CONDITIONS CONTRIBUTING TO POOR COAGULATION AND

SEDIMENTATION PERFORMANCE IN MUNICIPAL

WATER TREATMENT

Andre' L. Jenkins, Sr.

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VITA

Andre' Lemar Jenkins Sr., son of Barnett and Mary Jenkins, was born on June 17, 1964 in Columbus, Georgia. He graduated from William Henry Shaw High School in 1982. He attended Mercer University in Macon, Georgia for one year, then enlisted into the United States Army on August 3, 1983, where he served 4 years of active duty service. Immediately after discharge on July 2, 1987, he entered the Active Army Reserves and Columbus State University where he earned his Bachelor of Science Degree in Chemistry in June of 1991. He earned his commission as a Second Lieutenant in the Army Reserves at Georgia Military Institute in August of that same year and has presently achieved the rank of Major. After several years of working in the Chemical Industry, he applied to The Graduate School at Auburn University in August of 1997. After successfully completing a series of core engineering courses, he entered the Graduate School at Auburn University in Auburn, Alabama in September of 1999.

THESIS ABSTRACT

CONDITIONS CONTRIBUTING TO POOR COAGULATION AND

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WATER TREATMENT

Andre' L. Jenkins, Sr.

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The failure of the Auburn Water Works municipal water treatment coagulation and

sedimentation process causing the plant to shut down from June 29, 1999 to July 2, 1999

was investigated. The investigation proceeded in two phases. The first phase was a

series of jar tests consisting of pure, deionized water that was spiked with a combination

of substances to induce specific desired test parameters common to municipal waters

before treatment. The purpose of this phase of testing was to ascertain the variables that

have the most pronounced influence on coagulation and sedimentation behavior after

treatment with aluminum sulfate (alum, Al_2SO_4); an effort to reveal the key variables that

contribute to coagulation failure. The second phase of testing was to take the worst case

combination of variables from phase I and treat them with a matrix of other coagulant

chemicals. In this way, it may be determined which chemical, if any, would produce

better treatment results than alum. A matrix of jar testing for each of the two primary

variables (pH and alkalinity) was examined for all of the coagulants. This second phase

will focus primarily on determining proper processing conditions. Other coagulants used

were ferric chloride ($FeCl_3$), cationic polymer, anionic polymer, non-ionic polymer, and

poly-aluminum chloride.

Results of the investigation demonstrated that treating a water at pH 8 yields better

results than a pH of 6. Although some coagulants lower the pH in water to a pH closer to

6, those waters yielded better turbidity and color test results when the pH was raised back

up to 8 than did waters left at the lower pH. It was also revealed through the test results

that the waters with higher alkalinities treated at pH 8 yielded more favorable results than

did lower alkaline samples at the same pH. Also, the investigation showed that alum is

the best coagulant for municipal water treatment based on turbidity and color testing, but

ferric chloride yielded acceptable results as well. Results produced with all of the

polymeric coagulants except poly-aluminum chloride proved far less desirable than did

alum and ferric chloride results and in some cases had little to no effect whatsoever on

the final water quality. Poly-aluminum chlorides on the other hand did have some

possible benefit over alum in terms of dose requirements and range of pH during

coagulation.

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Computer software used   Microsoft Office 2003—Microsoft Word 2003 and

Microsoft Excel 2003

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I. INTRODUCTION

Every living organism requires water in some shape or fashion to survive. These requirements are met in numerous ways. Human beings have several methods by which to obtain water. We consume it through the foods we eat, but primarily we receive water directly into our bodies by drinking. Most drinking water comes from either groundwater wells or processed surface waters. Surface waters such as lakes, ponds, rivers and streams are major sources of fresh water for drinking, however these waters require treatment. A primary treatment step is the coagulation of turbidity causing particulate material by the addition of chemicals (coagulants) and mixing.

One of the most widely used coagulants used in municipal water treatment processes around the world is aluminum sulfate (Al_2SO_4), commonly referred to as alum, and the simultaneous addition of lime to alter pH. These chemicals are generally used for removing suspended solids in the water which contribute to high turbidity and color readings. Additionally, in the removal of the solids other contaminates such as bacteria and chemicals occur. Typically the suspended solids with the greatest potential to contribute to high turbidity and color contain humic substances, which are comprised of natural organic matter (NOM). Coagulants enhance the aesthetic qualities of the water by removing these suspended solid particles and NOM. To the consumer, good clean water will appear pure and clear. Alum is usually a very dependable coagulant, but requires

proper chemical conditions to be effective. Researchers have tested many different

chemicals and compounds for their effectiveness in the water treatment process. Some

chemicals obviously have no place in water treatment, while others may and sometimes

do play a significant role in the processes of water treatment. According to Eikebrokk

(1999), optimization of coagulation/direct filtration processes with respect to efficient

removal of humic substances, i.e. NOM has gained much attention in many countries

over the last years. NOM has also been identified as a major cause of color and high

turbidity in surface water sources. Thus, the successful removal of NOM and colloidal

compounds in general, plus co-precipitated metals and ions in the treated water is

required for purification.

II. RESEARCH OBJECTIVES

The goal of this research was to investigate and establish past conditions for poor coagulation and sedimentation performance experienced by the Auburn Water Works in the summer of 1999. The investigation proceeded in two phases. The first phase used a synthetic source water prepared by using a matrix of key water constituents that were examined to discover the influence each had on coagulation behavior. Pure, deionized water was spiked with a combination of specific variables in the amounts shown in Tables 2A and 2B. Two different types of suspended solids were used in the investigation. The first source of solid matter was derived from native Alabama soil. The clay soil was gathered, dried, and separated using ASTM standard sieves. The fraction passing the number 100 sieve was retained and used in the study. The other source of solid matter was gathered from a forested Alabama setting, dried, macerated, and sieved in a manner similar to the clay solids. Alkalinity was adjusted with calcium hydroxide, $(Ca(OH_2))$, and hardness by a combination of $Ca(OH_2)$ and/or calcium chloride $(CaCl_2)$. Oil was added in the amounts shown in Table 2A and 2B using a low viscosity straight mineral oil. Solution pH was adjusted using nitric acid (HNO_3) and/or sodium hydroxide $(NaOH)$.

A matrix of paired extremes (high and low value) of each of the variables in Tables 2A and 2B were examined using the jar testing procedure where six 1000 ml

beakers with identical water mixtures for the test runs were stirred in an identical manner. Into each beaker was added an increasing amount of coagulant, rapidly stirred, then gently agitated, and finally allowed to settle. After settling for a period of one half hour, a sample of the water was removed from the surface of the beaker and analyzed for turbidity and color. It was anticipated that the key variables that contribute to poor coagulation would be revealed.

The second phase of the investigation established proper coagulation procedures to deal with the worst case aqueous solution(s) in phase 1. The second phase focused primarily on determining the proper processing conditions (pH and alkalinity) and determining the chemicals that improved the ability to coagulate the worst case water. The investigation was investigated in a similar manner to the first phase by conducting a matrix of the experiments at high and low values of each variable. These variables are identified in Table 2C. Jar testing studies were individually conducted on a matrix for each of the two primary variables using all of the coagulants individually. Assuming that only one mixture from phase I is examined for each different type of TSS results in a total of 48 individual jar tests. The major objective of the sedimentation/coagulation study was to evaluate the effect of different coagulants on a design water in an effort to improve the treatment of source waters that defy normal procedures.

III. LITERATURE REVIEW

1.0 COAGULATION AND FLOCCULATION

Coagulation is essential for use in the treatment of the water we consume. In practice, more contamination is removed from the water by the combined processes of coagulation and sedimentation. Thus coagulation is an absolutely essential treatment process for removal of colloidal matter and other contaminates in water. Colloidal particulate removal is aesthetically important and essential for health reasons as well, such as the removal of heavy metals, pesticides, viruses, organic and inorganic matter. Heavy metals represent problems in terms of groundwater and there are concerns of chronic exposures to low levels of heavy metals in drinking water (Cheremisinoff, 2002). The water widely used as public water supplies are surface waters but some groundwater sources are used too but generally have more dissolved mineral concentrations than surface waters (Snoeyink and Jenkins, 1980). By definition, coagulation is a physiochemical process that alters the kinetics of particles causing stable colloids to become unstable and agglomerate into larger aggregates which can be removed by sedimentation and filtration (Amirtharajah and O'Melia, 1990).

1.1 <u>Colloids</u>

The definition of a colloid is defined by as a substance that consists of particles dispersed in throughout another substance which are too small for resolution with an ordinary light microscope but are incapable of passing through a semi permeable membrane (Webster, 2001). A more specific definition would be particles that are too small to settle out of suspension in a water that will be used for human consumption.

1.1.1 Characteristics

The particles that are found in water can generally be categorized into two major groups based on size. Particles that are considered larger than 0.5 μm are generally classified as suspended solids, and particles measuring an approximate size of 5 nm – 0.5 μm are classified as colloidal material.

Colloids are also characterized by their water-solid interfacial properties. Based on these properties, they are categorized as either hydrophobic or heterophobic particulates. Hydrophobic particulates, which include clays, metal oxides, and microorganisms, (Amirtharajah and O'Melia, 1990) have a well-defined interface between the water and the solid phase and have a low affinity for water molecules. They are also found to be thermodynamically unstable and will aggregate irreversibly over time (Montgomery, 1985).

1.1.2 Stability

A colloid is considered stable when there exists an equilibrium between associated attractive and repulsive forces. Some colloids exist in a state of indefinte stability.

Colloidal particles of this nature which are said to be irreversible, exist in a thermodynamically and energetically stable state. Colloids that exist in a state that is not indefinately stable are termed reversible which are the colloidal particles that will coagulate under certain conditions.

Although irreversible colloidal particles coagulate, all do not coagulate at the same rate. Most commonly, the stable and unstable classifications of colloids applied to irreversible colloids relate to their kinetic properties rather than their energetic or thermodynamic properties. Therefore kinetically unstable colloids are irreversible colloids that coagulate rapidly and kinetically stable colloids are irreversible colloids that coagulate very slowly.

Colloid stability is most often divided into two categories: electrostatic stabilization and steric stabilization. The electrostatic stabilization category is based on the fact that most colloids possess a negative charge. This surface charge results from one of two mechanisms:

1. Surface groups on the solid may react with water to either accept or donate protons.

2. Surface groups and ions can react in water within the structure of the particle.

The second reaction is the predominant cause of the charge associated with clay minerals. These negative charges are neutralized by positive ions. Steric stabilization results from the adsorption of non-ionic compounds at solid liquid interface. Sorbed polymers can perform either as stabilizers or destabilizers. Their behavior is dependent upon several factors such as the amount of polymer and amount of solid particle present, the polymers affinity for the solid particles in the water, and the electrolyte type and concentration

used. Quantitive equations that describe the interaction of the forces are difficult to

develop. However, two conditions produce repulsion:

1. Adsorbed layers can be compressed by *interparticulate collision,* which

   results in a reduced volume available for the sorbed molecule.

2. Interpenetration or collision of adsporbed layers which results in an increase

   of polymer segment concentration in the region being mixed, which is the

   most frequently occuring condition.

Layer interpenetration stabilization is widely used in the manufacturing of industrial

colloids such as paints and waxes (Amirtharajah and O'Melia, 1990).

1.1.3 Double Layer Theory

As previously stated, most colloidal particles carry a negative charge while the bulk

solution surrounding the colloids is electrically neutral (Faust and Aly, 1998,

Montgomery, 1985). When particles are placed in water, the surface of the particle

becomes charged. Ions of opposite charge (usually positive) of the particles surface

charge accumulates the particle surface in order to satisfy electroneutrality. This

accumulation is opposed by another normal tendency of particles to diffuse in the

   direction of decreasing concentration. The combination of the electrostatic attraction

and diffusion result in an electrical double layer. This double layer generates a diffuse

cloud of ions around a particle. An electric potential at the particle surface forms due to

the excess ions and decreases exponentially with distance from the particle surface as

seen in Figure 1.0 below. As a particulate moves in an electrical field, some portion of

the fluid

near its surface moves with developing a shear plane which separates the inner Stern

layer of adsorbed molecules from the outer layer of oppositely charged ions, referred to

as counterions. The depth of this layer is dependent on the ionic strength, with the

difference in electrical potential between the Stern layer and the bulk solution termed the

zeta potential (Montgomery, 1985).
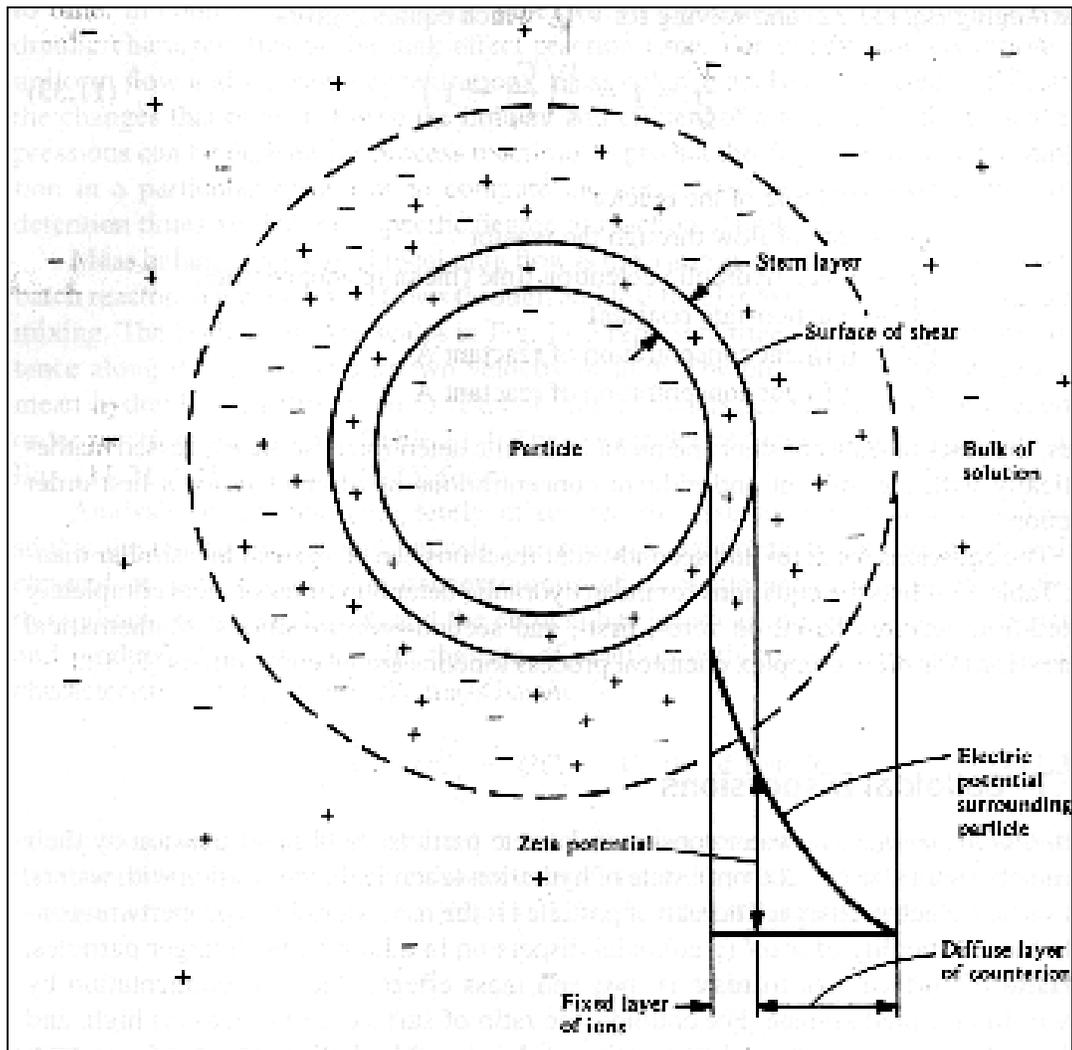
Figure 1.0. Electric Potential at a Particle Surface or Zeta Potential Diagram

1.2 Destabilization

   In order to remove colloidal particles from contaminated water, destabilization and/or "neutralization" of the charged particles or a reduction in particulate stability (Montgomery, 1995). Destabilization mechanisms that can be exploited to achieve particulate destabilization include compression of the electrical double layer, adsorption and charge neutralization, interparticle binding or bridging, and enmeshment or "sweep floc" (Montgomery, 1985, Amirtharajah and O'Melia, 1990)

1.2.1 *Double Layer Compression*

   One of the most popular and widely used methods of colloidal particlate destabilization is compression of the electrical double layer. The addition of positively charged counterions compresses the double-layer, lowering the volume of the diffuse layer necessary to maintain electroneutrality and thus reducing the effective thickness of that diffuse layer. The range of the repulsive interaction between similar colloidal particles also decreases, so that the attractive van der Walls interaction can dominate at all separations, the activation energy barrier can disappear, and electrostatic stabilization can be eliminated (Amirtharajah and O'Melia, 1990). The double layer compression process is achieved by the addition of electrolytes. Although the addition of electrolytes does not affect particle charges, double layer thickness and zeta potential will decrease resultingly. If the proper amount of electrolytes are added, coagulation will occur and colloids will settle out of solution (Faust and Aly, 1998). A similar process occurs at a freshwater river/seawater interface. Freshwater rivers with low ionic strength chemistry combines and mixes with high ionic strength seawater. This causes the particles to be destabilized by double layer compression and accumulation of particles results in the

formation of deltas at river mouths (Amirtharajah and O'Melia, 1990). In this example, seawater provides the electrolyte for the reaction.

1.2.2 Adsorption and Charge Neutralization

Research has shown that mechanisms other than electrostsatics are responsible for destabilization (Faust and Aly, 1998). In adsorption and charge neutralization, the mechanism is as the name implies: available counterions act to neutralize particles by being adsorbed and thus destabilization the particle. If ions are added in excess, charge reversal occurs and the destabilized particles are restablilzed. Also, some ions like sodium (Na^+) and dodecylamine ($C_{12}H_{25}NH_3^+$) have the same charge but behave differently in charge neutralization and require different amounts to destabilize particles and accordingly the quantity required in excess to induce charge reversal and restabilization. In fact, overdosing with sodium is not possible (Amirtharajah and O'Melia, 1990). This fact serves as verification that electrostatics are not the only mechanism controllong destabilization as electrostatically sodium and dodecylamine have equal destabilization abilities (Amirtharajah and O'Melia, 1990).

1.2.3 Adsorption and Interparticle Binding

Coagulation polymers added to solutions are adsorbed on specific sites of the particle, allowing the polymer to have *segments* with active sites that bind with other particles with similar polymer segmented particles to form a destabilized particle (Figure 1.1) If excess polymer is added, the free sites begin to bind soley to a single individual particle

and restabilization results. Restabilization results similarly with excess agitation of the

solution (Figure 1.)(Faust and Aly, 1998).
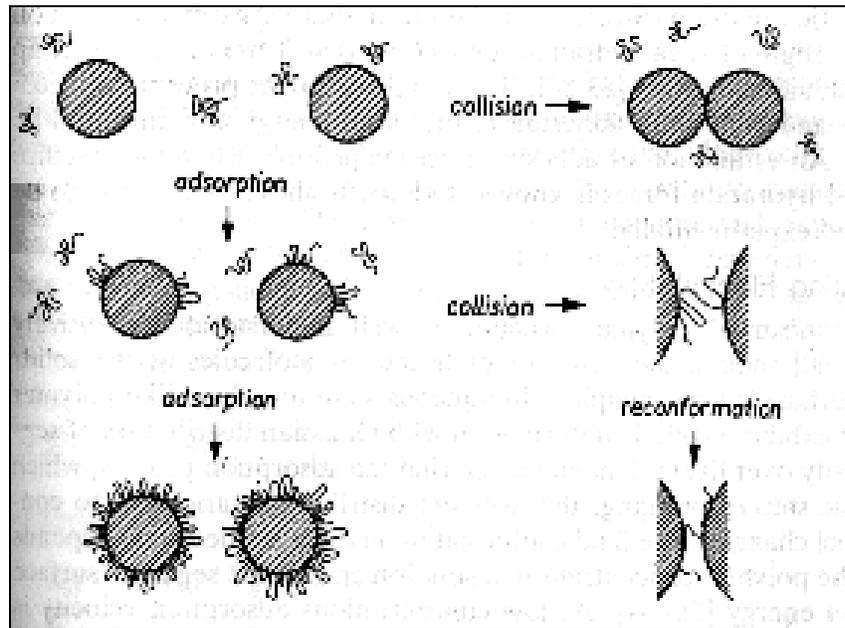
Figure 1.1. Polymer Adsorption and Interparticle Binding

1.2.4   Enmeshment

Enmeshment or entrapment in a particle is the final type of destabilization mechanism.

Metal salts such as aluminum sulfate [$Al_2(SO_4)_3$] or ferric chloride ($FeCl_3$) cause metal

hydroxides to precipitate. Colloidal particles can be enmeshed in these precipitants, most

often referred to as *sweep floc*. When sweep floc settles, it sweeps the colloidal particles

down with it. This process, which is a combination of destabilization mechanisms and

transport, is extensively used in water treatment to remove variable turbidity, and

dissolved organic carbon (DOC) (Amirtharajah and O'Melia, 1990). Entrapment

coagulation is not a chemical destabilization of the colloidal particles but a physical destabilization of the colloidal system. This physical destabilization process is often referred to as orthokinetic coagulation (Faust and Aly, 1998).

1.3 Transport Processes

In order for destabilized particles to collide and aggregate, the particle transport process must occur. There are three accepted transport processes: Brownian motion, also known as perikinetic coagulation, flow induced motion, also called orthokinetic coagulation, and differential settling (Faust and Aly, 1998, Amirtharajah, A, 1991) These three processes are used to account for particle aggregation during flocculation (Amirtharajah and O'Melia, 1990).

1.3.1 Brownian Motion

Brownian motion, or perikinetic flocculation, is defined as the random motion of the particles caused by their continuous bombardment by surrounding water molecules. The driving force for Brownian motion is thermal energy (Amirtharajah and O'Melia, 1990). With brownian motion colloidal particles collide with other colloidal particles. Some stay together via interparticle bonding and form larger particles called aggregates. This process and as long as conditions remain virtually constant, aggregation will continue until the aggregates become too large to be affected by brownian motion (Kramer, 1999).

The process theory centers around one particle acting as a central particle. Other particles around the central particle collide with that central particle and bond together to become one particle larger particle. Over time, a reduced concentration of particles

around the central particle will occur and diffusion causes a steady stream of particles

towards the central particle. These collisions are governed by the concentration of

particles present and their diameters and can be expressed as (Amirtharajah and O'Melia,

1990):

$$(N_{ij})_p = \frac{2kT\,(d_i + d_j)^2}{3\,\mu d_i\,d_j}\; n_i\,n_j \qquad\qquad (1.1)$$

where $(N_{ij})_p$ = rate of binary perikinetic collisions

k = Boltzmann constant

T = absolute temperature (^0K)

d_i and d_j = diameter of ith and jth particle respectively

n_i and n_j = concentration of ith and jth particle respectively

μ = dynamic viscocity

Consideration must also be given to other factors that effect rates of collisions such as

hydrodynamic and electrostatic interactions. The influence of coagulants is important as

well and must also be considered. Minute additions of coagulants increase the

concentration particles formed by nucleation and precipitation by several orders of

magnitude, and hence the process of perikinetic flocculation is accelerated considerably

(Amirtharajah and O'Melia, 1990).

1.3.2 Flow Induced Motion

The next kinetic transport process that will be discussed is flow-induced motion, or

orthokinetic flocculation. Orthokinetic flocculation results from a velocity gradient

existing between colliding particles. It involves particle movement by a gentle motion of water most often called agitation, with the knowledge that particles will agglomerate if they undergo collision with each other or become close enough to be within the *zone of influence* of one another. Since inducing a fluid motion is easily initiated and controlled, orthokinetic flocculation and coagulation can be and is often manipulated in numerous engineering systems. The rate of binary orthokinetic collisions in laminar flow is defined as (Amirtharajah and O'Melia, 1990):

$$(N_{ij})_o = 1/6 \; n_i \, n_j \, (d_i + d_I)^2 \; G \qquad\qquad (1.2)$$

where $(N_{ij})_o$ = rate of binary orthokinetic collisions

G = mean velocity gradient (dv/dz)

In turbulent flow it can be implied that since functional forms are similar the conceptual framework is similar and quantitative treatment results are consistent, thus the laminar flow equation can be used throughout (Amirtharajah and O'Melia, 1990).

1.3.3 Differential Settling

Differential settling is the particle transport process whereby heavier and/or larger settling particles of diameter d_i overtake those that are smaller and settle more slowly with a diameter of d_j, collide with them and agglomerate with them while settling. Differential settling can be defined quantitatively as (Amirtharajah and O'Melia, 1990):

$$(N_{ij})_d = \frac{\pi g(s\text{-}1)(d_i + d_I)^3\ (d_i + d_I)\, n_i\, n_j}{72v} \qquad\qquad (1.3)$$

where $(N_{ij})_d$ = rate of collision from differential settling
g = acceleration due to gravity

v = kinematic viscosity

s = specific gravity of particle

1.4   Coagulants

The uses of coagulants such as metal salts and polymers have long been recognized as an important basic component of the coagulation process. Coagulants work in part to help destabilize the colloidal particles present and in doing so increase the precipitation of particulate contributing to turbidity and color from suspension.

1.4.1   *Metal Salts*

Metal salts such as aluminum sulfate $[Al_2(SO_4)_3]$ or ferric chloride $(FeCl_3)$ produce hydrolyzing metal ions in aqueous solutions. When these salts are added to water, they will dissociate to form trivalent Al^{3+} and Fe^{3+} ions and then hydrate to form the complexes $Al(H_2O)_6^{3+}$ and $Fe(H_2O)_6^{3+}$. These complexes then proceed to undergo several hydrolytic reactions which form both mononuclear and polynuclear species. If the metal salts are added to water in concentrations less than their respective solubility limits of their metal hydroxides, the hydrolysis products will form and adsorb onto particles causing them to undergo destabilization and charge neutralization. When the concentrations then exceed the solubility limits of the metal hydroxides, the formation of metal hydroxide precipitate occurs. In this state, both charge neutralization and

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enmeshment in precipitate (section 1.2.2) contribute to coagulation (Faust and Aly, 1998).

1.4.1-a Aluminum Sulfate

The most commonly used coagulant in conventional water treatment is aluminum sulfate, most commonly referred to as *alum*. The formula for filter alum is $Al_2(SO_4)_3*14.3\ H_2O$ with a molecular weight of 600 grams per mole. Alum is commonly manufactured, shipped, and fed in a dry granular form although it is also available in powdered and liquid alum syrup forms as well. The reaction for aluminum sulfate addition is (Viessman and Hammer, 1998)

$$Al(SO_4)_3*14.3H_2O + 3Ca(HCO_3)_2 \rightarrow 2Al(OH)_3 \downarrow + 3CaSO_4 + 14.3H_2O + 6CO_2 \quad (1.4)$$
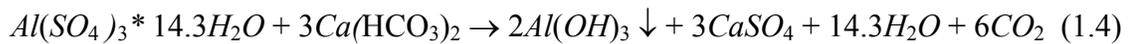
When commercial alum is added to water, a series of hydrolysis reactions occur as intermediate reactions to the precipitation of $Al(OH)_3$ (s), commonly referred to as *sweep floc* (Amirtharajah and O'Melia, 1990, Faust and Aly, 1998).

$$Al^{3+} + H_2O + 3Ca(HCO_3)_2 \leftrightarrow AlOH^{2+} + H^+ \qquad \log K = -4.97 \qquad (1.5)$$

$$AlOH^{2+} + H_2O \leftrightarrow Al(OH)_2^+ + H^+ \qquad \log K = -4.3 \qquad (1.6)$$

$$Al(OH)_2^+ + H_2O \leftrightarrow Al(OH)_3 + H^+ \qquad \log K = -5.7 \qquad (1.7)$$

$$Al(OH)_3 + H_2O \leftrightarrow Al(OH)_4^- + H^+ \qquad \log K = -8.0 \qquad (1.8)$$

$$2Al^{3+} + 2H_2O + \leftrightarrow Al_2(OH)_2^{4+} + 2H^+ \qquad \log K = -7.7 \qquad (1.9)$$

$$3Al^{3+} + 4H_2O + \leftrightarrow Al(OH)_4^{5+} + 4H^+ \qquad \log K = -13.94 \qquad (1.10)$$

$$13Al^{3+} + 28H_2O \leftrightarrow Al_{13}O_4(OH)_{24}{}^{7+} + 32H^+ \qquad \log K = -98.73 \qquad (1.11)$$

$$Al(OH)_3 \ (am) \leftrightarrow Al^{3+} + 3OH^- \qquad \log K = -31.5 \qquad (1.12)$$

$$Al(OH)_3 \ (c) \leftrightarrow Al^{3+} + 3OH^- \qquad \log K = -33.5 \qquad (1.13)$$
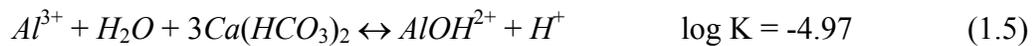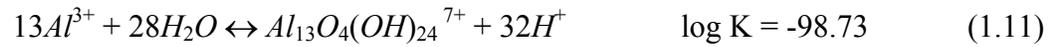
While precipitating Al(OH)$_3$ (s), the preceeding reactions produce hydrogen ions (H$^+$) which will affect pH. It is believed that for every mg/L of aluminum hydroxide precipitated, 0.5 mg/L of alkalinity as CaCO$_3$ is consumed. To accommodate this comsumption of alkalinity, lime or caustic soda is usually added to raise the pH in an effort to maintain the pH within the range of facilitating optimum coagulation (Amirtharajah and O'Melia, 1990).

As previously stated, aluminum hydroxide formation is pH dependent. The range for coagulation with alum is 5.8 – 8.0 with the optimum range depending on a relationship between concentration of aluminum sulfate added and pH (fig.)

1.4.1-b Iron Salts

Iron salts most commonly used come as ferrous [Fe(II)] salts and ferric [Fe(III)] salts. Fe(II) is used in the form of ferrous sulfate (FeSO$_4$) and Fe(III) in the form of ferric chloride (FeCl$_3$). Ferrous sulfate is sold as green crystals or granular material and fed via dry feeding while ferric chloride can be purchased in either crystalline of liquid forms. Iron salts are usually less restricted by pH range and more effective at color removal from water than are aluminum salts (aluminum sulfate). Alum is, however more cost effective and iron salts may require additional chemical addition for precipitate formation (Viessmann and Hammer, 1998). Iron salts are also very corrosive in nature and must be

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handles in specially-designed containers that are either rubber-lined or glass containers. The overall reactions of iron salts may be represented as (Amirtharajah and O'melia, 1990)

Ferrous Sulfate ($FeSO_4$)

$$2FeSO_4 \cdot 7H_2O + 2Ca(HCO_3)_2 + 0.5O_2 \rightarrow 2Fe(OH)_3 \downarrow +2CaSO_4 + 4CO_2 + 13H_2O \quad (1.14)$$

Ferric Chloride ($FeCl_3$)

$$FeCl_3 \cdot 6H_2O + 2Ca(HCO_3)_2 \rightarrow 2Fe(OH)_3 \downarrow + 3CaCl_3 + 6CO_2 + 6H_2O \quad (1.15)$$
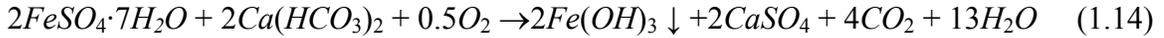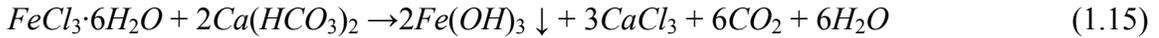
Reaction mechanisms of both iron salts are similar, but ferrous sulfate reactions require an additional chemical addition for ferric hydroxide precipitate formation to occur. For this to happen, Fe(II) must be oxidized to Fe(III) and then formation to iron hydroxide can occur.

Similar to the alum mechanism, a series of intermediate hydrolosis reactions occur to the formation of ferric hydroxide precipitate (Amirtharajah and O'Melia, 1990, Faust and Aly, 1998). They are represented as follows:

$$Fe^{3+} + H_2O \leftrightarrow FeOH^{2+} + H^+ \qquad \log K = -2.2 \qquad (1.16)$$

$$FeOH^{2+} + H_2O \leftrightarrow Fe(OH)_2{}^+ + H^+ \qquad \log K = -3.5 \qquad (1.17)$$

$$Fe(OH)_2{}^+ + H_2O \leftrightarrow Fe(OH)_3 + H^+ \qquad \log K = -0.6 \qquad (1.18)$$

$$Fe(OH)_3{}^+ + H_2O \leftrightarrow Fe(OH)_4{}^- + H^+ \qquad \log K = -0.1 \qquad (1.19)$$

$$2Fe^{3+} + 2H_2O \leftrightarrow Fe_2(OH)_4{}^{4+} + H^+ \qquad \log K = -2.9 \qquad (1.20)$$

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$$3Fe^{3+} + 4H_2O \leftrightarrow Fe_3(OH)_4{}^{5+} + 4H^+ \qquad\qquad \log K = -6.3 \qquad\qquad (1.21)$$

$$Fe(OH)_3 \, (am) \leftrightarrow Fe^{3+} + 3OH^- \qquad\qquad \log K = -38.7 \qquad\qquad (1.22)$$

$$\alpha\text{--}FeO(OH) + H_2O \leftrightarrow Fe^{3+} + 3OH^- \qquad\qquad \log K = -41.7 \qquad\qquad (1.23)$$
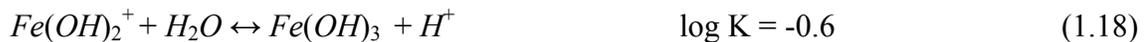
The precipitation of $Fe(OH)_3$ produces hydrogen ions which affect pH as does the alum mechanism, but the Fe(III) acid is less soluble and stronger than that of aluminum. Here pH correction/preservation must be exercised by the addition of lime or caustic soda to maintain optimum pH levels required for precipitate formation to occur (Amirtharajah and O'Melia, 1990).

The pH range for formation of ferric hydroxide is 4-9 (Viessmann and Hammer, 1998). At higher pH levels (pH>10), the predominant species present at equilibrium conditions with either solid is the monomeric anion $Fe(OH)_4{}^-$. At lower pH levels (pH<6), the dominant soluble species are cationic monomers such as Fe^{3+} and $Fe(OH)_2{}^+$ (Fig) Iron is least soluble at a ph of about 8 (Amirtharajah and O'Melia, 1990).
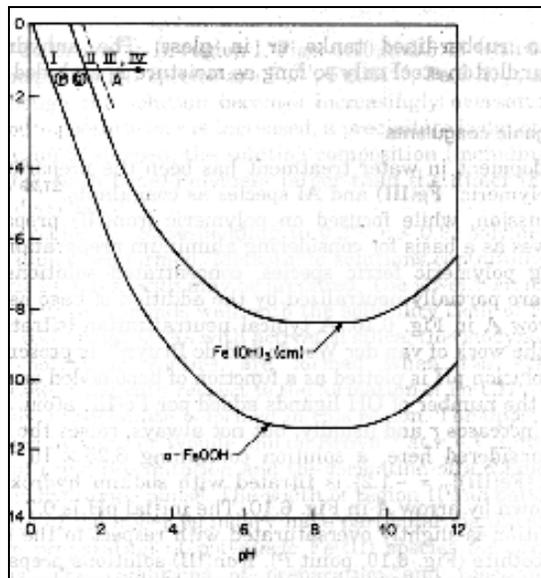
Figure 1.2. Solubility Range of Fe(III) ion

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1.4.2 *Polymers*

Polymers are either organic or inorganic. Organic polymers are either anionic such as polystyrene sulfonate, cationic such as polyethylene amine, or non-ionic such as polyacrylamide (Amirtharajah and O'Melia, 1990). Both can be effective coagulants or coagulant aids. Examples of inorganic polymers are polymeric ferric [Fe(III)] and aluminum species such as polyaluminum chloride.

1.4.2-*a Organic Polymers*

Organic polymers have gained widespread popularity in the water treatment industry since they were introduced in the early 1950's. These polymers are long-chain molecules of repeating chemical units or monomers designed to provide distinctive physicochemical properties to the polymer. They may contain one single monomer or may be composed of different types of subunits, which may vary in number and produce polymers with different molecular weights and different charge densities if the subunits are charged. They may also form as linear or branched chain structures in varying degrees. Although some polymers are non-ionic and uncharged, many polymers often possess an ionic nature that produces an electrical charge. These polymers have at least one monomeric unit with an attached ionizable group in its structure such as a carboxyl, amino, or sulfonic group and are called *polyelectrolytes*. Depending on the attached ionizable group, the polyelectrolyte may be either cationic, anionic, or *ampholytic*. Ampholytic polyelectrolytes contain both positive and negative groups, one example would be proteins (Amirtharajah and O'Melia, 1990).

1.4.2-b Inorganic Polymers

The two primary inorganic polymers used in water treatment are salts of ferric and

aluminum ions. Both hydrolizable cations are readily available as sulfate or chloride salts

in both liquid and solid form but in the United States the predominate water treatment

coagulant is aluminum sulfate or "alum," sold in a hydrated form as $Al_2(SO_4)_3*xH2O$,

where x is usually 14 (Montgomery, 1985).

   "As a rule, any polymer adsorbs on any surface" (Amirtharajah and O'Melia, 1990).

Polymers behave as if they have many arms like an octopus.   Many of the bonding

portions or segments may be in contact with a surface at the same time. This

characteristic of polymeric coagulants and coagulant aids serves to greatly enhance their

overall adsorption performance, sometimes to the point of apparent irreversibility. There

is definitely strength in numbers, and such is definitely the case for polymeric substances,

for even polymers possessing lower bonding energies per segment can have a very high

collective affinity for a surface. In many cases, bonds may be directed in that bonds can

be formed between particular functional groups on the polymer molecule and specific

sites on a solid surface (Amirtharajah and O'Melia, 1990). If a monomeric unit in a

polymer contains ionizable groups, the polymer is termed polyelectrolyte and depending

upon the type of ionizable group on the monomeric groups, a polyelectrolyte can be

cationic, anionic, or ampholytic with both positive and negative groups present (Gregory,

1978). Figure 1.3 represents examples of these materials:

Some Synthetic Polymers [1]

Nonionic	Anionic	Cationic
$\begin{bmatrix} -CH-CH_2- \\ \quad\ \ CONH_2 \end{bmatrix}_n$	$\begin{bmatrix} -CH-CH_2- \\ \quad\ COO^-\ Na^+ \end{bmatrix}_n$	$\begin{bmatrix} -CH_2-CH_2-NH_2^+ \end{bmatrix}_n$
Polyacrylamide M.W. = 10^6	Sodium polyacrylate M.W. = 10^6	Polyethylene imine M.W. = 500 to 100,000
$\begin{bmatrix} -CH-CH_2- \\ \quad\ OH \end{bmatrix}_n$	$\begin{bmatrix} -CH-CH_2- \end{bmatrix}_n$ with phenyl–$SO_3^-Na^+$	Polydiallyldimethyl ammonium chloride ("Cat-Floc") M.W. = 10,000 to 100,000
Polyvinyl alcohol	Sodium polystyrene sulfonate	
$\begin{bmatrix} -CH_2-CH_2-O \end{bmatrix}_n$		$\begin{bmatrix} -CH-CH_2- \end{bmatrix}_n$ with pyridinium N^+ $H Br^-$
Polyethylene oxide		Polyvinylpyridinium bromide

Figure 1.3. Some Synthetic Polymers by Charge (Gregory, 1978)

IV. MATERIALS AND EXPERIMENTAL METHODS

4, 0 SYNTHETIC SURFACE WATER PREPARATION

Synthetic surface water samples were produced by a Barnstead/Thermolyne (Dubuque, IA) NANOpure[TM] Reagent Grade ultra pure water system that produced 17.4 $M\Omega$-cm water and stored in Nalgene 50-liter HDPE carboys. In order to achieve the desired total suspended solids concentrations, two different soils were required. The inorganic TSS soil was taken from the area along US 29 in Auburn, Al, and the other soil was taken from a heavily wooded, damp area along highway 231 in Montgomery, AL. The organic soil was dried at a temperature of 105 degrees Celsius using a Lindberg/Blue M (Ashville, NC) MO 1450 Mechanical Convection Oven. The inorganic soil was dried at a temperature of 103 degrees Celsius using a GCA/Precision Scientific (Chicago, IL) Thelco Model 28 furnace. Both soils were separated using an ASTM standard sieve set and a sieve shaker with impacter. Soils retained in the pans passing the #100 sieve were used in all experiments. A Hach (Loveland, CO) Model One laboratory pH meter was used to measure pH. The pH was adjusted using either a 0.1 M solution made from EM Science (Gibbstown, NJ) certified ACS grade nitric acid solution or a 0.1 M sodium hydroxide solution made from Curtin Matheson Scientific (Houston, TX) Chempure[TM] certified ACS grade sodium hydroxide. Two separate concentrations.

of aluminum sulfate solutions were required for use in phase I jar testing. One was a

1mg/L solution and the other was 10 mg/L solution. Each was made from NANOpure[TM]

Water and EM Science (Gibbstown, NJ) USP specification grade aluminum sulfate

hydrate crystals.

Table 4A – Matrix of Variables for Phase I Part 2 Experiments

Run	Suspended Solids (mg/L)	Alkalinity (mg/L as CaCO3)	Hardness (mg/L as CaCO3)	pH	Oils (mg/L)
1	200	100	150	8	50
2	200	100	150	8	5
3	200	100	150	6	50
4	200	100	150	6	5
5	200	100	50	8	50
6	200	100	50	8	5
7	200	100	50	6	50
8	200	100	50	6	5
9	200	50	150	8	50
10	200	50	150	8	5
11	200	50	150	6	50
12	200	50	150	6	5
13	200	50	50	8	50
14	200	50	50	8	5
15	200	50	50	6	50
16	200	50	50	6	5
17	20	100	150	8	50
18	20	100	150	8	5
19	20	100	150	6	50
20	20	100	150	6	5
21	20	100	50	8	50
22	20	100	50	8	5
23	20	100	50	6	50
23	20	100	50	6	5
25	20	50	150	8	50
26	20	50	150	8	5
27	20	50	150	6	50
28	20	50	150	6	5
29	20	50	50	8	50
30	20	50	50	8	5
31	20	50	50	6	50
32	20	50	50	6	5

4.1 JAR TEST PROCEDURE

Two separate concentrations of aluminum sulfate solutions were required for use in phase I jar testing. One was a 1mg/L solution and the other was 10 mg/L solution. Each was made from NANOpure$^{TM.}$ water and EM Science (Gibbstown, NJ) USP specification grade aluminum sulfate hydrate crystals. One milligram of aluminum sulfate crystals was carefully measured into a weigh boat that was placed in a Shimadzu (Kyoto, Japan) Libror Model AEG 220 analytical balance.

For phase II jar testing, the same two separate stock solutions were used to coagulate the worst case waters from phase I for the aluminum sulfate coagulation/flocculation portion of this phase of testing. For the additional ferric chloride, cationic polymer, non-ionic polymer, anionic polymer, and poly aluminum chloride coagulants tested in phase II of the jar testing, one stock solution with concentration of 1mg/ml for each coagulant was prepared and used in the jar test experiments. The ferric chloride coagulant solution was prepared from NANOpure$^{TM.}$ water and Merck KgaA's EM Science (Darmstadt, Germany) anhydrous ferric chloride crystals mixed for a 24 hour period on a Corning (Big Flats, NY) Model PC-320 Stirrer/Hotplate. The cationic (IC-7219 PWG), anionic (IC-7110 PWG), and non-ionic (IC-4800), polymers tested in this project were obtained from Industrial Chemicals, Inc. (Birmingham, AL) in crystalline form. The poly-aluminum chloride (PAC 2000) polymer was obtained in liquid form. The cationic polymer, non-ionic polymer and anionic polymer solutions were all prepared for jar testing by mixing 1 gram of each polymer in crystalline form with 1L of the NANOpure$^{TM.}$ water and allowing them to dissolve and mix for a period of 24 hours on the Corning PC-320 Stirrer/Hotplate (without heat).

The jar tests were conducted by placing 900mL of the water to be tested into each of 6 – 1L beakers and labeling them 1 to 6. The individual concentration of each jar tested water can be found in matrix form in *Table 4A, p.24*. The beakers were then placed in a Phipps and Bird, Inc. (Richmond, VA) Model 300 six paddle stirrer jar test apparatus in ascending numerical order. Amounts of coagulant solution was then carefully pipetted into 50 mL beakers in the amounts shown in *Table 4B* below:

Table 4B Coagulant Concentrations per Beaker in Jar Testing

Beaker #	mL of 1mg/ml Coagulant added to beaker (mL)	Coagulant Concentration Added (mg/L)
1	0	0
2	10	10
3	20	20
4	40	40
5	50	50
6	100	100

The paddles of the apparatus were then lowered into the samples. The apparatus was started and adjusted to a speed of 100 rotations per minute (rpms). The coagulants first poured into the 50mL beakers were then simultaneously poured into the 1L beakers. Small beakers were rinsed with distilled water into larger respective beakers to insure minimize residual coagulant in small beakers. Samples were then mixed for additional 30 seconds at 100 rpms, and then rpms were reduced to 20 rpms and allowed to mix an additional 15 minutes. At the conclusion of this second mixing period, the mixing was stopped, the paddles raised out of the samples, and then the samples remained quiescent for 30 minutes to allow the flocculated material to settle out of solution.
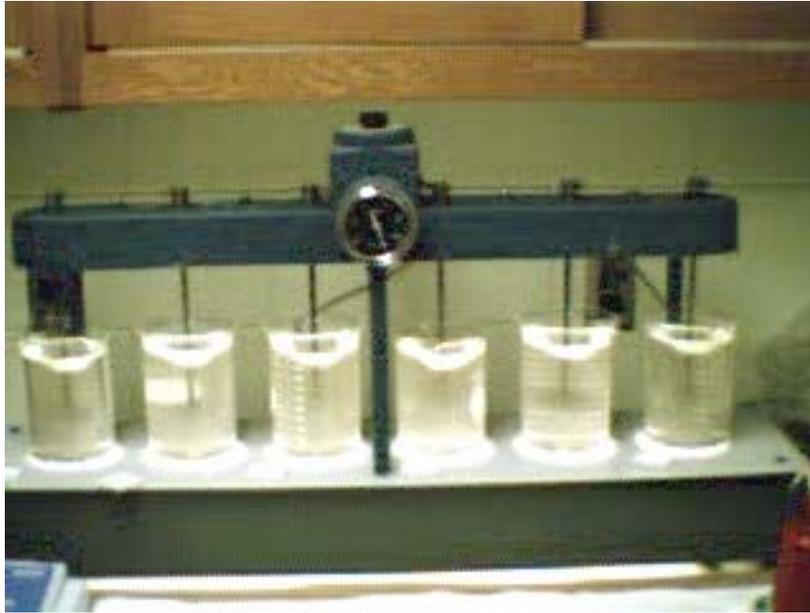
Figure 4.0. Jar Test apparatus mixing at 100 rpms with FeCl$_2$ Coagulant.
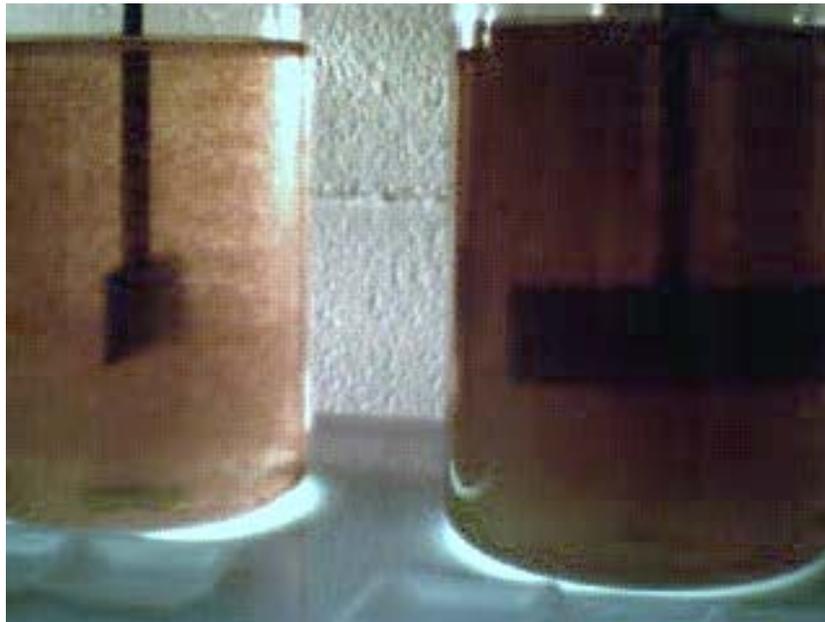
Figure 4.1. Jars with 50 mg/L and 100 mg/L FeCl$_2$ Coagulant added to jars with 200 mg/L inorganic TSS and 8.0 pH after mixing 15 minutes @ 20 rpm.

Once the settling period was over, 30 mL of the supernatant was extracted from the very top of the beaker and transferred to a Hach (Loveland, CO) Model 2100A turbidimeter sample cell for testing.

4.2 DATA COLLECTION AND ANALYSIS

Samples of supernatant collected were analyzed for two variables: turbidity and color. The samples were first collected 35 mL (+/- 1 mL) in a Hach (Loveland, CO) Model 2100A turbidimeter sample cell. Following collection, the samples were analyzed for turbidity using a HACH (Loveland, CO) 2100A turbidimeter with the data reported in the standard unit for turbidity measurement, the nephalometric turbidity unit (NTU). The samples were then transferred to a clean, empty HACH (Loveland, CO) COD model DR/3000 Spectrophotometer COD sample cell and analyzed for true color using Hach procedure code C.11. This procedure code program is calibrated in color units based on the American Public Health Association (APHA) and American Water Works Association) recommended standard of 1 color unit being equal to 1mg/L platinum as chloroplatinate ion. This method is not only applicable for drinking water color determination, but for wastewater and seawater color determination as well.
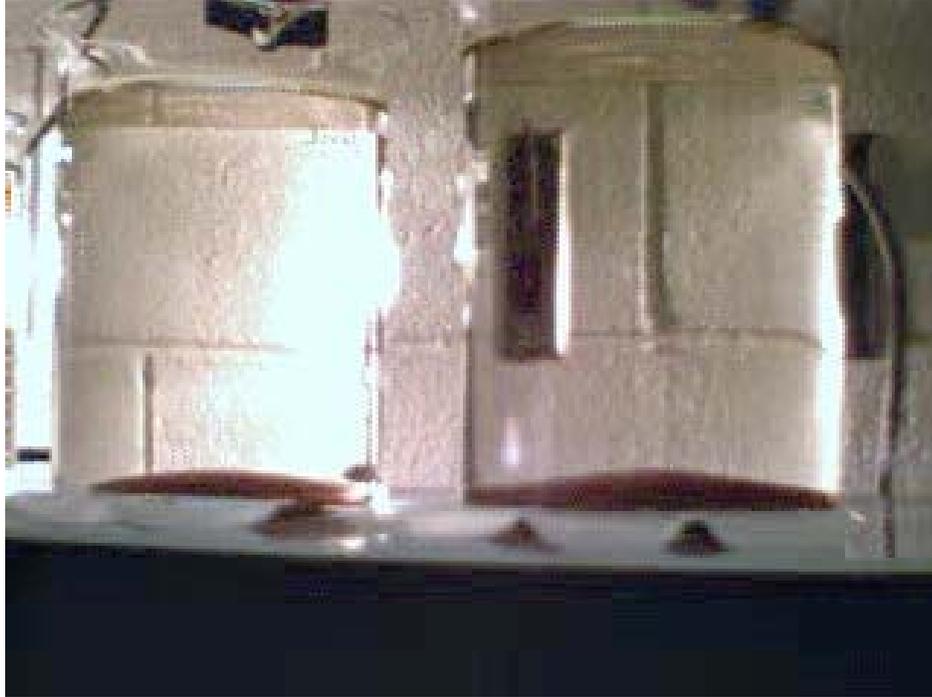
Figure 4.2. Jars with 50 mg/L and 100 mg/L FeCl$_2$ Coagulant added to jars with 200 mg/L inorganic TSS and 8.0 pH after settling period.

V. RESULTS AND DISCUSSIONS

5.1. PHASE I EXPERIMENTS

One aspect of this research was to evaluate the turbidity removal abilities and capabilities of alum under various treatment conditions that may and do occur in municipal drinking water treatment. The variation of conditions tested here were based on a matrix of specific variables identified as key influences in water treatment and water quality. The experimental phase of this evaluation proceeded in two phases, and each phase was composed of an inorganic battery of jar tests and an organic battery of jar testing.

The first step in the phase I experimental phase of the research was conducted in an effort to evaluate the influence of each of several key water constituents on coagulation behavior shown in Tables 5A and 5B. Synthetic source waters were prepared by mixing reagent grade ultra pure water obtained from a Barnstead/Thermolyne NANOPure^{TM} system producing 17.4 MΩ-cm water and two distinctly different soils for achieving the desired organic and inorganic total suspended solid concentrations. The pure water was spiked with a combination of specific variables (total suspended solids, alkalinity, hardness, pH, and oil) in varied amounts and combinations in order to achieve specific water characteristics for testing. Two different types of suspended solids were

used in the investigation. The first source of solid matter was derived from native

Alabama soil. The clay was gathered locally and then dried and separated using ASTM

standard sieves. The fraction of solid material passing the number 100 (150micron)

sieve. The other source of solid material was gathered from a forested Alabama area.

The soil was then dried, macerated, and sieved in a manner similar to the clay solids.

Alkalinity was adjusted with calcium hydroxide, and hardness was adjusted by

combination of calcium hydroxide and/or calcium chloride. Oil, which was a low

viscosity straight mineral oil, was added in the amounts shown in table 5.1 and 5.2.

Solution pH was adjusted using diluted nitric acid and/or sodium hydroxide.

   A matrix of paired extremes (high and low values) of each of the variables in tables

5.1 and 5.2 were examined using the jar testing procedure where six 1000 ml beakers

with identical water mixtures for the test runs were stirred in an identical manner. Into

each beaker was added an increasing of amount of coagulant. They were next rapidly

stirred at 100 rpms for 30 seconds, then gently agitated at 20 rpms for an additional 30

minutes. Finally, they were allowed to settle for one half hour. After completing the

settling period, a sample of water is removed from each of the six beakers and analyzed

for turbidity and color. It was anticipated that the key variables that contribute to poor

coagulation would be revealed in this phase of testing. The testing was divided as

inorganic and organic total suspended solids testing, each with 4 additional parameters

each (alkalinity, hardness, pH, and oil) with a high and low concentration of each. The

testing matrix of variables indicated that 32 individual jar tests would be required to

adequately test of the two types of soil for a total of 64 individual jar test procedures.

However, by conducting a statistically designed experiment the number of experiments

can be reduced by a factor of two with no loss of information. The factorial designed

experiment thus results in the 32 individual tests (16 per soil source). A matrix of these

test variables appears in Table 5C. The anticipated outcome of the phase I experimental

matrix of jar testing is an indication of the key constituent in the source water

contributing to the coagulation problems.

Table 5.1 **- Parameters for Coagulation Studies Using Clay for Suspended Solids**

Parameter	High Concentration	Low Concentration
Suspended Solids - Clays	200 mg/L	20 mg/L
Alkalinity	100 mg/L (as CaCO3)	50 mg/L (as $CaCO_3$)
Hardness	100 mg/L (as CaCO3)	50 mg/L (as $CaCO_3$)
pH	8	6
Oils	50 mg/L	5 mg/L

Table 5.2 **- Parameters for Coagulation Studies Using Biological Material for Suspended Solids**

Parameter	High Concentration	Low Concentration
Suspended Solids - Clays	200 mg/L	20 mg/L
Alkalinity	100 mg/L (as CaCO3)	50 mg/L (as $CaCO_3$)
Hardness	100 mg/L (as CaCO3)	50 mg/L (as $CaCO_3$)
pH	8	6
Oils	50 mg/L	5 mg/L

Table 5.3 - Matrix of Variables for Part 2 Experiments

Run	Suspended Solids (mg/L)	Alkalinity (mg/L as CaCO3)	Hardness (mg/L as CaCO3)	pH	Oils (mg/L)
1	200	100	150	8	50
2	200	100	150	8	5
3	200	100	150	6	50
4	200	100	150	6	5
5	200	100	50	8	50
6	200	100	50	8	5
7	200	100	50	6	50
8	200	100	50	6	5
9	200	50	150	8	50
10	200	50	150	8	5
11	200	50	150	6	50
12	200	50	150	6	5
13	200	50	50	8	50
14	200	50	50	8	5
15	200	50	50	6	50
16	200	50	50	6	5
17	20	100	150	8	50
18	20	100	150	8	5
19	20	100	150	6	50
20	20	100	150	6	5
21	20	100	50	8	50
22	20	100	50	8	5
23	20	100	50	6	50
23	20	100	50	6	5
25	20	50	150	8	50
26	20	50	150	8	5
27	20	50	150	6	50
28	20	50	150	6	5
29	20	50	50	8	50
30	20	50	50	8	5
31	20	50	50	6	50
32	20	50	50	6	5

5.1.1. PHASE I RESULTS WITH INORGANIC TSS

    The inorganic soil was jar tested with varying parameter concentrations according to the designed matrix of variables, treated with increasing amounts of alum and the resulting supernatants from each jar tested were gathered and tested for turbidity and color. The jar test results for each of the six beakers required for one jar test procedure were recorded. The best results from each jar test were recorded as was the amount and type of coagulant used to obtain it. Those results were plotted in order to more easily compare which parameters and in what concentration these parameters had the most affect on both turbidity and color in the source water. The results were plotted as the individual jar test number, which directly correlates to a specific combination of parameters vs. average color and average turbidity per jar test. Color was measured in standard color units based on the APHA-recommended standard of 1 color unit being equal to *1mg/L platinum as chloroplatinate ion* on a Hach DR/3000 Spectrophotometer. Turbidity was measured in the standard turbidity unit, which is NTU (Nephalometric Turbidity Unit) on a Hach model 2100A turbidimeter.

    Upon viewing the tabulated and plotted test results of this portion of the testing, several parametric combinations are noteworthy and one is outstanding. One of the first things that is visibly evident is that alum appears to be much effective in removing turbidity than it is in removing color from waters contaminated with inorganic TSS and high or low pH values. When examining the individual jar tests for the different parameter combinations in Table 4A, the most prominent differences in turbidity removal and color removal performances are jar tests #2, which was composed of high suspended solids, alkalinity, hardness, and pH concentration and low oil concentration, #4,

composed of high suspended solids, alkalinity, and hardness concentration but low pH and oil, #7 with high alkalinity, suspended solids and oil concentration but low hardness and pH concentration, #13 with high suspended solids, pH, and oil concentration but low alkalinity and hardness concentration and Jar test #16 with high suspended solids and oil concentration and low concentrations of alkalinity, hardness, and pH. Jar test #2 yielded a poor color result but an acceptable turbidity reading, yielding the lowest color reading of the higher color test results. Further, it is one of only two jar tests that performed poorly with a high pH concentration which indicates that coagulants performed better in waters with higher pH than they in waters with lower pH values.

Examination of jar tests #4, composed of high suspended solids, alkalinity, and hardness concentration but low pH and oil, and #13 with high suspended solids, pH, and oil concentration but low alkalinity and hardness concentration reveal that even though their test results were very similar in measured values and differences between those values, their test parameters were quite different. Both tests had identical inorganic TSS parameters, but Jar test 4 was composed of high alkalinity and hardness concentrations combined with low pH and oil concentrations, while jar test 13 was the exact opposite in composition with low alkalinity and hardness concentrations but high oil and pH concentration, yet results remained similar even after secondary jar tests were performed on each of the two different variable combinations. This would tend to indicate that water with high concentrations of inorganic TSS, alkalinity, and hardness but low pH and little oil has a similar effect on turbidity and color in water with high concentrations of inorganic TSS, oil, and pH but low alkalinity and hardness.

Jar test #7 with high alkalinity, suspended solids and oil concentration but low hardness and pH concentration seems to further substantiate the low pH and high alkalinity in a high inorganic solid water hypothesis even though its high oil concentration and low hardness would lend to test 13's indications. In fact, test number 7 results were worse than both test 4 and 13, as depicted graphically in Figure 5.1 with only a high inorganic solids concentration common between the three, which could indicate that high inorganic solids is much more important to poor results than are the other variables.

Jar test #16 with high suspended solids and oil concentration but low concentrations of alkalinity, hardness, and pH resulted in the worst test results of the inorganic total suspended solids jar tests that were treated with aluminum sulfate. It resulted in a color reading of 42.83 color units (mg/L platinum as chloroplatinate ion) and a turbidity reading of 7.87 NTU, which were the highest values measured throughout the research. It was composed of only one variable in a high concentration, which was the inorganic total suspended solids variable. All the other variables were present in the lower concentrations. Upon closer examination of these results, it may be possible to hypothesize that in this battery of testing inorganic total suspended solid concentration and pH were the most influential variables for poor performance of alum in treatment of the water. It may also be that the other variables present in smaller concentrations somehow aid alum in its removal efforts of turbidity and color.
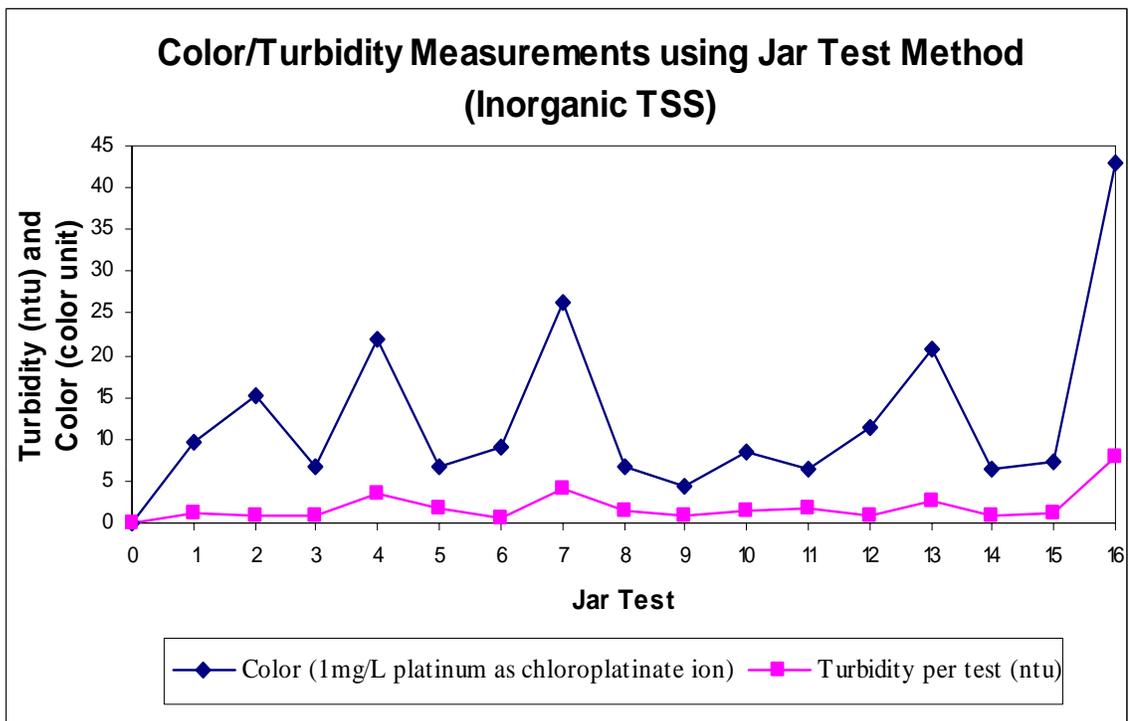
Figure 5.1. Phase I Inorganic Solid Variable Matrix Jar Test Results

5.1.2 PHASE I RESULTS WITH ORGANIC TSS

Upon examining the jar test results for the effect of alum on the variable matrix using organic total suspended solids instead of inorganic, it was observed that different yet similar results were obtained . For the organic portion of the phase I testing, the worst performers for turbidity and color removal by alum are jar test #7 with high alkalinity, suspended solids and oil concentration but low hardness and pH concentration, jar test #11 containing high suspended solids, hardness, and oil and low alkalinity and pH, jar test #14 with high suspended solids and pH but low alkalinity, hardness, and oil concentrations, and jar test #16 with high suspended solids and oil concentration but low concentrations of alkalinity, hardness, and pH.

Jar test #14 with high suspended solids and pH but low alkalinity, hardness, and oil concentrations yielded poor color results, but acceptable turbidity readings, much like jar test #2 consisting of high suspended solids, alkalinity, hardness, and pH but low oil content in the inorganic matrix of tests. Jar test #14 was the only low performer that was not initially high in organic suspended solids, which could indicate a possible explanation for its acceptable turbidity reading of less than 1 NTU. In fact, this jar test was initially low in all test variables except for pH, which incidentally was initially low for all other poor-performing jar tests with organic solids. This could indicate that in the absence of other known contaminants, pH may have a direct, negative impact on alum performance with organic solids present.

Jar tests #11 with high suspended solids, hardness, and oil and low alkalinity and pH and test #16 with high suspended solids and oil concentration but low concentrations of alkalinity, hardness, and pH yielded very similar test results for turbidity and color

removal. Also, these two jar tests were very similar in initial composition. Both jar test 11 and 16 began with high organic suspended solids, and low in alkalinity, and pH, but hardness and oil concentrations were initially opposite in high and low concentration. The fact that the two jar tests performed extremely similar to jar testing with alum as the coagulant despite differences in initial hardness and oil content seem indicate that the effects of these two contaminants have little influence on the coagulation process of alum in waters with high organic TSS content, alkalinity, and low pH.

Upon examining jar test #7 which was composed of high alkalinity, suspended solids and oil concentration but low hardness and pH concentration, it seems that alkalinity and oil can affect the performance of alum in a low pH water. It may be more correct to say that alum's affect on turbidity and color in the presence of a highly alkaline, oily water with a high concentration of organic suspended solids may be directly affected by the presence of that organic solid. The results observed increased substantially with the increase of alkalinity and oil, leading one to believe that in the presence of the organics, the alum was ineffective altogether.

The results of the Organic TSS matrix of jar tests are different from the results of the Inorganic TSS matrix of jar tests in that the worst case results of the Organic TSS matrix are not as profound to the Inorganic TSS matrix jar tests for the most part, but similar to each other in that two of the four poor performers with the Inorganic TSS matrix are poor performers in the Organic TSS matrix as well. In fact among the worst two performers in both cases are the same as far as water composition and jar test number is concerned. They are jar tests test #7 which was composed of high alkalinity, suspended solids and oil concentration but low hardness and pH concentration and jar test #16 with

high suspended solids and oil concentration but low concentrations of alkalinity, hardness, and pH. Test 7 is the by far the worst performer of all the tests in this battery of testing, and so it would probably be feasible to further jar test this particular combination of variables using other coagulants in an effort to identify one that will prove effective in these conditions.

Based on the results of the two batteries of testing in phase I of this research, it has been revealed that there are two most profound negative performers present, one from each battery of tests. They are jar test parameters from jar test 16 of the inorganic TSS testing phase and the parameters for jar test 7 of the organic TSS testing phase. Jar test #16's parameters are high inorganic suspended solids, but low alkalinity, hardness, pH, and oil content and jar test #7 has parameters of high organic suspended solids, alkalinity, and oil content, but low hardness and pH. These two jar tests with their specific variable combinations shall be examined in phase II of this research in an effort to determine effective alternate chemicals for coagulation in cases such as these that would be more effective than alum.
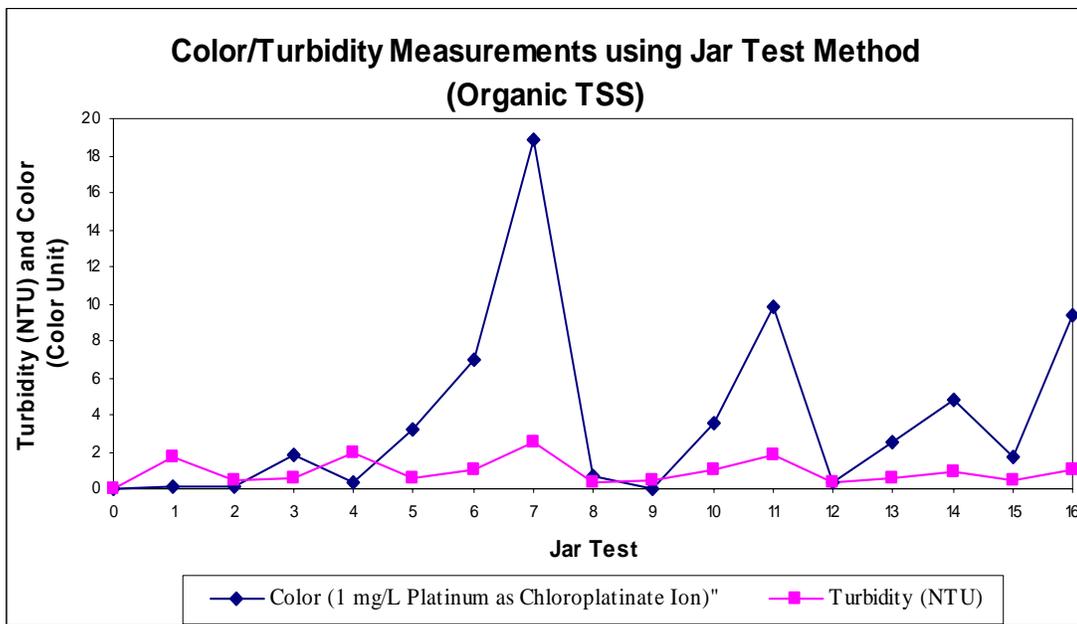
Figure 5.2. Phase I Organic Solid Variable Matrix Test Results

5.2 PHASE II EXPERIMENTS

The second phase of the investigation will deal with the worst case aqueous solution identified in the phase I testing. Phase II focused primarily on determining the proper process conditions (pH and alkalinity) and determine the chemical coagulants that improve the ability of the waters being tested to coagulate. The investigation proceeded in a manner very similar to the first phase in that a matrix of experiments and were conducted with high and low values of each variable. Tentatively, these variables are identified as:

1. pH   6 and 8

2. Alkalinity   50 and 100 mg/L as $CaCO_3$

3. Chemical Coagulants

    3.1 Alum

    3.2 Ferric Chloride

    3.3 Cationic Polymer

    3.4 Non-ionic Polymer

    3.5 Anionic Polymer

    3.6 Poly-aluminum chloride (PAC)

Jar testing studies were conducted on the matrix of combinations for each of the two primary variables and all of the chemical coagulants as shown in Table 5.1 on the preceding page. Since a worst case water has been identified water for both the inorganic and organic phases of testing, each of them must undergo an identical matrix of testing. One matrix results in 24 individual tests, and so a total of 48 individual jar tests were conducted in this phase.

Table 5.4. Phase II Worst Case Water Matrix

Alum	Run	Suspended Solids (mg/L)	Alkalinity (mg/L as CaCO₃)	Hardness (mg/L as CaCO₃)	pH	Oil (mg/L)
	1	200	100	50	6.0	50
	2	200	50	50	8.0	50
	3	200	100	50	8.0	50
	4	200	50	50	6.0	50
Ferric Chloride	Run	Suspended Solids	Alkalinity	Hardness	pH	Oil
	5	200	100	50	6.0	50
	6	200	50	50	8.0	50
	7	200	100	50	8.0	50
	8	200	50	50	6.0	50
Cationic Polymer	Run	Suspended Solids	Alkalinity	Hardness	pH	Oil
	9	200	100	50	6.0	50
	10	200	50	50	8.0	50
	11	200	100	50	8.0	50
	12	200	50	50	6.0	50
Non-Ionic Polymer	Run	Suspended Solids	Alkalinity	Hardness	pH	Oil
	13	200	100	50	6.0	50
	14	200	50	50	8.0	50
	15	200	100	50	8.0	50
	16	200	50	50	6.0	50
Anionic Polymer	Run	Suspended Solids	Alkalinity	Hardness	pH	Oil
	17	200	100	50	6.0	50
	18	200	50	50	8.0	50
	19	200	100	50	8.0	50
	20	200	50	50	6.0	50
Poly-Aluminum	Run	Suspended Solids	Alkalinity	Hardness	pH	Oil
	21	200	100	50	6.0	50
	22	200	50	50	8.0	50
	23	200	100	50	8.0	50
	24	200	50	50	6.0	50

5.2.1   PHASE II EXPERIMENTS WITH INORGANIC TSS (JAR TEST 16)

Investigation of coagulation effects on the combination of variables identified as the

worst case water using inorganic solid soil was continued in this phase of testing.

Coagulation effects are measured as turbidity readings, with lower readings being better

than higher ones. The parameters being used for the prepared water were high inorganic

suspended solid content of 200 mg/L and oil concentration of 50 mg/L, but low alkalinity

content of 50 mg/L, low hardness concentration of 50 mg/L, pH of 6.0. Jar tests were

performed using all six of the alternate chemical coagulants according to the Table 5.1.

The jar testing was conducted in four basic groups based also on the matrix that included

all 6 coagulants. The categories of testing were waters with high alkalinity and low pH,

low alkalinity and high pH, high alkalinity and high pH, and low alkalinity and low pH

with specific values shown in Table 5.1.

5.2.1.1 *Turbidity Results with High Alkalinity and Low pH*

Of all the coagulants tested under the condition of high alkalinity and low pH, three of

the six performed to yield acceptable turbidity readings. The ferric chloride, the anionic

polymer, and the poly-aluminum chloride were the three who performed to the standard

of less than 1 NTU, with the ferric chloride performing best. In the second jar of this jar

test with a ferric chloride addition in the amount of 10 mg/L, the turbidity reading went

from 3.3 NTU down to 0.18 NTU, well below the accepted threshold of 1.0 NTU as seen

in Figure 5.1 and Table 6.2. Additional amounts in subsequent jars resulted in equally

low turbidity readings for this water. The anionic polymer also performed well under these conditions, although not quite as well as the ferric chloride. The initial addition of anionic polymer yielded a turbidity reading of 0.6 ntu and all subsequent additions yielded readings under the 1.0 ntu standard, while the poly aluminum did not bring the water to an acceptable turbidity level until it reached a dose level of 50 mg/L, but once this dosage was reached, performance level of PAC was better than the anionic polymer at the same dose level. At 100 mg/L , PAC and ferric chloride removed almost all the turbidity from this water. The non-ionic polymer coagulant reached an acceptable level of turbidity removal at the 40 mg/L dosage and improved turbidity removal at the 50 mg/L dose, but at a dosage of 100 mg/L added turbidity back to the water. This indicates that at the correct dosage, a non-ionic polymer coagulant is effective in waters of this type.

The cationic polymer and alum coagulants did not perform well in the water with high alkalinity and low pH. At the initial dosage levels of 10 mg/L, both chemicals removed some turbidity, but from the 20 mg/L dosage and beyond the cationic polymer tested was ineffective as seen in Figure 5.1 and Table 5.2. These results tend to indicate that the turbidity causing colloids in this water exhibit an anionic charge and repel the cationic based chemical polymeric coagulants, having an adverse effect on the coagulation process in waters of this type.
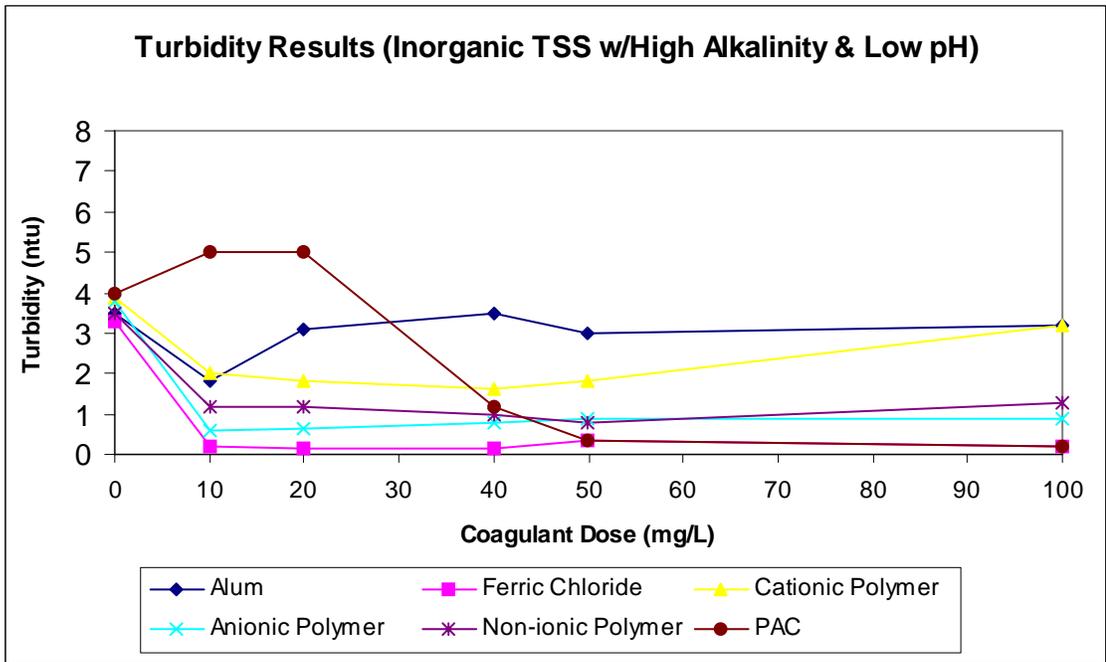
Figure 5.3 Turbidity Results of Worst case Jar Test with Inorganic TSS, High Alkalinity

and Low pH

Table 5.5

Concentration	Alum	FeCl$_3$	Cationic	Anionic	Non-ionic	PAC
0	3.5	3.3	3.9	3.8	3.5	4
10	1.8	0.18	2	0.6	1.2	5
20	3.1	0.15	1.8	0.65	1.2	5
40	3.5	0.16	1.6	0.8	1	1.2
50	3	0.35	1.8	0.9	0.8	0.35
100	3.2	0.2	3.2	0.9	1.3	0.2

5.2.1.2 Turbidity Results with Low Alkalinity and High pH

The coagulants tested in this type of water composition that exhibited the best

turbidity removal characteristics overall were ferric chloride, anionic polymer, and poly-

aluminum chloride coagulants, but in water with low alkalinity and high pH values, the

cationic polymer also performed well at lower doses as seen in Figure 5.2 and Table 5.3.

The ferric chloride outperformed all the others by far. After the initial dosage of 10

mg/L, the turbidity reading of the ferric chloride treated jar went from 3.4 NTU down to

was 0.1 NTU and remained the same for all subsequent doses up to 100 mg/L. The

anionic polymer coagulant reached acceptable levels down from 3.6 NTU to 1.0 after the

initial 10 mg/L dose and readings remained below 1.0 NTU throughout. After adding the

second dosage of 20 mg/L of coagulant, the poly-aluminum chloride and the cationic

polymer coagulants both brought turbidity levels down from 3.2 NTU to 0.8 NTU and

3.7 NTU to 0.7 NTU respectively in the water with low alkalinity and high pH. Based on

pure numerical results, the cationic polymer outperformed the PAC at the dose level of

20 mg/L and they performed almost identically until a 100mg/l dosage was reached,

where the cationic polymer seemed to display some reversal of its coagulation ability and

go above the 1.0 NTU turbidity level. The reason for this reversal could be that the level

of contaminant that this coagulant could affect was reached. It is possible that Van Der

Waals forces between the cationic polymer molecules and other particles in the mixture

began to coagulate to cause turbidity but not enough to become heavy enough to fall out

of suspension. This could also indicate that the colloids became just large enough to

cause turbidity but since they shared the same surface charges repelled each other

continuously, keeping them in suspension. The non-ionic polymer initially removed

some turbidity from the test water, but seemed to reach coagulation capacity after 10 mg/L was added and removed no more turbidity after that point. Reasons for the inability to remove turbidity by the non-ionic polymer could be that there were limited active sites available to this polymer and once it was ineffective on the more dominant, turbidity-causing colloidal particles. The alum was simply ineffective removal of turbidity in water with low concentrations of alkalinity and high pH. Alum initially increased turbidity in the water and caused turbidity readings to remain elevated past their initial reading without coagulant throughout the entire series of dosing.

Turbidity Results (Inorganic TSS w/Low Alkalinity & High pH)
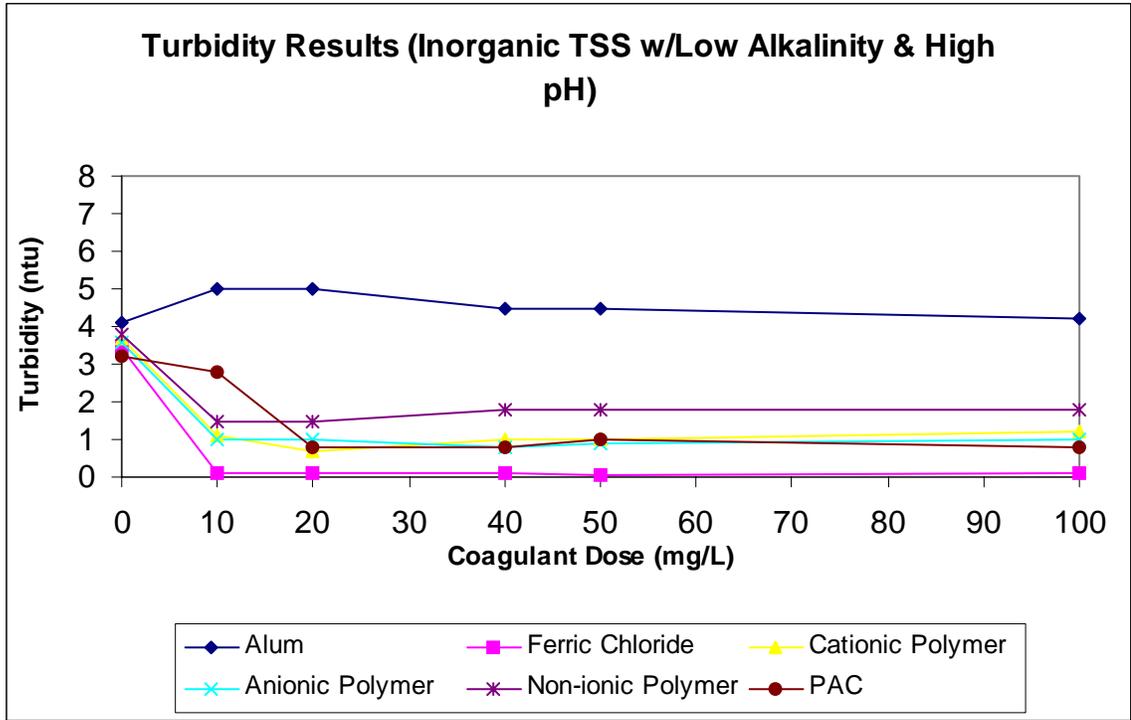
Figure 5.4 Turbidity Results of Worst case Jar Test with Inorganic TSS, Low Alkalinity

and High pH

Table 5.6. Accompanying Data for *Figure 5.4*

Concentration	Alum	FeCl$_3$	Cationic	Anionic	Non-ionic	PAC
0	4.1	3.4	3.7	3.6	3.8	3.2
10	5	0.11	1.1	1	1.5	2.8
20	5	0.1	0.7	1	1.5	0.8
40	4.5	0.1	1	0.8	1.8	0.8
50	4.5	0.07	1	0.9	1.8	1
100	4.2	0.1	1.2	1	1.8	0.8

5.2.1.3 Turbidity Results with High Alkalinity and High pH

In Figure 5.3 and Table 5.4 the data shows that the tested water with properties of high

alkalinity and high pH, ferric chloride coagulant, anionic polymer coagulant, non-ionic

polymer coagulant and poly-aluminum chloride (PAC) coagulant all performed to bring

turbidity readings of the water which exhibited average initial turbidity readings of 3.8

NTU to less than 1.0 NTU. Water with high alkalinity and high pH that was treated with

cationic polymer coagulant and the alum coagulants did not perform as well. The

cationic polymer coagulant dropped the turbidity reading of the water to 1.1 NTU after

the initial 10 mg/L dosage and 1.0 NTU after 20mg/L of the coagulant were added. Upon

the addition of 40 mg/L of the cationic polymer coagulant, the turbidity reading was 0.6

NTU, which is within the standard. The Alum on the other hand increased turbidity

readings almost 2.5 times the original untreated reading. Addition of Alum coagulant

increased turbidity from an initial 3.7 NTU to 9.1 NTU after 100mg/L were added. After

the initial 10mg/L were added, turbidity rose from the 3.7 NTU to 6.8 NTU. The reason

for this increase is most likely due to repulsion forces between negatively charged

colloidal particles and Aluminum ions from the Alum coagulant keeping each other in

suspension instead of coagulating as they would if the colloidal particles exhibited a

positive charge in the suspension.
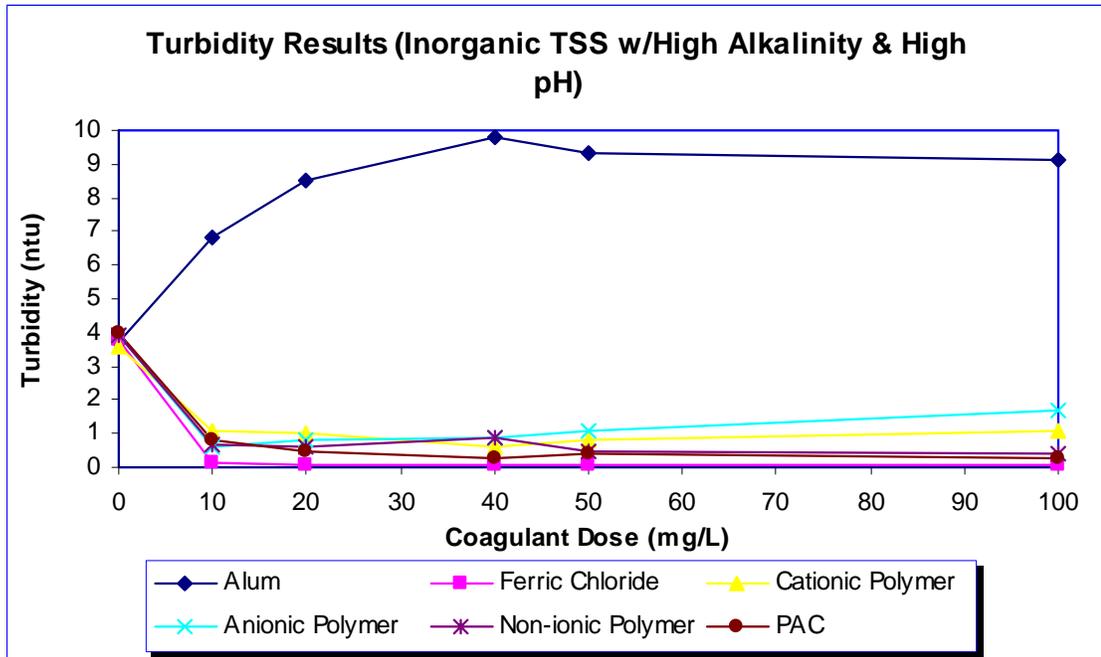
Figure 5.5 Turbidity Results of Worst case Jar Test with Inorganic TSS, High Alkalinity

and High pH

Table 5.7. Accompanying Data for *Figure 5.5*

Concentration	Alum	$FeCl_3$	Cationic	Anionic	Non-ionic	PAC
0	3.7	3.8	3.6	3.9	3.9	4
10	6.8	0.13	1.1	0.6	0.7	0.8
20	8.5	0.08	1	0.8	0.6	0.5
40	9.8	0.09	0.6	0.9	0.9	0.3
50	9.3	0.06	0.8	1.1	0.5	0.4
100	9.1	0.1	1.1	1.7	0.4	0.3

5.2.1.4 Turbidity Results with Low Alkalinity and Low pH

In Figure 5.4 and Table 5.5, the data indicates that jar tests of water with the conditions of

low alkalinity and low pH, all the coagulants performed well upon the initial dosage

except for the PAC, which increased turbidity with the initial 10 mg/L dosage added. But

after the addition of a 20 mg/L dosage, turbidity dropped from 5.8 NTU to 1.0 NTU,

which is within the standards. Conversely, both the cationic and anionic polymer

coagulants additions of 20 mg/L and beyond seemed to increase turbidity readings in

proportion with increasing amounts of coagulant added. The cationic polymer turbidity

readings were above 1.0 after the 20 mg/L dosage and the anionic polymer water

remained within standard up until the addition of 50 mg/L coagulant was added. This

would indicate that the charged polymer coagulants should be used in smaller amounts

than others such as alum and ferric chloride in this type of water.
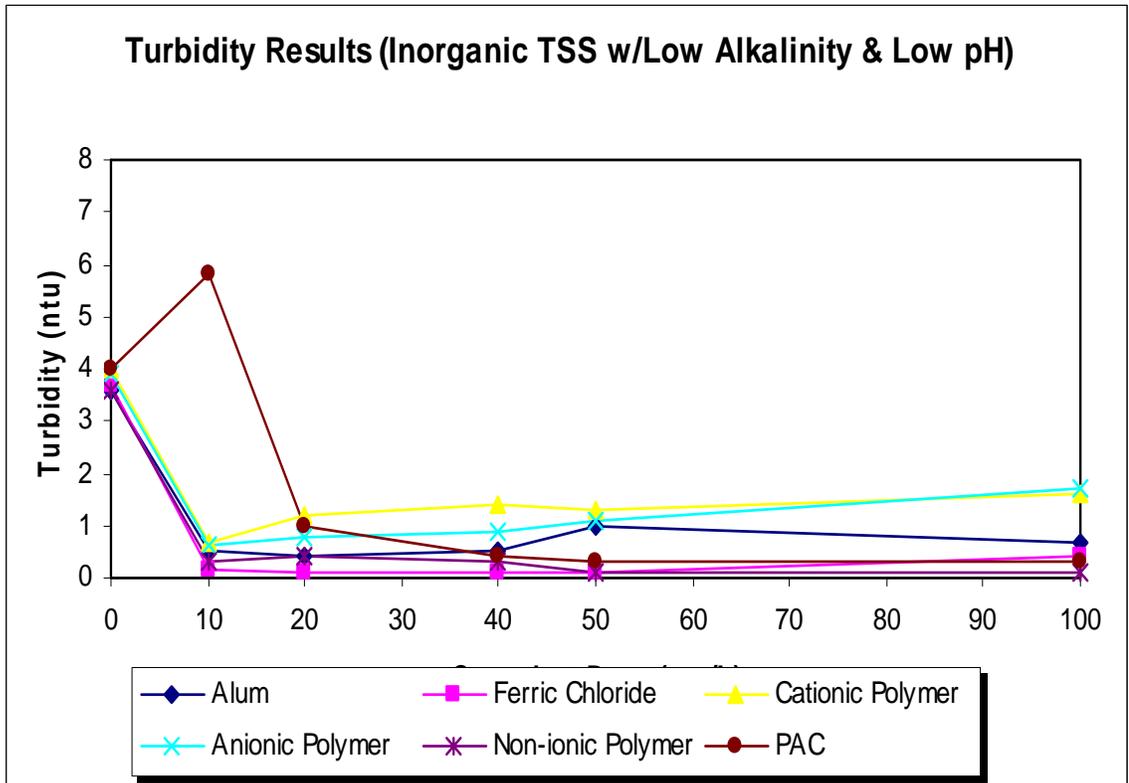
Figure 5.6 Turbidity Results of Worst case Jar Test with Inorganic TSS, Low Alkalinity

and Low pH

Table 5.8 Accompanying Data for *Figure 5.6*

Concentration	Alum	FeCl$_3$	Cationic	Anionic	Non-ionic	PAC
0	3.6	3.7	4	3.9	3.6	4
10	0.5	0.17	0.7	0.6	0.3	5.8
20	0.43	0.1	1.2	0.8	0.4	1
40	0.5	0.11	1.4	0.9	0.3	0.4
50	1	0.1	1.3	1.1	0.1	0.3
100	0.65	0.4	1.6	1.7	0.1	0.3

5.2.2   PHASE II EXPERIMENTS WITH ORGANIC TSS (JAR TEST 7)

Investigation of coagulation effects on jar test #7 which was composed of high organic suspended solid content of 200 mg/L, high alkalinity content of 100 mg/L, and high oil concentration of 50 mg/L, but low hardness concentration of 50 mg/L, the combination of variables identified as the worst case water using organic solid soil in phase I testing was continued in this phase of testing. Jar tests were performed as with the inorganic suspended solid testing portion of this phase.

5.2.2.1 *Turbidity Results with High Alkalinity and Low pH*

Jar testing the worst case water phase I water with organic suspended solids which was jar test #7 with a concentration of high organic suspended solid content of 200 mg/L, high alkalinity content of 100 mg/L, and high oil concentration of 50 mg/L, but low hardness concentration of 50 mg/L and low pH yielded different results than did the inorganic suspended solids in a similar mixture. This data is graphically and numerically represented in Figure 5.5 and Table 5.6. Ferric chloride coagulant performed much the same as it did with inorganic TSS. After the first addition of ferric chloride, the turbidity was removed to an acceptable level and remained at a very low level for all subsequent doses. PAC performed second best instead of the cationic polymer, bringing turbidity to acceptable levels of less that 1.0 NTU after the addition of 40 mg/L and maintaining acceptable levels for additional jar test method additions of 50 mg/L and 100 mg/L of

coagulant. All the other chemical coagulants failed to bring turbidity levels to an acceptable level throughout the dosing cycle and were thus considered ineffective for turbidity removal for waters with similar compositions with NOM as their source of TSS. Alum came close to achieving an acceptable level of turbidity removal after 20 mg/L, but after the next dose of 40 mg/L, the turbidity returned to close to the initial, untreated level and was ineffective as well.
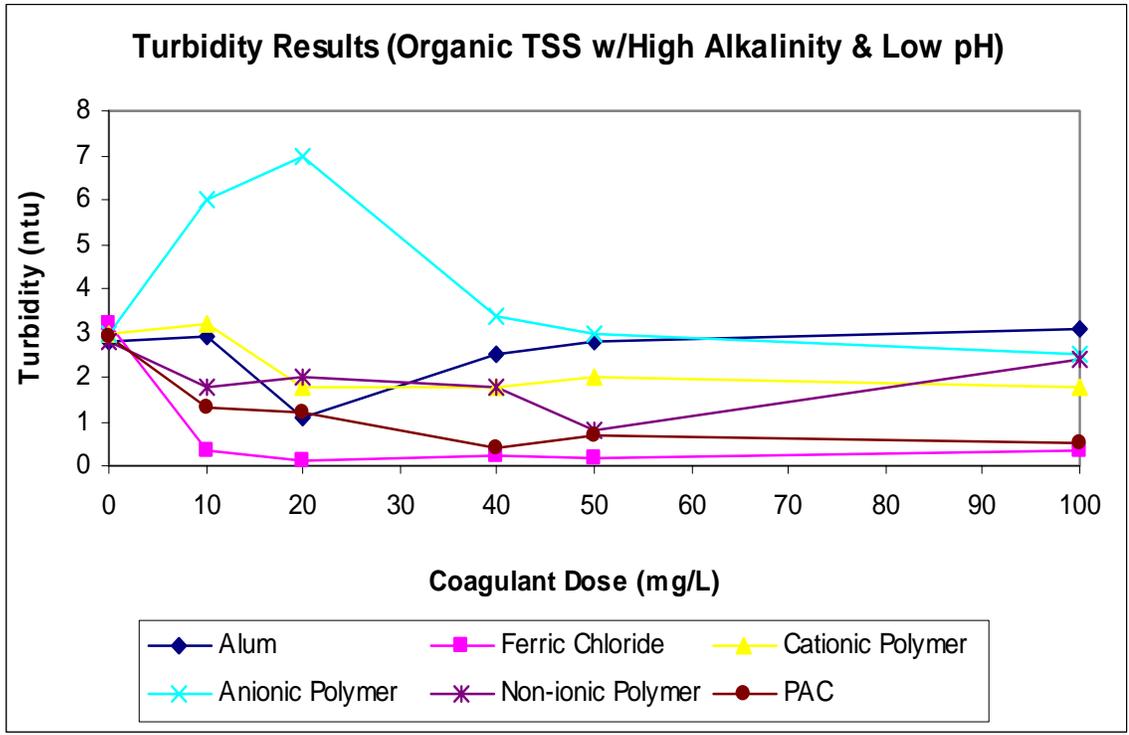
Figure 5.7 Turbidity Results of Worst case Jar Test with Organic TSS, High Alkalinity

and Low pH

Table 5.9 Accompanying Data for *Figure 5.7*

Concentration	Alum	FeCl$_3$	Cationic	Anionic	Non-ionic	PAC
0	2.8	3.2	3	3	2.8	2.9
10	2.9	0.34	3.2	6	1.8	1.3
20	1.1	0.1	1.8	7	2	1.2
40	2.5	0.25	1.8	3.4	1.8	0.4
50	2.8	0.2	2	3	0.8	0.7
100	3.1	0.35	1.8	2.5	2.4	0.5

5.2.2.2 *Turbidity Results with Low Alkalinity and High pH*

Upon examining the results in Figure 5.6 and Table 5.7, the data suggests that ferric chloride is clearly the most effective coagulation chemical. It achieves the desired turbidity levels after the initial 10 mg/L dose and maintains excellent levels throughout the dosing cycle. Anionic polymer coagulant also performs well in water with low alkalinity and high pH. Although not as effective as the ferric chloride, Anionic Polymer does remove turbidity to an acceptable level of 1.0 NTU and maintain an acceptable level for the entire dosing cycle as well. The cationic polymer and the PAC perform to standards after 20 mg/L of polymer are added and the PAC maintains its removal capabilities throughout the dosing cycle. After 100 mg/L, the cationic polymer turbidity reading is no longer acceptable. The non-ionic polymer initially removes some turbidity, but does not improve with additional amounts of coagulant added, and can only remove a small amount and does not remove to standard. Alum performs poorly in water with a concentration of high organic suspended solid content of 200 mg/L, high alkalinity content of 100 mg/L, and high oil concentration of 50 mg/L, but low hardness concentration of 50 mg/L and low pH . It increases turbidity to a high level upon the initial dosing and does not seem to further affect turbidity readings after that dosing. Subsequent doses neither improve nor increase turbidity readings.
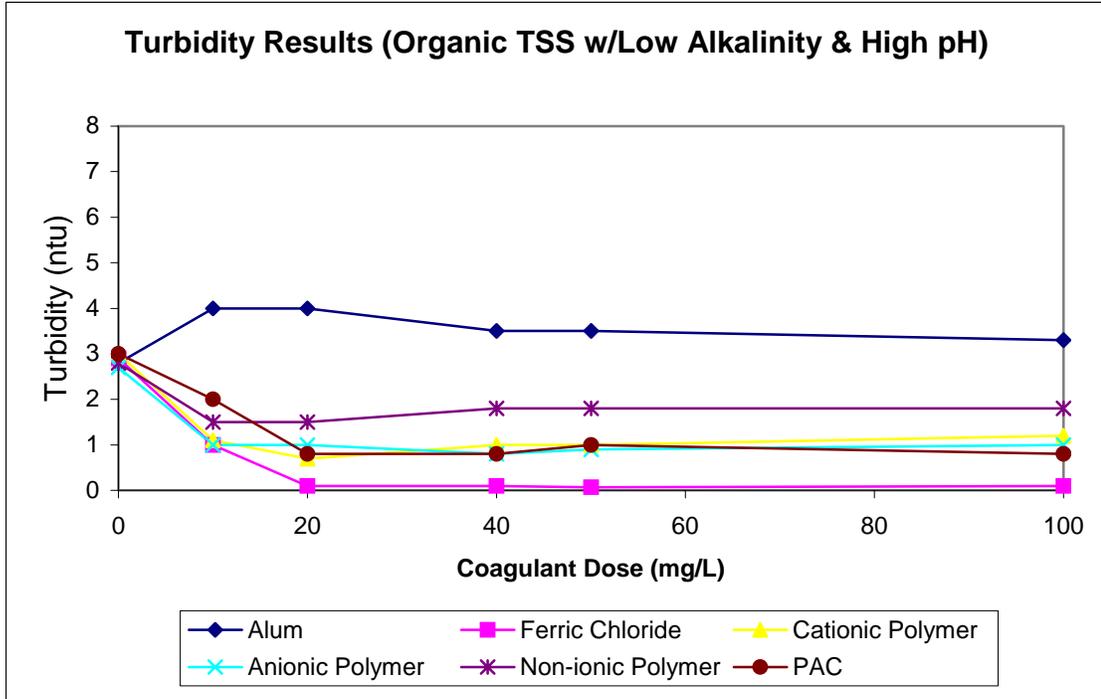
Figure 5.8 Turbidity Results of Worst case Jar Test with Organic TSS, Low Alkalinity

and High pH

Table 5.10 Accompanying Data for *Figure 5.8*

Concentration	Alum	FeCl$_3$	Cationic	Anionic	Non-ionic	PAC
0	2.8	2.9	3	2.7	2.8	3
10	4	1	1.1	1	1.5	2
20	4	0.1	0.7	1	1.5	0.8
40	3.5	0.1	1	0.8	1.8	0.8
50	3.5	0.07	1	0.9	1.8	1
100	3.3	0.1	1.2	1	1.8	0.8

5.2.2.3 *Turbidity Results with High Alkalinity and High pH*

Figure 5.7 and Table 5.8 reveals that in waters with a concentration of high organic suspended solid content of 200 mg/L, high alkalinity content of 100 mg/L, and high oil concentration of 50 mg/L, but low hardness concentration of 50 mg/L and low pH the initial doses of ferric chloride, anionic, non-ionic, and poly-aluminum chloride coagulants bring the water to acceptable turbidity levels and maintain them for the entire dosing cycle. Upon subsequent dosing of high alkalinity and high pH water the anionic polymer did not perform to turbidity standards after 50mg/L or more of the polymer was added. The ferric chloride basically removed all of the turbidity. Also the Alum was again ineffective in coagulating organic TSS or NOM.
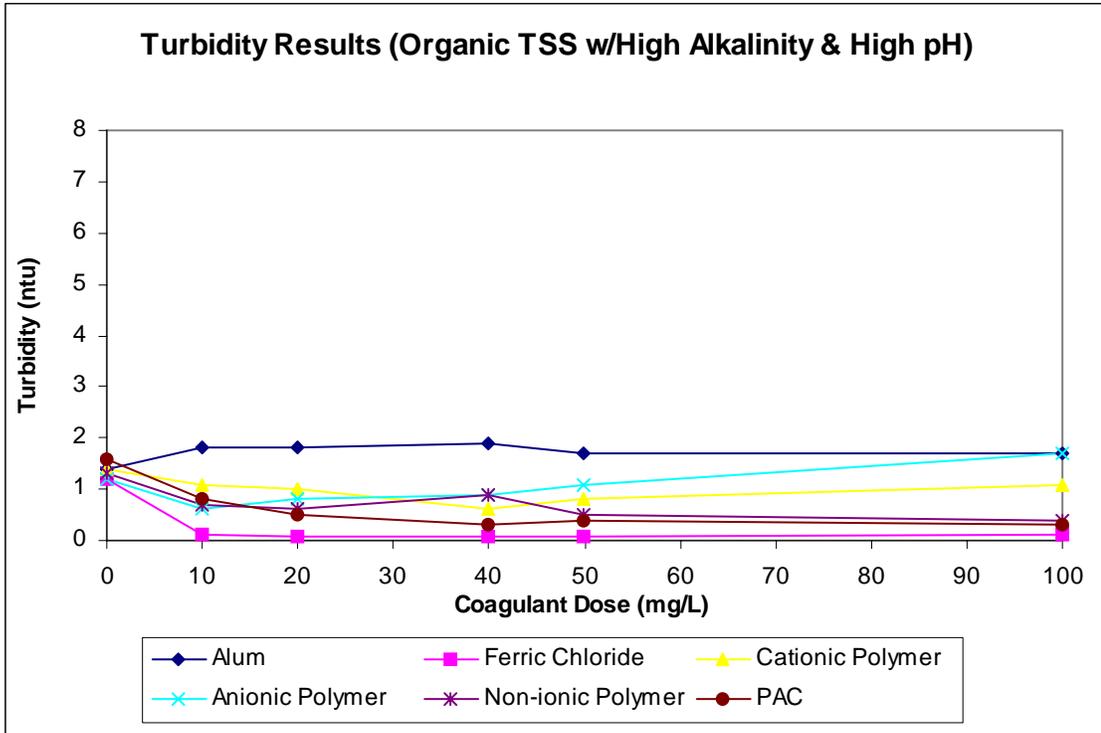
Figure 5.9 Turbidity Results of Worst case Jar Test with Organic TSS, High Alkalinity,

and High pH

Table 5.11 Accompanying Data for *Figure 5.5*

Concentration	Alum	FeCl$_3$	Cationic	Anionic	Non-ionic	PAC
0	1.4	1.2	1.4	1.2	1.3	1.6
10	1.8	0.13	1.1	0.6	0.7	0.8
20	1.8	0.08	1	0.8	0.6	0.5
40	1.9	0.09	0.6	0.9	0.9	0.3
50	1.7	0.06	0.8	1.1	0.5	0.4
100	1.7	0.1	1.1	1.7	0.4	0.3

5.2.2.4 *Turbidity Results with Low Alkalinity and Low pH*

Data displayed in Figure 5.8 and Table 5.9 show that turbidity readings for water with low alkalinity and low pH were low, indicating that waters with this particular composition will require little to no coagulant-aiding chemical for the water to meet specified turbidity levels. Regardless, a sample water with an alkalinity of 50 mg/L and pH of 6.0 was jar tested the same as the others. Here ferric chloride, non-ionic polymer, and poly-aluminum chloride all improved coagulation in the low alkaline and low ph concentration water. Initial cationic and anionic polymer coagulants enhanced coagulation and improved turbidity readings, but additional dosing of each of these coagulants increased turbidity in the waters in proportion to the increase in coagulant added. Alum again was ineffective in enhancing the coagulation process in the water because of the negatively charged organic colloidal particles in suspension.
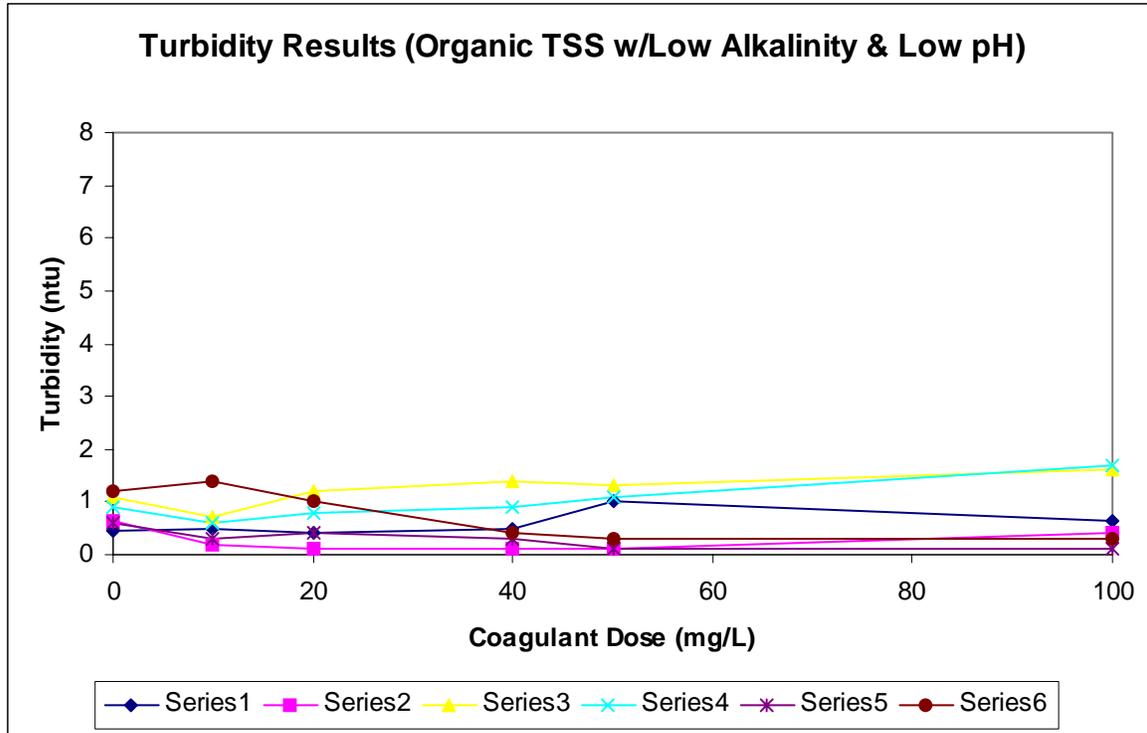
Figure 5.10 Turbidity Results of Worst case Jar Test with Organic TSS, Low Alkalinity

and Low pH

Table 5.12 Accompanying Data for *Figure 5.5*

Concentration	Alum	FeCl$_3$	Cationic	Anionic	Non-ionic	PAC
0	0.45	0.65	1.1	0.9	0.6	1.2
10	0.5	0.17	0.7	0.6	0.3	1.4
20	0.43	0.1	1.2	0.8	0.4	1
40	0.5	0.11	1.4	0.9	0.3	0.4
50	1	0.1	1.3	1.1	0.1	0.3
100	0.65	0.4	1.6	1.7	0.1	0.3

VI. CONCLUSIONS

The results of this research clearly verify that different coagulants with varying properties behave differently as far as treatment efficiency and results under different conditions. They performed differently in waters with organic total suspended solids than they do in those with inorganic total suspended solids. Cationic polymers and Alum are not very effective in treating water with Natural Organic Matter because they have similar electrical charges and repel each other rather than attract or allow themselves to be be in contact with each other so that they may coagulate and agglomerate. Conversely they usually perform well in waters with higher inorganic solids content due to the fact that inorganic solids usually exhibit a negative charge and attract or coagulate with positive ions in the water. Further, they perform differently in those same waters at different pH and alkalinity content levels as well.

In terms of general suspended solid removal, all coagulants performed better overall in waters contaminated with organic particulate than with inorganic contaminates, with some such as being outstanding and some poor. Ferric chloride performed well in water with organic and inorganic total suspended solids and with high and low concentrations of alkalinity and pH. PAC performed well in all situations as well, but not quite as good as ferric chloride. Anionic Polymer coagulant performed best in waters with inorganic TSS and was not greatly affected by pH values. Cationic Polymer performed

best in Organic TSS situations with higher pH values that it did in waters with Inorganic

solids and lower pH. Nonionic Polymer did not perform very well in any situation in

small amounts but performance improved when greater amounts (in excess of 50 mg/L)

were added to low ph, organic TSS waters. Alum, which is what the Auburn Water

treatment Facility usually uses, performed best in water with Organic Suspended solids

than it did with water with inorganic suspended solids concentration and it performed

best in Low pH conditions in most cases.

6.1 *Organic Total Suspended Solids*

In the testing where organic total suspended solids were used, ferric chloride was the

best performer as far as turbidity and color removal under every tested condition. Ferric

chloride performed equally as well in water contaminated with organic solids as it did in

waters contaminated with inorganic solids and it performed in waters with high and low

ph levels and alkalinity content. There was not a test condition where the initial addition

of 10 mg/L ferric chloride was not sufficient in bringing turbidity readings in the water to

1NTU or less, and only one situation where the turbidity reading was more than 0.4 NTU.

The anionic and non-ionic polymers performed next best in the waters with organic total

suspended solids. The anionic and non-ionic polymers both performed better ultimately

under low ph with low alkalinity water and high ph with high alkalinity water conditions

than in the low pH with high alkalinity water or high pH with low alkalinity combination

of variables. The water treated with anionic and nonionic high alkalinity/high pH

variable combinations both brought turbidity levels to less than 1ntu after the initial 10

mg/L doses were added, while the low alkalinity/low pH combinations treated with the

two polymers never ultimately came into a reliable compliance. As can be seen in figures

5.1 through 5.8, polyaluminum chloride (PAC) performed well in the water with high pH

levels, but was less effective in the waters having lower pH. High pH water turbidity

levels were below 1 NTU after 10-20 mg/L PAC dosing, while lower pH water needed

twice as much to achieve acceptable turbidity readings. The cationic polymer performed

to standards with the addition of 40-50 mg/L to water with high pH and high alkalinity.

Upon additional coagulant to these water conditions, the turbidity results increased,

indicating a decreased ability to coagulate due to overdosing. Cationic polymer was

ineffective on organic matter period. Turbidity readings of all waters treated with alum

possessing organic total suspended solids increased in every individual jar test performed

and measured. The measured test results of alum coagulation performance indicates that

alum serves to greatly increase turbidity levels in waters that were contaminated with

organic particulate rather than remove it, and that any efforts to coagulate organic

colloidal particles with it under conditions similar to those investigated will more than

likely prove unsuccessful.

6.2 *Inorganic Total Suspended Solids*

   Jar tests conducted using inorganic suspended solids yielded some similar coagulation

performance results as far as performance ranking goes. Ferric chloride was the best

performing coagulant under all investigated test conditions using inorganic particulate.

Ferric chloride coagulant consistently brought turbidity levels well below 1.0 NTU upon

initial dosing of 10 mg/L. In all but one reading, results were measured below 0.2 ntu,

and the one exception yielded a measurement of 0.35 NTU. The next best performing

polymer was the polyaluminum chloride (PAC). It performed best under high pH and

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low alkaline conditions in treating water with organic TSS and worst at low pH and high alkaline conditions. Turbidity measurements were within standards after the initial 10 mg/L dosing and in the worst case, 50 mg/L were required to bring the measurement below 1.0 NTU. The anionic polymer performed next best, and a little better than the non-ionic polymer. The anionic polymer performed well in waters with high alkaline/low pH concentrations, low alkaline/low pH concentrations and the high alkaline/high pH water. In all three of these waters, the turbidity levels measured 0.6 ntu after the initial 10 mg/L dose, which is well below 1.0 NTU. In the last case, the readings were at or just below 1.0 NTU after the initial dose. The non-ionic polymer performed best in two different water and variable combinations. The non-ionic polymer performed best in water with low alkalinity and low pH solution and the and in water with high alkalinity solution and high pH. In these two water types, non-ionic polymer brought turbidity readings down to acceptable levels of no higher than 1.0 NTU after the initial dosing. In the water with high alkalinity and low pH value, the non-ionic polymer brought the water into compliance after a 50 mg/L dose was added, but fell out of compliance after the 100 mg/L dosing. The cationic polymer was ineffective at removing turbidity in water with high alkalinity and low pH value. Only after a 10 mg/L dosing of the low alkaline, low pH water, a 30 mg/L dosing of the low alkaline, high pH water, and 40-50 mg/L dose of the high alkaline and high pH water was the turbidity ever reduced to below 1.0 NTU. 40 and 50 mg/L dosing of this same water brought levels to 1.0 NTU, but not lower. All other testing of cationic polymer under these conditions was ineffective. In the water consisting of low alkaline and low pH concentration, alum performed well, bringing the water into compliance after initial dosing and keeping it

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there throughout the dosing cycle. In all other water variable combinations, served to greatly enhance turbidity rather than reduce it, sometimes doubling turbidity measurements. Overall performance of the alum was poor under these conditions as well.

In conclusion, ferric chloride performed the best under all conditions and alum performed worst based on the experimental data gathered in this research. The polymers performed generally well, with the anionic performing better than the cationic in most situations.   Since Auburn Water Treatment Facility uses alum as its primary coagulant for water treatment, the coagulation problem was most likely due to the introduction of some inorganic substance or some other material whose turbidity causing particles were positively charged as were the ions in the Alum.

VII. RECOMMENDATIONS

The results of this research successfully demonstrated the performance of the six different coagulants studied under most common varying conditions of a source water quality which are pH, alkalinity, and the organic and inorganic characteristics of turbidity causing colloidal particle present in the water. However, there are certain areas where future research could be improved or focused and steps that a municipal could take to treat waters that exhibit persistent turbidity levels despite traditional treatment methods.

1.0 Sample Collection and Testing

The major aspect of this research that could have made a difference in the results would be the common characteristics of the laboratory prepared waters and the actual water that would not coagulate in the Auburn Water Works Treatment Facility. Based on previous research conducted on similar occurrences and observations in and around the treatment plant, it is logical to hypothesize probable and possible contaminates that may have entered the system and prevented the alum used in the process from causing coagulation to occur, but without an actual sample of the water in question, a definitive cause is difficult to determine. If there were some way that some of the actual water that experienced the coagulation problems could have been retained and some type of testing or research could have been conducted on it, some simple explanation may have been

ascertained for the irregular behavior exhibited by the water and the coagulant combination. But since this did not happen, we must rely on laboratory samples that attempt to simulate possible contaminated water characteristics. The actual water would have made the research more specific in that it would have directly addressed the problem at its source.

1.0 Alternate Coagulants on Site

Based on this research and countless other investigations, it has certainly evident that any one coagulant does not always perform to standard in every situation. It is also obvious that the characteristics of a municipal water treatment plant's sourcewater changes constantly due to the instability of nature and may often do so without warning, changing the characteristics that a coagulant and/or treatment process must address. For these reasons, a treatment plant should always have alternate coagulants either on site or available at a moments notice in order to be more ready to address these sudden and sometimes extenuating circumstances that will probably occur occasionally.

VIII. REFERENCES

Amirtharajah, A., and C. R. O'Melia (1990) Coagulation Processes: Destabilization, Mixing, and Flocculation. p. 269-361., Water Quality and Treatment. AWWA, New York, N.Y, McGraw-Hill, Inc.

Amirtharajah, A., M. M. Clark, and R. R. Trussell (1991) Mixing in Coagulation and Flocculation. AWWARF, Denver, CO, AWWA.

Berube, Margery S (2001). Webster's II New College Dictionary. P. 213, Houghton Mifflin Co.

Cheremisinoff, N. P. (2002). Handbook of Water and Wastewater Treatment Technologies. Woburn, MA, Butterworth-Heinemann.

Clark, M..M. (1996). Transport Modeling for Environmental Engineers and Scientists. New York, NY, John Wiley and Sons.

Dobiáš, Bohuslav (1993). Coagulation and Flocculation: Theory and Applications. New York, NY, Marcell Dekker, Inc.

Faust and Aly (1987). Adsorption Processes for Water Treatment. Stoneham, MA, Butterworth Publishers.

Faust and Aly (1998). Chemistry of Water Treatment., Chealsea, MI, Ann Arbor Press, Inc.

Fryters, T. (2002). Removal of Total Organic Carbons from Drinking Water. *Technical Services, Hydro-Tech Limited:* 1-10.

Kramer, T. A. (2000). Analytical solutions for Bikenitic Coagulation: Incorporation of a Maximum Size Class. *Journal of colloid and Interface Science,* **216**, 116

Fulton, George P. (1998). Master Planning and Treatment Process Selection. p.7-20., Water Treatment Plant Design. New York, NY, AWWA, McGraw-Hill, Inc.

Montgomery, J. M. (1985). Water Treatment Principles and Design. New York, N.Y., John Wiley and Sons, Inc.

Riesman, Warren and Mark J. Hammer (1998). Water Supply and Pollution Control.
    Menlo Park, CA, Addison Wesley Longman, Inc.

Scott, K. N., et al. (1995). Arsenic Removal by Coagulation. *AWWA Journal*: 114-126.

Snoeyink, V.L. and D. Jenkins (1980). Water Chemistry. Canada, John Wiley and Sons,
    Inc.

APPENDIX

PHASE I JAR TEST DATA

Table 5.13: Phase I Inorganic Solid Variable Matrix Jar Test Results Data

Jar Test #	Color	Turbidity
0	0	0
1	9.5	1.083
2	15.17	1
3	6.667	0.883
4	21.83	3.567
5	6.667	1.75
6	9	0.73
7	26.17	3.975
8	6.667	1.567
9	4.333	0.875
10	8.333	1.433
11	6.333	1.667
12	11.333	0.917
13	20.83	2.633
14	6.333	0.917
15	7.167	1.183
16	42.83	7.867

Table 5.14: Phase I Organic Solid Variable Matrix Jar Test Results Data

Jar Test #	Color	Turbidity
0	0	0
1	0.167	1.7
2	0.167	0.462
3	1.83	0.58
4	0.33	2
5	3.16	0.572
6	7	0.997
7	18.83	2.467
8	0.667	0.397
9	0	0.405
10	3.5	1
11	9.833	1.867
12	0.4	0.367
13	2.5	0.621
14	4.83	0.918
15	1.667	0.513
16	9.333	0.975