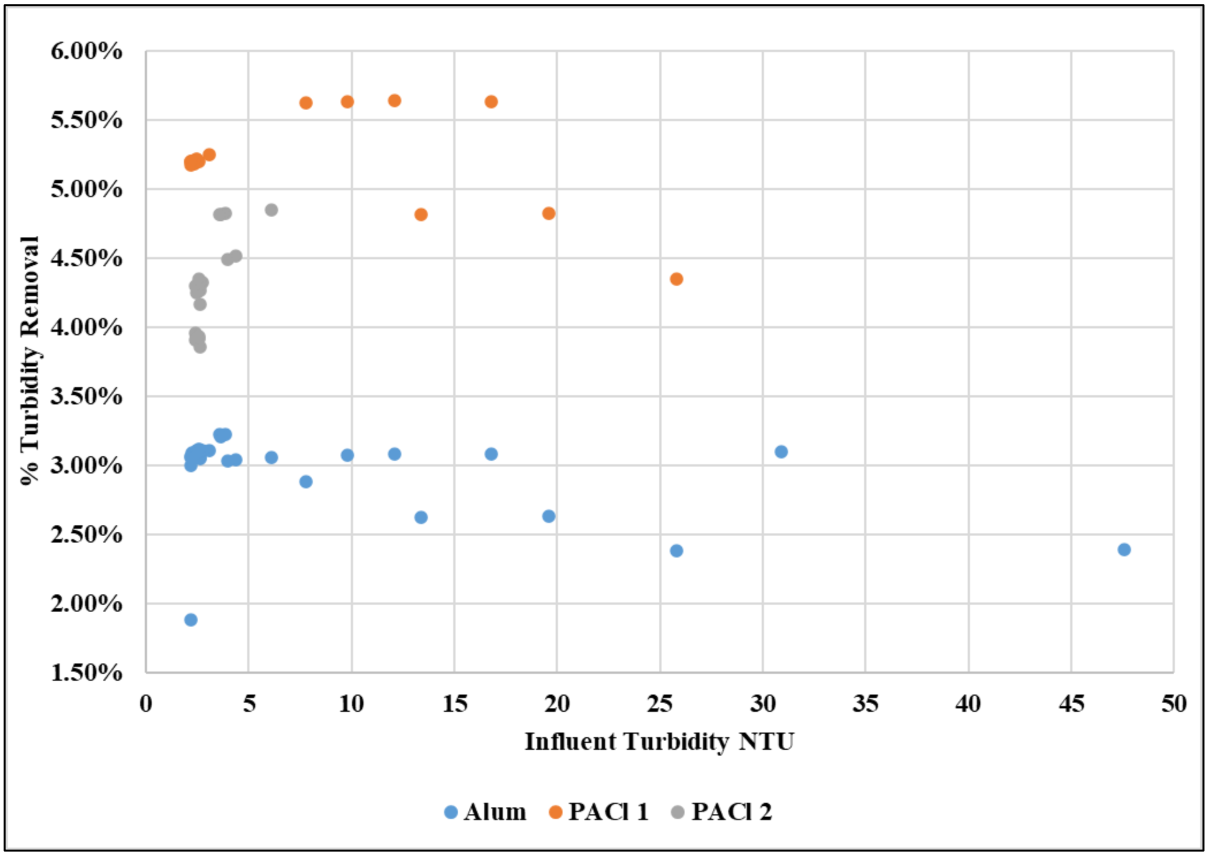


Figure 19: Turbidity Removal Per mg/L Coagulant Addition Viewed Against Influent Turbidity.

In Figure 20 below, the % Turbidity removal per mg/L of coagulant addition is compared to the influent pH for each coagulant. This data set contains both the summer and fall pilot plant runs. There were multiple data points for each coagulant as the influent pH changed throughout the experiments. From this chart, PACl 1 and PACl 2 both outperformed Alum in terms of % Turbidity removal across the whole array of pH levels. PACl 1 exhibited higher removal % rate around pH 7.3-7.4. PACl 2 exhibited a higher removal % rate from pH 7.5-7.9. Alum had a very steady % removal rate across the varying pH levels with the highest removal from 7.5-7.9.

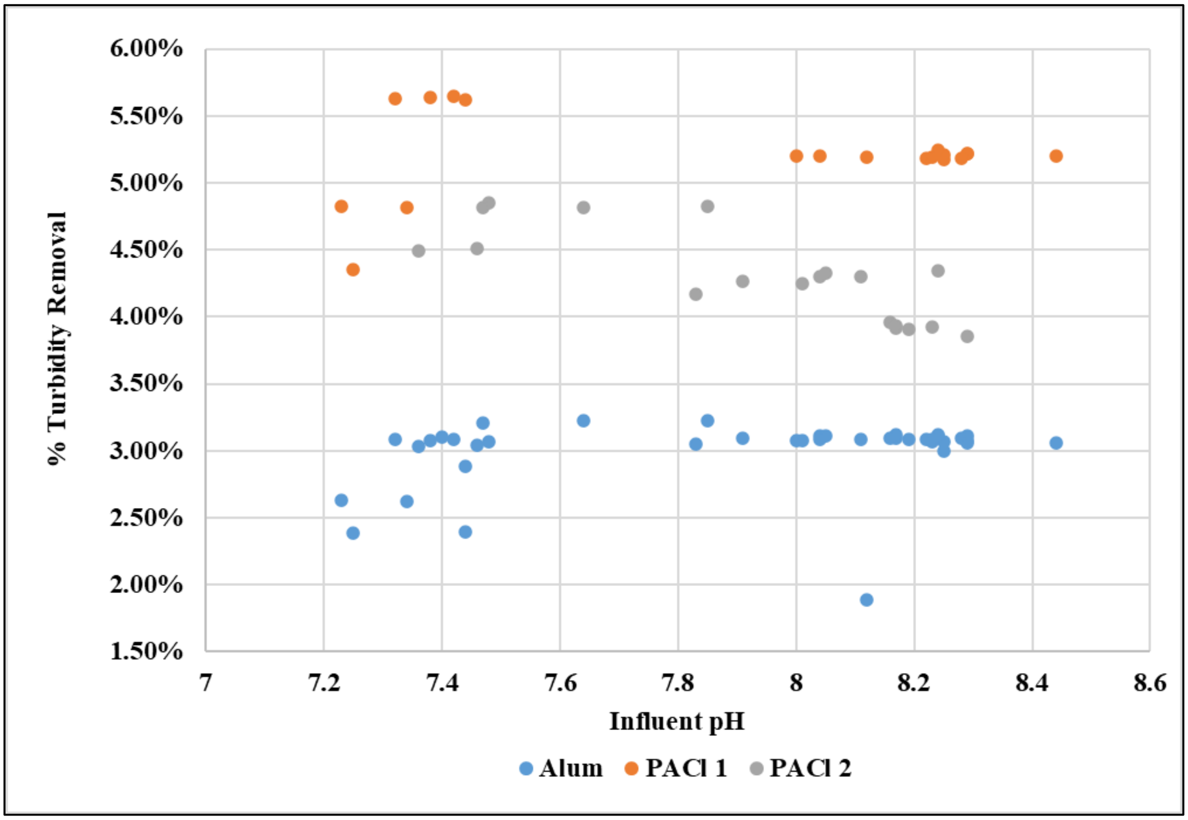


Figure 20: Turbidity Removal Per mg/L Coagulant Addition Viewed Against Influent pH.

While turbidity is one of the primary concerns when it comes to drinking water and public health, other parameters must also be examined. The corrosivity rates of the different coagulants is an important factor that plays a big role in the distribution system. Higher corrosivity levels could potentially pull lead and copper out of plumbing or cause iron and steel to rust reducing the water quality and leading to both health and aesthetic issues. To examine corrosivity, the chloride, sulfate, and alkalinity levels of the finished water samples from the pilot plant were used to calculate a couple of different theoretical corrosion factors. To look at the water's potential effects on lead and copper leaching, the Chlorite to Sulfate Mass Ratio (CSMR) was calculated for each coagulant during each season. The values were averaged to give one result per coagulant per season. To examine the effects of each coagulant on iron and steel pipe corrosion, the Larson Ratio was calculated. These results were also averaged to give one result per coagulant per season. These results can be seen summarized in Table 20 below.

All coagulants register as mildly corrosive on the CSMR scale. A ratio value >0.500 is Highly corrosive unless the alkalinity is <50 mg/L (EDWARDS and TRIANTAFYLLIDOU 2007). Since all alkalinities measured were greater than 50 mg/L throughout this experiment, the index value was degraded to Moderately corrosive. If the alkalinity had fallen below 50 mg/L, Alum in the Fall as well as both PACl 1 and PACl 2 during both seasons would have been classified as Highly Corrosive.

On the Larson Scale, the alkalinity is part of the calculation, and all analytes are converted to their millimolar equivalents (Vasconcelos et al. 2015). Using this scale, PACl 1 and PACl 2 as well as Alum in the fall were less corrosive to iron and steel than Alum in the summer. Based on this, the PACl coagulants might become an issue to lead and copper corrosion were the Alkalinity to fall below 50 mg/L. This could be corrected for by increasing chemical lime addition during treatment. During the pilot study, the decrease in alkalinity consumption by the PACl coagulants led to a decrease in lime addition so needing to add lime in increase alkalinity might not be costly.

Table 20: Corrosivity of Coagulants Ran in Pilot Plant 2020 Study.

		Lead and Copper			**Iron and Steel**	
Coagulant	**Season**	**CSMR AVG**	**CSMR St Dev**	**CSMR Corrosivity**	**Larson Ratio**	**Larson Corrosivity**
Alum1	Summer	0.385	0.013	Moderate	0.510	Mid
Alum2	Summer	0.383	0.008	Moderate	0.479	Low
Alum1	Fall	0.589	0.010	Moderate	0.349	Light
Alum2	Fall	0.584	0.013	Moderate	0.329	Light
PACl1	Summer	0.776	0.040	Moderate	0.321	Light
PACl1	Fall	0.932	0.019	Moderate	0.278	Light
PACl2	Summer	0.723	0.087	Moderate	0.335	Light
PACl2	Fall	0.786	0.302	Moderate	0.294	Light

Trihalomethane formation is another factor monitored and regulated in drinking water for public health purposes. Trihalomethane are disinfection by products formed when natural organic matter in the raw water interacts with disinfectants. Trihalomethanes are formed when the water is generally alkaline, as is the case with the treated water at BWD. Total

Trihalomethanes consist of the compounds; chloroform, bromodichloromethane, dibromochloromethane, and bromoform. Long Term Exposure to Total Trihalomethanes above the MCL can cause issues in the liver, kidney, or central nervous system as well as increase the risk of developing cancer. The US EPA set a maximum allowable annual average of 80 ug/L in 2001 for larger surface water public water systems (US EPA 2015b). The THM samples taken to meet these standards are from within the system's distribution system. The pilot plant data for finished water Total THM formation as well as 7 Day Total THM formation can be found in Table 21. The 7 Day Total THM formation test consist of collecting a finished water sample in a demand free amber glass bottle without preservative or headspace. The bottle was placed in the dark at room temperature and analysis was run after 7 days had passed. The conditions were used to simulate the water aging subsequent chemical reactions within a water storage facility or pipeline in the distribution system. Based on the results of the Pilot Study, there was not an increase in THM formation or THM formation potential when PACl coagulants were used instead of Aluminum Sulfate. None of the THM formation results went above the 80 ug/L MCL limit. In addition, neither PACl consistently performed better than the other when it came to THM formation.

Table 21: Disinfection by Product Formation of Coagulants Ran in 2020 Pilot Study.

Coagulant	Season	Total THM Avg ug/L	THM Formation St Dev	7 Day Total THM Avg ug/L	THM Formation St Dev
Alum1	Summer	21.5	1.04	69.1	5.35
Alum2	Summer	19.7	2.21	64.1	3.76
Alum1	Fall	17.2	3.01	71.5	10.2
Alum2	Fall	15.7	3.78	63.5	11.5
PACl1	Summer	19.4	0.80	62.7	2.97
PACl1	Fall	14.8	1.08	69.2	7.57
PACl2	Summer	19.1	2.31	70.9	4.29
PACl2	Fall	13.4	0.35	63.1	9.87

While THM formation is expected when using chlorine species to disinfect surface water there are ways to mitigate the concentrations produced. Total Organic Carbon, TOC, removal is regulated by both federal and state agencies to remove disinfection by product pre-cursors in conventional treatment facilities. Compliance requirements can be found in Table 22 below ("Disinfectants and Disinfection Byproducts Rules (Stage 1 and Stage 2) What Do They Mean to You?," n.d.).

Table 22: EPA Required Percent Removal of TOC.

	Source Water Alkalinity, mg/L as CaCO3		
	0-60	**>60-120**	**>120**
>2.0 to 4.0	35%	25%	15%
>4.0 to 8.0	45%	35%	25%
>8.0	50%	40%	30%

The compliance rules require a certain removal percentage based on the source water alkalinity and source water TOC. In the pilot plant study performed during this experiment, the source water alkalinity stayed between 60-120 mg/L as $CaCO_3$. The source water TOC during this experiment stayed between 1.97 and 2.85 mg/L. Based on this data and the required removal table, the treatment needed to achieve at least a 25% removal of TOC. Based on the calculated TOC % removal, shown in Table 23, Alum met this criteria during both summer runs but neither fall run, PACl1 met this criteria during both the summer and fall, and PACl2 met the removal criteria during both the summer and fall runs.

Table 23: TOC and DOC Removal of Coagulants Ran in 2020 Pilot Study.

Coagulant	Season	TOC % Removal Avg	TOC % Removal St Dev	DOC % Removal Avg	DOC % Removal St Dev
Alum1	Summer	38%	0.07	31%	0.03
Alum2	Summer	42%	0.02	28%	0.04
Alum1	Fall	19%	0.03	18%	0.02
Alum2	Fall	21%	0.03	15%	0.04
PACl1	Summer	42%	0.03	29%	0.04
PACl1	Fall	28%	0.04	29%	0.02
PACl2	Summer	40%	0.02	25%	0.02
PACl2	Fall	30%	0.02	21%	0.08

4.4 Phase 3: Cost and Environmental Impact Analysis

The pilot plant treatment chemical dosages were used to determine the cost of running the full scale water treatment plant at BWD using the same treatment parameters. To do this, the chemical pump RPMs that were recorded throughout the experiments were converted to mg/L additions. This was done using the pump calibration curves for each pump completed prior to each pilot plant run as well as the concentration of each chemical dosed. Since the pump speeds were varied throughout each experiment to optimize treatment of each pilot plant trains, the dosages of each pump were averaged for the days running each coagulant chemical. After dosages were determined, the price per pound (typical water treatment cost unit) of each chemical as it is bought by BWD in 2022 was used to calculate the chemical costs per MG (million gallons) treated. The cost of each chemical per MG treated was totaled and the 2018 production average of 55 MG per day was used to calculate the estimated chemical cost per calendar year. The raw and calculated data can be seen in the tables that follow. Table 24 showed the Summer Pilot Plant Cost of running T1 with Alum while optimizing the chemical additions for optimum turbidity removal. The dates used were from July 24, 2020 to July 26, 2020.

Table 24: Summer PP Run Cost of T1- Alum From 7/24/2020 to 7/26/2020.

Treatment Chemical	Concentration (mg/L)	Dry Feed Rate (mg/L)	Price/lb	Chemical Cost ($/MG)
Alum*	49.00	15.21	$0.06	$16.13
Ferrous	5.50	1.67	$0.10	$25.32
Lime	100.00	5.56	$0.11	$5.21
Caustic	25.00	1.97	$0.13	$8.70
Nonionic Polymer	100.00	0.02	$2.72	$0.45
NaClO2	12.00	1.00	$0.49	$34.06
Cl2**	100.00	2.50	$0.27	$5.53
PACl 1	100.00	NA	$0.35	
PACl 2	100.00	NA	$0.35	
Fluoride	60.00	0.7	$0.91	$8.83
			Total ($/MG)	$104.24
			Annual Total ($)	$2,092,569

Table 25 showed the Summer Pilot Plant Cost of running T2 with PACl 1 while optimizing the chemical additions for optimum turbidity removal. The dates used were from July 24, 2020 to July 26, 2020.

Table 25: Summer PP Run Cost of T2- PACl1 from 7/24/2020 to 7/26/2020.

Treatment Chemical	Concentration (mg/L)	Dry Feed Rate (mg/L)	Price/lb	Chemical Cost ($/MG)
Alum*	49.00	NA	$0.06	
Ferrous	5.50	2.20	$0.10	$33.36
Lime	100.00	5.22	$0.11	$4.90
Caustic	25.00	0.00	$0.13	$0.00
Nonionic Polymer	100.00	0.02	$2.72	$0.45
NaClO2	12.00	1.00	$0.49	$34.06
Cl2**	100.00	2.50	$0.27	$5.53
PACl 1	100.00	18.63	$0.35	$54.38
PACl 2	100.00	NA	$0.35	
Fluoride	60.00	0.7	$0.91	$8.83
			Total ($/MG)	$141.51
			Annual Total ($)	$2,840,837

Table 26 showed the Summer Pilot Plant Cost of running T1 with Alum while optimizing the chemical additions for optimum turbidity removal. The dates used were from July 31, 2020 to August 6, 2020.

Table 26: Summer PP Run Cost of T1- Alum From 7/31/2020 to 8/6/2020.

Treatment Chemical	Concentration (mg/L)	Dry Feed Rate (mg/L)	Price/lb	Chemical Cost ($/MG)
Alum*	49.00	15.21	$0.06	$16.13
Ferrous	5.50	1.67	$0.10	$25.32
Lime	100.00	5.56	$0.11	$5.21
Caustic	25.00	1.38	$0.13	$6.08
Nonionic Polymer	100.00	0.02	$2.72	$0.45
NaClO2	12.00	1.00	$0.49	$34.06
Cl2**	100.00	2.50	$0.27	$5.53
PACl 1	100.00	NA	$0.35	
PACl 2	100.00	NA	$0.35	
Fluoride	60.00	0.7	$0.91	$8.83
			Total ($/MG)	$101.61
			Annual Total ($)	$2,039,860

Table 27 showed the Summer Pilot Plant Cost of running T2 with PACl 2 while optimizing the chemical additions for optimum turbidity removal. The dates used were from July 31, 2020 to August 6, 2020.

Table 27: Summer PP Run Cost of T2- PACl2 from 7/31/2020 to 8/6/2020.

Treatment Chemical	Concentration (mg/L)	Dry Feed Rate (mg/L)	Price/lb	Chemical Cost ($/MG)
Alum*	49.00	NA	$0.06	
Ferrous	5.50	2.00	$0.10	$30.33
Lime	100.00	2.96	$0.11	$2.78
Caustic	25.00	0.00	$0.13	$0.00
Nonionic Polymer	100.00	0.02	$2.72	$0.45
NaClO2	12.00	1.00	$0.49	$34.06
Cl2**	100.00	2.50	$0.27	$5.53
PACl 1	100.00	NA	$0.35	
PACl 2	100.00	22.82	$0.35	$66.61
Fluoride	60.00	0.7	$0.91	$8.83
			Total ($/MG)	$148.58
			Annual Total ($)	$2,982,841

Table 28 showed the Fall Pilot Plant Cost of running T1 with Alum while optimizing the chemical additions for optimum turbidity removal. The dates used were from October 30, 2020 to November 5, 2020.

Table 28: Fall PP Run Cost of T1- Alum From 10/30/2020 to 11/5/2020.

Treatment Chemical	Concentration (mg/L)	Dry Feed Rate (mg/L)	Price/lb	Chemical Cost ($/MG)
Alum*	49.00	17.31	$ 0.06	$18.35
Ferrous	5.50	1.40	$ 0.10	$21.26
Lime	100.00	6.07	$ 0.11	$5.70
Caustic	25.00	4.05	$ 0.13	$17.91
Nonionic Polymer	100.00	0.02	$ 2.72	$0.45
NaClO2	12.00	1.00	$ 0.49	$34.06
Cl2**	100.00	2.50	$ 0.27	$5.53
PACl 1	100.00	NA	$ 0.35	
PACl 2	100.00	NA	$ 0.35	
Fluoride	60.000	0.7	$ 0.91	$8.83
			Total ($/MG)	$112.09
			Annual Total ($)	$2,250,246.92

Table 29 showed the Fall Pilot Plant Cost of running T2 with PACl 1 while optimizing the chemical additions for optimum turbidity removal. The dates used were from October 30, 2020 to November 5, 2020.

Table 29: Fall PP Run Cost of T2- PACl1 from 10/30/2020 to 11/5/2020.

Treatment Chemical	Concentration (mg/L)	Dry Feed Rate (mg/L)	Price/lb	Chemical Cost ($/MG)
Alum*	49.00		$0.06	$0.00
Ferrous	5.50	1.49	$0.10	$22.66
Lime	100.00	6.02	$0.11	$5.65
Caustic	25.00	2.40	$0.13	$10.61
Nonionic Polymer	100.00	0.02	$2.72	$0.45
NaClO2	12.00	1.00	$0.49	$34.06
Cl2**	100.00	2.50	$0.27	$5.53
PACl 1	100.00	19.43	$0.35	$56.72
PACl 2	100.00	NA	$0.35	
Fluoride	60.00	0.7	$0.91	$8.83
			Total ($/MG)	$144.51
			Annual Total ($)	$2,900,943

Table 30 showed the Fall Pilot Plant Cost of running T1 with Alum while optimizing the chemical additions for optimum turbidity removal. The dates used were from November 6, 2020 to November 12, 2020.

Table 30: Fall PP Run Cost of T1- Alum From 11/6/2020 to 11/12/2020.

Treatment Chemical	Concentration (mg/L)	Dry Feed Rate (mg/L)	Price/lb	Chemical Cost ($/MG)
Alum*	49.00	15.44	$0.06	$16.37
Ferrous	5.50	1.07	$0.10	$16.16
Lime	100.00	6.07	$0.11	$5.70
Caustic	25.00	3.27	$0.13	$14.44
Nonionic Polymer	100.00	0.02	$2.72	$0.45
NaClO2	12.00	1.00	$0.49	$34.06
Cl2**	100.00	2.50	$0.27	$5.53
PACl 1	100.00	NA	$0.35	
PACl 2	100.00	NA	$0.35	
Fluoride	60.00	0.7	$0.91	$8.83
			Total ($/MG)	$101.53
			Annual Total ($)	$2,038,247

Table 31 showed the Fall Pilot Plant Cost of running T1 with Alum while optimizing the chemical additions for optimum turbidity removal. The dates used were from November 6, 2020 to November 12, 2020.

Table 31: Fall PP Run Cost of T2- PACl2 from 11/6/2020 to 11/12/2020.

Treatment Chemical	Concentration (mg/L)	Dry Feed Rate (mg/L)	Price/lb	Chemical Cost ($/MG)
Alum*	49.00		$0.06	$0.00
Ferrous	5.50	1.17	$0.10	$17.74
Lime	100.00	6.02	$0.11	$5.65
Caustic	25.00	1.12	$0.13	$4.95
Nonionic Polymer	100.00	0.02	$2.72	$0.45
NaClO2	12.00	1.00	$0.49	$34.06
Cl2**	100.00	2.50	$0.27	$5.53
PACl 1	100.00	NA	$0.35	
PACl 2	100.00	20.76	$0.35	$60.58
Fluoride	60.00	0.7	$0.91	$8.83
			Total ($/MG)	$137.79
			Annual Total ($)	$2,766,194

Since sludge disposal is also a large part of expenses at BWD water treatment plant, and a parameter with the potential to change based on coagulant selection, this was also calculated. The estimated sludge production was determined using a mass balance that included average flow rate per day of BWD based on 2018 production data, influent TSS, or total suspended solids, during each pilot plant run (calculated based on influent turbidity measurements and a conversion factor of Turbidity to TSS as measured in the laboratory at BWD), chemical additions, and effluent TSS calculated in the same manner as influent TSS.

The average solids percentage from sludge at BWD was used to calculate the tons wet sludge per year. The cost of sludge disposal and handling for BWD WTP based on 2021 pricing was used to calculate the final disposal costs.

$$\frac{m3\ sludge}{day} = Influent\ Flow\ Rate, Q\ \left[\left(Sum\ of\ Chemical\ Additions, C_{1,2,3} + Influent\ TSS, C_{In}\right) - Effluent\ TSS, C_{out}\right]$$

Equation 6 Sludge Calculation

Table 32 and Table 33 below summarize the values used to calculate Sludge Production amounts and subsequent sludge disposal costs.

Table 32: Sludge Production and Cost Calculated Based on Summer 2020 Pilot Plant Data.

Measurement	Variable	Unit	T1 Alum 7/24/2020 - 7/26/2020	T1 Alum 7/31/2020 - 8/6/2020	T2 PACl1 7/24/2020 - 7/26/2020	T2 PACl2 7/31/2020 to 8/6/2020
Flow Rate	Q	m3/day	208197.65	208197.65	208197.65	208197.65
Alum	C1	mg/L	31.04081633	31.04081633	18.63	22.82
Ferrous	C2	mg/L	1.67	1.67	2.20	2
Lime	C3	mg/L	5.56	5.557	5.22	2.96
Caustic	C4	mg/L	1.97	1.375	0.00	0
NonIonic	C5	mg/L	0.02	0.02	0.02	0.02
Turbidity In		NTU	2.37	2.55	2.37	2.55
TSS In	C6	mg/L	3.35355	3.60825	3.35355	3.60825
Turbity Out		NTU	0.13	0.1	0.09	0.11
TSS Out	C_{out}	mg/L	0.18395	0.1415	0.12735	0.15565
Sludge		m3/day	9042110.62	8979474.35	6100232.78	6506717.88
		mg/day	9042110617.71	8979474354.70	6100232784.53	6506717876.39
		kg/day dry weight	9042.11	8979.47	6100.23	6506.72
	Annual totals	kg/year	3300370.38	3277508.14	2226584.97	2374952.02
		ton/year dry weight	3300.37	3277.51	2226.58	2374.95
		ton/year wet	15716.05	15607.18	10602.79	11309.30
Annual Cost for hauling and disposal at			**$1,063,662**	**$1,056,294**	**$717,597**	**$765,413**

Table 33: Sludge Production and Cost Calculated Based on Fall 2020 Pilot Plant Data.

Measurement	Variable	Unit	T1 Alum 10/30/2020 - 11/5/2020	T1 Alum 11/6/2020 - 11/12/2020	T2 PACl1 10/30/2020 - 11/5/2020	T2 PACl2 11/6/2020 - 11/12/2020
Flow Rate	Q	m3/day	208197.65	208197.65	208197.65	208197.65
Alum	C1	mg/L	35.32419003	31.5	19.43	20.755
Ferrous	C2	mg/L	1.402	1.066	1.49	1.17
Lime	C3	mg/L	6.0749	6.07	6.02	6.02
Caustic	C4	mg/L	4.0519	3.266	2.40	1.12
NonIonic	C5	mg/L	0.02	0.02	0.02	0.02
Turbidity In		NTU	2.37	4.38	2.37	4.38
TSS In	C6	mg/L	3.35355	6.1977	3.35355	6.1977
Turbity Out		NTU	0.13	0.098	0.09	0.08
TSS Out	C_{out}	mg/L	0.18395	0.13867	0.12735	0.1132
Sludge		m3/day	10418749.64	9989537.69	6785327.97	7322207.25
		mg/day	10418749643.79	9989537690.58	6785327971.62	7322207251.68
		kg/day dry weight	10418.75	9989.54	6785.33	7322.21
	Annual totals	kg/year	3802843.62	3646181.26	2476644.71	2672605.65
		ton/year dry weight	3802.84	3646.18	2476.64	2672.61
		ton/year wet	18108.78	17362.77	11793.55	12726.69
Annual Cost for hauling and disposal at			**$1,225,602**	**$1,175,112**	**$798,187**	**$861,343**

The cost of each run and thus the cost of using each coagulant chemical when extrapolated to the full scale of treatment at BWD based on 2018 production values are summarized in Table 34 and Table 35. PACl 1 and PACl 2 both present higher total costs than Alum during both the summer and fall season runs. Something to note when reviewing this data is that the PACl costs used were based on the initial sticker prices of the coagulants. Large scale utilities, such as BWD often do not pay full sticker price for chemicals, with price reductions of 20-30% not uncommon. Also to note are waste disposal fees and waste uses. Recent legislation has shed light on the threat of PFAS contained in treatment plant sludges as pertaining to land applications. This is an issue that could directly impact how water and wastewater treatment facilities dispose of their waste products as well as the costs associated with the process.

Table 34: Summer 2020 Pilot Plant Trial Total Cost Summary.

Summer 2020 Pilot Plant Trial

	Alum 1	**Alum 2**	**PACl 1**	**PACl 2**
Alum*	$16.13	$16.13	$0.00	$0.00
Ferrous	$25.32	$25.32	$33.36	$30.33
Lime	$5.21	$5.21	$4.90	$2.78
Caustic	$8.70	$6.08	$0.00	$0.00
Nonionic Polymer	$0.45	$0.45	$0.45	$0.45
$NaClO_2$	$34.06	$34.06	$34.06	$34.06
Cl_2**	$5.53	$5.53	$5.53	$5.53
PACl 1	$0.00	$0.00	$54.38	$0.00
PACl 2	$0.00	$0.00	$0.00	$66.61
Fluoride	$8.83	$8.83	$8.83	$8.83
Total Chemical Cost/MG	$104	$102	$142	$149
Cost at avg 55 MGD/Year	$2,092,569	$2,039,860	$2,840,837	$2,982,841
Sludge Disposal	$1,063,662	$1,056,294	$717,597	$765,413
Treatment and Sludge Annual Cost	**$3,156,231**	**$3,096,154**	**$3,558,433**	**$3,748,254**
Cost Difference From Alum			**$402,203**	**$652,100**

Table 35: Fall 2020 Pilot Plant Trial Total Cost Summary.

	Alum 1	Alum 2	PACl1	PACl 2
Alum*	$18.35	$16.37	$0.00	$0.00
Ferrous	$21.26	$16.16	$22.66	$17.74
Lime	$5.70	$5.70	$5.65	$5.65
Caustic	$17.91	$14.44	$10.61	$4.95
Nonionic Polymer	$0.45	$0.45	$0.45	$0.45
$NaClO_2$	$34.06	$34.06	$34.06	$34.06
Cl_2**	$5.53	$5.53	$5.53	$5.53
PACl 1	$0.00	$0.00	$56.72	$0.00
PACl 2	$0.00	$0.00	$0.00	$60.58
Fluoride	$8.83	$8.83	$8.83	$8.83
Total Chemical Cost/ MG	$112.09	$101.53	$144.51	$137.79
Cost at avg 55 MGD/Year	$2,250,247	$2,038,247	$2,900,943	$2,766,194
Sludge Disposal	$1,225,602	$1,175,112	$798,187	$861,343
Treatment and Sludge Annual Cost	**$3,475,849**	**$3,213,359**	**$3,699,131**	**$3,627,537**
Cost Difference From Alum			**$223,281**	**$414,177**

CHAPTER 5 CONCLUSION AND FURTHER RESEARCH

5.1 How the Data Fits the Primary Experiment Motivation

The primary motivation behind this experiment, as explained in Section 1.2 was to examine the performance and feasibility of switching to polyaluminum chloride coagulants in the treatment process at a large surface water treatment facility in Northwest Arkansas. This examination took place using a Triple Bottom Line approach looking at:

1) Public Health
2) Financial Viability
3) Environmental Impact

5.1.1 Public Health

Safe drinking water is one of the most important and oftentimes overlooked aspect of public health. It is imperative that all treatment chemicals utilized be safe to add without imparting a harmful quality on the finished water and in combination with physical treatment, bring the raw water to the quality standards for drinking water as set by federal and state agencies. Based on the data from both the preliminary jar tests and the pilot scale testing, the two main alternative coagulants examined both performed as well or better than the standard coagulant, Aluminum Sulfate when it came to treating water from Beaver Lake. The PACl coagulants maintained the high turbidity removal rate expected of a coagulant and outperformed Aluminum Sulfate in the lowest turbidity level reached in both the summer and fall pilot plant trials with alum getting down to 0.08 NTU and both PACls reaching 0.07 NTU. PACl 1, and PACl 2 achieved a turbidity less than 0.15 NTU in 97%, 100%, 95% of samples respectively and a turbidity of less than 0.10 NTU in 53%, 95%, and 74% of samples respectively. When standardized based on turbidity removal % per mg/L of coagulant added, alum, PACl 1, and PACl 2 averaged 3.00%, 5.21%, and 4.30% removal respectively. This is important as a treatment plant is able to maintain the same standard of treatment with a lower amount of chemical addition allowing the treatment facility to maintain smaller chemical storage capacities which reduce the plant foot print and the plant’s vulnerability to supply chain disruptions.

When looking at the way drinking water impacts public health, disinfection by product creation is a necessary component to examine. Both polyaluminum chloride coagulants performed similarly to aluminum sulfate in THM formation and THM formation potential. All results were within the recommended guidelines of less than 80 mg/L. TOC removal rates, which are used to confirm compliance when chlorine disinfectants are in use, improved when either of the polyaluminum chloride coagulants were used compared to alum. The PACl coagulants did not fal below 25% TOC removal (EPA Guideline based on Alkalinity) while alum fell below this level with 19% and 21% removal in the fall pilot plant runs.

Treatment facilities must also ensure the finished water leaving the treatment plant maintains its characteristics. One way to examine this is to ensure the finished water is non corrosive to both distribution system and household plumbing. To examine this, CSMR and Larson corrosivity ratios were calculated using lab analysis data. Based on the CSMR results, all coagulants were moderately corrosive for lead and copper pipes as long as the alkalinity remains over 40 mg/L. If alkalinity was to drop, the Polyaluminum Chloride coagulants might be corrosive. Alkalinity is something controllable by the addition of lime. Based on the Larson ratio results, polyaluminum chloride coagulants were actually less corrosive on steel pipes than alum. Based on all parameters studied during this coagulant trial, polyaluminum chloride coagulants maintained all drinking water standards pertinent to protecting public health.

5.1.2 Financial Viability

Running a treatment trial on a pilot plant calibrated to the specifications of the full treatment facility is a good way to approximate the chemical application and thus financial implications of the trial at full treatment plant scale. During this trial, we were able to run the pilot plant trains in a way that mimics the coagulants running in the BWD treatment facility.

Many factors came into play when comparing alum to the polyaluminum chloride coagulant examined in the scope of this project. Polyaluminum chloride coagulants are more expensive by volume than alum. Although the turbidity removal rate per mg/L coagulant added was higher in the polyaluminum chloride coagulants, meaning less volume was needed to achieve the same standard of treatment, the chemical costs were still higher. Less lime and sodium hydroxide was also needed for the polyaluminum chloride coagulants, but as these are relatively cheap chemicals the reduced volume did not outweigh the higher cost of the coagulants.

It was assumed that the deciding factor would be the sludge removal costs. Because much less chemical volume was needed with polyaluminum chloride coagulants to treat water to the same standard as alum, sludge production was indeed lower. Even with this, the sludge removal costs did not add up enough to offset the chemical costs. With PACl 1 averaging $312,000 and PACl 2 averaging $533,000 more than treatment with alum when extrapolated across a year of treatment using BWD 2018 produciton data. This leaves alum as the most financially viable coagulant option of those examined within the scope of this project.

5.1.3 Environmental Impact

Oftentimes the environmental impact of actions are overshadowed by other more obvious factors. Environmental impacts are harder to quantify than financial impacts or public health impacts. In drinking water treatment public health takes top priority and financial impact second, but environmental impact deserves a spot at the table for consideration. Watershed management is taking a spotlight at drinking water treatment facilities because providing clean and cost effective water begins with having a clean and abundant source of raw water. There are a couple of ways that this experiment looked at environmental impact. Through a literature review, it was discovered that polyaluminum chloride coagulants could potentially have a lower environmental impact than monomeric aluminum chloride or aluminum sulfate coagulants. During the treatment process, a study by Krupinska found that monomeric and polymerized aluminum coagulants, such as alum, impart a lower aluminum residual in the finished water than colloidal aluminum coagulants, such as PACls (Krupińska 2020). Aluminum is listed by the USEPA as a secondary contaminant with a standard Maximum Contaminant Level of 0.05 to 0.2 mg.L.

Because, less aluminum is imparted into the drinking water with colloidal aluminum coagulants, such as PACls, this must mean that the residual ends up in the sludge. Aluminum hydroxide formed during the coagulation process is bioavailable and able to be taken up by various plants. It can also travel through soil to infiltrate the water table. While more aluminum will end up in treatment sludge by using polyaluminum chloride coagulants, this aluminum was found to be easier to remove from the sludge through aluminum recovery by pH adjustment than that from monomeric or polymerized aluminum residual (Nair and Ahammed 2017) .

Prior to running this experiment, it was postulated based on literature information that the use of PACl as the primary coagulant vs alum would produce less sludge. This held true during the experimental phase. Between the Summer and Fall Pilot Plant trials conducted in 2020 as part of this project, using the PACl coagulants averaged 5,091 tons of sludge less per year. This equates to 255 Semi Dump loads at 20 tons each or 727 average dump truck loads at 7 tons each. This equates to 721 gallons of diesel in a semi dump or 2060 gallons of diesel in a regular dump truck based on a 17 mile one way trip from BWD to the local landfill at 6 MPG. This is a big reduction in fuel consumption as well as emissions. This also equates to a big reduction in overall footprint with less waste sludge ending up in the landfill.

5.2 CCD Jar Test Experiment

5.2.1 Determination of the optimal range of operating parameters

The optimal ranges of the two independent variables provided in Figure 11 were very different in terms of both coagulant dosage and pH. For instance, according to Figure 11a, any combinations of the coagulant dosage and pH that fall onto the “zero” contour curve will produce an optimal final settled turbidity result. If a vertical line is drawn at any dosage value greater than 21.7 mg/L, there will be two optimal pH values (one upper and one lower) due to the two intersecting points on the “zero” contour curve. This observation makes it difficult to determine the unique values for the two independent variables that can achieve the optimal final settled turbidity in the water purification process. To obviate this issue, a condition must be defined, i.e., it is expected that the optimal dosage for the treatment must be the lowest dosage of the chemical used to achieve the same treatment effect. Therefore, it is suggested that the vertical line is drawn in such a way that it is tangent to the “zero” contour curve, and its intercept with the x-axis indicates the lowest dosage value, which is 21.7 mg/L (shown in Figure 11a). This operation clearly identifies the optimal values for coagulant dosage and adjusted raw pH, which are 21.7 mg/L and 7.53, respectively. For final filtered turbidity, the determination of the optimal combination for coagulant dosage and adjusted raw pH is much simpler because the values of these two independent variables can be obtained from the graph in Figure 11b directly (not shown), which are 27.95 mg/L for coagulant dosage and 7.91 for pH.

Optimizing coagulant dosage in water treatment has been an active research field for years as new complex organic and inorganic coagulants are being developed and presented to the market on a continuous basis. However, to date, many studies have mainly focused on comparing the new coagulant products with the traditional one (alum) to show how well these new products perform in cleaning up water impurities at a lower dosage. For instance, Khairul Zaman et al. (Khairul Zaman et al. 2021) recently reported a study using Jar test that compared chitosan and polyaluminum chloride (PACl) with alum in treating various water samples from different treatment plants with turbidity and pH ranging from 20 - 826 NTU and 5.21 - 6.8, respectively. Their findings showed that PACl worked well at a dosage level of 20 mg/L, which was consistent with the result obtained from this study (21.7 mg/L). There have been some studies attempting to optimize coagulant dosage and adjusted raw pH to achieve the best treatment results. Fard et al. (Fard et al. 2021) optimized the dosage and pH by employing PACl as a coagulant to treat wastewater(drinking water?) based on the CCD/RSM methodology. However, their data showed that the optimal operating conditions for PACl were dosage = 301.8 mg/L and pH = 6.53, which achieved water turbidity removal by 99.92%. Compared to the optimized dosage determined in this study, their dosage appeared to be excessive; however, this could be due to the difference of the initial water turbidity between our study (range: 1 – 270) and theirs (range: 20 – 826 NTU), which made direct comparisons of the data between the two studies difficult. On the other end of the spectrum, a study reported that the optimal conditions for PACl used as a coagulant in treating tropical freshwater were between 2.0 and 3.1 mg Al_2O_3/L for PACl and within a range of 7.7 – 8.1 for pH (Arruda et al. 2018). The pH range used in their study was similar to that found in this study; however, the PACl dosage was much lower than that used in this study. Obviously, this could also be attributed to the initial water quality. In their study, the range of initial water turbidity was from 16 to 59 NTU, while in ours it ranged from 1 to 270 NTU. Thus, the difference in coagulant dosage used was understandable because higher initial water turbidity would need larger coagulant dosages to achieve similar treatment results. Therefore, according to the results from this study and the information from past studies, it can be inferred that the optimization results of the operating variables such as coagulant dosage and pH are site- and/or water-specific. That means that for different waters with various quality characteristics, the purification process needs to be optimized specifically to deal with the water under treatment. The optimized operating conditions are not universal and should not be used for general applications.

5.3 Future Studies

While this project resulted in Alum being the best fit for the BWD Water Treatment facility based on experimental results and information in 2020, that is not to say this outcome would occur based on current data. Looking at the triple bottom line approach used in this experiment, alum and PACl performed similarly with regards to public health and maintaining standards of drinking water treatment. It was during the second tier of the triple bottom line, profit and financial viability, that PACl did not perform as well as alum. However, the national and local economy have changed dramatically since the study was conducted. With fuel prices rising, chemical costs rising, and landfill space becoming more expensive, it is recommended that the data from this study be re-figured with current price points. It was also brought to light that the prices used in calculating chemical costs should be better evaluated as the prices used for the polyaluminum chloride coagulants was market cost while the alum price used was the negotiated price at BWD at the time the study was conducted. Large treatment facilities like BWD are often able to get reduced prices based on the volume of chemicals they purchase. With the potential reduced price of polyaluminum chloride coagulants and the increase in landfill and transportation fees, the price dynamics between the two types of coagulants could differ.

Other potential studies resulting from this project are the measurement of sludge produced from alum and PACl coagulants instead of theoretical calculations. A solids percentage analysis of the sludge produced would be beneficial as well. In looking at both the pubic health and environmental tiers of the triple bottom line approach, running aluminum analysis to determine the concentration and speciation within the finished water and the sludge produced by both coagulants would be valuable and interesting.

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