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THESIS

IMPACT OF
DUAL ALUM AND POLYALUMINUM CHLORIDE COAGULATION
ON FILTRATION

Submitted by

Michael G. Haines

Department of Civil Engineering

In partial fulfillment of the requirements

For the Degree of Master of Science

Colorado State University

Fort Collins, Colorado

Summer 2003

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July 9, 2003

WE HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER OUR SUPERVISION BY MICHAEL G. HAINES ENTITLED "IMPACT OF DUAL ALUM AND POLYALUMINUM CHLORIDE COAGULATION ON FILTRATION" BE ACCEPTED AS FULFILLING IN PART REQUIREMENTS FOR THE DEGREE OF MASTER OF CIVIL ENGINEERING.

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ABSTRACT OF THESIS

Impact of Dual Alum and Polyaluminum Chloride Coagulation on Filtration

The process of treating drinking water with a combination of alum and polyaluminum chloride (dual coagulant) has been performed by at least one utility along the Colorado Front Range since the early 1990s. Previous bench-scale research with water containing low concentration of natural organic matter (NOM) showed the dual treatment developed larger non-settleable floc than alum and these floc re-aggregated faster than polyaluminum chloride (PACL) or alum after experiencing induced shearing. Pilot-scale studies showed longer filter run volumes with low-NOM waters treated with dual coagulant. Full-scale testing using reservoir water with stable water quality parameters, including relatively low levels of NOM, was conducted to determine if bench-scale and pilot-scale studies were indeed indicative of full-scale performance. The coagulants were administered at typical, plant-established doses and finished water quality was continuously monitored to ensure that the overall water quality was not sacrificed. Turbidity, filter loss of head, and filter run length were monitored during the sample periods. Total organic carbon (TOC) samples were collected and analyzed during each of the coagulant monitoring periods. Full-scale data shows that the dual treatment provided significantly longer filter run times than alum or PACL alone. However, TOC removal for alum treatments proved better than for PACL or the dual coagulant. Bench-scale experiments were conducted with high-NOM water to further the understanding of the mechanisms involved for the dual coagulants improved performance and to determine if high-NOM water treated with dual coagulant performed similarly as low-NOM water. The same three coagulant regimes as previously mentioned were examined and their optimum doses were determined based on turbidity and TOC removal. A photometric dispersion analyzer was used to study the effects of shearing by measuring the size of the floc formed by the coagulants and the rate of floc formation. Bench-scale results indicate that the increased concentration of NOM places an additional demand on coagulant dose, causes increased rate of particle settling and shows that floc formed in dual treated water forms stronger bonds that are less likely to shear than alum or PACL alone.

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I want to acknowledge the one person who set me straight and sparked my desire to "get good grades," my wife Without her, none of what I have achieved in the past 10 years would have been possible. you are too young to know what an influence you have been but I thank you now.

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My gratitude goes out to the folks who work at Soldier Canyon Water Treatment Plant. Without their insight and willingness to work, this thesis would never have taken shape.

Few graduate students, if any, can claim they reached their goals without the help of fellow grad students. My confidants include Kevin McCurdy, Dean Gregory and fellow AF officers Dave Byer and John Frazey.

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CHAPTER 1. INTRODUCTION

Since the introduction of coagulation in the late 19th century, aluminum sulfate (alum) has been the metal salt of choice for coagulation processes. Coagulant aids were developed in the 1930s, followed by synthetic organic polymers in the 1960s (Letterman et al, 1999). The use of synthetic organic polymers such as polyaluminum chloride (PACL) has gained in popularity since their introduction but have yet to dominate the water treatment industry, most likely due to their increased cost as compared to alum. Experimentation with combinations of alum and polymers resulted in an effort to utilize the somewhat unique advantages of both coagulants and to minimize their disadvantages.

When used individually, either alum or PACL are capable of treating water to acceptable levels, as supported by studies and proven in full-scale operations. Little conclusive evidence is available about the effects of using both chemicals as dual coagulants, as previous studies have produced conflicting results. Dual coagulation for this study is defined as the process by which two coagulants are applied to the raw water at the site of rapid mixing. Young et al (2000) defined polymer-aided flocculation "as the coagulation and flocculation process which is accomplished by using alum in conjunction with a small dosage of polymer." For purposes of this study, polymer-aided flocculation will be defined as a coagulation process with a dose ratio of inorganic metal salt to polymer greater than 3:1. The definition for dual coagulation will be extended to include the requirement of a dose ratio less than or equal to 3:1, either metal salt to polymer or polymer to metal salt.

The literature available concerning dual coagulation is more in line with Young et al (2000) definition of polymer-aided flocculation and not true dual coagulation, even when the researchers used dual coagulation terminology in their papers. However, in a recent study the effects associated with cyclic shearing and floc morphology for waters containing low levels of natural organic matter (NOM) treated with alum, PACL and dual coagulation. Bench-scale and pilot-scale analyses were performed by McCurdy (2003) to further the understanding of the dual coagulation process and serve as the basis for comparing the results achieved in this study.

The hypothesis that bench-scale and pilot-scale analysis data for low NOM water is predictive of full-scale performance, due to the formation of fundamentally different aggregates that are distinct to the coagulant treatment implemented, was tested. A full-scale plant treated water with alum alone, PACL alone and dual coagulant (1:2 by weight, alum to PACL) and provided water quality data for comparison with previously obtained bench-scale and pilot-scale data. Additionally, the hypothesis that water with high levels of NOM would negatively alter the flocculation kinetics for water treated with dual coagulants was also investigated. The purpose of this study was to look at the effects of cyclic shearing on high levels of NOM laden water treated with alum alone, PACL alone and dual coagulant (1:2 by weight, alum to PACL). Bench-scale analysis incorporating the use of a photometric dispersion analyzer (PDA) to measure floc aggregation response to cyclic shearing was used.

CHAPTER 2. LITERATURE REVIEW

Coagulation has three steps: coagulant formation, particle destabilization and interparticle collisions (Letterman et al, 1999; Matsui et al, 1998). Coagulant formation occurs in-situ (upon the addition of a chemical, such as alum, to the water) or can take place in the chemical manufacturing process (as occurs when PACL is created). Destabilization of particles, making particles "sticky," can happen by charge neutralization or sweep enmeshment (Yao et al, 1971). Interparticle collisions begin in the rapid mix stage and continue on through the flocculation stage and even occur within the filters.

Removal of natural organic mater (NOM) has become a concern, not only due to studies that show NOM reduction leads to reduced disinfection by-product (DBP) formation but also due to the EPA mandated Surface Water Treatment Rule, which dictates Enhanced Coagulation requirements (Exall and VanLoon, 2000; Edzwald and Tobiason, 1999; Eikebrokk, 1999; Letterman et al, 1999; Tseng and Edwards, 1999). As a result of increased regulation and further understanding of the relationship between NOM and DBPs, coagulants are required to do more. Coagulant manufacturers have thus been prompted to produce polymers with only slightly differing chemical composition in the hopes that their product will offer better performance than another. Furthermore, unique means of employing the chemicals, such as dual and two-stage coagulation, have been developed and studies of their effects have been undertaken.

In light of the voluminous research available on alum and PACL as single coagulants, only a refresher on the chemistry involved with each individual coagulant will be presented. A discussion of the limited and inconclusive literature available on the dual coagulation process will come next. The effects of NOM on the coagulation process discovered by other researchers will also be discussed. Only a brief review of the PDA literature will be presented here, due to the thoroughness of the PDA literature available elsewhere.

2.1 Coagulation with Alum and PACL

Alum is a metal salt that hydrolyses in water quickly and is almost immediately adsorbed to colloidal particles (Kawamura, 2000). The aluminum hydrolysis products (including aluminum hydroxide sols, $Al(OH)_{3(s)}$ formed in-situ) comprise the coagulant formation step of the coagulation process previously mentioned. Particle destabilization comes about from initial charge neutralization of the natural particles by aluminum hydroxide sols (Licskó, 1997). The interparticle collisions occur because alum is present in larger numbers than the natural particles demand, thus coagulating with one another (precipitating out) and sweeping the natural particles, including NOM, into floc (Lettermen et al, 1999; Matsui et al, 1998). Since the interparticle collision rate occurs much more slowly than the rate at which charge neutralization occurs, the collision rate is the rate-limiting step.

PACL is not as acidic as alum due to its high basicity and contains preformed (not in situ like alum), positively-charged polymers and monomers resulting in a more readily formed, denser floc that produce less sludge when used in drinking water treatment processes versus metal salts (Edzwald et al, 2000). Basicity is a relationship of the OH^- to the Al concentrations expressed in percent. In the case of high basicity PACL, the Al_{13} positively charged polymer is dominant and the polymer would then function by charge neutralization. Basically, charge neutralization is the process where the negatively charged natural particles are neutralized by the positively charged metal hydrolysis products causing destabilization. Instantaneous dispersion is important for a process to be governed by charge neutralization (Kawamura, 2000; Matsui et al 1998). According to some, the flocculation rate is slower for charge neutralization than for sweep coagulation (Lettermen et al, 1999).

Enhanced coagulation involves elevated coagulant doses along with pH control to remove a higher percentage of NOM, thus decreasing the amount of disinfection byproducts (DBP) that form in the drinking water system. Elevated coagulant doses (overdosing) produce more sludge, higher chemical costs, shorter filter run lengths and increased backwash water consumption, while underdosing can lead to residual metals and sub-optimal turbidity and TOC removal (Eikebrokk, 1999). Therefore, a WTP must have a treatment process that optimizes the coagulant dose as well as the coagulant type.

Currently, the EPA does not give compliance credit for meeting its Step 2 Enhanced Coagulation requirements if a surface-water treatment plants uses dual coagulation or any polymer as its primary coagulant (Edzwald and Tobiason, 1999). Edzwald and Tobiason believed this exclusion could prove detrimental for some utilities and performed studies to develop an *optimum coagulation* approach to water treatment operations. Optimum coagulation is defined as operating a plant at the coagulant dose and pH that maximize particle, turbidity, TOC and other DBP precursor removal while minimizing the residual coagulant. Comparing alum to polymer-aided flocculation (dose ratio = 15:1, alum to polymer) at a full-scale dissolved air flotation plant, their results showed better dissolved organic carbon (DOC) removal and lower yearly costs for the polymer-aided flocculation (Edzwald and Tobiason, 1999).

2.2 Coagulation with Dual Coagulants

The National Center for Environmental Research (which falls under the auspice of the Environmental Protection Agency, EPA) funded a project from 1995-1999 that "investigated the effectiveness of combinations of organic and inorganic coagulants on NOM removal from potable water sources" (Benjamin and Edwards, 1999). Their research focused on the effect ferric chloride in combination with cationic and anionic polymers on NOM removal. Distinctions between their work and the work presented here include the use of ferric chloride versus alum and the use of anionic polymers in addition to cationic polymers used in this study. The research applied the polymer in combination with the metal salt in doses more consistent with the definition of polymer-aided flocculation, not true dual coagulation. The study investigated the effects of each coagulant dose administered by itself and in combination with one another (the effects of dual cationic and anionic polymer were not studied). Their findings for the effect of ferric chloride and cationic polymer on dissolved organic carbon (DOC) removal were negligible at higher ferric doses and slightly better than ferric chloride at lower doses. However, the research concluded "conventional doses of ferric chloride and small doses of polymer appear to offer the greatest advantage in terms of combined particle and NOM removal."

B.Y. Ammary performed one of the most extensive research efforts regarding "dual coagulation" in 1995 (Ammary, 1995). The ratio of metal salt to cationic polymer dose examined by Ammary was on a decreasing scale of 125 to 8.3 parts ferric to 1 part polymer, by weight. The dose ratio used by Ammary is in sharp contrast to the 1:2 metal salt to polymer ratio examined in this study and is therefore more in line with polymer-aided flocculation. However, the bench-scale experiments Ammary performed with the PDA were similar to those utilized for the high NOM experiments performed in this study and as well as those performed by McCurdy (2003). The dissertation looked at ferric nitrate alone, cationic polymer alone and a combination of the two. The effects of temperature, coagulant addition sequence, mixer speed and sulfate concentration on polymer-aided coagulation performance using synthetic water were monitored with a photometric dispersion analyzer (PDA). A significant difference between work performed by Ammary and work performed by this author centers on the use of NOM. Ammary could not examine the effects of NOM on polymer-aided flocculation since the water used in those bench-scale analyses was synthesized in the laboratory without NOM addition. In contrast, work performed by this author used natural water containing low levels of NOM spiked with reference NOM to a known concentration. Among Ammary's conclusions were that polymer-aided flocculation processes were better than either type of coagulant alone when the metal hydroxide precipitates were formed (i.e. sweep coagulation) but that polymer-aided flocculation was worse than polymer alone when charge neutralization was the main mechanism of coagulation. Ammary did succinctly state "the combined use of these coagulants [ferric nitrate and cationic polymer] is intended to utilize the benefits of both coagulants through the reduction of the inorganic coagulant dose and the production of a larger and stronger floc."

McBride et al (1977) looked at dual coagulation in the ratio range of true dual coagulation when evaluating process trains for treating river water. Using a pilot plant, McBride found that 2 mg/L polymer to 2 mg/L alum used in all process trains (conventional, direct and in-line filtration) treated the river water the most effectively. Water treated with the dual coagulant under conventional or direct processes always met filtered water turbidity requirements. The study stopped short of performing full-scale studies.

Another study concluded that combining alum and ferric chlorides in a 1:1 ratio does not produce a more effective coagulant (Johnson and Amirtharajah, 1983). Indeed, the study indicated the dual coagulant performed similar to alum alone based on a review of empirical data obtained by others as well as jar tests performed on their own. The lack of improved performance for the dual coagulant could be explained by competition between the coagulants, as proposed by Johnson and Amirtharajah. Another explanation is that the dual coagulant (alum and ferric) functions by two similar coagulation mechanisms when used individually, thus replacing half the dose of one with the other does not change the coagulation process. Other researchers have proposed that the metal salt/polymer dual coagulant described in this paper versus the metal salt/metal salt dual coagulant examined by Johnson and Amirtharajah, functions by two distinct coagulation mechanisms, a combination of charge neutralization (polymer) and sweep coagulation (alum) (McCurdy, 2003; Petruševski et al, 1996; Ammary, 1995). The current study will examine if the effects of two different class of coagulants combined together can improve process performance.

2.3 Natural Organic Matter

The water quality parameters affecting coagulant choice and dose include pH, alkalinity, temperature, NOM concentration and NOM speciation (Edzwald et al, 2000). Edzwald et al (2000) state that coagulants that destabilize primarily by charge neutralization are controlled by turbidity. O'Melia et al (1999) concluded that for high TOC waters, NOM controls the coagulant dose, not turbidity. The coagulation pH, coagulation dose and the type of TOC determines how much NOM will be removed (O'Melia et al, 1999; Tseng and Edwards, 1999). Optimizing coagulant dose based on the point of minimum settled turbidity might not occur at the same dose as that required to achieve the point of minimum settled TOC.

Exall and VanLoon (2000) examined organic matter (OM) removal using alum and PACL alone. They did not examine the effects of dual coagulation, nor did they use the PDA. Based on jar tests, alum was found to be a poor cold-water choice regardless of the OM concentration. PACL performed well in cold water but the presence of higher levels of OM, particularly tannic acid, described as "a useful model compound for NOM," in warm water negatively affected PACL ability to reduce turbidity and remove OM.

Gregory and Carlson (2003) and Carlson and Gregory (2000) performed research looking at the effects of a two-stage coagulation process on waters containing various levels of NOM. Two-stage coagulation involves the application of a single coagulant type at two separate times (bench-scale) or locations (full-scale). The dose ratio of the metal salt to metal salt applied to water is 1:1. The bench and pilot-scale results indicate that two-stage coagulation increases the collision efficiency, increases particle removal during sedimentation, and increases the time for particle breakthrough to occur (longer filter runs). The authors theorize that the two-stage process resulted in particles that are not restabilized by NOM because they were more uniformly destabilized than a single-stage coagulation process. The effects witnessed in the two-stage study may be applicable to this study in that dual coagulation is similar to two-stage coagulation with respect to the split dose (time and/or location). Dual coagulation, as defined by this author, uses a different coagulant at a lower dose in the "second stage," instead of the same coagulant and coagulant dose as in two-stage coagulation.

Graham et al (1992) examined coagulant dose ratios on the order of 1:1, alum to polymer, however the majority of the experiments were performed within the range of 3:2 to 12:1, alum to polymer. The research used jar tests and a bench-scale filtration apparatus, both of which can produce results that are significantly different from pilot-scale or full-scale experiments. Graham et al (1992) used color in their experiments in the range of 40-80 Hazen units and the samples were filtered to remove undissolved humic material (i.e. turbidity). Color consists of colloidal metallic hydroxides or organic compounds; however, the later is usually more dominant. Graham et al (1992) concluded that any dual coagulant or polymer-aided experiment was not as effective at coagulating color. Graham et al (1992) stated that when dual or polymer-aided coagulation is employed, complete charge neutralization is not necessary for efficient performance in direct filtration applications. His rationale for this phenomenon was that unabsorbed polymer enters the filter and attaches to the grains giving the floc something to adhere. Gregory and Carlson (2003) also noted this phenomenon in their study examining floc formation kinetics in granular media filtration performance.

Hubel and Edzwald (1987) used a jar test apparatus to test dual coagulants (1:1 alum to polymer) on high NOM water. The initial concentration of the TOC in the water was 9.4 mg/L. After water and polymer were mixed for 5 minutes, alum was added and a 2-minute rapid mix (100 RPM) followed. Their results indicate that alum alone at lower pH (5.5) produced better turbidity and total organic carbon (TOC) removal than either 1:1 or 8:1 alum to polymer. At a pH of 7.2, the 8:1 alum to polymer dose produced the best turbidity (significantly better) and TOC removal (slightly better). The removal achieved by the 8:1 polymer-aided flocculation for the pH = 7.2 water did not exceed the removals achieved by alum only at pH 5.5. One of their final conclusions was that the "dual" coagulant might be useful for water containing 5 mg/L or less

TOC. Jar tests are excellent sources for developing general trends and determining reference doses but having pilot–scale and full-scale data is always preferable.

The final relevant study regarding NOM and coagulants showed that addition of small amounts of polymer (0.5 –1.0 mg/L) reduced the optimum alum dose by 43-67% for waters spiked to 5 mg/L DOC (Bolto et al, 1999). The dose ratio of alum to polymer was variable from 20-40:1, thus the experiments more closely fit the definition for polymer-aided flocculation and not true dual coagulation as examined here for high TOC water. The study employed jar tests and used reconstituted water prepared from concentrated NOM. The 67% reduction was linked to the increased hydrophobic NOM concentration of the treated water versus a lower concentration of hydrophobic NOM for the 43% reduction. Bolto et al (1999) concluded that the polymers perform better when particles are present and that the polymer-aided flocculation is more effective due to the increased particulate concentration contributed by alum.

2.4 Photometric Dispersion Analyzer

Many researchers have related the PDA output (flocculation index, FI) to the state of aggregation and have shown that a larger FI implies a larger floc size (Gregory and Carlson, 2003; McCurdy, 2003; Wang et al, 2002; Matsui et al, 1998; Ohto et al, 1993; Glasgow and Kim, 1989). John Gregory (1985) is generally considered the pioneer who first developed the method of using the PDA to measure flocculation kinetics. David Nelson designed the original PDA and Ohto et al (1993) developed a PDA that adjusted for fouling.

Three recent studies performed at Colorado State University (CSU) used the PDA to study flocculation kinetics. The first study concluded that the rate of floc formation, as measured by the PDA, was indicative of overall process performance (Gregory and Carlson, 2003). The second study concluded that shear recovery is indicative of pilot-scale filtration performance (McCurdy 2003). The third study showed that high NOM waters did not adversely affect the PDA and that the FI was a reliable measure of floc size (Gregory, 2003). All three studies conclude FI can be related to filtration performance. The link from FI to filter performance can be made on the theory that FI relates aggregate formation to the coagulant and coagulant dose employed and aggregates become their own receptor within a filter. Gregory and McCurdy also concluded that increased filter performance at the pilot scale (i.e. longer runtimes) was not due solely to solids mass loading since similar settled water particle counts were noted for all treatments. A final relative conclusion by Gregory regarding the slope of the FI stipulated that choosing the lowest alum dose that does not increase the FI slope (the steepest slope) would in effect be choosing the optimum alum dose. Gregory's (2003) work is supported independently by work performed by Ammary (1995) who concluded the flocculation kinetics are better and the flocs are bigger with steeper FI slopes. McCurdy (2003) also lends support to Gregory (2003) by concluding that the coagulant that resulted in better recovery slopes (steeper slopes) after induced shearing would be the optimum coagulant choice.

Work performed by personnel outside CSU also show that the PDA output is a useful tool in determining optimal coagulant dose (Kan et al, 2002; Kan and Huang, 1998; Huang and Chen, 1996). Additionally, studies by other researchers using the PDA experienced a decreasing FI that is relevant to this study (Kan et al, 2002; Ammary, 1995; Li and Gregory, 1991). They explained the decrease in FI was from the large floc settling and being effectively excluded from the calculation. Basically, the time it takes for the FI to reach a maximum value corresponds with the time it takes for particles to begin settling.

CHAPTER 3. RESEARCH OBJECTIVE

Researchers have examined the effects of single coagulants on the drinking water treatment process to great detail. Research on the combined effects of dual coagulation is much more limited. The majority of "dual-coagulation" studies have used a dose ratio more appropriately defined as polymer-aided flocculation (Ammary, 1995; Graham et al; 1992; Hubel and Edzwald, 1987; Johnson and Amirtharajah, 1983). Of the studies that have looked at a dose ratio of metal salt to polymer on the order of 1:1, bench-scale experiments dominate as the preferred method of research. Pilot-scale studies are surprisingly limited and application of full-scale data is almost non-existent (McCurdy, 2003; Edzwald and Tobiason, 1999). Studies have attempted to examine the effects of NOM on dual coagulation but those studies were limited in scope (bench-scale experiments only), used synthesized water instead of natural water or used a dose ratio more in line with polymer-aided flocculation (Bolto, 1999; Ammary, 1995; Graham et al, 1992; Hubel and Edzwald, 1987). A recent study examined true dual coagulation using alum to PACL (dose ratio 1:2) with bench-scale and pilot-scale experiments for natural, low NOM water (McCurdy, 2003).

The primary objective of this research was to determine if full-scale performance data obtained from a local water treatment plant proved a recent study that showed dual coagulation performed better than alum and PACL at the bench-scale and pilot-scale level using similar natural source water. Full-scale data developed from implementing each of the three coagulant treatments were obtained from a local water treatment plant. A secondary objective was to determine if the trends noted for the low NOM study were applicable to high

NOM water. Bench-scale analyses were performed using natural reservoir water spiked with NOM and the floc aggregation kinetics were monitored using a PDA.

CHAPTER 4.

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WATER TREATMENT USING DUAL COAGULATION

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Abstract: The process of treating drinking water with a combination of alum and polyaluminum chloride (dual coagulant) has been performed by at least one utility along the Colorado Front Range since the mid 1990s. Previous bench-scale research with low total organic carbon (TOC) water using a photometric dispersion analyzer showed the dual treatment developed larger non-settleable floc than alum alone and re-aggregated faster than PACL or alum alone after experiencing induced shearing. Pilot-scale studies showed longer filter run volumes with the dual treatment. The current study proved that at the full-scale level, the dual treatment provided significantly longer filter run times and slightly increased turbidity removal versus either PACL or alum alone when treating low TOC water. TOC removal using alum as a single coagulant proved better than for PACL alone or the dual coagulant. In order to determine the effects of higher natural organic matter concentrations on the treatment process, bench-scale analysis were performed.

4.1 Introduction

Since the introduction of coagulation in the late 19th century, aluminum sulfate (alum) has been the metal salt of choice for coagulation processes. Coagulant aids were developed in the 1930s, followed by synthetic organic polymers in the 1960s (Letterman et al, 1999). The use of synthetic organic polymers such as polyaluminum chloride (PACL) has gained in popularity since their introduction but have yet to dominate the water treatment industry, most likely due to their increased cost as compared to alum. Experimentation with combinations of alum and polymers resulted in an effort to utilize the somewhat unique advantages of both coagulants and to minimize their disadvantages.

When used individually, either alum or PACL are capable of treating water to acceptable levels, as supported by studies and proven in full-scale operations. Little conclusive evidence is available about the effects of using both chemicals as dual coagulants, as previous studies have produced conflicting results. Dual coagulation for this study is defined as the process by which two coagulants are applied to the raw water at the site of rapid mixing. Young et al (2000) defined polymer-aided flocculation "as the coagulation and flocculation process which is accomplished by using alum in conjunction with a small dosage of polymer." For purposes of this study, polymer-aided flocculation will be defined as a coagulation process with a dose ratio of inorganic metal salt to polymer greater than 3:1. The definition for dual coagulation will be extended to include the requirement of a dose ratio less than or equal to 3:1, either metal salt to polymer or polymer to metal salt.

The literature available concerning dual coagulation is more in line with Young et al's (2000) definition of polymer-aided flocculation and not true dual coagulation, even when the researchers used dual coagulation terminology in their papers. However, a recent study did look at the effects associated with cyclic shearing and floc morphology for waters containing low levels of NOM treated with dual coagulation. Bench-scale and pilot-scale analysis were performed by McCurdy (2003) to further the understanding of the dual coagulation process and serve as the basis for comparing the results achieved in this study.

The hypothesis that bench-scale and pilot-scale analysis data for low NOM water is predictive of full-scale performance, due to the formation of fundamentally different aggregates that are distinct to the coagulant treatment implemented, was tested. A full-scale plant treated water with alum alone, PACL alone and dual coagulant (1:2 by weight, alum to PACL) and provided water quality data for comparison with previously obtained bench-scale and pilot-scale data. Additionally, the hypothesis that water with high levels of NOM would negatively alter the flocculation kinetics for water treated with dual coagulants was also investigated. The purpose of this study was to look at the effects of cyclic shearing on high levels of NOM laden water treated with alum alone, PACL alone and dual coagulant (1:2 by weight, alum to PACL). Bench-scale analysis incorporating the use of a photometric dispersion analyzer (PDA) to measure floc aggregation response to cyclic shearing was used.

4.2 Literature Review

Coagulation has three steps: coagulant formation, particle destabilization and interparticle collisions (Letterman et al, 1999; Matsui et al, 1998). Coagulant formation occurs in-situ (upon the addition of a chemical, such as alum, to the water) or can take place in the chemical manufacturing process (as occurs when PACL is created). Destabilization of particles, making particles "sticky," can happen by charge neutralization or sweep enmeshment (Yao et al, 1971). Interparticle collisions begin in the rapid mix stage and continue on through the flocculation stage and even occur within the filters.

Removal of natural organic mater (NOM) has arisen as a concern, not only due to studies that show NOM reduction leads to reduced disinfection by-product (DBP) formation but also due to the EPA mandated Surface Water Treatment Rule, which dictates Enhanced Coagulation requirements (Exall and VanLoon, 2000; Edzwald and Tobiason, 1999; Eikebrokk, 1999; Letterman et al, 1999; Tseng and Edwards, 1999). As a result of increased regulation and further understanding of the relationship between NOM and DBPs, coagulants are required to do more. Prompting coagulant manufacturers to produce polymers with only slightly differing chemical composition that supposedly offer better performance. Furthermore, unique means of employing the chemicals, such as dual and two-stage coagulation, have been developed and studies of their effects have been undertaken.

Having a firm understanding of the individual chemistry of the two ingredients that make up the dual coagulant is a must. In light of the voluminous research available on alum and PACL as individual coagulants, minimal background information will be presented first on alum, followed by PACL. A discussion of the limited and inconclusive literature available on the dual coagulation process will come next. The effects of NOM on the coagulation process discovered by other researchers will also be discussed. Only a brief review of the PDA literature will be presented here, due to the thoroughness of the PDA literature available elsewhere.

4.2.1 Coagulation with Alum and PACL

Alum is a metal salt that hydrolyses in water quickly and is almost immediately adsorbed to colloidal particles (Kawamura, 2000). The aluminum hydrolysis products (including aluminum hydroxide sols, $Al(OH)_{3(s)}$ formed in-situ) comprise the coagulant formation step of the coagulation process previously mentioned. Particle destabilization comes about from initial charge neutralization of the natural particles by aluminum hydroxide sols. The interparticle collisions occur because alum is present in larger numbers than the natural particles demand, thus coagulating with one another (precipitating out) and sweeping the natural particles, including NOM, into floc (Lettermen et al, 1999; Matsui et al, 1998). Since the interparticle collision rate occurs much more slowly than the rate at which charge neutralization occurs, the collision rate is the rate-limiting step.

PACL is not as acidic as alum due to its high basicity and contains preformed (not in situ like alum), positively-charged polymers and monomers resulting in a more readily formed, denser floc that produce less sludge when used in drinking water treatment processes versus metal salts (Edzwald et al, 2000). Basicity is a relationship of the OH^- to the Al concentrations expressed in percent. In the case of high basicity PACL, the Al_{13} positively charged polymer is dominant and the polymer would then function by charge neutralization. Basically, charge neutralization is the process where the negatively charged natural particles are neutralized by the positively charged metal hydrolysis products causing destabilization. Instantaneous dispersion is important for a process to be governed by charge neutralization (Kawamura, 2000; Matsui et al 1998). According to some, the flocculation rate is slower for charge neutralization than for sweep coagulation (Lettermen et al, 1999).

Enhanced coagulation involves elevated coagulant doses along with pH control to remove a higher percentage of NOM, thus decreasing the amount of disinfection byproducts (DBP) that form in the drinking water system. Elevated coagulant doses (overdosing) produce more sludge, higher chemical costs, shorter filter run lengths and increased backwash water consumption, while underdosing can lead to residual metals and sub-optimal turbidity and TOC removal (Eikebrokk, 1999). Therefore, a WTP must have a treatment process that optimizes the coagulant dose as well as the coagulant type.

Currently, the EPA does not give compliance credit for meeting its Step 2 Enhanced Coagulation requirements if a surface-water treatment plants uses dual coagulation or any polymer as its primary coagulant (Edzwald and Tobiason, 1999). Edzwald and Tobiason believed this exclusion could prove detrimental for some utilities and performed studies to develop an *optimum coagulation* approach to water treatment operations. Optimum coagulation is defined as operating a plant at the coagulant dose and pH that maximize particle, turbidity, TOC and other DBP precursor removal while minimizing the residual coagulant. Comparing alum to polymer-aided flocculation (dose ratio = 15:1, alum to polymer) at a full-scale dissolved air flotation plant, their results showed better dissolved organic carbon (DOC) removal and lower yearly costs for the polymer-aided flocculation (Edzwald and Tobiason, 1999).

4.2.2 Coagulation with Dual Coagulants

The National Center for Environmental Research (which falls under the auspice of the Environmental Protection Agency, EPA) funded a project from 1995-1999 that "investigated the effectiveness of combinations of organic and inorganic coagulants on NOM removal from potable water sources" (Benjamin and Edwards, 1999). Their research focused on the effect ferric chloride in combination with cationic and anionic polymers on NOM removal. Distinctions between their work and the work presented here include the use of ferric chloride versus alum and the use of anionic polymers in addition to cationic polymers used in this study. The research applied the polymer in combination with the metal salt in doses more consistent with the definition of polymer-aided flocculation, not true dual coagulation. The study investigated the effects of each coagulant dose administered by itself and in combination with one another (the effects of dual cationic and anionic polymer were not studied). Their findings for the effect of ferric chloride and cationic polymer on dissolved organic carbon (DOC) removal were negligible at higher ferric doses and slightly better than ferric chloride at lower doses. However, the research concluded "conventional doses of ferric chloride and small doses of polymer appear to offer the greatest advantage in terms of combined particle and NOM removal."

B.Y. Ammary performed one of the most extensive research efforts regarding "dual coagulation" in 1995 (Ammary, 1995). The ratio of metal salt to cationic polymer dose examined by Ammary was on a decreasing scale of 125 to 8.3 parts ferric to 1 part polymer, by weight. The dose ratio used by Ammary is in sharp contrast to the 1:2 metal salt to polymer ratio examined in this study and is therefore more in line with polymer-aided flocculation. The dissertation looked at ferric nitrate alone, cationic polymer alone and a combination of the two. The effects of temperature, coagulant addition sequence, mixer speed and sulfate concentration on polymer-aided coagulation performance using synthetic water were monitored with a photometric dispersion analyzer (PDA). A significant difference between work performed by Ammary and work performed by this author centers on the use of NOM. Ammary could not examine the effects of NOM on polymer-aided flocculation since the water used in those bench-scale analyses was synthesized in the laboratory without NOM addition. In contrast, work performed by this author used natural water containing low levels of NOM spiked with reference NOM to a known concentration. Among Ammary's conclusions were that polymer-aided flocculation processes were better than either type of coagulant alone when the metal hydroxide precipitates were formed (i.e. sweep coagulation) but that polymer-aided flocculation was worse than polymer alone when charge neutralization was the main mechanism of coagulation. Ammary did succinctly state "the combined use of these coagulants [ferric nitrate and cationic polymer] is intended to utilize the benefits of both coagulants through the reduction of the inorganic coagulant dose and the production of a larger and stronger floc."

McBride et al (1977) looked at dual coagulation in the ratio range of true dual coagulation when evaluating process trains for treating river water. Using a pilot plant, McBride found that 2 mg/L polymer to 2 mg/L alum used in all process trains (conventional, direct and in-line filtration) treated the river water the most effectively. Water treated with the dual coagulant under conventional or direct processes always met filtered water turbidity requirements. The study stopped short of performing full-scale studies.

Dual coagulation using two different metal salts was examined and one of the conclusions was that combining alum and ferric chlorides in a 1:1 ratio does not produce a more effective coagulant (Johnson and Amirtharajah, 1983). Indeed, the study indicated the dual coagulant performed similar to alum alone based on a review of empirical data obtained by others as well as jar tests performed on their own. The lack of improved performance for the dual coagulant could be explained by competition between the coagulants, as proposed by Johnson and Amirtharajah. Another explanation is that the dual coagulant (alum and ferric) functions by two similar coagulation mechanisms when used individually, thus replacing half the dose of one with the other does not change the coagulation process. Other researchers have proposed that the metal salt/polymer dual coagulant described in this paper versus the metal salt/metal salt dual coagulant examined by Johnson and Amirtharajah, functions by two distinct coagulation mechanisms, a combination of charge neutralization (polymer) and sweep coagulation (alum) (McCurdy, 2003; Petruševski et al, 1996; Ammary, 1995). The current study will examine if the effects of two different class of coagulants combined together can improve process performance.

4.2.3 Natural Organic Matter

The water quality parameters affecting coagulant choice and dose include pH, alkalinity, temperature, NOM concentration and NOM speciation (Edzwald et al, 2000). Edzwald et al

(2000) state that coagulants that destabilize primarily by charge neutralization are controlled by turbidity. O'Melia et al (1999) concluded that for high TOC waters, NOM controls the coagulant dose, not turbidity. The coagulation pH, coagulation dose and the type of TOC determines how much NOM will be removed (O'Melia et al, 1999; Tseng and Edwards, 1999). Thus, treating water for maximum pathogen and NOM removal are two opposing goals since turbidity is a surrogate measure of the pathogen concentration.

Exall and VanLoon (2000) examined organic matter (OM) removal using alum and PACL alone. They did not examine the effects of dual coagulation, nor did they use the PDA. Based on jar tests, alum was found to be a poor cold-water choice regardless of the OM concentration. PACL performed well in cold water but the presence of higher levels of OM, particularly tannic acid, described as "a useful model compound for NOM," in warm water negatively affected PACL ability to reduce turbidity and remove OM.

Gregory and Carlson (2003) and Carlson and Gregory (2000) performed research looking at the effects of a two-stage coagulation process on waters containing various levels of NOM. Two-stage coagulation involves the application of a single coagulant type at two separate times (bench-scale) or locations (full-scale). The dose ratio of the metal salt to metal salt applied to water is 1:1. The bench and pilot-scale results indicate that two-stage coagulation increases the collision efficiency, increases particle removal during sedimentation, and increases the time for particle breakthrough to occur (longer filter runs). The authors theorize that the two-stage process resulted in particles that are not restabilized by NOM because they were more uniformly destabilized than a single-stage coagulation process. The effects witnessed in the two-stage study may be applicable to this study in that dual coagulation is similar to two-stage coagulation with respect to the split dose (time and/or location). Dual coagulation, as defined by this author, uses a different coagulant at a lower dose in the "second stage," instead of the same coagulant and coagulant dose as in two-stage coagulation.

Graham et al (1992) examined coagulant dose ratios on the order of 1:1, alum to polymer, however the majority of the experiments were performed within the range of 3:2 to 12:1, alum to polymer. The research used jar tests and a bench-scale filtration apparatus, both of which can produce results that are significantly different from pilot-scale or full-scale experiments. Graham et al (1992) used color in their experiments in the range of 40-80 Hazen units and the samples were filtered to remove undissolved humic material (i.e. turbidity). Color consists of colloidal metallic hydroxides or organic compounds; however, the later is usually more dominant. Graham et al (1992) concluded that any dual coagulant or polymer-aided experiment was not as effective at coagulating color. Graham et al (1992) stated that when dual or polymer-aided coagulation is employed, complete charge neutralization is not necessary for efficient performance in direct filtration applications. His rationale for this phenomenon was that unabsorbed polymer enters the filter and attaches to the grains giving the floc something to adhere. Gregory and Carlson (2003) also noted this phenomenon in their study examining floc formation kinetics in granular media filtration performance.

Hubel and Edzwald (1987) used a jar test apparatus to test dual coagulants (1:1 alum to polymer) on high NOM water. The initial concentration of the TOC in the water was 9.4 mg/L. After water and polymer were mixed for 5 minutes, alum was added and a 2-minute rapid mix (100 RPM) followed. Their results indicate that alum alone at lower pH (5.5) produced better turbidity and total organic carbon (TOC) removal than either 1:1 or 8:1 alum to polymer. At a pH of 7.2, the 8:1 alum to polymer dose produced the best turbidity (significantly better) and TOC removal (slightly better). The removal achieved by the 8:1 polymer-aided flocculation for the pH = 7.2 water did not exceed the removals achieved by alum only at pH 5.5. One of their final conclusions was that the "dual" coagulant might be useful for water containing 5 mg/L or less TOC. Jar tests are excellent sources for developing general trends and determining reference doses but having pilot–scale and full-scale data is always preferable.

The final relevant study regarding NOM and coagulants showed that addition of small amounts of polymer (0.5 –1.0 mg/L) reduced the optimum alum dose by 43-67% for waters spiked to 5 mg/L DOC (Bolto et al, 1999). The dose ratio of alum to polymer was variable from 20-40:1, thus the experiments more closely fit the definition for polymer-aided flocculation and not true dual coagulation as examined here for high TOC water. The study employed jar tests and used reconstituted water prepared from concentrated NOM. The 67% reduction was linked to the increased hydrophobic NOM concentration of the treated water versus a lower concentration of hydrophobic NOM for the 43% reduction. Bolto et al (1999) concluded that the polymers perform better when particles are present and that the polymer-aided flocculation is more effective due to the increased particulate concentration contributed by alum.

4.2.4 Photometric Dispersion Analyzer

Many researchers have related the PDA output (flocculation index, FI) to the state of aggregation and have shown that a larger FI implies a larger floc size (Gregory and Carlson, 2003; McCurdy, 2003; Wang et al, 2002; Matsui et al, 1998; Ohto et al, 1993; Glasgow and Kim, 1989). John Gregory (1985) is generally considered the pioneer who first developed the method of using the PDA to measure flocculation kinetics. David Nelson designed the original PDA and Ohto et al (1993) developed a PDA that adjusted for fouling.

Three recent studies performed at Colorado State University (CSU) used the PDA to study flocculation kinetics. The first study concluded that the rate of floc formation, as measured by the PDA, was indicative of overall process performance (Gregory and Carlson, 2003). The second study concluded that shear recovery is indicative of pilot-scale filtration performance (McCurdy 2003). The third study showed that high NOM waters did not adversely affect the PDA and that the FI was a reliable measure of floc size (Gregory, 2003). All three studies conclude FI can be related to filtration performance. The link from FI to filter performance can be made on the theory that FI relates aggregate formation to the coagulant and coagulant dose employed and aggregates become their own receptor within a filter. Gregory and McCurdy also concluded that increased filter performance at the pilot scale (i.e. longer runtimes) was not due solely to solids mass loading since similar settled water particle counts were noted for all treatments. A final relative conclusion by Gregory regarding the slope of the FI stipulated that choosing the lowest alum dose that does not increase the FI slope (the steepest slope) would in effect be choosing the optimum alum dose. Gregory's (2003) work is supported independently by work performed by Ammary (1995) who concluded the flocculation kinetics are better and the flocs are bigger with steeper FI slopes. McCurdy (2003) also lends support to Gregory (2003) by concluding that the coagulant that resulted in better recovery slopes (steeper slopes) after induced shearing would be the optimum coagulant choice.

Work performed by personnel outside CSU also show that the PDA output is a useful tool in determining optimal coagulant dose (Kan et al, 2002; Kan and Huang, 1998; Huang and Chen, 1996). Additionally, studies by other researchers using the PDA experienced a decreasing FI that is relevant to this study (Kan et al, 2002; Ammary, 1995; Li and Gregory, 1991). They explained the decrease in FI was from the large floc settling and being effectively excluded from the calculation. Basically, the time it takes for the FI to reach a maximum value corresponds with the time it takes for particles to begin settling.

4.2.5 Research Objective

Researchers have examined the effects of single coagulants on the drinking water treatment process to great detail. Research on the combined effects of dual coagulation is much more limited. The majority of "dual-coagulation" studies have used a dose ratio more appropriately defined as polymer-aided flocculation (Ammary, 1995; Graham et al; 1992; Hubel and Edzwald, 1987; Johnson and Amirtharajah, 1983). Of the studies that have looked at a dose ratio of metal salt to polymer on the order of 1:1, bench-scale experiments dominate as the preferred method of research. Pilot-scale studies are surprisingly limited and application of full-scale data is almost non-existent (McCurdy, 2003; Edzwald and Tobiason, 1999). Studies have attempted to examine the effects of NOM on dual coagulation but those studies were limited in scope (bench-scale experiments only), used synthesized water instead of natural water or used a dose ratio more in line with polymer-aided flocculation (Bolto, 1999; Ammary, 1995; Graham et al, 1992; Hubel and Edzwald, 1987). A recent study examined true dual coagulation using alum to PACL (dose ratio 1:2) with bench-scale and pilot-scale experiments for natural, low NOM water (McCurdy, 2003).

The primary objective of this research was to determine if full-scale performance data proved a recent study that showed dual coagulation performed better than alum and PACL at the bench-scale and pilot-scale level. Full-scale data developed from implementing each of the three coagulant treatments were obtained from a local water treatment plant. A secondary objective was to determine if the trends noted for the low NOM study were applicable to high NOM water. Bench-scale analyses were performed using natural reservoir water spiked with NOM and the floc aggregation kinetics were monitored using a PDA.

4.3 Materials and Methods

4.3.1 Raw Water Conditions

Source water used for the bench-scale and full-scale portions of this project was Horsetooth Reservoir (HT) Water. HT water quality remains fairly consistent throughout the year, relative to river water sources. Some change in initial water conditions has been noted during the spring run-off season; however, the change is minimal and does not result in dramatic changes to the treatment process (Reed, 2003). The raw (untreated, no additional NOM added) HT water used for the bench-scale portion was collected from a tap located in the hydraulics laboratory of the Colorado State University Environmental Research Center (CSU-ERC). Refrigerator limitations dictated the amount of water that could be stored at one time, however, water was collected in approximately 60 L batches each time. Due to the intermittent demand for raw HT water and the desire to collect water with as similar initial water conditions as possible, the line was flushed for approximately five minutes each time a batch was collected. Water was collected four times over a two-month period and was stored at 4° C when not in use. The parameters in Table 1 highlight the minimum, maximum and average values obtained over the course of the bench-scale experiments.

	pH	Alkalinity (mg/L as $CaCO_3$)	Raw HT TOC (mg/L)	High HT TOC (mg/L)	Turbidity (NTU)
Min	7.1	24	2.3	7.7	11
Max	7.6	26	2.7	8.5	13
Avg	7.4	25	2.5	7.8	12

Table 1. Typical Raw Water Quality for HT Water Collected at the ERC

4.3.2 Dose Optimization for High TOC Water

Reference aquatic natural organic matter (NOM) was obtained from the International Humic Substance Society (IHSS) located at the University of Minnesota. Suwannee River NOM was isolated by IHSS using reverse osmosis. Graham et al (1992) provides a thorough description of the process IHSS follows in creating its humic material. According to IHSS, the NOM contained 52.47% carbon in a dry, ash-free sample. Calculations to determine the appropriate amount of NOM to add in order to create synthetic water (high TOC) with a concentration of approximately 8 mg/L TOC were performed initially using the weight analysis data provided by IHSS. After the NOM was measured using the Mettler AE100 scale, the appropriate amount of NOM was added to raw HT water to create high TOC water. The TOC concentration of the synthetic HT water was verified using the Hach AstroTOC UV meter, which operates on the EPA-approved UV-persulfate oxidation method (Hach 2002). If necessary, additional NOM was added to increase the TOC concentration to approximately 8 mg/L. High HT TOC data is presented in Table 1.

The bench-scale optimum coagulant dose was determined for high TOC water using alum alone, PACL alone, and dual coagulant. The alum used was aluminum sulfate ($Al_2(SO_4)_3$

$\cdot 14.3H_2O$, 9 % Al_2O_3). The PACL was manufactured by Summit Research Labs under the label Sumaclear 820B (18-20% Al_2O_3, 80% basicity, no sulfate). The 1:2 ratio, alum to PACL by weight, was not optimized but rather developed from typical practices implemented by Soldier Canyon Water Treatment Plant, SCWTP (Reed, 2003). Based on previous experience with optimum dose jar testing experiments, the optimum alum dose was determined first, followed by the optimum PACL dose. The optimum PACL dose obtained served as a reference point for determining the initial dual coagulant dose range. Additional data regarding the actual doses administered during the jar tests is available in Appendix A.

The bench-scale optimum dose determination used a Phipps & Bird PB-900 programmable jar tester, see Figure 1, following typical jar-testing protocol (Kawamura, 2000). Each coagulant was individually pippetted onto separate Teflon-coated septa that were resting on the edge of each jar. Using the septa allowed for timely delivery of all chemicals and at the appropriate times the coagulant (i.e. septa) would be introduced into the two-liter jars for mixing. During their individual optimization experiments, alum and PACL were introduced at the start of a rapid mix cycle that would last 30 seconds. When the dual coagulant optimum dose was being determined, the PACL was introduced first, followed by alum 15 seconds later for a total rapid mix of 30 seconds. Separating the doses in this manner allowed the bench-scale experiments to mirror pilot-scale and full-scale practices that administer the coagulants at different in-line injection points. Ammary (1995) reports that numerous studies have been performed on the coagulant addition sequence with contrary results.

Figure 1. Jar Test Apparatus

A cationic polymer coagulant aid manufactured by Allied Colloid under the label LT-22s was used during each optimization experiment and was introduced with approximately 5 seconds of rapid mix remaining. SCWTP, as well as at least one other local drinking water plant, use the cationic polymer (Reed, 2003). Using the coagulant aid allowed the bench-scale experiments to mirror pilot-scale and full-scale practices. A previous study showed little affect between the addition of coagulant aid during the bench-scale monitoring versus experiments performed without coagulant aid as monitored by the PDA (McCurdy, 2003).

A three-stage, decreasing energy flocculation followed the 30-second rapid mix, each flocculation stage lasted 15 minutes. The mixer was operated at 300 RPM during the rapid mix stage ($G = 300\ s^{-1}$). The mixing in the flocculation stages was performed at 48 RPM, 32 RPM and 18 RPM, respectively ($G = 48, 32, 18\ s^{-1}$). A 15-minute settling period succeeded the flocculation stage, at which time samples were collected for turbidity, TOC and pH. Optimum doses were based on the dose that corresponded with the point of minimum settled turbidity.

4.3.3 Cyclic Shearing Experiments

No shear and shear experiments were performed using a Label programmable mixer and a Hach PDA. The mixer blade extended into the PDA jar containing 2.2 L of the high TOC water. High TOC water was treated using the optimized dose determined by the methods described in section

3.3.2. The coagulant and coagulant aid doses were adjusted for the increased volume of water used in the PDA experiments versus the standard jar test experiments.

For the no shear experiments, the mixer blade operated at 330 rpm for three minutes while the pump and PDA were on, allowing the PDA measurements to stabilize. For the single coagulant experiments, alum or PACL was introduced at the end of the 3-minute stabilization period. The rapid mix continued for 15 seconds, at which time the mixing speed dropped to 50 RPM (slow mix). Just prior to the mixer speed decrease, coagulant aid was introduced. When the dual coagulant was used, PACL was added after 2.75 minutes of stabilization and alum was added at 3 minutes. The mixer remained at 50 rpm until the experiment timed out (usually within 15 minutes). The no shear experiments were performed to allow stable, consistently sized floc to form that would create a baseline for comparing with shear experiments and with results obtained previously by McCurdy for low NOM water.

For shear experiments, the mixer blade operated at the same speeds as the no shear experiments. However, the initial 50 RPM slow mix period lasted for five minutes followed by a 220 RPM shear period that lasted for 1.5 minutes that was intended to shear the floc. At the end of this shearing period, the mixer speed was again lowered to 50 RPM for 5 minutes. This slow/rapid mix shear cycle was repeated for a total of four shearing periods and four recovery periods.

A downstream peristaltic pump would pull water from the jar through tubing that allowed the water to flow through the PDA and then deposit the water to waste. No recycling of the water took place in these experiments, unlike experiments performed by others using the PDA (Kan et al, 2002; Kan and Huang, 1998; Ammary, 1995). In a study examining shearing on activated sludge, researchers stated that their previous studies showed that changes in FI were due to conditions in the reactor and not to shearing conditions in the tubing (Chaignon et al, 2002). The pump was set at 20 ml/min to decrease the effect of changing volume on the mixing energy within the 2 L container. A picture of the PDA set-up is presented in Figure 2.

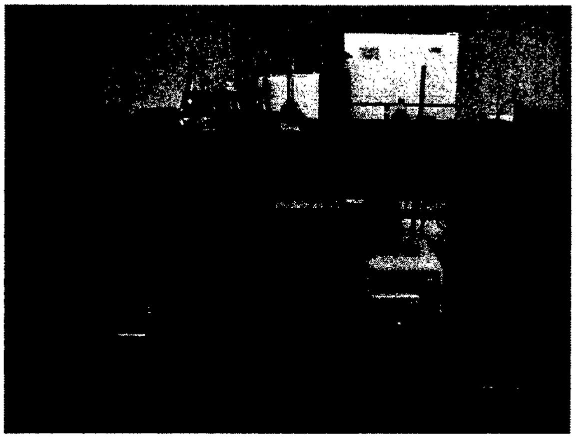

Figure 2. PDA set-up

No pH control for either the dose optimization or the PDA experiments was implemented. Literature supports the notion that the PDA response is not affected by different pH but that the PDA can be used to correctly measure aggregation in samples of varying pH (Kan and Huang, 1998). The decision to not adjust pH was based in part on research performed by McCurdy (2003) that did not adjust for pH. Since the pH used in these experiments was typical of those experienced by WTPs and the PACL used was a high basicity coagulant, adjusting the pH for these experiments is not necessary but may be something to consider in future studies. Ching (1994) showed that decreasing the pH of the raw water and increasing the coagulant dose, removed more TOC than allowing the pH to float. Ching concluded the metal hydroxide precipitates formed at the higher doses contributed to the TOC removal.

4.3.4 Full-Scale Water Treatment Plant Study

A conventional water treatment plant was used to determine if the trends noted from previous pilot scale plant experiments, as well as bench-scale experiments, treating low TOC waters proved to be reliable indicators of full-scale performance (McCurdy, 2003). SCWTP, located in the City of Fort Collins, treats water obtained from HT and a simplified schematic is presented as

Figure 3. Depending on the experiment, PACL and dual coagulant were injected at the location labeled alum. Also, the treatment plant has 4 flocculation basins not 3 as depicted in the figure.

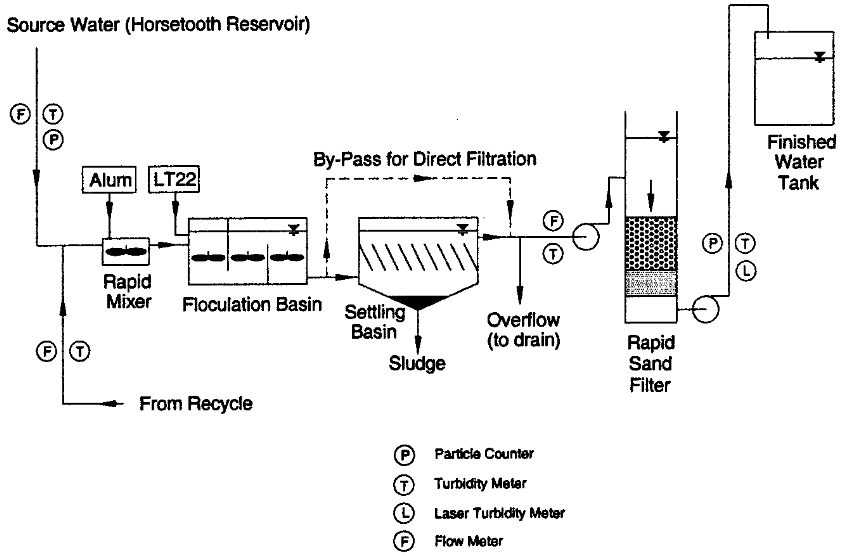

Figure 3. Schematic of WTP.

The WTP process includes rapid mixing with an inline mechanical mixer (Water Champ) and an inline hydraulic jet rapid mixer, four-stage flocculation basin (total detention time @ 8 mgd = 48 min), two inclined parallel plate settling basins (hydraulic loading rate = 0.15 gpm/ft^2), and dual media filters (35” anthracite, 12” sand) with filter bed area equal to 360 ft^2. Pictures of the rapid mix set-up are shown in Figures 4 and 5 and the flocculation basin is shown in Figures 6 and 7.The rapid mix portion of the treatment process occurs over a distance of approximately 30 feet from the initial polymer addition point to the inline hydraulic jet mixer. The plant operates the filters in a constant rate, declining head manner. The average filter-loading rate varied from 2.27 gpm/ft^2, 2.71 gpm/ft^2, and 2.41 gpm/ft^2 for each coagulant dosing scheme (alum, PACL, dual, respectively). Filter runs ended as head loss and turbidity counts approached but never exceeded unacceptable levels (i.e. terminal head loss and turbidity breakthrough were not allowed to occur).

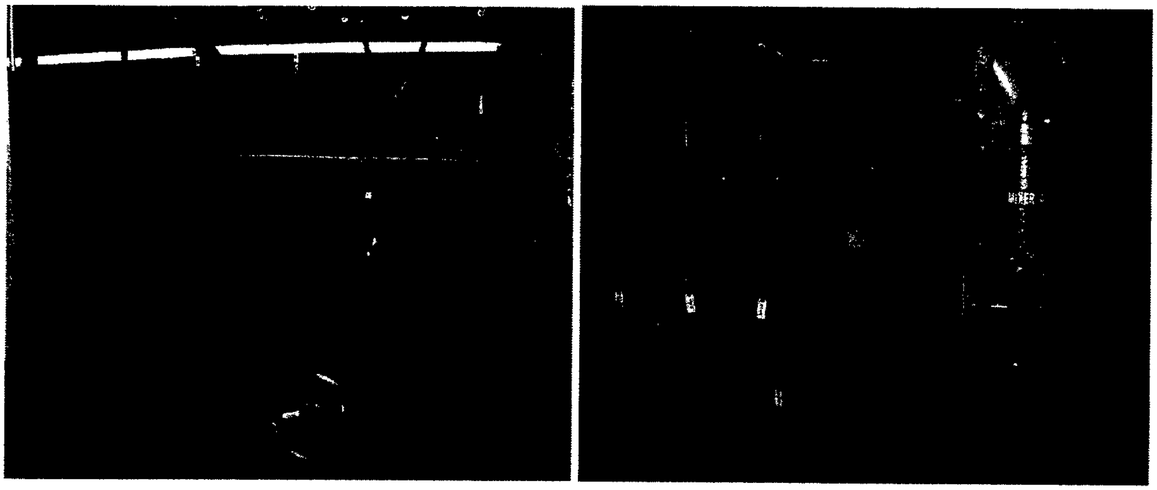

Figure 4 and 5. In-line mechanical mixer and inline hydraulic jet mixer.

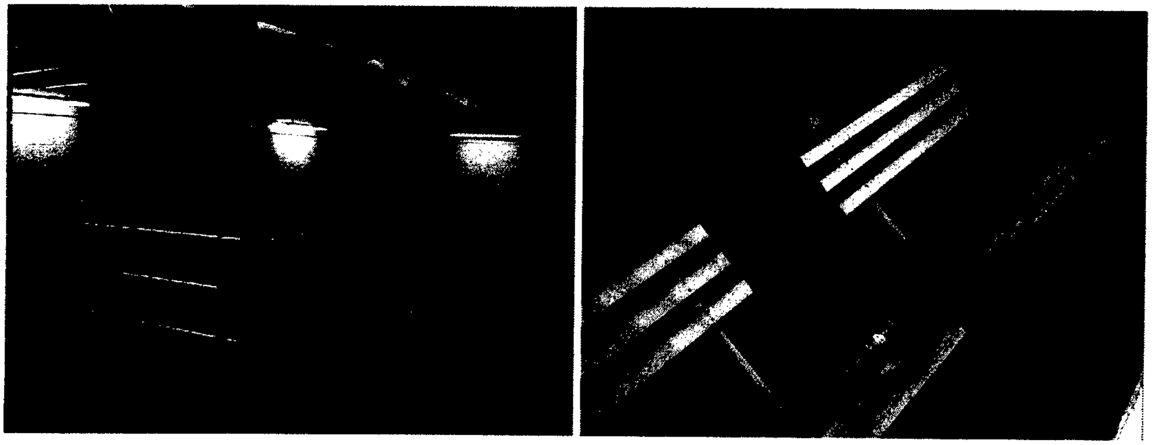

Figure 6 and 7. Flocculation basin and paddles.

The filter flow rate is evenly distributed to all on-line filters. The plant has up to 20 filters available; during the course of dual and PACL testing, 6 filters (filters 13-20) were in service and were rotated on- and off-line. During the course of the alum operations (which occurred after PACL and dual testing had completed), filters numbered 5 – 12 were placed in service to handle the additional summer flow. However, filters 9-12 differ from the other 16 filters in that they are tri-media and contain a high-density sand and gravel barrier layer. For this reason, the data obtained from these filters has been excluded from the results and discussion section. As a result of filters coming on-line and off-line, the total number of filter runs varied for each coagulant dosing operation. The number of filter runs available for comparison were 14, 15, and 18 (alum, PACL, dual, respectively). Figure 8 is the filter room depicting filters 12 through 20.

Figure 8. Filter room

Backwash operations were performed using finished water contained in two backwash tanks (40,000 gal and 80,000 gal each) at a flow rate of 17 gpm/ft^2 for approximately 20 min. The backwash included air scouring and rotary arm surface wash. A third tank (120,000 gal) is also usually available but was off-line during due to maintenance.

The WTP used alum and coagulant aid identical to that described in section 4.3.2. However, the WTP used Nalco 8233 (19% Al_2O_3, 76% basicity, no sulfate), a high molecular weight polymer similar to Summit 820B, when performing the dual and PACL alone operations. According to the plant supervisor, the two polymers provide nearly identical performance (Reed, 2003). Due to the nearly identical comparison between the two PACLs, the relationship between dual coagulation performance at the bench-scale and pilot-scale levels (which used Summit 820B) to the full-scale operations (which used Nalco 8233) should still hold true. Letterman and Sricharoenchaikit (1982) found that using three different cationic polymers in their preliminary studies produced similar residual turbidity and electrophoretic mobility values. The polymer feed locations (two of them) are located approximately 4 feet upstream of the alum feed/mechanical mixer as can be seen in Figure 4. Figure 5 shows coagulant feed lines upstream of the inline hydraulic jet mixer that were not in operation during the course of these experiments. Figure 9 presents the manual control panel and daily-use dual coagulant tanks located at the WTP.

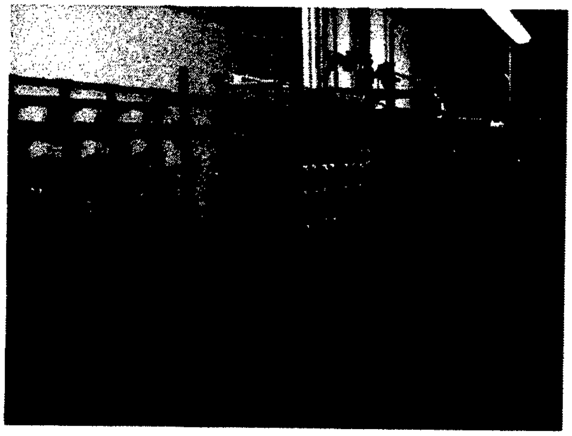

Figure 9. Daily dual coagulant feed tanks and control board.

Raw water flows, filter loss of head and filtered water turbidity were monitored on-line during each coagulant dosing operation. Raw water turbidity, raw water pH, raw water alkalinity, raw water temperature and settled water turbidity were collected and analyzed by WTP operators. Raw and finished water TOC samples were collected by plant operators and sent to the City of Fort Collins Water Quality Lab for analysis. Particle counts were unavailable due to upgrades being performed on the sampling board at the time of the coagulant dose operations.

4.4 Results and Discussion

4.4.1 Full-Scale Operations

The main purpose of these experiments served to determine if the conclusions reached by McCurdy (2003) for bench-scale and pilot-scale experiments dealing with low TOC water, proved indicative of full-scale performance. The load rate, head loss accumulation rate (HLAR) and the unit filter run volumes (UFRV) are presented in Table 2. Similar, but not exact, load rates were witnessed during each of the three coagulant treatments. The optimum dual dose as presented in the results section will be in terms of alum to PACL, unless stated otherwise. For example, the optimum dose listed for the dual treatment in Table 2 under the "Coagulant" heading is "3.9/8.1" which should be read as "3.9 mg/L alum to 8.1 mg/L PACL."

	Dose (mg/L)		Load rate	HLAR	UFRV
Treatment	Coagulant	Coagulant Aid	(gal/min/ft2)	(ft/hr)	(gal/ft2)
Alum	23	0.16	2.27	0.413	2040
PACL	8.4	0.14	2.64	0.149	6650
Dual	3.9/8.1	0.13	2.41	0.154	6800

Table 2. Average headloss and run length comparison for each full-scale treatment.

Full-scale dosing data presented in Table 2 were optimized doses determined by plant operators. The average doses administered by the WTP are nearly identical to those determined by McCurdy (2003) for bench-scale and pilot scale experiments and are presented in later in the dose optimization section (Table 6). The similar doses allow comparison between bench-scale and pilot-scale studies performed by McCurdy to the full-scale data obtained in this study.

Full-sale data show PACL and dual treatments had almost identical HLAR as one another. The run volumes for PACL and dual treatments were also similar. The most noticeable difference came in the HLAR and UFRV for the alum treatment versus PACL or dual. The runs treated with alum were only able to treat 30% of the water as either the PACL or dual before backwashing became a necessity. McCurdy (2003) found that for similar load rates, the dual coagulant was able to treat a higher UFRV (14713 gal/ft^2) than either PACL (11160 gal/ft^2) or alum (9144 gal/ft^2) treatments. The data in Table 2 indicate that bench-scale results obtained by McCurdy (2003) are indeed indicative of full-scale performance. Figure 10 dramatically illustrates the difference in run lengths.

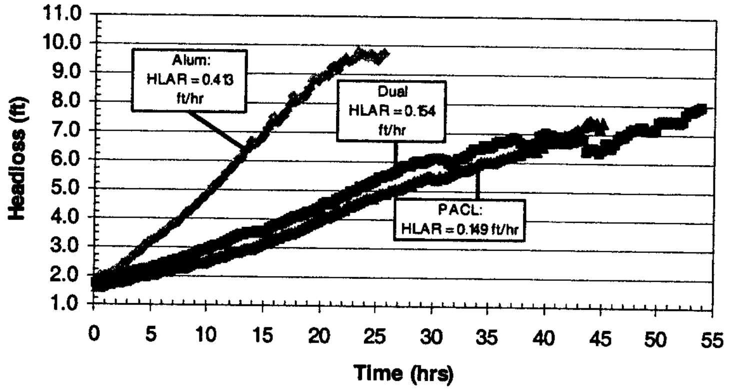

Figure 10. Full-scale average filter headloss plots for each treatment.

Figures 10 presents the average headloss plot for each treatment. Despite the slightly higher HLAR exhibited by the dual treatment the dual run length lasted almost 10 hours longer than the PACL and 25 hours longer than alum, on average. From Figures 10 and 11, the average alum run ended almost twice as early as the average dual run and never achieved approached the filtered turbidity values for either the dual or PACL treatments. Examining Figure 11, PACL achieved the lowest filtered turbidity values but ended approximately 8 hours earlier than the dual. The longer filter runs exhibited by the dual treatment may indicate that the ability of the floc to resist shearing, along with its ability to attach to media and itself within the filter, is greater than the ability of alum or PACL floc.

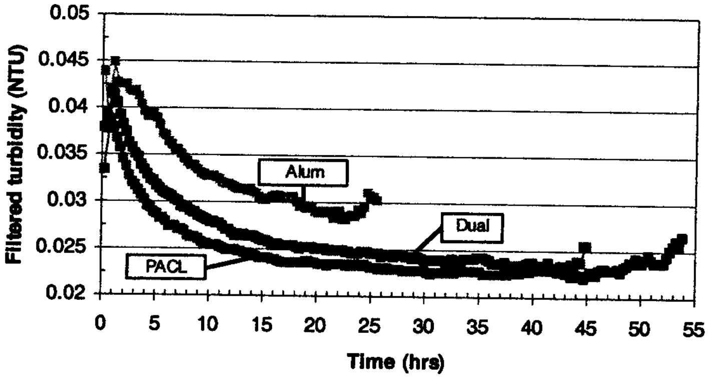

Figure 11. Full scale average filtered water turbidity for treatment.

As can been seen from the turbidity data presented in Table 3 the average settled water turbidity for each treatment at the full-scale plant were similar to one another (alum = 1.3 NTU, PACL = 1.1 NTU, and dual = 1.1 NTU). The dual treatment produced nearly identical filtered water quality as the PACL treatment, other than a slightly larger settled water turbidity removal. The alum produced slightly lower water quality than the other two treatments, however, the difference was minimal (0.04 versus 0.03, alum versus dual or PACL, respectively) and the water was not compromised. The filtered turbidity removals for the three treatments were 99.7%, 99.7% and 99.6% (dual, PACL and alum, respectively). Thus, no significant difference in the three treatments based on filtered water quality could be discerned.

Treatment	Raw Water Turbidity (NTU)	Settled Water		Filtered water	
		Turbidity (NTU)	Turbidity Removal	Turbidity (NTU)	Turbidity Removal
Alum	9	1.3	86.3%	0.04	99.6%
PACL	9	1.1	88.0%	0.03	99.7%
Dual	10	1.1	89.0%	0.03	99.7%

Table 3. Average turbidity removal for full-scale filter runs.

The data suggests that if there is a difference in settleable and non-setteable floc between the three treatments, filter performance with respect to turbidity removal is negligibly affected. The data in Table 3 also indicates that coagulant choice for full-scale operations treating low TOC water should be based on criteria other than turbidity removal. McCurdy (2003) found minimal difference in settled and filtered water turbidity for the three treatments at the pilot-scale level.

McCurdy (2003) also found minimal difference in TOC removal as presented in Table 4 in which the average removal centered at 55% for the filtered water.

Treatment	Raw TOC (mg/L	Settled Water		Filtered water	
		TOC (mg/L)	Removal (%)	TOC (mg/L)	Removal (%)
Alum	1.5	1.0	31%	0.63	58%
PACL	1.9	1.2	38%	0.80	57%
Dual	1.8	1.1	37%	0.84	53%

Table 4. Average TOC removal for pilot filter runs.

Table 5 contains the TOC data for each of the three treatments at the full-scale level. Alum is able to remove significantly more TOC at full-scale than either the PACL or dual treatments. However, alum is not able to lower the finished water TOC to a level that is significantly greater than either the dual or PACL. The TOC removals for the alum treatments between pilot and full-scale are comparable to one another. However, TOC removals for the PACL and dual are significantly less at full-scale than pilot-scale. Additional samples should be analyzed to determine the repeatability of the removals noted in Tables 4 and 5.

Treatment	Raw Water TOC (mg/L)	Finished Water TOC (mg/L)	% TOC removal (finished)
Alum	3.1	1.6	48%
PACL	2.7	1.9	31%
Dual	2.8	1.9	34%

Table 5. Average TOC removal for full-scale filter runs.

For low TOC water, bench-scale experiments using the PDA were indicative of full-scale performance. The full-scale data indicates that the dual treatment provides the longest filter run volumes. The turbidity removal for all three coagulants is similar and should not be the primary reason for coagulant choice. The TOC removal indicates that alum may be a more appropriate choice for utilities with DBP issues.

4.4.2 Dose Optimization

The optimum dose for each coagulant treatment was determined as the point of minimum settled water turbidity from the jar-test experiments and is presented in Table 6. In addition to containing the optimum doses for high TOC water, the results from low TOC optimization experiments performed by McCurdy (2003) are also included. McCurdy based the optimum coagulant dose on the point of minimum settled turbidity. Settled turbidity and TOC results will be presented later in this section. Appendix A contains additional information regarding the jar test experiments, including the individual water quality results for each dose administered for the high TOC water. The optimum dual dose as presented in the results section will be in terms of PACL to alum, unless stated otherwise. For example, the optimum dose listed for the dual treatment in Table 6 under the "mg/L" heading is "26/13" which should be read as "26 mg/L PACL to 13 mg/L alum." For high TOC water the average initial TOC = 8 mg/L and initial turbidity = 12.4 NTU. For the low TOC experiments the average initial TOC = 3.7 mg/L and turbidity = 2.2 NTU.

	Optimum dose - high TOC			Optimum dose - low TOC		
	mg/L	µl/L	mg/L as Al	mg/L	µl/L	mg/L as Al
alum	40	62	3.6	20	30	1.8
PACL	50	38	5.0	10	7.5	1.0
dual	26/13	20/20	2.6/1.2	8.0/4.0	6.0/6.1	0.8/0.4

Table 6. Optimum dose jar test results (low TOC from McCurdy, 2003).

As can be seen from Table 6, the optimum alum dose doubled from low to high TOC conditions, the optimum dual dose increased approximately 3 times and the optimum PACL dose increased 5 times. The high NOM water placed additional coagulant demand on PACL treated water, while alum was the least effected.

Examining the doses based on volume gives the reader a practical quantitative dose comparison. For the low TOC water, dual coagulant required 1.6 times the volume of coagulant as PACL. For high TOC water, dual coagulant required the same volume of coagulant as the PACL treatment. For low TOC water, alum required 4 times the volume of PACL and 2.5 times the volume of dual coagulant. For the high TOC water, alum required only 1.5 times the volume of coagulant as when PACL or dual were used. Basically, the presence of NOM eroded the volume-based advantages of PACL and dual versus alum. Volume relates directly to cost since the coagulants are sold per volume. PACL is more expensive than alum and having to purchase additional quantities to treat high NOM water may not be cost effective.

Table 7 was created from research presented by McCurdy (2003) and presents the settled turbidity and TOC values based on the respective optimum dose listed in Table 6. From these results the reader can conclude that the dual treatment produced the lowest settled turbidity and TOC results for bench-scale experiments. Differences in the settled water results are insignificant indicating that additional parameters outside turbidity and TOC would decided coagulant choice.

	Initial		Settled	
	Turbidity (NTU)	TOC (mg/L)	Turbidity (NTU)	TOC (mg/L)
alum	2	3.7	0.5	1.8
PACL	2	3.7	0.7	1.6
dual	2	3.7	0.4	1.6

Table 7. Jar test turbidity and TOC results for low TOC water (McCurdy, 2003).

The percent removal data presented in Figure 12 sheds additional light on the coagulants' performance. The dual produced the largest percent removals for both turbidity and TOC. The advantage of the dual treatment over PACL is clear with respect to turbidity but the TOC removal was only negligibly better. McCurdy concluded that for low TOC water, coagulant choice would not depend on TOC removal because of the similar removals.

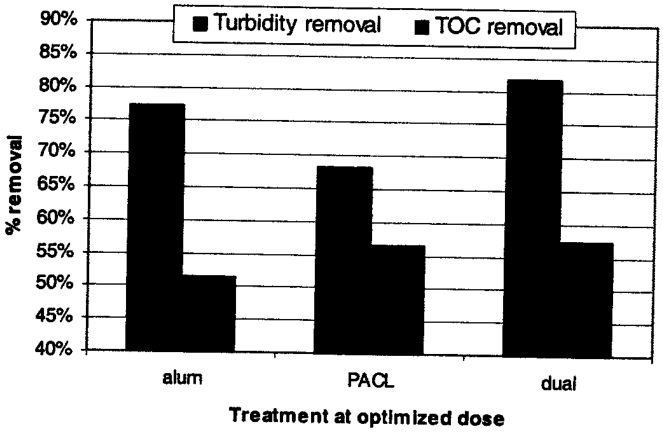

Figure 12. Coagulant performance for turbidity and TOC (low TOC water, created from McCurdy, 2003).

Jar tests for the high TOC water indicate alum produced the lowest settled turbidity while PACL produced the lowest settled TOC, as seen in Table 8. The differences in settled water results are minimal. Surprisingly, the dual treatment performed marginally during the jar test experiments for high TOC water. Obviously, the additional NOM in the high TOC jar tests placed an additional demand on the dual treatment.

	Initial		Settled	
	Turbidity (NTU)	TOC (mg/L)	Turbidity (NTU)	TOC (mg/L)
alum	12	7.8	3.2	4.3
PACL	12	7.8	3.4	4.1
dual	12	7.8	3.9	4.3

Table 8. Jar test turbidity and TOC results for high TOC water.

The removal efficiency of each treatment is presented in Figure 13 for both turbidity and TOC removal. Alum removes the largest percentage of turbidity while PACL removes the largest percent of TOC. Dual coagulant provides the least amount of turbidity removal of the three treatments and the same amount of TOC removal as alum. On a normalized Al basis, the PACL has the largest concentration of Al monomers and polymers that may contribute to the increase TOC removal.

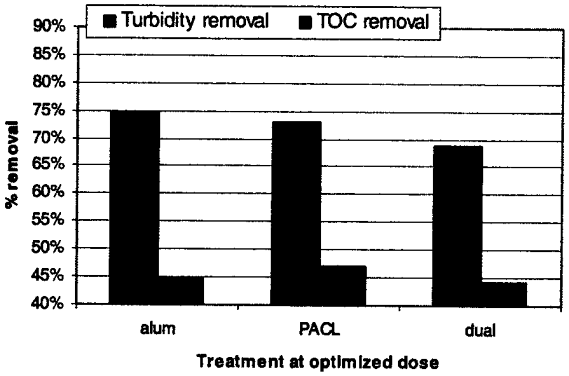

Figure 13. Coagulant performance for turbidity and TOC (high TOC water).

The jar tests served as a tool for determining appropriate doses to use in the PDA experiments. Jar test data indicates similar performance for all three coagulants, with a slight advantage toward alum for turbidity and PACL for TOC. However, one must be careful when examining jar test data, as the conclusions can be misleading. Jar test data indicates that in the presence of high TOC, factors outside water quality (i.e. cost, chemical availability, etc.) will play a larger role in determining the choice of coagulant dose.

4.4.3 Floc Shearing

the floc aggregation kinetics for each treatment under low energy mixing conditions (i.e. no shear) for high TOC water are presented in Figure 14. Figure 14 serves two purposes: first, the figure allows comparison of each treatment with one another for high TOC water; second, the figure can be compared with a similar one developed by McCurdy (2003) for low TOC water.

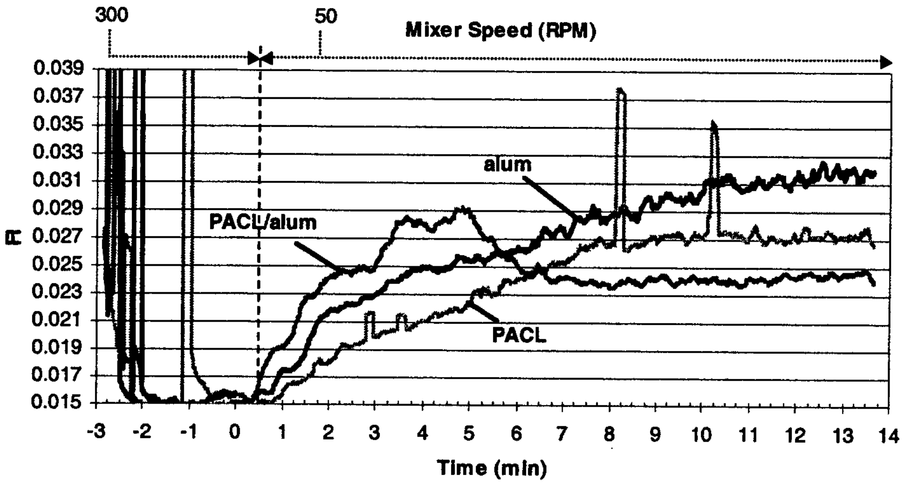

Figure 14. Average floc aggregation monitored by PDA (no induced shear, high TOC water).

The zero on the time scale is the point at which coagulant was added for alum and PACL experiment. For the dual treatment, -0.25 minute is when PACL was added, followed by alum at 0 minute. For all three treatments, coagulant aid was added just prior to the hatched line (0.25 minutes), which indicates the decrease in mixing energy from rapid mix to slow mix. The large, sharp spikes that occur most noticeably before zero and occasionally during the PACL treatments are due to air bubbles that passed through the PDA causing interference.

The most notable trend from Figure 14 is the sharp decline in the dual treatment after approximately 5 min. The dual treatment reaches a maximum particle size just prior to the decline and then the size of the dual particles decreases distinctly and plateaus. The decrease is most likely due to the particles settling out at a rate much greater than the aggregation rate, as documented by Kan et al (2002), Ammary (1995) and Li and Gregory (1991). The plateau witnessed with the dual treatment could be indicative of a lack of continued particle growth or could indicate that particles have started to settle at a rate proportional to particle growth.

For high TOC water, the PDA indicates that the aggregation rate for alum is slightly steeper than for PACL. At approximately 8 minutes the PACL plateaus while the alum continues to grow. The plateau recorded for the PACL treatment is most likely due to the same relationship of particle growth to settling rate that occurs with the dual treatment. Alum continues to grow at a rate faster than its associated particle settling rate. In other words, alum requires more time to form particles that have achieved enough density to settle.

Applying Gregory and Carlson (2003) theory regarding optimum dose as "the lowest dose beyond which FI does not increase more rapidly," one could conclude the dual is the optimum coagulant since all the treatments represented in Figure 14 are at their respective optimum doses and the dual has the largest initial FI slope.

The FI response for low TOC water is quite opposite from high TOC water in that the aggregation kinetics for the three coagulants were similar to one another, as can be seen in Figure 15 from McCurdy (2003). For the low TOC water, alum is the coagulant that first results in the settling of particles. Alum reaches a distinct plateau after 13 minutes during the low TOC experiments, similar to PACL during the high TOC no shear experiment.

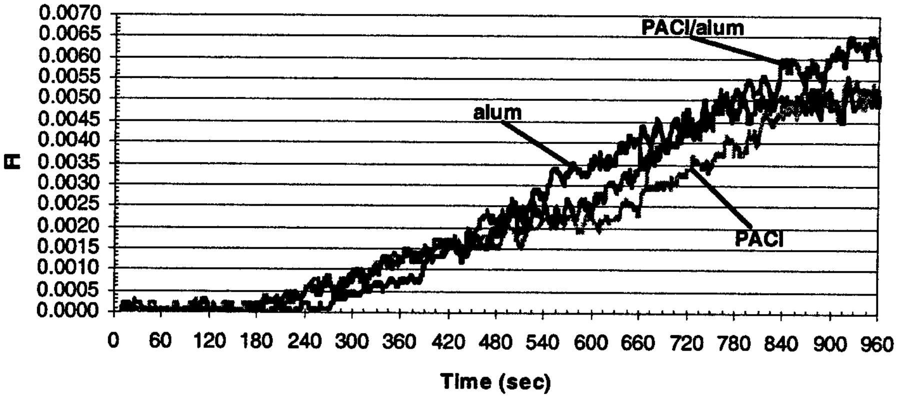

Figure 15. Average floc aggregation monitored by PDA (no induced shear, low TOC, from McCurdy, 2003).

The differences between floc aggregation kinetics for the three treatments from low TOC water to high TOC water (Figure 15 versus Figure 14, respectively) indicate that NOM places additional constraints on floc growth. Of the three treatments, the dual coagulant's flocculation kinetics are the most obviously effected by the increase in NOM. The dual reaches a size that is conducive to settling under high TOC conditions relatively quickly, this could be due to the PACL causing effective charge neutralization that aids the alum in "sweeping" the NOM from the suspension.

Particle settling for any PDA experiment is not necessarily desirable. When large particles settle, they are no longer able to aggregate with other smaller particles. Adjusting the PDA experiments (increasing mixer speed during flocculation) would allow the larger particles to remain suspended. Increasing the mixer speed too much would cause pre-mature shear, which is also not desirable.

In Figure 16 the vertical hatched lines represent the change in mixing speed. The mixing speeds are labeled at the top of the plot. The coagulants were dosed at the same times as explained earlier for Figure 14.

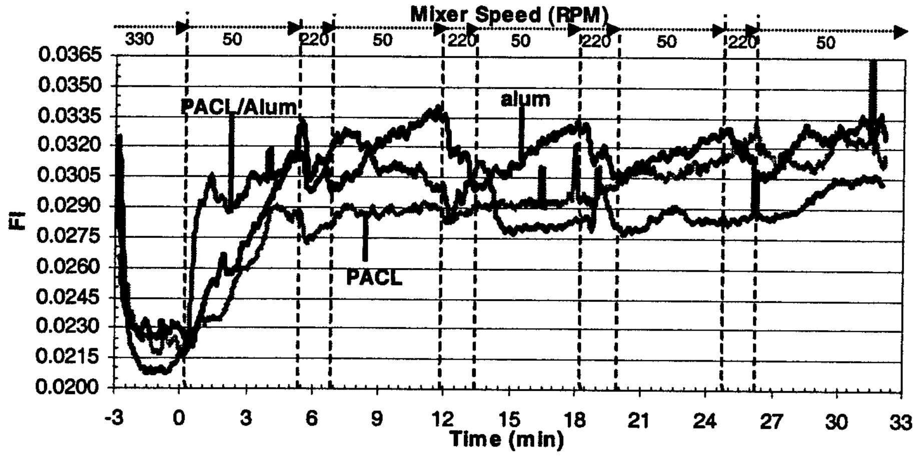

Figure 16. Average floc aggregation response to shear cycling (high TOC water).

As can be seen in Figure 16, the dual treatment exhibits the most perplexing behavior of the three treatments. After initially increasing in FI at a rate significantly larger than either the alum or PACL treatments, the aggregation kinetics slow down to a rate that allows alum to reach equivalent size by the start of the first shear event. During the first recovery period, the dual treatment decreases in FI, presumably due to particle settling. During the second recovery period the dual treatment plateaus and no significant change in FI occurs until the fourth recovery period, at which time the FI plateaus at a slightly higher level than the second and third recovery period. The final increase in FI is most likely due to the decrease in volume that effectively changes the mixing energy of the PDA jar, re-suspending previously settled aggregates and changing the ratio of the PDA output.

The PACL treatment for the high TOC water maintains the FI achieved under the initial aggregation during the first two shear events. However, the FI increases during the third shear event and behaves erratically during the fourth recovery period. This is most likely due to particles that had settled in the first two recovery periods being re-suspended in large enough numbers that the collision efficiency increases and the particle size increases. Because this re-suspension occurs for the PACL before it occurs for the dual treatment, one could conclude that the particles formed by the dual treatment are more dense than those formed by the PACL treatment.

The alum treatment does not plateau or decrease in any recovery period. The ability of the alum to re-aggregate after experiencing shear gradually declines with each event. The last recovery period shows a slight increase in recovery, however, this can be accounted for due to the change in mixing energy as explained previously for PACL and dual treatments. The fact that particles do not settle under the alum treatment but do settle to varying degrees for PACL and dual treatments, lends credence to the theory proposed by McCurdy (2003) that alum, PACL and dual treatments form fundamentally different aggregates. In fact, the data indicates that PACL and dual coagulant form denser aggregates under these mixing conditions.

McCurdy (2003) studied the floc morphology for the three treatments and concluded the size of the coagulated floc was similar for the treatments, however, the non-settleable floc formed during PACL and dual treatments are distinctly different than the floc formed for the alum treatment. He noticed a shift in charge distribution that indicated the previous statement was highly probable. This author finds the difference in shear behavior between the three treatments for high TOC water and the settling of dense floc for the PACL and dual experiments are also indicative of a fundamental difference in floc formation. Performing additional experiments at higher mixing energy to ensure shear is induced in the dual treatment is the next step in understanding shear effects on high TOC water.

Upon close examination, the dual coagulant actually experiences an increase in FI to some extent within the first two shear events. During the first two shear events, the dual FI decreases with the onset of the shear as expected and then actually increases in FI within the shear event. This increase in FI could be explained by the re-suspension of settled particles in large enough numbers that the ratio output is affected. Or the increase could be due to more ideal mixing conditions experienced under the high mix shear that actually allows for particle growth through increased particle collision and aggregate re-arrangement.

An additional insight into coagulant behavior with respect to induced shear is the relative floc strength witnessed in Figure 16. PACL and dual do not shear under the mixing conditions tested in these experiments for high TOC water. From this observation, one could conclude that the PACL and dual coagulants form stronger bonds than alum, presumably due to their charge neutralization characteristics.

Unlike McCurdy's (2003) low TOC experiments in which all three coagulants experienced gradually decreasing recovery slopes after undergoing shear (presented in Figure 17), the behavior for the three coagulants used for the high TOC water is more complicated as explained previously.

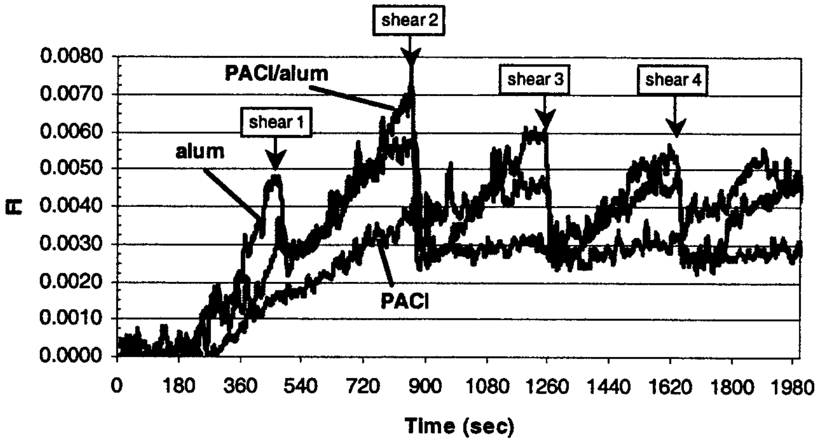

Figure 17. Average FI response to cyclic shearing for HT water (low TOC water, from McCurdy, 2003).

McCurdy (2003) theorized that under low TOC conditions, the dual treatment was more effective due to PACL initially charge neutralizing the particles prior to enmeshment by alum during sweep coagulation. When the particles experienced shear, the aggregates were broken into smaller floc with newly exposed surfaces that were still near charge neutral, leading to better recovery. When water treated with alum alone experienced shear, the newly exposed particles were not near charge neutral and re-stabilized. For high TOC water the alum treatment exhibits the same gradual decreasing shear recovery response as witnessed for the low TOC water. However, during the high TOC experiments, the alum treatments were less effected by shear than during low TOC, perhaps due to a larger volume fraction of solids (i.e. increased alum dose) that allowed for continued sweep coagulation.

McCurdy also theorized for low TOC water that dual aggregates have a greater potential to recover from breakup due to the higher degree of destabilization during floc development. Research with high TOC water indicates that alum has the greater potential to recover from break-up. The dual did not exhibit the ability to recover from shear under high TOC conditions as it did with low TOC conditions. A possible explanation is that for high TOC water, the dual treatment will effectively form dense aggregates that will not shear at the same energy that causes shear in low TOC water treated with dual coagulant. The stronger bonds could stem from the combined charge neutralization and sweep enmeshment mechanisms exerting a greater effect under the higher doses associated with high TOC water.

4.5 Application to Utilities

Most utilities operate with the goal of producing water that meets or exceeds federal, state and local regulations while minimizing their production cost. Performing a cost-benefit analysis is a common tool used by utilities in determining operations and management decisions. Excluding regulatory compliance and public health issues, a utility should not implement a treatment process when the benefits are out-weighed by the cost. However, the importance assigned to a benefit may differ from one utility to the next. In general, most plant supervisors would agree that adding chemicals at their respective optimum doses outweighs the costs of under- or over-dosing chemicals. A utility that under-doses chemicals during its coagulation process risks pathogens being allowed to enter the drinking water supply, while overdosing could place additional strain on downstream unit processes (i.e. filters) and lead to increased operation costs.

Relevant yearly operation costs faced by utilities fall into one of three categories: chemical costs, sludge disposal costs and power costs. Chemical cost obviously includes the cost associated with purchasing and delivery of each coagulant. Additional expense could be incurred depending on the coagulant choice, as is the case with alum. It is generally accepted that alum performs better at lower pH than the pH of typical raw water. In order to drop the pH to optimum coagulation conditions acid is sometimes added and a base (e.g. lime) is added to raise the pH before the water is released to the system. The necessity of these pH-adjusting chemicals increases the chemical cost associated with alum. Alum is by far the most commonly used coagulant in the drinking water industry, due to its ease of use, low toxicity, low cost and ability to treat water to acceptable levels. However, the overall yearly operating cost for treating water with PACL could be less than the yearly operating cost of alum. PACL offers the same benefits as alum but is not as widely used because the cost of PACL is 4 to 8 times the cost of alum. PACL is able to operate in a broader pH range and does not require pH adjustment, thus the cost difference for the two coagulants decreases. Full-scale data from this study show that PACL requires half the volume as alum to treat water to the same acceptable water quality. Not only does this decrease the coagulant cost by 50%, the PACL would require less storage space and half the deliveries as required for alum.

Regardless of the coagulant type, utilities must dispose of the sludge produced in the settling process. The disposal options include sending the sludge to a landfill, discharging the sludge to the sewer system for a wastewater plant to treat, and land application of sludge. The first two options require paying another party to handle the sludge while the third option requires an adequate amount of land for the sludge to dry. Alum takes longer to dewater than PACL and for small utilities this cost of land application can be prohibitively expensive with alum but acceptable for PACL. The WTP that participated in this study land applies the sludge and sees a cost benefit from the decreased drying time associated with PACL (Reed, 2003).

Full-scale data from this study indicate that the alum filter runs required backwashing 3 times as frequently as PACL or dual coagulant. Since finished water is used to clean filters, a small percentage of the finished water must be diverted to the backwashing operation. Over the course of their associated filter runs, alum required 4.0% of the finished water be diverted, dual and PACL required 2.6%. The costs associated with backwashing include finished water cost and energy costs from operating pumps that deliver the water to the backwash tank. Backwash water that has been used to clean the filter is usually recycled back through the treatment process (i.e. it is blended with raw water and treated to drinking water standards again).

This study showed an increased UFRV for the dual and PACL treatments versus alum. UFRV is a means of normalizing one filter run with another with respect to their HLAR. In this study, dual and PACL treatments resulted in larger UFRV than alum. A plant that has a larger

UFRV with one coagulant dose versus another dose with the same coagulant could conclude that the larger UFRV is indicative of an optimized treatment process. A utility could also conclude that a larger UFRV associated with one treatment versus another would be indicative of the optimum coagulant choice. When comparing different treatments, the treatment with the largest UFRV and lowest yearly operating cost would be the logical choice of coagulant.

If a plant is unable to meet the demands of its customers, increasing the plant capacity could be achieved by building additional filters or adding storage tanks, both of which would increase the plant's footprint. The plant may not have the space available to expand or capital available to finance such a project. With dual coagulation, a plant could add an additional coagulant addition point (if it did not already have multiple points) so that both alum and PACL could be delivered. With the ability to treat water with dual coagulants, a plant would increase capacity from having fewer filters off-line due to backwashing and would have a smaller percentage of its finished water being used for backwashing.

To fully understand the benefits of dual coagulation for a particular plant, a detailed cost analysis based on the concepts discussed above would need to be completed. The potential cost savings should be compared with the costs of retrofitting the plant and a decision on using the process could be made. In this study, a slight improvement in filtered turbidity was observed. Particle counting would be needed to determine if there is a significant difference between the treatment processes. This could be done with full-scale tests since there is no risk to the public with this sort of testing.

4.6 Conclusions

Full-scale data proved the hypothesis that bench-scale and pilot-scale analysis data for low NOM water is predictive of full-scale performance. Full-scale data indicated dual coagulation provided similar turbidity removal and longer run volumes than either alum or PACL alone. The combined charge neutralization and sweep coagulation ability of the dual coagulant is the most likely mechanism for the observed improvements. Longer run volumes are indicative of increase productivity and can be used to compare one treatment with another. Additional benefits from using dual coagulation would come from the cost benefit of using less polymer and increased TOC removal than when PACL alone is used, and lower sludge generation than when alum alone is used.

Bench-scale data does not prove the hypothesis that water with high levels of NOM would negatively alter the flocculation kinetics for water treated with dual coagulant. Bench-scale data indicates that NOM laden waters require larger coagulant doses that may negatively impact the benefits of dual coagulation to treat drinking water at the full-scale level. Floc formed during dual and PACL coagulation in high TOC water was denser and stronger than floc formed for the same treatments for low TOC water, as evidenced by the increased settling rate. Additionally, dual and PACL aggregates did not experience shear under that same mixing conditions that induced shear for low TOC water. This phenomenon may be due to the increased coagulant doses associated with treating high TOC water that allowed for more effective charge neutralization.

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PREFACE TO THE APPENDICES

The appendices section provides additional detail of procedures and results that are meant to supplement the main paper that will be submitted for journal publication. Some of this material covers additional experiments that are not irrelevant to the previous discussion, but are added as an appendix due to space restrictions and to keep the journal paper concise and focused on the main findings of this research.

APPENDIX A:

DUAL COAGULATION SUPPLEMENTAL INFORMATION

A-1 Additional detail on dose optimization experiments

Source water

McCurdy (2003) used the City of Longmont Water Treatment Plant's pilot plant located on the St. Vrain River. The river water is part of the Colorado-Big Thompson (CBT) system that collects mountain run-off and distributes the water throughout the Front Range. Horsetooth Reservoir (HT) water is also part of the CBT project. McCurdy (2003) performed bench-scale with CBT (St. Vrain) and with HT water. All the data and graphs presented with respect to bench-scale experiments in this research were developed using HT water. The pilot scale data taken from McCurdy used CBT water, which is share many similar water quality parameters as HT and is presented in Table A.1.

	pH	Alkalinity (mg/L as CaCO3)	Raw HT TOC (mg/L)	Turbidity (NTU)
CBT	7.4	22	3.7	2.2
HT[1]	7.6	26	2.1	2.7
HT[2]	7.4	25	2.5	12

[1] as measured by McCurdy (2003)

[2] as measured by Haines (2003)

Table A.1. Initial water quality for bench and pilot scale testing

The turbidity for difference between HT samples could be due to seasonal variations, insufficient flushing of the sample line prior to collection and/or equipment measurement differences. Regardless of the exact reason for the differences, comparing the experimental results to one another is acceptable since variations in water quality when dealing with natural water will occur.

Creating high NOM water

An example of the spreadsheet created by the author to determine the amount of NOM to add to any given amount of water is presented in Table A.2. The spreadsheet requires that the user know the raw TOC and have an estimate of the percent carbon (C). Of course these numbers can be manipulated to determine what the actual percentage of C was for the NOM supplied by IHSS. For the spreadsheet in Table A.2, the percentage C was assumed to be 45%.

Raw HT TOC =	3.5	mg/L
Syn HT TOC =	10	mg/L
Need to add	6.5	mg/L C

Volume H2O =	1	L needs	6.5	mg C =	14	mg NOM	=	0.0144	g NOM
Volume H2O =	2	L needs	13	mg C =	29	mg NOM	=	0.0289	g NOM
Volume H2O =	10	L needs	65	mg C =	144	mg NOM	=	0.1444	g NOM
Volume H2O =	20	L needs	130	mg C =	289	mg NOM	=	0.2889	g NOM
Volume H2O =	21	L needs	137	mg C =	303	mg NOM	=	0.3033	g NOM
Volume H2O =	22	L needs	143	mg C =	318	mg NOM	=	0.3178	g NOM
Volume H2O =	24	L needs	156	mg C =	347	mg NOM	=	0.3467	g NOM

Table A.2. Spreadsheet for determining NOM addition

In reality the C concentration was equal to 39%, because adding the equivalent amount of NOM listed in Table A.2 did not increase the TOC to 10 mg/L. Instead the final TOC equaled approximately 8 mg/L. The decision was made that 8 mg/L is reflective of high NOM conditions and the experiments were allowed to continue.

Coagulant dosing

A copy of the spreadsheet used to determine alum and coagulant aid doses and their corresponding settled water quality parameters are contained in Table A.3 below.

Sample ID	Chemical Dose Information					Setteled Water	
	Alum			Coag Aid		Turbidity (NTU)	pH
	mg/L	uL	mg/L as Al	mg/L	uL		
A-Raw	0	0	0	0	0	12.3	7.15
A-1	50	154	4.55	0.05	57	5.9	5.83
A-2	55	170	5.00	0.05	57	7.54	5.67
A-3	60	185	5.45	0.05	57	7.04	5.45
A-4	65	201	5.91	0.05	57	6.69	5.23
A-5	70	216	6.36	0.05	57	6.89	5.04
A-6	30	93	2.73	0.05	57	8.29	6.44
A-7	40	123	3.64	0.05	57	4.73	6.35
A-8	45	139	4.09	0.05	57	4.75	6.19

Table A.3. Spreadsheet of alum dose determinations and results.

The first 5 jars were based on an overestimate of the amount of alum that would be necessary to produce the minimum settled turbidity. Samples A-6 through A-8 were performed to expand the sample range.

The settled water turbidity results for alum are plotted in Figure A.1 below. The plot provided a visual representation of the turbidity response to the coagulant dose and clearly showed an alum dose of 3.6 – 4.1 mg/L as Al produced the lowest turbidities.

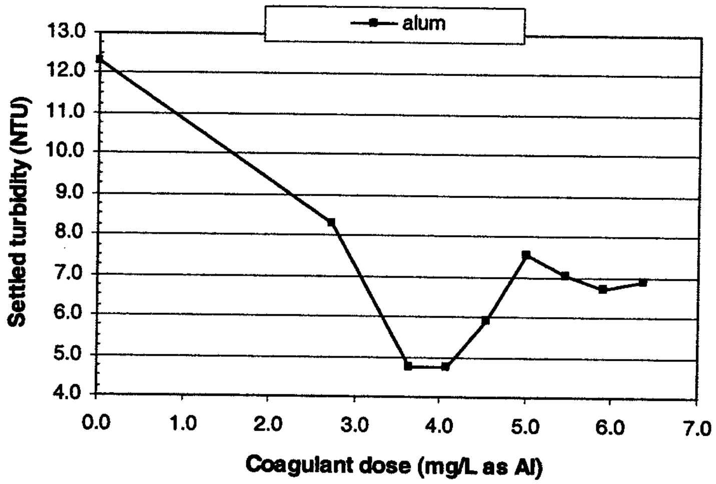

Figure A.1. Settled turbidity plot for alum jar test.

A copy of the spreadsheet used to determine PACL and coagulant aid doses and their corresponding settled water quality parameters are contained in Table A-4 below.

Sample ID	Chemical Dose Information					Settled Water		
	PACL			Coag Aid		Turbidity (NTU)	pH	TOC (mg/L)
	mg/L	uL	mg/L as Al	mg/L	uL			
P-Raw1	0	0	0	0	0	12.3	7.15	7.91
P-1	15	23	1.50	0.05	57	13.2	7.25	7.12
P-2	20	30	2.00	0.05	57	8.85	7.20	4.48
P-3	22.5	34	2.25	0.05	57	8.64	7.12	4.10
P-4	25	38	2.50	0.05	57	9.01	7.14	3.85
P-Raw2	0	0	0	0	0	12.7	7.13	8.53
P-5	20	30	2.00	0.05	57	14.4	7.10	7.74
P-6	25	38	2.50	0.05	57	7.85	6.99	5.45
P-7	30	45	3.00	0.05	57	8.68	7.00	5.46
P-8	35	53	3.50	0.05	57	7.79	6.89	5.59
P-9	40	60	4.00	0.05	57	7.66	6.97	5.66
P-Raw3	0	0	0	0	0	13.3	7.53	8.23
P-10	20	30	2.00	0.05	57	10.9	7.18	6.92
P-11	30	45	3.00	0.05	57	11.1	7.07	6.35
P-12	40	60	4.00	0.05	57	10.4	7.03	5.54
P-13	50	75	5.00	0.05	57	3.37	6.94	4.01
P-14	80	120	8.00	0.05	57	18.3	6.94	9.84

Table A.4. Spreadsheet of PACL dose determinations and results.

Samples P-1 through P-4 indicated the optimum alum dose occurred at approximately 2.1 mg/L as Al based on the slight upward response of the curve at the higher doses. The settled water turbidity and TOC results for PACL samples P-1 through P-4 are plotted in Figure A.2 below.

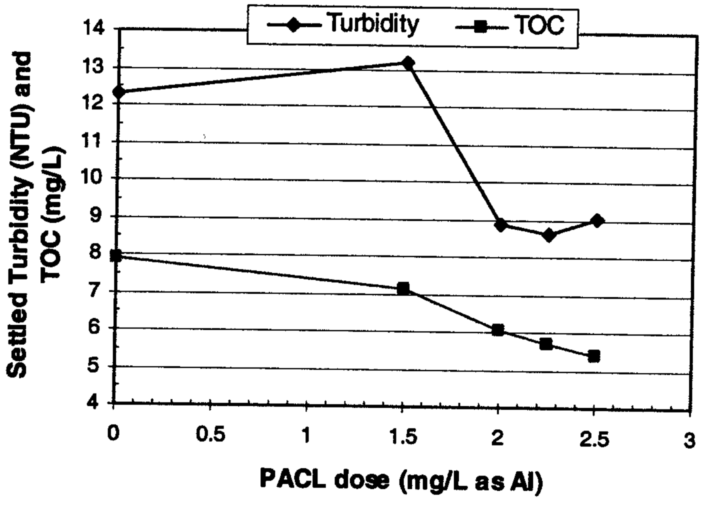

Figure A.2. Settled turbidity and TOC plot for PACL jar test (P1- P4).

The optimum dose of 2.1 mg/L as Al (which is approximately 50% of the optimum alum dose) corresponded with McCurdy (2003) optimum dose determinations for alum and PACL that indicated the optimum PACL dose occurred at approximately 50% of the alum dose. Additional jar tests (P-5 through P-14) were performed to expand the dose range to verify that 21 mg/L was indeed the optimum dose. The settled water turbidity and TOC results from these 14 jars were averaged and are presented in Figure A.3.

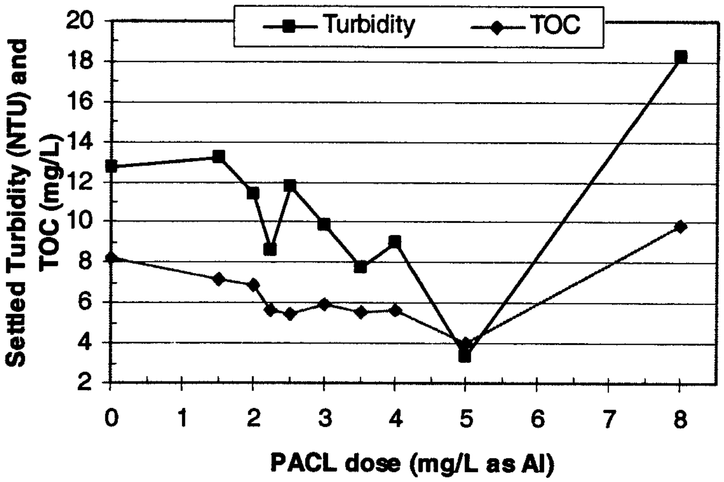

Figure A.3. Settled turbidity and TOC plot for PACL jar test (average P1- P14).

The plot from Figure A.3 indicates the optimum PACL dose for the high TOC water actually occurs at 5 mg/Las Al, 30% more than what the high TOC water requires when treated with alum. McCurdy (2003) also noted that the point of minimum settled TOC did not occur at the point of minimum settled turbidity but that increased coagulant doses would eventually bring about the decreased performance of the coagulation, sedimentation and filtration process. As can be seen from Figure A.3, that negative performance is evident at the highest administered coagulant dose.

A copy of the spreadsheet used to determine dual and coagulant aid doses and their corresponding settled water quality parameters are contained in Table A.5 below.

Sample ID	Chemical Dose Information								Settled Water		
	PACL			Alum			Coag Aid		Turbidity (NTU)	pH	TOC (mg/L)
	mg/L	uL	mg/L as Al	mg/L	uL	mg/L as Al	mg/L	uL			
D-Raw1	0	0	0	0	0	0	0.00	0	12.3	7.15	7.91
D-1	15	23	1.50	7.5	23	0.68	0.05	57	15.0	7.10	7.12
D-2	20	30	2.00	10	31	0.91	0.05	57	5.65	7.00	4.48
D-3	22.5	34	2.25	11.25	35	1.02	0.05	57	4.56	6.98	4.10
D-4	26	39	2.60	13	40	1.18	0.05	57	3.19	6.85	3.85
D-Raw2	0	0	0	0	0	0	0.00	0	10.0	6.95	7.72
D-5	20	30	2.00	10	31	0.91	0.05	57	6.30	6.82	5.64
D-6	26	39	2.60	13	40	1.18	0.05	57	4.56	6.79	4.81
D-7	32	48	3.20	16	49	1.45	0.05	57	5.01	6.77	4.56

Table A.5. Spreadsheet of dual dose determinations and results.

Jars D-1 through D-4 were performed initially based on the optimum PACL dose and D-5 through D-7 were performed to expand the range to ensure the point of minimum settled turbidity and TOC were recorded. The settled water turbidity and TOC results from these experiments were averaged and are presented in Figure A.4.

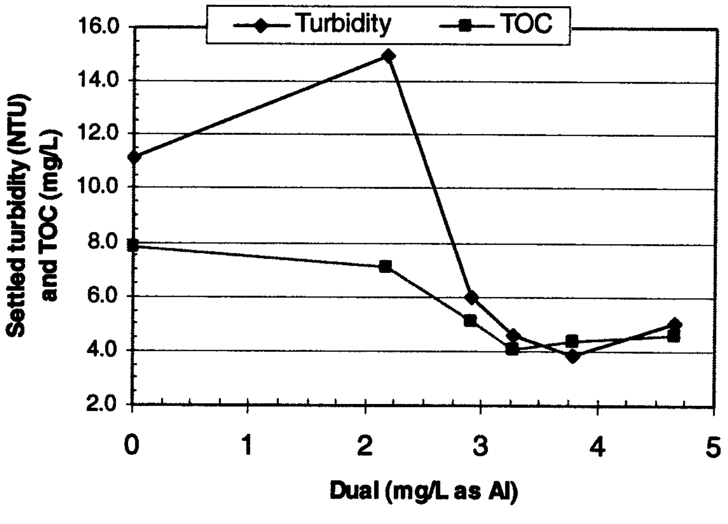

Figure A.4. Settled turbidity and TOC plot for dual jar test.

As can be seen from Figure A.4. the point for minimum settled turbidity occurs at slightly less than 4 mg/L as Al (combined Al from PACL and alum)or 26.0 mg/L PACL to 13.0 mg/L alum. The point of minimum settled TOC actually occurs at approximately 3.25 mg/L as Al. Seemingly implying that the dual treatment causes the points of minimum settled turbidity and minimum settled TOC to occur at the same dose for high TOC. Meaning that TOC, not turbidity, places a larger demand on the coagulant under high TOC conditions.

TOC analyzer

TOC samples were collected 15 minutes after the jar test had completed the third flocculation stage. The first draw (approximately 10 ml) was discarded from each sample to prevent non-characteristic water that had collected in the sample tube. Samples when then analyzed for turbidity, pH and TOC. Figure A.5.a-b contains pictures of the TOC analyzer. The Toc analyzer is located in the same laboratory as the jar test and other water quality meters. This set-up allowed for immediate analysis by the author. The time to take to run one TOC sample took approximately 15 minutes. The TOC analyzer needs an additional 15 minutes (approximately) between consecutive samples to purge the line. In this manner, two samples could be analyzed in one hour. For jar test experiments this could mean a lag time of approximately 2.5 hours between sample collection to the last TOC analysis. Samples were stored with their lids on and in the refrigerator until ready for TOC analysis. The two plastic containers as circled in Figure A.5.a are typical of the containers used to store the samples. The jar on the right (with tubing extending into it) is the sample, the jar on the left was used hold rinse water from cleaning the probe.

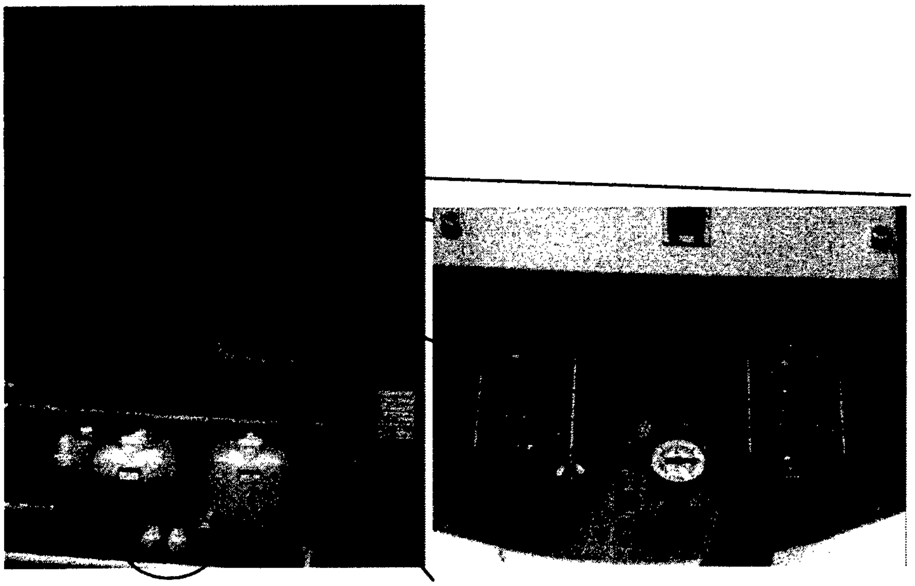

Figure A.5 (a – b). Hach astroTOC UV analzer.

The individual coagulant PDA data gathered to develop Figure 13 in the results and discussion section are presented in Figure A.6 through A.8. PDA experiments were performed for the purpose of FI and particle correlation for each coagulant. The FI plots used are shown in Figure A-4. The plot line for each graph is actually the trendline (moving average = 10) calculated for each data set to minimize interference in the measurements. The hashed vertical lines are representative of the change in mixer speed but are not exact due to scaling errors within Excel.

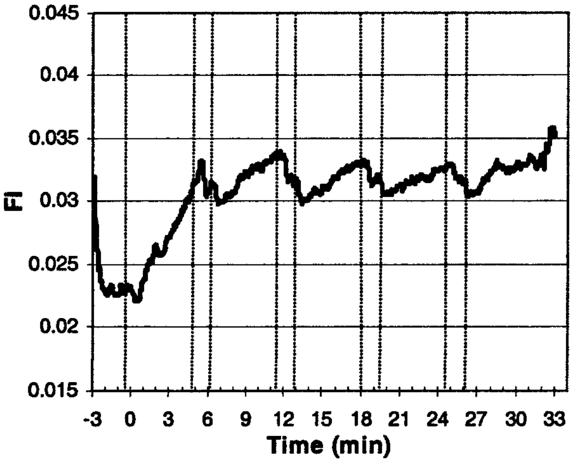

Figure A.6. Alum FI response data.

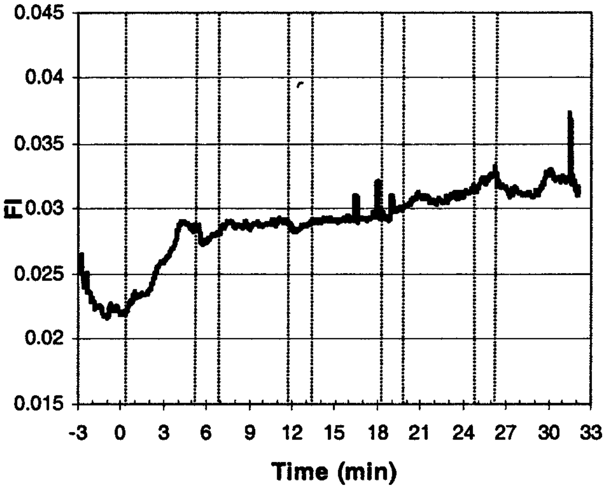

Figure A.7. PACL FI response data.

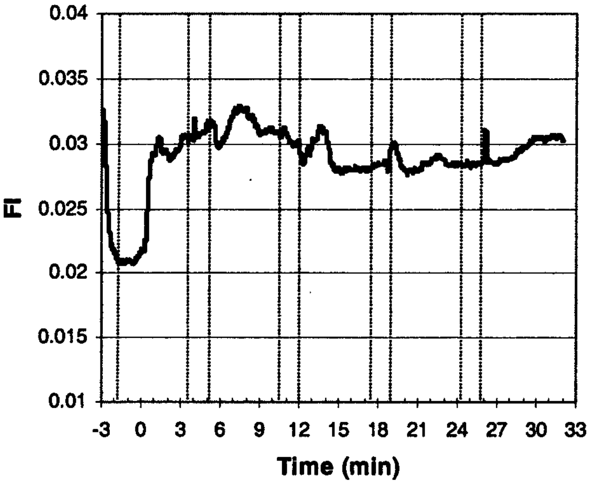

Figure A.8. Dual FI response data.

The procedure for calculating the slope recovery used the FI values at the start and end of each shear cycle. The elapsed time in minutes between shear events was used to determine the slope as rate of change in FI per unit time. The FI data used for these calculations is shown below in Table A-5.

Time (min)	Alum (FI)	Slope (FI/min * 10^2)	PACL (FI)	Slope (FI/min * 10^2)	Dual (FI)	Slope (FI/min * 10^2)
0.25	0.230		0.225		0.215	
5.25	0.315	1.7	0.285	1.2	0.310	1.9
6.75	0.310		0.280		0.305	
11.75	0.335	0.5	0.290	0.2	0.300	-0.1
13.25	0.315		0.285		0.300	
18.25	0.330	0.3	0.295	0.2	0.285	-0.3
19.75	0.305		0.300		0.285	
24.75	0.325	0.4	0.315	0.3	0.285	0
26.25	0.310		0.325		0.290	
31.25	0.330	0.4	0.315	-0.2	0.305	0.3

Table A.6. Shear cycle slope calculations from FI data.

The data in Table A.6 was used to create the graphs contained in the next section (A.2)

A-2 Additional detail on PDA experiments

As shown by Wang et al (2002) and applied by McCurdy (2003), FI slope is indicative of collision efficiency and higher FI slopes imply higher collision efficiency. Applying this theory to Figure 17 leads to the conclusion that alum had the highest collision efficiency.

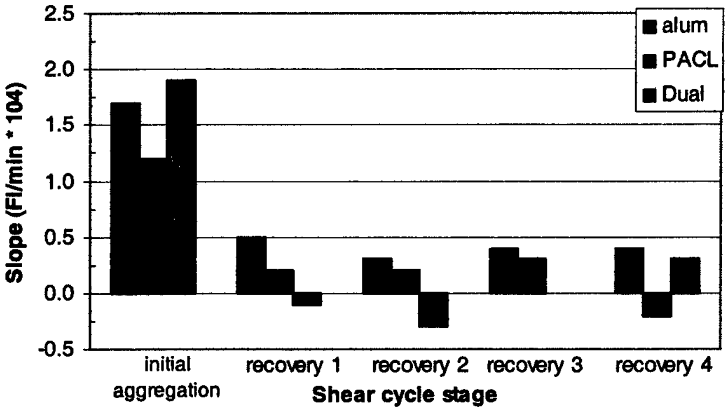

Figure A.9. Shear cycle initial aggregation and recovery slopes (high TOC).

PACL and dual treatments had, on average, similar recovery slopes as one another, implying that neither one is more advantageous than the other. One can determine the ability of a treatment to recover from shear by calculating its initial aggregation slope and calculating the average recovery as presented in Figure A.10.

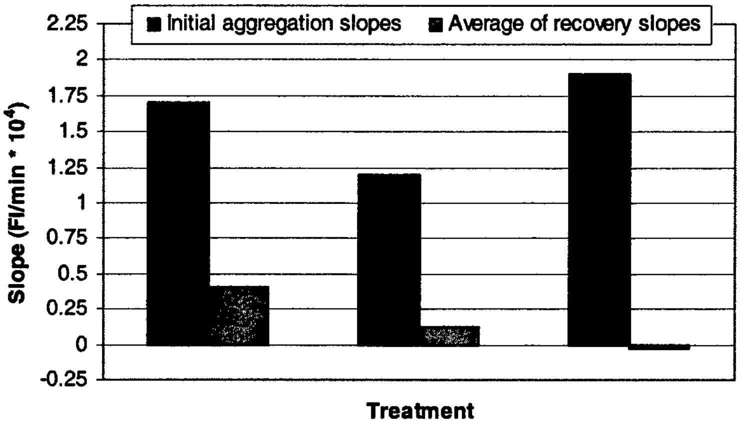

Figure A.10. Shear cycle initial aggregation slopes and recovery slope averages.

The data seems to indicate that under high TOC conditions, the alum treatment is more likely to recover from shear induced breakup due to its ability to retain 24% of its initial aggregation slope, versus 10% for PACL and a negative 1% recovery for the dual. The bench-scale results may indicate that alum results in increased performance when treating high TOC waters at pilot-scale and full-scale operations. Which is in stark contrast to effects of shear on low TOC aggregation rates and recovery slopes presented in Figures A.11 and A.12 (McCurdy, 2003).

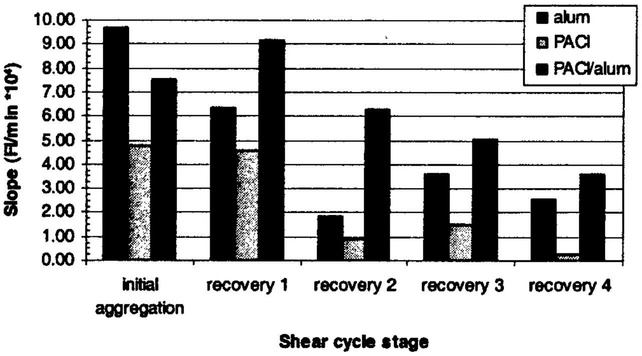

Figure A.11. Shear cycle initial aggregation and recovery slopes for HT water.

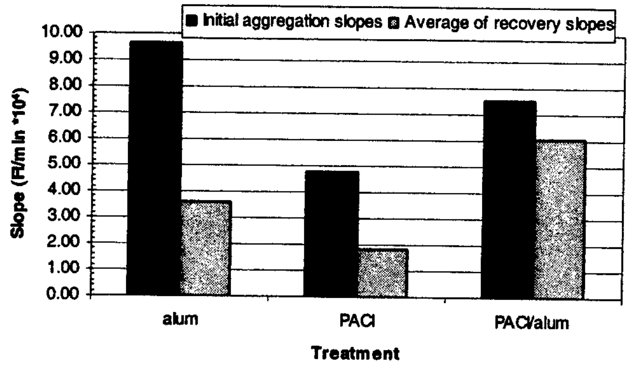

Figure A.12. Plot of slope averages for HT water.

Figures A.11 shows that alum had the highest initial aggregation, which McCurdy concluded was due to higher solids content associated with alum versus PACL or dual at the doses administered by McCurdy. Figure A.12 shows that that the dual treatment recovers the best under conditions of induced shear for low TOC water. Also from Figure A.12, McCurdy concluded that alum was the most affected by shear, indicating that alum was less effective in shear recovery. One of McCurdy's primary conclusion was that the since dual performed best and this increased performance corresponded with the highest degree of recovery for low TOC conditions, then the degree of recovery may be indicative of pilot-scale and full-scale filtration performance.