The Effect of Selected Coagulants on Chloride-to-Sulfate Mass Ratio for Lead Control and on Organics Removal in Two Source Waters

by

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Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

Abstract

Lead is a known toxin, with the ability to accumulate in the human body from as early as fetal development. Lead exposure is known to cause a myriad of health effects which are more prominent among children. Health effects upon exposure can range from renal and heart disease or potentially cancer in adults to neurotoxicity in children.

The continued presence of old lead service lines and plumbing in distribution systems as well as lead-containing solders and brass fixtures in homes may contribute lead to drinking water. Recent studies have highlighted the importance of a predictor known as the chloride-to-sulfate mass ratio (CSMR) in controlling lead release. A ratio above 0.5 – 0.6 theoretically increases the aggressiveness of lead leaching in galvanic settings, while a lower ratio controls lead corrosion. A switch in coagulant type could significantly alter the ratio. However, a coagulant switch could also trigger changes in finished water turbidity and organics, including disinfection by-product (DBP) precursors, as well as impact sludge production.

Anecdotal evidence from an Ontario water treatment utility suggested the potential applicability of a newly formulated polymer, cationic activated silica (CAS), in improving DBP precursor removal when used in concurrence with a primary coagulant. No previous scientific research had been dedicated to testing of the polymer.

The present research had three primary objectives: The first was to investigate the effect of conventional coagulation with six different coagulants on the chloride-to-sulfate mass ratio as it pertains to lead corrosion in two Ontario source waters of differing quality. Additionally, the effect of coagulant choice on pH, turbidity, and organics removal was investigated. The second objective was aimed at testing potential reductions in CSMR and organics that could be brought about by the use of two polymers, cationic and anionic activated silica (CAS and AAS, respectively), as flocculant aids. Finally, the performance of a high-rate sand-ballasted clarification process was simulated at bench-scale to gauge its performance in comparison with conventional coagulation simulation techniques.

The first series of jar-tests investigated the effectiveness of CAS as a primary coagulant on Lake Ontario water. In comparison with the conventional coagulants aluminum sulfate and polyaluminum chloride, CAS did not offer any apparent advantage with respect to turbidity and organics removal.

Testing of CAS and AAS as flocculant aids was also conducted. Results from a full factorial experiment focused on CAS testing on Lake Ontario water showed that coagulant dose is the most significant contributor to CSMR, turbidity, DOC removal, and THM control. Generally, improvements resulting from CAS addition were of small magnitude (<15%). Reductions in CSMR were attributed to the presence of the sulfate-containing chemicals alum and sulfuric acid in the CAS formulation. Testing of sulfuric acid-activated AAS on Grand River water showed that pairing of AAS with polyaluminum chloride provides better results than with alum with respect to DOC removal (39% and 27% respectively at 60 mg/L coagulant dose). Highest turbidity removals (>90%) with both coagulants were achieved at the tested coagulant and AAS doses of 10 mg/L and 4 mg/L respectively. CSMR reductions in the presence of AAS were also attributable to sulfate contribution from sulfuric acid. Bench-scale simulation of a high-rate sand-ballasted clarification process on Grand River water showed comparable removal efficiencies for turbidity (80 – 90% at 10 mg/L), and DOC (30 – 40% at 50 mg/L).

Finally, six different coagulants were tested on the two source waters for potential applicability in CSMR adjustment in the context of lead corrosion. The two chloride-containing coagulants polyaluminum chloride and aluminum chlorohydrate increased CSMR in proportion to the coagulant dose added, as would be expected. Average chloride contribution per 10 mg/L coagulant dose was 2.7 mg/L and 2.0 mg/L for polyaluminum chloride and aluminum chlorohydrate, respectively. Sulfate-contributing coagulants aluminum sulfate, ferric sulfate, pre-hydroxylated aluminum sulfate, and polyaluminum silicate sulfate reduced CSMR as coagulant dose increased, also as would be expected. The highest sulfate contributors per 10 mg/L dose were pre-hydroxylated aluminum sulfate (6.2 mg/L) and ferric sulfate (6.0 mg/L). The lowest CSMR achieved was 0.6 in Lake Ontario water at a 30 mg/L dose and 0.8 in Grand River water at a 60 mg/L dose. Highest DOC removals were achieved with the chloride-containing coagulants in both waters (35 – 50%) with aluminum chlorohydrate showing superiority in that respect. DOC removals with sulfate-containing coagulants were less, generally in the range of 22 – 41%.

Specificity of critical CSMR values to source water needs to be investigated. Additionally, long term effects of sustained high or low CSMR values in distribution systems need to be further looked into. Finally, the effect of interventions to alter CSMR on other water quality parameters influencing lead corrosion such as pH and alkalinity still represent a research deficit.

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To my mother and father,

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Glossary

AAS	Anionic activated silica
Alum	Aluminum sulfate
CAS	Cationic activated silica
CSMR	Chloride-to-sulfate mass ratio
DBPs	Disinfection by-products
DIC	Dissolved inorganic carbon
DO	Dissolved oxygen
DOC	Dissolved organic carbon
DWSP	Drinking Water Surveillance Program
GRCA	Grand River Conservation Authority
HAAFP	Haloacetic acid formation potential
LCR	Lead and Copper Rule
MAC	Maximum acceptable concentration
MOE	Ministry of Environment
NOM	Natural organic matter
ORP	Oxidation-reduction potential
PACl	Polyaluminum chloride
PASS 100	Polyaluminum silicate sulfate
PAX-XL 1900	Aluminum chlorohydrate
PHAS	Pre-hydroxylated aluminum sulfate
SDS-THM	Simulated distribution system trihalomethane
SHE	Standard hydrogen electrode
SUVA	Specific UV absorbance
THM	Trihalomethane
TIC	Total inorganic carbon
TOC	Total organic carbon
USEPA	U.S. Environmental Protection Agency
UV_{254}	UV absorbance (254 nm)
WHO	World Health Organization
WTP	Water treatment plant

Chapter 1 INTRODUCTION

1.1 Background

1.1.1 Lead in drinking water

Lead is widely recognized as a toxin. Health effects can range from renal and heart disease, premature birth, and cancer in adults to impaired neurological and bone development in pediatric populations (USEPA, 2008; Health Canada, 2007; Deng and Poretz, 2001; Masters and Coplan, 1999; Hamilton and Flaherty, 1995). Despite the ban on the use of lead pipes for the conveyance of drinking water in the US and Canada, particulate and dissolved lead in drinking water may still source from old lead service lines and plumbing and from the use of lead-containing solder and brass fixtures (Vasquez et al., 2006; Kimbrough, 2007; Triantafyllidou et al., 2007; Edwards and Triantafyllidou, 2007).

Recent experimental and utility evidence has highlighted the importance of the chloride-to-sulfate mass ratio as one of the factors controlling lead release in potable water (Edwards and Triantafyllidou, 2007; Edwards et al., 1999). Ratios below 0.5 – 0.6 tend to control lead corrosion while higher ratios trigger lead release at galvanic connections (Edwards and Triantafyllidou, 2007). Water utility practices such as coagulant choice and the use of anion exchange (a more limited practice) are the predominant contributors to the ratio (Edwards and Triantafyllidou, 2007), though disinfectant dose and type may also play a role.

While a coagulant switch has the ability to substantially influence the chloride-to-sulfate mass ratio of the water, the cascade of processes following coagulation will also be impacted. The most noticeable change(s) in water quality that may result from a coagulant switch are the removal efficiencies of turbidity and organics, specifically those implicated in the formation of disinfection by-products.

1.1.2 Coagulants and flocculant aids

Commonly used coagulants in drinking water treatment can generally be classified into two groups; those based on aluminum, and those based on iron. Aluminum and iron based coagulants are popular due to their efficiency, relatively low cost, and abundance. Some examples include: aluminum sulfate (alum), polyaluminum chloride (PACl), ferric sulfate, aluminum chlorohydrate, pre-hydroxylated aluminum sulfate, and polyaluminum silicate sulfate. The application of the former 3 coagulants is common in drinking water treatment while relatively little is known about the applicability of the latter 3 coagulants with respect to CSMR adjustment and DBP control.

The utilization of polymers as flocculant aids in drinking water treatment has been documented to be advantageous in the reduction of coagulant dose requirements and hence metal residuals in the treated water (Bolto and Gregory, 2007). Increased filter run time and reductions in floc volume are also potential advantages of the use of polymers, which can also be used as coagulant aids. This propagates to overall cost reductions for a water treatment utility. Additionally, polymer performance is less sensitive to variations in raw water temperature and pH (Graham et al., 2008) which would consequently result in the production of finished waters of more consistent quality. Being of high molecular weight, polymers exhibit their advantages by improving the settleability and toughness of the formed flocs.

Two examples of silica-based polymers of potential application in drinking water treatment are anionic and cationic activated silica. Anionic activated silica is commonly applied as a flocculant aid, with alum or polyaluminum chloride as the primary coagulants. Anecdotal evidence from a water treatment utility in Ontario suggested the potential applicability of the new silica-based polymer, cationic activated silica, in increasing the removal efficiency of DBP precursors when used as a flocculant aid. The potential applicability of that polymer in drinking water treatment therefore warranted further research into the subject.

1.1.3 Disinfection by-products in drinking water

The practice of employing chlorination for the inactivation of pathogenic organisms in potable water is by far the most common disinfection method employed in water treatment utilities (Clark and Sivangensen, 1998) although UV is increasingly being used. Though it has demonstrated its ability to efficiently reduce disease-causing agents in the water, chlorination can result in the formation of toxicological and carcinogenic disinfection by-products (DBPs) when chlorine reacts with natural organic matter (NOM) (Rodriguez, 2007; Pirkle, 2007). The presence of bromide will contribute to the production of brominated DBPs. An important class of chlorinated disinfection by-products is trihalomethanes (THMs), which include chloroform, dichlorobromomethane (DCBM), dibromochloromethane (DBCM), and bromoform (Rodriguez, 2007).

In light of the detrimental health effects associated with the presence of chlorinated DBPs in potable water, maximum allowable concentrations of THMs have been set by regulatory agencies in the US and Canada to 80 µg/L and 100 µg/L respectively (USEPA, 2008; MOE, 2008). Stringent regulations with respect to chlorinated DBP concentrations in potable water have in some cases necessitated the removal of DBP precursors and natural organic matter (NOM) prior to disinfection. Coagulation and flocculation can achieve NOM removal from water to address such a goal.

1.2 Research motivation and objectives

In their research, Edwards and Triantafyllidou (2007) highlighted the importance of coagulant choice on the chloride-to-sulfate mass ratio and consequently galvanic lead release in potable water. However, the individual effect of different coagulants on the chloride-to-sulfate mass ratio has not been previously compared.

Previous scientific research pertaining to the application of the newly developed polymer cationic activated silica in drinking water treatment is not currently available, either for CSMR adjustment or as a flocculation aid.

To address these deficiencies, bench-scale jar testing was conducted on two substantially different Ontario surface waters with the following main objectives:

1. To investigate the effect of conventional coagulation and flocculation with new and existing coagulants on chloride-to-sulfate mass ratio.

2. In parallel, evaluate the effect of changing coagulants and dosages on pH, turbidity, and organics removal.

3. To investigate the effect of anionic and cationic activated silica, typically used as flocculation aids, on CSMR, pH, turbidity, and organics removal.

4. For the case of a high-rate sand-ballasted clarification process for the coagulation/flocculation of water, to validate the use of standard jar test procedures by comparing them to a bench-scale jar test apparatus that was designed to simulate the performance of the sand-ballasted clarification process.

1.3 Thesis organization

Chapter 2 of this thesis provides relevant background information on coagulation and flocculation including mechanisms and commonly used chemicals. The chemistry, sources, toxicity, and corrosion of lead are also discussed.

The equipment, analysis methods, and chemicals employed in this research are discussed in detail in Chapter 3.

Chapters 4 and 5 explore the experimental designs and results pertaining to tests conducted on Lake Ontario and Grand River waters, respectively. Chapter 6 provides an insight into coagulant performance by comparing results from the two waters at the common doses tested.

Finally, Chapter 7 provides a list of conclusions from this research and recommendations for future research.

Chapter 2 LITERATURE REVIEW

2.1 Natural organic matter

Natural organic matter (NOM) can be described as a heterogeneous collection of organic substances with varying molecular weight, structure, and acidity. NOM may originate from decaying vegetation, aquatic biomass, soil, or from aquatic organisms (Sharp et al., 2006; Fabris et al., 2008; Lovins et al., 2003). The organic material present in NOM predominantly contains phenolic and carboxylic functional groups. Hydroxyl radicals may also be present (Srinivasan and Viraraghavan, 2004; Tseng and Edwards, 1999).

The presence of elevated levels of NOM in water is highly undesirable since it contributes to color and may cause unpleasant taste and odours. In addition, NOM may induce microbial growth, affect coagulant dose, cause membrane fouling, and reduce the availability of adsorption sites in activated carbon filters during treatment (Fabris et al., 2008; Bolto and Gregory, 2007). More importantly, NOM that is not removed during treatment may react with oxidants to produce disinfection by-products (DBPs). Many of the DBPs so formed are halogenated organic compounds known or suspected to have carcinogenic effects on humans (Tan et al., 2005). The two most common types of DBPs in terms of quantities formed are trihalomethanes (THMs) and haloacetic acids (HAAs). THMs were first discovered in disinfected waters in 1974 and are suspected to induce bladder and colorectal cancers, as well as birth defects in humans (Simpson and Hayes, 1998). HAAs showed potential to induce liver tumours in animals and are believed to have the same effects on humans (Kleiser and Frimmel, 2000). As such, removal of elevated levels of NOM from the water is highly desirable.

NOM can be broadly classified into two main groups, namely non-humic and humic solutes. Non-humic solutes include relatively simple compounds belonging to carbohydrates, amino acids, lipids, hydrocarbons, as well as other well known classes of organic compounds (Fabris et al., 2008). On the other hand, humic substances incorporate a highly heterogeneous mixture of solutes with varying acidities (pK_a 3 – 5), molecular weights (hundreds to thousands), and molecular structure (predominantly phenolic and carboxylic). Humic substances exhibit surface active properties via the presence of aliphatic and aromatic regions in their structure (Bolto and Gregory, 2007). Humic substances are often described as weak anionic polymers since they are negatively charged at typical pH values (Sharp et al., 2006). Humic substances may further be classified into two fractions based on molecular weight (MW) and response to a specific fractionation procedure, namely fulvic (MW: 200 – 1000 g/mole) and humic (MW: up to 200,000 g/mole) (MWH, 2005).

Direct measurement of concentrations of various NOM components in water is challenging due to the complex nature of its constituents and the virtually countless number of compounds that would have to be measured. As such, certain surrogate or global, easily measured parameters can be used to quantify NOM presence in the water of which the most common are total organic carbon (TOC) (Lovins et al., 2003) and dissolved organic carbon (DOC) (Bolto and Gregory, 2007). TOC analyzes for dissolved and suspended organic matter through the complete oxidation of NOM and the measurement of the resulting CO_2 (MWH, 2005). DOC incorporates those compounds which will pass through a 45 µm filter and typically constitutes 90 % of TOC. The global average of DOC in natural waters was reported by Bolto and Gregory (2007) as 5.75 mg/L.

2.2 Coagulation and flocculation

Chemical coagulation can be defined as the process whereby the destabilization of a colloidal suspension is achieved through chemical addition. The primary goal of coagulation is to overcome the colloidal stability in a given system. This is achieved by rapid mixing of a coagulant in solution for short durations in order to achieve complete and uniform coagulant dispersion. Insufficient coagulant mixing may result in uneven coagulant dispersion throughout the solution, resulting in the presence of too much coagulant in certain areas and too little in others thereby degrading the overall process. Coagulant over-mixing on the other hand is not believed to have an effect on coagulation performance. During rapid mix, primary aggregates or “flocs” may form. Flocculation is the process of inducing the destabilized particles resulting from coagulation to attach or agglomerate together thereby forming larger “flocs” that can more readily be settled (Bratby, 2006; Horne, 2005).

Particulate destabilization through coagulation by metal salts can occur via two mechanisms, namely charge neutralization and complexation/precipitation or colloid enmeshment. Both mechanisms may occur concurrently during coagulation of drinking water. In charge neutralization, cationic hydrolyzed and prehydrolyzed metal salts as well as polymers can adsorb to the anionic particulates predominantly present in the water thereby neutralizing the charge on the colloid surface. This will consequently enhance the ability of the particulates to agglomerate (flocculate) together due to the elimination of electrostatic inter-particle repulsion. Overdosing of the coagulant may cause charge reversal and colloid restabilization. During colloid enmeshment, insoluble metal hydroxides (such as $Al(OH)_3$ from alum) form and entrap colloids during their formation. Additional removal may potentially be established through colloid adsorption to the insoluble metal salts as they precipitate. Enmeshment predominates at high coagulant doses and high pH (Pernitsky and Edzwald, 2006; Alshikh, 2007; Sharp et al., 2006; Bratby, 2006; Horne, 2005; MWH, 2005).

2.2.1 Enhanced coagulation

Enhanced coagulation (EC) is an optimization process aimed to achieve both turbidity and NOM removal (DOC more specifically). Optimization necessitates proper coagulant selection, proper coagulant dispersal in solution, and more importantly, pH adjustment (usually pH reduction) in order to achieve optimal removal efficiencies with the chosen coagulant (Allpike et al., 2005; Childress et al., 1999). Sharp et al. (2006) reports that the optimum pH for iron based coagulants is in the range of 4.5 – 5.5 while that for aluminum based coagulants is in the range of 5 – 6.

At lower pH, DOC removal using enhanced coagulation was believed to have been achieved via colloid enmeshment which not only involved the precipitation of metal salts in solution, but also the formation of insoluble metal humates and fulvates (Vrijenhoek et al., 1998). Childress et al. (1999) also reported that charge neutralization could be in effect during enhanced coagulation.

Figure 2-1 shows results from work conducted by Boyer and Singer (2005) to determine the effect of enhanced coagulation with alum on parameters such as UV_{254} absorbance, dissolved organic carbon (DOC), trihalomethane formation potential (THMFP), and haloacetic acid formation potential (HAAFP) from four source waters. As illustrated, removal efficiencies of up to 45 % (UV_{254}) were observed in a water which coincidentally had higher humic content (higher SUVA). Enhanced coagulation therefore shows improved performance in high SUVA waters.

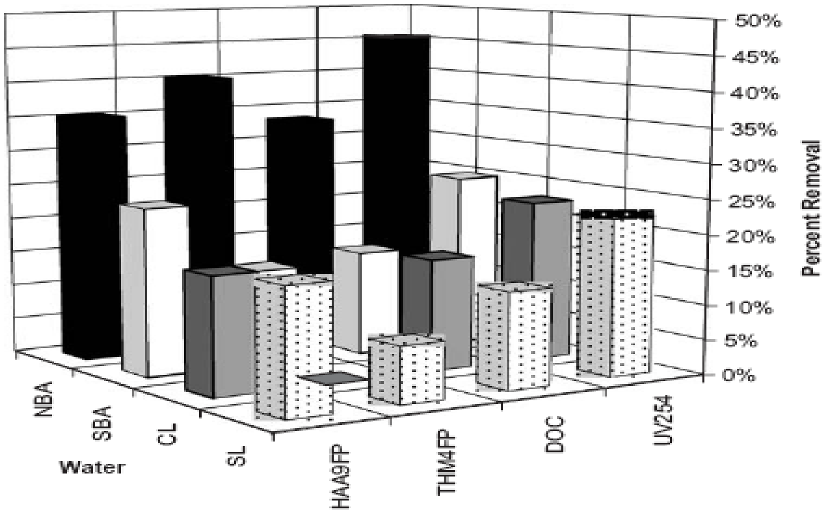


Figure 2-1: Effect of enhanced coagulation on four surface waters with different SUVA

(Reprinted by permission of the Journal of Water Research, from “Bench-scale testing of a magnetic ion exchange resin for the removal of disinfection by-product precursors”, by Boyer, T., and Singer, P. (2005), Water Research Vol. 39, No. 7)

The effectiveness of ferric chloride in enhanced coagulation was tested in experiments conducted by Childress et al. (1999). It was concluded that high coagulant doses (> 16 mg/L) and lower water pH (5.5) favoured enhanced coagulation. At optimal enhanced coagulation conditions, TOC and UV254 removals were 48% and 53% respectively and the removal of the higher molecular weight fraction of NOM was favoured.

2.2.2 Coagulants

The most commonly used coagulants are metal salts. These are generally classified into two groups; those based on aluminum, and those based on iron. Aluminum and iron based coagulants are popular due to their relatively low cost and their abundance. Some examples include: aluminum sulfate (alum), polyaluminum chloride (PACl), ferric sulfate, aluminum chlorohydrate, pre-hydroxylated aluminum sulfate, and aluminum hydroxide sulfate (also known as polyaluminum silicate sulfate). The application of the first four chemicals in drinking water treatment has been documented, while the application of aluminum hydroxide sulfate has been documented for industrial wastewater treatment. Little is known about the application of pre-hydroxylated aluminum sulfate. All coagulants can form polynuclear complexes in solution, which may be a function of pH (Bratby, 2006).

This section briefly discusses the chemical and physical characteristics of selected representative coagulants.

Aluminum sulfate (alum): is the most common coagulant used in drinking water treatment. It has a formula of $Al_2(SO_4)_3.14H_2O$ or $Al_2(SO_4)_3.18H_2O$ and has an aluminum content close to 9% as Al (Bratby, 2006). The addition of alum to a solution immediately followed by proper rapid mixing will result in the dissolution of aluminum sulfate to form $Al(H_2O)_6^{3+}$ (more commonly represented as Al^{3+}). This is followed by the hydrolysis of Al^{3+} to form dissolved Al species such as $Al(OH)^{2+}$, $Al(OH)_2^{1+}$, or $Al(OH)_4^{1-}$ or a precipitate such as $Al(OH)_3(s)$. In addition, polymerization of Al species may occur to form $Al_{13}(OH)_{24}^{7+}$. However aluminum polymers are not normally present during normal coagulation conditions (Pernitsky and Edzwald, 2006).

Al speciation is a function of pH and temperature as shown in Figure 2-2. At a given temperature, lower pH values will result in the predomination of the strongly charged Al^{3+} species, as in pH below 5 for water at 20°C. Increasing pH will result in the domination of Al species with lower positive charges, and eventually the domination of the negatively charged $Al(OH)_4^{1-}$ at $pH > 6.5$. At lower temperatures, positively charged Al species may form at relatively higher pH values (Pernitsky and Edzwald, 2006). Iron containing coagulants are also known to behave in a similar fashion to alum.

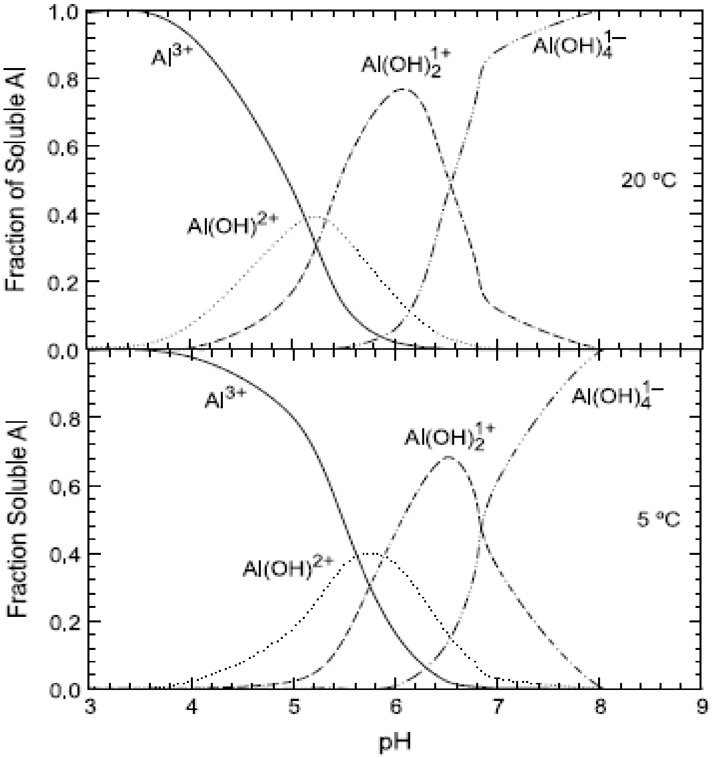


Figure 2-2: Effect of temperature and pH on Al speciation for alum solutions

(Reprinted by permission of the Journal of Water Supply: Research and Technology - AQUA, from "Selection of alum and polyaluminum coagulants: principles and applications", by Pernitsky, D., and Edzwald, J. (2006), AQUA Vol. 55, No. 2)

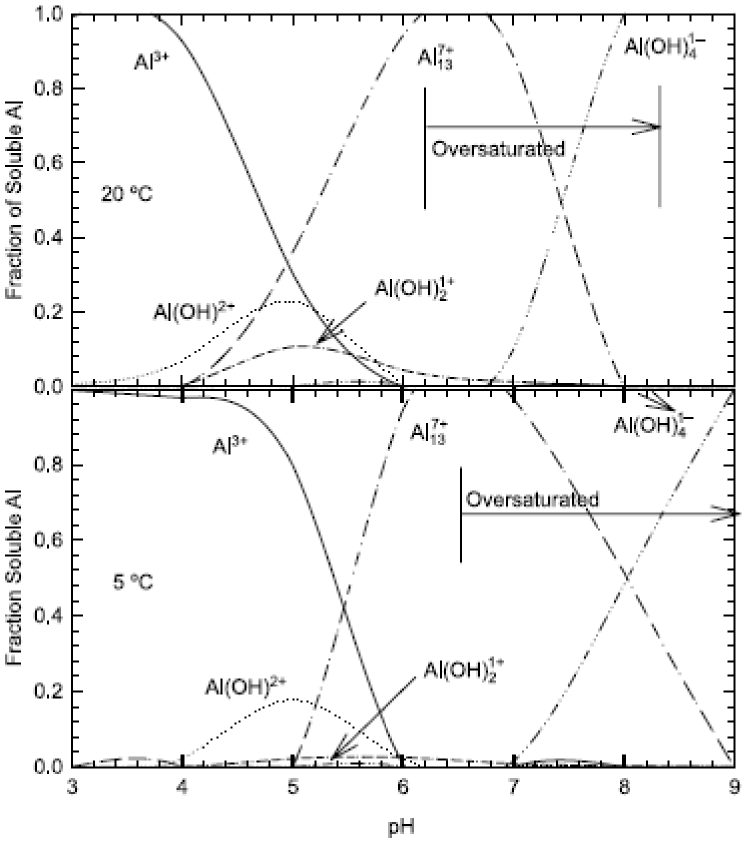
Polyaluminum chloride: is produced by the reaction of base with aluminum salts. Polymers are characterized by their basicity which can be expressed as:

Basicity % = $\{[OH^-]/[Al_T]\}x\{100/3\}$

Basicities can range from 15 – 85 % and can affect the presence of polymers in solution. In general, higher basicity PACl solutions have bigger polymer fractions and vice versa.

Figure 2-3 shows the effect of pH and temperature on Al speciation in the presence of an Al concentration of 1 mg/L. As in the case of alum, increasing pH results in the predominance of Al species with lower positive charge. At 20°C, Al_{13}^{7+} polymers dominate at a pH range of 5 – 7.5 with a higher pH range for water at 5°C. At a pH between 6 – 6.5, a decrease in soluble Al^{3+} might be expected due to oversaturation and aluminum precipitation in the form of $Al(OH)_3(s)$.

Polyaluminum chlorides also include aluminum chlorohydrate (high density PACl) which has a formula of $Al_2(OH)_5Cl$, a basicity of 83%, and an aluminum content of 13%. Polyaluminum chlorides also incorporate polyaluminum silicate sulfates, which are prepared by incorporating aluminum sulfate with activated silica (for wastewater treatment applications) (Bratby, 2006).



1. Note that at Al_T=1mg/L, the solution is theoretically oversaturated with $Al(OH)_{3(am)}$ for pH greater than 6.2 at 20 °C and greater than 6.5 at 5 °C

Figure 2-3: Effect of temperature and pH on Al speciation for PACl solutions (Al_T=1mg/L)

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2.3 Polymers

Polymers can function either as primary coagulants or as coagulant/flocculant aids. The utilization of polymers as coagulant/flocculant aids in drinking water treatment has been documented to be advantageous in the reduction of coagulant dose requirements and hence metal residuals in the treated water (such as aluminum from aluminum salts) (Bolto and Gregory, 2007); increased filter run time; reductions in floc volume, producing an overall smaller sludge hence reducing sludge handling and disposal expenses (Bolto and Gregory, 2007; Graham et al., 2008); the production of waters with more consistent quality due to low polymer sensitivity to variations in pH (Graham et al., 2008); improvements in coagulation performance and NOM removal even at low temperatures (Graham et al., 2008); and finally cost savings of up to 30% (Nozaic et al., 2001). Polymers exhibit their advantages by improving the settleability and toughness of the formed flocs.

Polymers are long-chained macromolecular compounds consisting of individual repeating units known as monomers attaching together by covalent bonds. Homopolymers consist of monomers of similar molecular structure, whereas copolymers can contain more than one type of monomer. Monomers may contain ionizable functional groups that can dissociate in the water resulting in an overall electrical charge for a polymer chain (cationic – positively charged; anionic – negatively charged; or ampholytic – both positively and negatively charged). In the scenario where a polymer is ionic in nature, it can be referred to as a polyelectrolyte. All polyelectrolytes are hydrophilic in nature (Bolto and Gregory, 2007; Bratby, 2006).

The molecular weight and degree of polymerization of a polymer are determined based on the sum of the molecular weights and the number of monomers in a polymer molecule, respectively. It is generally assumed that polymers of high molecular weights have long monomer chains and vice versa (Bratby, 2006; MWH, 2005).

Polymers can be either natural or synthetic. While the use of natural polymers has been previously applied in drinking water treatment due to their low toxicity and relative biodegradability (Graham et al., 2008; Folkard and Sutherland, 2002), synthetic polymers are more common due to their relatively lower cost, availability, and ease of preparation (Bolto and Gregory, 2007; MWH, 2005; Demers, 2002).

Polymers are generally characterized either based on their molecular weights (low – MW < 10^5; medium – MW 10^5 – 10^6; high – MW > 10^7) or their ionic nature (cationic, anionic, or non-ionic), with the latter being the most common mode of characterisation. Polyelectrolytes are generally characterised not only based on their ionic nature, but more importantly on their charge density, which is measured in terms of the molar percentage of the charged groups (mol %) or as milliequivalents per gram (meq/g) (Graham and Gregory, 2007). In addition to the molecular weight and charge density of a polymer, additional parameters that may be useful for polymer evaluation include the concentrations of active ingredient and monomers; viscosity; proportion of ionizable groups; and the amount of insoluble material present (Ghosh et al., 1985; Bratby, 2006).

Polymers in aqueous solutions generally adopt a “random coil” configuration with coil lengths that could be in the order of up to a hundred nm in higher molecular weight polymers. The coil length is proportional to the square root of the molecular weight (Bolto and Gregory, 2007). The extent of coil “spread” in a solution is dependent upon the attractive and repulsive forces existing between the different polymer segments. In the presence of a solution of low ionic strength, repulsion between the segments of a cationic or anionic polyelectrolyte will result in polymer expansion in solution; a configuration which is favourable in the context of coagulation/flocculation. The presence of a high ionic strength solution on the other hand will result in less substantial coil expansion (Bolto and Gregory, 2007).

2.3.1 Mode of action

Two principal mechanisms govern particle flocculation with polyelectrolytes, namely polymer bridging and electrostatic patch effects (Bolto and Gregory, 2007; Bratby, 2006). These two mechanisms may occur concurrently and are described below:

2.3.1.1 Polymer bridging

The phenomenon of particle flocculation by polyelectrolytes through polymer bridging has been recognized for quite some time (Ruehrwein and Ward, 1952). Polymer bridging occurs when long-chain polymers irreversibly adsorb to particles. The adsorbed polymers may essentially have free segments extending into the solution, creating the possibility of adsorption to additional particles thereby “bridging” between them. Adsorption may occur either through electrostatic interaction, where polyelectrolytes with charges opposite to those on particles will attach to the particles due to electrostatic attraction; through hydrogen bonding such as those which may form in the presence of hydroxyl groups on the polymer surface; or through ionic binding, where an anionic polyelectrolytes may attach to particles of the same charge in the presence of divalent metal cations such as Ca^{2+}. The adsorption of long-chain polymers to particles is described as essentially irreversible since long-chain polymers can attach to a particle surface at many sites, reducing the possibility of complete polymer detachment from the particle (Bolto and Gregory, 2007).

The effectiveness of bridging by polymers has been documented to be a function of polymer dose. A polymer overdose may result in the saturation of all adsorption sites on a particle surface thereby reducing chances of adsorption with other polymers and causing particle restabilization, while a polymer underdose will result in relatively few bridging contacts between particles. As such, an optimum dose for polymer bridging is essential (Bolto and Gregory, 2007; MWH, 2005).

In addition, Bolto and Gregory (2007) assert that charge density may play an essential role in polymer bridging; where a high charge density would reduce the chances of polymer adsorption to a particle of a similar charge thereby reducing flocculation effectiveness. On the contrary, Kleimann et al. (2005) argued that polyelectrolytes of high charge density are favourable since they deliver a higher charge per dose thereby achieving more effective charge neutralization of the particles. In any event, proper choice of a polymer based on charge density seems to be a crucial factor in the optimization of the flocculant performance.

2.3.1.2 Electrostatic patch effects

This mechanism essentially revolves around the idea that in the presence of a highly charged polyelectrolyte and a weakly charged particle of opposite charge such as in the example of a cationic polyelectrolyte in a water solution (where particles are predominantly negatively charged), the polyelectrolyte will adsorb completely to the particle leaving no free segments in the solution. Despite the potentially resulting overall "neutrality" of the particle, it is argued that some "patches" or "islands" of the original charge may still exist on the particle surface, resulting in an overall electrostatic attraction between "patches" of opposite charges from different particles, thereby resulting in particle attachment and flocculation (Bratby, 2006; Bolto and Gregory, 2007; Gregory, 1973; Kasper, 1971).

2.3.2 Polymer applications in drinking water treatment

Polymers as primary coagulants: numerous studies have documented the successful use of polyelectrolytes as primary coagulants for the removal of turbidity (Nozaic et al., 2001; Graham et al., 2008), organics, particularly humic substances using cationic polyelectrolytes (Bolto et al., 1999; Bolto and Gregory, 2007; Bolto et al., 1998), and micro-organisms (Amirhor and Engelbrecht, 1975). Results comparable to those obtained with alum coagulation were reported both for turbidity and organics removal.

Polymers as flocculant aids: by far, the most common use for polyelectrolytes has been in the form of flocculant aids in conjunction with aluminum and iron salts as the primary coagulants. The mechanism of particle removal in that setting is as described above. Ideally, a good polymer is one that increases floc size and strength thereby enhancing settleability (Bolto and Gregory, 2007). Polymers have also been successfully utilized as filter aids and sludge conditioners (Bratby, 2006).

2.3.3 Activated silica

Activated silica has been widely used in water and wastewater treatment applications. The anionic form of activated silica is the most commonly used form (Bratby, 2006; Demers, 2002), although cationic activated silica has also been formulated (Robles, 2007). The preparation of activated silica (both cationic and anionic) involves the use of commercially available sodium silicate solutions (with a pH of approximately 12). Acid reagents are used to neutralize the sodium silicate solution to a pH below 9, causing oversaturation of the solution with silica, resulting in the formation of silicates. Examples of commonly used reagents include sulfuric acid and aluminum sulfate, though the use of chlorines and sodium bicarbonate has also been documented (Bratby, 2006). The addition of an acid reagent commences the gelation (activation) of silica compounds to silica precipitates; a reaction that is stopped prior to completion by dilution with water, resulting in the formation of an activated silica sol (Demers, 2002). Silica activation is usually carried out on-site since gelling and deposit formation may occur from long durations of storage. A comparison between the preparation of cationic activated silica and common methods of preparation of anionic activated silica is shown in Table 2-1.

Table 2-1: Difference in preparation of cationic and anionic activated silica

	Cationic Activated Silica (1 % CAS)	**Anionic Activated Silica**		
		Baylis Sol (H_2SO_4)	**Alum Sol ($Al_2(SO_4)_3.18H_2O$)**	**Ferriclear Sol $Fe_2(SO_4)_3$**
Constituent chemicals	• 925 mL D.I. water • 50 mL N Sodium Silicate • 7 - 10 mL 96% H_2SO_4 • 25 mL 49% alum ($Al_2(SO_4)_3.14H_2O$)	• 80.8 mL Milli Q water • 20 mL 1:1 Sodium Silicate (500 mL N Sodium Silicate + 500 mL Milli Q water) • 14 mL 10% H_2SO_4	• 104 mL Milli Q water • 16 mL 1:1 Sodium Silicate (500 mL N Sodium Silicate + 500 mL Milli Q water) • 11.4 mL 16% $Al_2(SO_4)_3.18H_2O$	• **120 mL Milli Q water** • **14 mL 1:1 Sodium Silicate (500 mL N Sodium Silicate + 500 mL Milli Q water)** • **11.3 mL 8 % $Fe_2(SO_4)_3$**
Preparation of 2 L of 5000 mg/L (SiO_2)	1 L sol + 1 L H_2O (with 1 mL H_2SO_4)	295.2 mL sol + 1.7 L H_2O	410.4 mL sol + 1.59 L H_2O	**520 mL sol + 1.48 L H_2O**
Gel/polymerization time	**1 minute**	**13 minutes**	**8 minutes**	**5 minutes**

2.4 Lead corrosion in drinking water

Lead is a known toxin, causing a myriad of adverse health effects upon exposure ranging from delayed physical and neurological development in children to high blood pressure, impaired reproductive capabilities and even death in adults (USEPA, 2008; Health Canada, 2007). Human exposure to lead is largely anthropogenic in nature and may occur through food, air, dust and soil, or water (Lenntech, 2008; USEPA, 2008; Health Canada, 2007). The contribution of drinking water to blood lead in the US is currently believed to be in the range of 7 – 20 % (Edwards and Dudi, 2004; Triantafyllidou et al., 2007). While drinking water is not currently considered as a major source of lead exposure in the US and Canada, recent instances of childhood lead poisoning were attributed to drinking water (Lytle and Schock, 2005; Edwards and Dudi, 2004) which warrants further investigation of the sources, chemistry, and levels of lead in drinking water and measures to reduce lead release in distribution systems.

2.4.1 Lead prevalence and sources

Lead (Pb) is a metallic element in group IV-A of the periodic table. It is a stable end product resulting from the radioactive decay of uranium. Lead is one of the heavy metals and it occurs naturally in the earth's crust, most commonly as galena (PbS). Other forms of lead which may be present in the earth's crust but are less abundant than galena include cerrusite (PbCO3), anglesite ($PbSO_4$), pyromorphite ($Pb_5(PO_4)_3Cl$), leadhillite,($Pb_4SO_4(CO_3)_2(OH)_2$), and lanarkite ($Pb_2(SO_4)O$) (Partington, 1967). Lead ore deposits existing naturally in the environment are most commonly associated with ores of zinc and silver. Lead may also be found in association with copper, arsenic, and antimony (Lovering, 1976; Heyl, 1976; Huff, 1976; Durrant, 1952).

The contribution of naturally occurring lead to environmental contamination is relatively minimal. This is attributed to lead's high tendency to combine and form low solubility compounds with common anions present in natural waters such as sulfates, carbonates and hydroxides (Hem, 1976). Naturally occurring lead can be mobilized in the environment by mechanical disintegration of lead ores, where low solubility lead compounds can be eroded off the surface of ore bodies thereby dispersing the lead compounds to a certain extent. Another form of lead mobilization in the environment is leaching in the presence of highly acidic or highly alkaline conditions. This may have a dispersal effect of a greater magnitude as lead becomes soluble and may form harmful complexes with organic material naturally present in the water. Soluble forms of lead may consequently enter and accumulate in the food chain if deposited in the soils or taken up by plants and animals (Lovering, 1976). Although such a pathway of lead entry into the food chain is possible, it is only responsible for very minute traces and is relatively rare. Concentrations of lead in waters resulting from the natural processes aforementioned are believed to be less than 10 µg/L (MWH, 2005).

Anthropogenic sources, or sources associated with human activities, are by far the most significant contributors of lead contamination in the environment. Historically, lead has been used in a variety of applications such as in jewellery, cooking utensils, paint, ceramics, and glass. More common uses of lead include the production of batteries, shielding for X-ray apparatus and atomic reactors, and in gasoline as an anti-knock additive (Lovering, 1976) which has been banned in Canada since 1990 (Health Canada, 2008).

Of most relevance within the context of drinking water is the use of leaded materials to convey water within the distribution system. The use of lead service lines, pure lead pipes in home plumbing, and leaded solders (50:50 lead:tin) to seal joints between copper pipes was common until lead pipes were banned in the US in 1986 as they can contribute lead to the water (Zhang and Edwards, 2006; Lytle and Schock, 1996; Triantafyllidou et al., 2007). In addition, leaded brass materials (containing lead, copper, zinc, and nickel) such as those used in newer faucets and fixtures have been recently shown to be a major source of lead in the water (Kimborough, 2007; Triantafyllidou et al., 2007). Although lead pipes are no longer installed in the US and Canada, many older districts still contain lead service lines pending replacement. As such, the presence of lead in drinking water will likely pose a problem in the foreseeable future.

2.4.2 Lead toxicity and drinking water regulations

As a heavy metal, particulate lead has the ability to accumulate in the body by lodging in the folds of the intestine or by being absorbed by the body in dissolved form and depositing in the bones. Lead accumulation can begin as early as fetal development (Triantafyllidou et al., 2007; Hamilton and Flaherty, 1995; Cannon, 1976). Acute adult exposure to lead has been linked with increased susceptibility to develop high blood pressure, hypertension, anaemia, heart disease, renal (kidney) disease or even cancer (USEPA, 2008; Masters and Coplan, 1999; Hozalski et al., 2005). Infants and children are especially vulnerable to the detrimental effects of lead due to greater relative exposure and increased sensitivity of the nervous system (Deng and Poretz, 2001; Deng et al., 2001). Infant and childhood exposure to lead has been linked with premature birth, learning deficits and low IQ, Attention Deficit Disorder (ADD), hyperactivity, poor bone mineralization during growth, poor enamel formation in teeth, and neurotoxicity (Gerlach et al., 2002; Banks et al., 1997; Hamilton and Flaherty, 1995; Masters and Coplan, 1999).

In Canada, the Maximum Acceptable Concentration (MAC) of lead in drinking water, established based on known health effects of lead exposure in children is set at 10 µg/L (MOE, 2008; Health Canada, 2008). This is consistent with the guideline established by the World Health Organization (WHO). On the other hand, in the United States the Action Level (AL) for lead in drinking water set by USEPA currently stands at the higher value of 15 µg/L (USEPA, 2008). USEPA also promulgated the Lead and Copper Rule (LCR) in 1991 to protect and educate the consumers about lead exposure via drinking water and to require utilities to monitor their water for lead and to take corrective actions if necessary. While the promulgation of the LCR resulted in classification of drinking water as a less significant source of lead, it did not eliminate it completely. This was illustrated in light of recent events of childhood lead-poisoning associated with drinking water in Greenville, N.C., Durham, N.C., and in Washington, D.C. where some water samples contained as much as 48,000 µg/L of lead (Triantafyllidou et al., 2007; Renner, 2006).

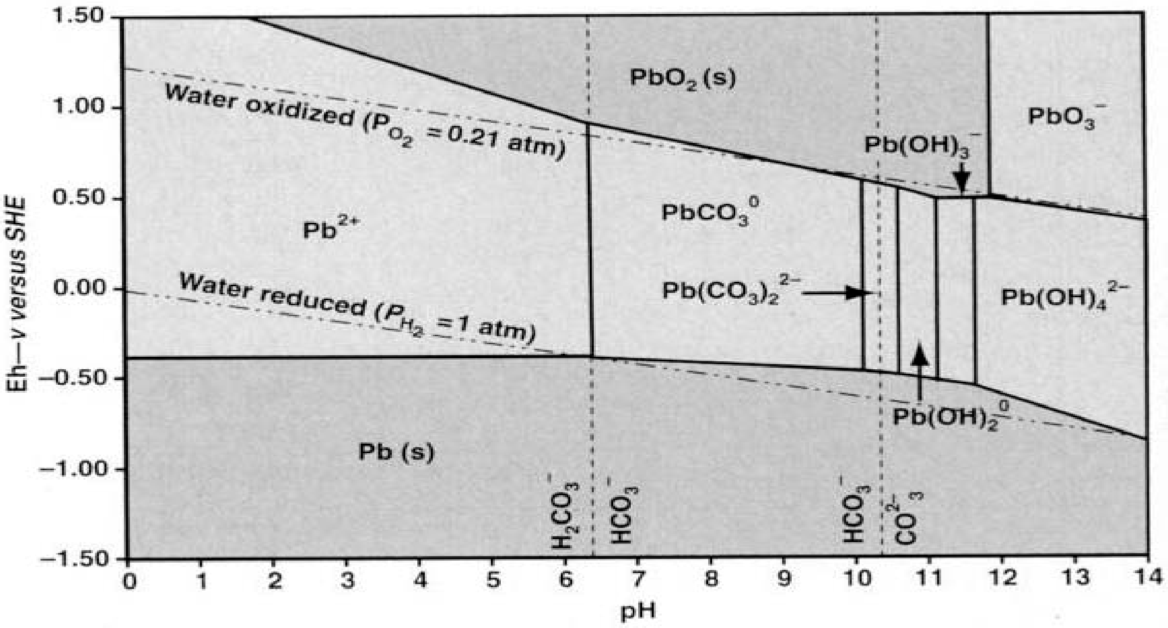
Sampling protocols developed by USEPA LCR and those recommended by Health Canada to monitor, protect, and reduce lead leaching in drinking water are very similar in nature. Both protocols set the action level at 15 µg/L for residential areas based on the 90th percentile level of lead in 1 L first draw samples collected after 6 hours of stagnation time (Lytle and Schock, 2005; Health Canada, 2008). However, it has to be noted that compliance with the 90th percentile lead action limit does not ensure the safety of lead levels in all the waters sampled (Triantafyllidou et al., 2007). In both protocols, residences are classified based on risk of exposure which is assessed depending on a number of criteria such as the presence of lead service lines, lead-containing solders or lead bearing pipes in home plumbing systems, or lead-containing brass fixtures in the distribution systems supplying a residential area. Based on these criteria, residences facing the highest risk of lead exposure are chosen as the sampling sites, with the frequency and number of samples required for lead analysis determined based on the number of people served under a particular distribution system. Sampling sites that do not meet the 90th percentile lead action limit of 15 µg/L are then required to conduct additional sampling, educate the consumers of potential problems, and investigate possible sources of the lead problem, taking corrective mitigation actions if necessary (Health Canada, 2008; USEPA, 2008).

While the sampling protocol developed by USEPA is a useful tool in detecting lead occurrences in drinking water in many circumstances, it has been reported in recent literature that the ability of the protocol to account for the presence of particulate lead in the water is very limited due to the low solubility of lead particulates and Pb (IV) compounds in 0.15% HNO_3 ; the acid used in the protocol to dissolve lead in sample waters before analysis. Triantafyllidou et al. (2007) demonstrated in lab experiments that the actual lead levels in water samples containing lead particulates such as Pb (IV) oxides could be up to 500% higher than those detected by the regular USEPA protocol and that the protocol only detected 20% of the actual lead content of a water sample containing lead particles. This is important in light of the recent case of elevated lead exposure in Greenville, N.C. from drinking water containing particulate lead. Water samples that contain particulates as the predominant form of lead may therefore be classified as safe under the USEPA protocol when in fact they are not (Triantafyllidou et al., 2007; Hozalski et al., 2005).

2.4.3 Lead Chemistry

Lead can form two classes of compounds in solution; namely plumbous and plumbic compounds. Plumbous compounds (Pb^{2+}) have 4 electrons in the valence shell of the lead atom, of which 2 are inert, and the remaining 2 are used to form covalent or ionic bonds, hence the name bivalent lead. Examples of plumbous compounds of relevance to drinking water systems include lead carbonate ($PbCO_3$), lead sulfate ($PbSO_4$), and lead hydroxide ($Pb(OH)_2$). In plumbic compounds (Pb^{4+}), the number of electrons in the valence shell is increased from 4 to 8 through the formation of 4 covalent bonds, hence the name quadrivalent (or more commonly, tetravalent) lead (Partington, 1967; Durrant, 1952). The significance of tetravalent lead in drinking water was not acknowledged until recently, when a seemingly innocuous switch in disinfectant type in Washington, D.C. triggered a lead release in significant amounts into the distribution system (Schock et al., 2001; Schock et al., 1996; Lytle and Schock, 2005; Edwards and Dudi, 2004). Of most relevance in drinking water systems is the presence of tetravalent Pb (IV) oxides (PbO_2).

The predominant form of lead present in the water is highly a function of the pH and the redox potential (Boyd et al., 2008; Lytle and Schock, 2005; Cantor et al., 2003; Renner, 2006). Pourbaix diagrams can provide a pictorial view of the predominant forms of lead (soluble or insoluble) that may be present in the water as a function of both pH and the electromotive force (Eh). Electromotive force (Eh) represents the electrical potential or the oxidation-reduction potential for the reactions of interest. The electromotive force is usually reported in reference to a standard hydrogen electrode (also denoted as SHE) (MWH, 2005). High (positive) Eh values therefore represent oxidizing conditions and vice versa. The Eh of the water is dependent on a variety of factors such as its oxygen content; residence time in the distribution system; the activity of organic matter and other reducing agents; and the presence of buffers (Lytle et al., 1998). Figure 2-4 shows the Eh-pH diagram for the lead-water-carbonate system, illustrating lead complexes that may form in a lead-water-carbonate system. However, limitations of Pourbaix diagrams have to be acknowledged at the outset; such diagrams oversimplify the conditions that may exist in real water systems, and are constructed based on assumptions about the ionic strength, temperature, and species present in the water. These factors indeed have an effect on lead species predominance, for example, carbonate concentrations in the water (Vasquez et al., 2006). Such diagrams can therefore only be used to predict the viability of corrosion in the distribution systems based on principles of thermodynamics but not the electrokinetic phenomena such as the rate of corrosion.



H_2CO_3—carbonic acid, HCO_3^-—bicarbonate ion, P—pressure, Pb—lead, PbO_2 (s)—lead(IV) oxide, (s)—solid, SHE—standard hydrogen electrode

Lead species = 0.015 mg/L, dissolved organic carbon = 10 mg/L C, ionic strength correction = 0

Figure 2-4: Eh-pH diagram for lead-water-carbonate system

(Reprinted by permission of the American Water Works Association, from "Formation of Pb (IV) oxides in chlorinated water", by Lytle, D., and Schock, M. (2005), AWWA Vol. 97, No. 11)

Figure 2-4 shows the domains of predominance of lead and its various complexes in the presence of carbonates. The two dashed lines on the figure represent the water stability domain; the pH and potentials at which the water is thermodynamically stable. At potentials above the upper dashed line, water is not thermodynamically stable and is oxidized thereby liberating oxygen. At potentials below the lower dashed line, water is also thermodynamically unstable and is reduced thereby liberating hydrogen gas. It has to be noted that any change in the gas pressure/concentration in the water system may result in a boundary shift for the water stability domain. The water stability domain constructed in Figure 2-4 was constructed based on an oxygen pressure (P_{O2}) of 0.21 atm and a hydrogen pressure (P_{H2}) of 1 atm. At a given pH, if P_{O2} in the water decreases, the upper dashed line will shift downwards and vice versa.

The solid lines existing between various lead species in Figure 2-4 represent equilibriums and stability. For example, at a pH between 6 and 7 and within the region of water stability, the vertical solid line indicates equimolar amounts of soluble plumbous ion (Pb^{2+}) and insoluble lead carbonate or cerrusite ($PbCO_3$). The vertical line also indicates that speciation is not sensitive to the redox potential but solely to pH. A shift in pH from a range of 7 – 10 to below 6 will therefore cause PbCO3 to dissolve to form soluble plumbous ions (Pb^{2+}); a condition that is highly unfavourable as it indicates lead corrosion and leaching into the water (Pourbaix et al., 1951). In that respect, pH adjustment to control lead release is highly influential in distribution systems.

Of recent interest with respect to drinking water applications is the formation of the tetravalent lead compound – lead dioxide (PbO_2(s)). Very little is known about the speciation characteristics of Pb (IV) in water. As such, accurate predictions pertaining to the solubility of PbO_2 in the water cannot be obtained (Lytle and Schock, 2005). Vasquez et al. (2006) claim that PbO_2 is less readily soluble in water than hydrocerrusite ($Pb_3(CO_3)_2(OH)_2$ (s)). From literature on the formation of PbO_2 in lead-acid batteries and in water, it is known that PbO_2 may exist in two different phases (polymorphs), namely α- PbO_2 and β- PbO_2 (Switzer et al., 2006). The polymorphs can be distinguished physically through observation of their color and structure; α- PbO_2 is orthorhombic in structure and is dark reddish brown in color; while β-PbO_2 is described as tetragonal with a brownish black to black color. Insoluble PbO_2 is known to form only at very high potentials, such as in the presence of a strong oxidant (free chlorine, chlorine dioxide). The presence of Pb (IV) is believed to be of special importance in distribution systems with lead-bearing materials. The relatively insoluble PbO_2 can form a thick, dense layer on the inner surface of pipes, which prevents further lead release into the water (Boyd et al., 2008). However, soluble forms of Pb (IV) were reported in the presence of sulfuric acid and phosphoric acid (Lytle and Schock, 2005). Other factors influencing lead release into the water are discussed in the following sections.

2.4.4 Lead Corrosion

Metallic corrosion of pipes in plumbing and distribution systems has been a major concern for decades. Corrosion results in the loss of pipe mass and the accumulation of tubercles which results in increased head loss and the reduced water carrying capacity of the pipes (McNeill and Edwards, 2000). More importantly, corrosion results in water contamination due to the release of soluble or particulate corrosion by-products into drinking water (McNeill and Edwards, 2000; MWH, 2005; Vasquez et al., 2006). The following section discusses corrosion specifically as it pertains to lead presence in service lines, pipes, solders, and brass.

In order for corrosion to occur, four components have to be present, namely an electron donor (anode), an electron acceptor (cathode), a conductor, and an electrolyte (Vasquez et al., 2006; MWH, 2005). In the absence of a galvanic connection, lead most commonly corrodes due to the presence of dissolved oxygen (DO). The most common oxidized form of lead present in the water is Pb^{2+} (Hozalski et al., 2006). However, as illustrated previously (Figure 2-4), in the presence of highly oxidizing conditions, tetravalent lead Pb^{4+} may also form. A classical example of lead corrosion in the presence of oxygen (and no galvanic connection) is illustrated below:

$$2\text{ Pb (s)} \longleftrightarrow 2\text{ Pb}^{2+} + 4\text{ e}^-$$

$$\text{O}_2\text{ (aq)} + 4\text{ H}^+ + 4\text{ e}^- \longleftrightarrow 2\text{ H}_2\text{O}$$

$$\overline{2\text{ Pb (s)} + \text{O}_2\text{ (aq)} + 4\text{ H}^+ \longleftrightarrow 2\text{ Pb}^{2+} + 2\text{H}_2\text{O}}$$

In the above reaction, all the components necessary for corrosion to occur are present. Lead (anode) is oxidized (loses electrons) to Pb^{2+} which is released into solution. Oxygen (cathode) is reduced to water in the presence of hydrogen ions adsorbed to the lead surface. The ions move between the cathode and the anode through water (conductor) to complete the electrical circuit. Finally, the electrolyte could be the water or any other chemical species (Vasquez et al., 2006; MWH, 2005). Edwards and Triantafyllidou (2007) assert that as a result of the corrosion of pure lead, the pH of the water in contact with the lead pipe may increase due to the neutralization of the OH^- ions produced by the cathodic reaction by the acid produced by the anodic reaction.

Pourbaix diagrams such as Figure 2-4 can be expanded to illustrate the corrosion behaviour of lead. The modified Pourbaix diagram with relevance to lead corrosion is used to identify three discrete regions; namely immunity, corrosion, and passivity/passivation. The region of immunity represents areas where the corrosion of lead is not thermodynamically possible (areas that exist outside the water stability domain). Regions of corrosion represent areas where lead is soluble, such as the areas of Pb^{2+} and $Pb(OH)_3^-$. According to Pourbaix et al. (1951), passivity can be used to refer to the region where lead is metallic and will not corrode (area represented as Pb (s) in Figure 2-4). Pourbaix et al. (1951) contrasts this to the region of “passivation” which represents the formation of insoluble lead compounds such as cerrusite ($PbCO_3$) and lead dioxide (PbO_2) which can form a layer of protective coating on the inner lining of the pipes thereby retarding corrosion (Pourbaix, 1951). However, in practical applications the regions of passivity and passivation are not discretely distinguished (MWH, 2005).

2.4.4.1 Galvanic Corrosion

Of most relevance to this research is the galvanic corrosion of lead in distribution systems and home plumbing. Galvanic corrosion occurs when two dissimilar metals or metal alloys are electrically connected with each other in water (Dudi and Edwards, 2004; Dudi, 2004; MWH, 2005). Galvanic corrosion is therefore expected to occur in solders (lead, tin) and brass fittings (lead, copper, zinc, nickel) (Kimborough, 2007). Galvanic corrosion occurs due to differences in corrosion potential. The severity of galvanic corrosion is a function of three influential factors, namely, the respective position the metals of interest in the galvanic series (difference in corrosion potential); the relative areas of the metals of interest; and the conductivity of the medium (in this case is water) (MWH, 2005).

Metals commonly used in drinking water supplies can be ranked based on their relative corrosion potentials in seawater into a galvanic series (MWH, 2005; Dudi and Edwards, 2004):

1. Zinc (Anodic or least noble – most likely to corrode)
2. Iron
3. Lead-tin solders
4. Lead
5. Brass (with lead)
6. Copper (Cathodic or most noble – least likely to corrode)

A glance at the galvanic series of metals could therefore help in the identification of the metals that are most likely to corrode in the presence of other metals. For example, lead, lead containing solders, and lead-containing brass are likely to be sacrificed (corrode) relative to copper tubing. In galvanic corrosion, the cathodic and anodic reactions are separated (Edwards and Triantafyllidou, 2007). Dudi and Edwards (2004) note that during galvanic corrosion, the pH at the anode (lead) surface may decrease. However, if the pH doesn't decrease at the surface during corrosion, no protective scale will be produced on the lead surface.

Limitations of the galvanic series need to be acknowledged. MWH (2005) note that the galvanic series presented above has been prepared for seawater and is not truly reliable in drinking water applications. In addition, galvanic series is known to be highly water-specific. As an illustration, Dudi and Edwards (2004) noted that in the presence of non standard water conditions, the electrochemical potential for copper may rise from a common potential of 0 mV to as high a potential as 800 mV. In that scenario, copper can become highly cathodic and can corrode metals that were originally believed to be cathodic with respect to copper. Such a condition is also important in that it will have an influence on the rate of corrosion. If copper becomes more cathodic, lead corrosion in water supplies is expected to increase.

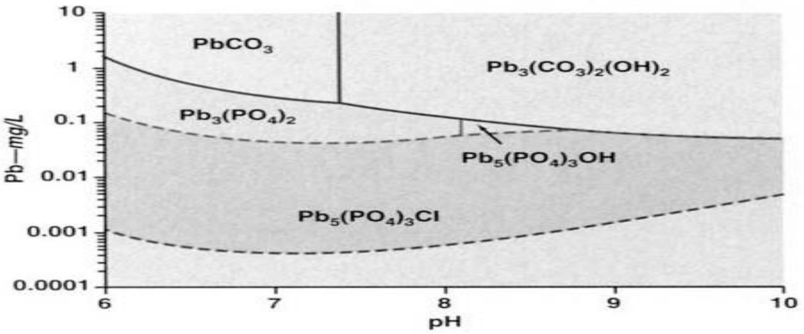
Finally, a galvanic phenomenon that is underappreciated is deposition corrosion. Deposition corrosion may occur if two dissimilar metals are not physically connected, but the presence of soluble ions of the cathodic metal in the water may mobilize and deposit on the anodic metal thereby causing corrosion (Dudi and Edwards, 2004).

2.4.4.2 Factors Influencing Lead Corrosion

Proper understanding of the factors that influence lead corrosion in water systems is the key to corrosion control. This section discusses a number of factors believed to influence lead corrosion. The factors are discussed below.

2.4.4.2.1 pH

Re-examination of the Pourbaix diagram in Figure 2-4 shows that the solubility of lead in water is largely a function of pH. As previously discussed, regions of corrosion, immunity and passivity are predominantly dependent on the pH of the contacting water. While lead is considered the most non-galvanic corrosion-resistant metal relative to the other metals commonly used to convey water (copper, iron), it becomes unstable in the presence of highly acidic or highly alkaline conditions (regions of corrosion). Such conditions are unfavourable. Lead solids that are thought to control lead solubility in drinking water are lead carbonate ($PbCO_3$), hydro-cerrusite ($Pb(CO_3)_2(OH)_2$), lead phosphate ($Pb_3(PO_4)_2$; hydroxy-pyromorphite ($Pb_5(PO_4)3OH$), chloropyromorphite ($Pb_5(PO_4)_3Cl$), and the tetravalent form of lead; lead dioxide (PbO_2), which becomes stable at very high potentials. Few data are available about the stability of other tetravalent lead species such as tetravalent lead hydroxide and tetravalent lead carbonates and phosphates (Schock et al., 2005; Pourbaix, 1951; Lytle and Schock, 2005; Edwards et al., 1999). Figure 2-5 shows the solubility diagram for stable Pb (II) compounds as a function of the operating pH range of 6 – 10. These compounds are believed to have the ability to form the passivating layer on the inner lining of lead pipes (Schock et al., 2005). An interesting observation from this figure is that the solubility of lead in the presence of chloropyromorphite as the passivating layer could be considerably lower than the most commonly present layer of lead carbonate. This observation illustrates a potential advantage of phosphate addition for corrosion control in drinking water which is consistent with previous research on the use of phosphates for corrosion inhibition (Cantor et al., 2000; Edwards and Mcneill, 2002).



Pb—lead, $PbCO_3$—lead carbonate, $Pb_3(CO_3)_2(OH)_2$—hydrocerrusite, $Pb_3(PO_4)_2$ —lead phosphate, $Pb_5(PO_4)_3OH$—hydroxypyromorphite, $Pb_5(PO_4)_3Cl$—chloropyromorphite

Diagram assumes 25°C, an ionic strength of 0.0005, and dissolved inorganic carbonate, orthophosphate, sulfate, and chloride concentrations of 15 mg/L C, 1 mg/L PO_4, and 5 mg/L sulfate and chloride, respectively. Polyphosphate complexation not included.

Figure 2-5: Solubility diagram for lead showing different solid-phase stability fields

(Reprinted by permission of the American Water Works Association, from "Replacing polyphosphate with silicate to solve lead, copper, and source water iron problems", by Schock, M., Lytle, D., Sandvig, A., Clement, J., and Harmon, S. (2005), AWWA Vol. 97, No. 11)

A simpler illustration of the direct effect of pH on lead release in water is shown in Figure 2-6. Edwards et al. (2002) conducted pipe rig tests on old and new pipes to determine the effect of pH on lead release into the water in both pipes. As illustrated in the figure, lead release in the water responded favourably to pH increase up to a pH of 9.5, regardless of pipe age. Results from Dudi and Edwards (2004) also confirmed that at a 90% confidence, the lead released at a pH of 7.5 is significantly higher than lead released at a pH of 8.5. Additionally, Lytle and Schock (2005) demonstrated that the rate of formation of the relatively insoluble PbO_2 increased with increasing pH, with tetravalent lead dominating or co-existing with Pb (II) species at higher pH.

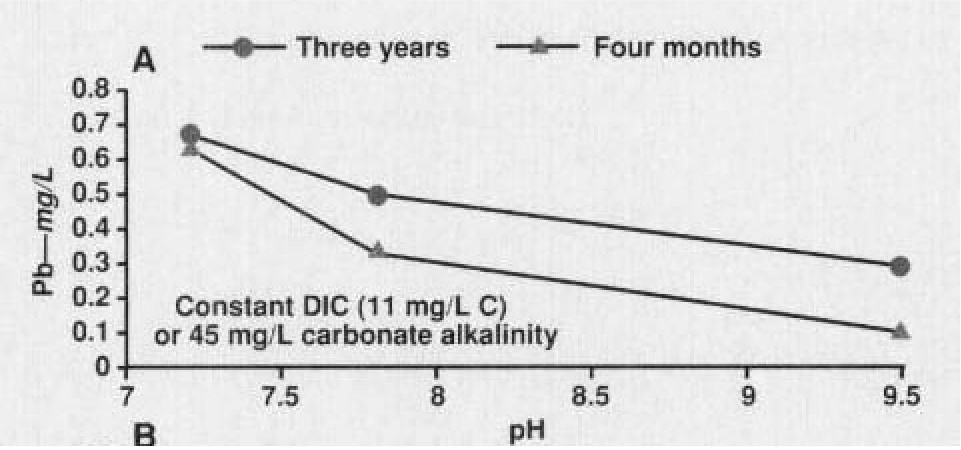


Figure 2-6: Effect of pH on lead release in new and old pipes

(Reprinted by permission of the American Water Works Association, from "Effect of phosphate inhibitors on lead release from pipes", by Edwards, M., and McNeill, L. (2002), AWWA Vol. 94, No. 1)

2.4.4.2.2 Alkalinity

Alkalinity refers to the capacity of a solution to neutralize a strong acid or the buffering capacity of water upon the addition of a strong acid (Snoeyink and Jenkins, 1980). In other words, it provides a measure of the ability of the water to resist changes in pH upon acid addition. The predominant source of alkalinity in a water system is the carbonate species (CO_3^{2-}, HCO_3^-), less significant sources of alkalinity include phosphates, silicates, borates, and carboxylates (MWH, 2005). Bicarbonate (HCO_3^-) concentrations are directly proportional to alkalinity for a pH range of 5.3 – 8.7 and for alkalinities greater than 10 mg/L as $CaCO_3$ (with a 3% error) (Edwards et al., 1996). Therefore for all practical purposes, bicarbonate concentrations are considered as a representation of the alkalinity of the water. Total inorganic carbon (TIC) as well as dissolved inorganic carbon (DIC) can also be used as representative measures of the degree of water alkalinity.

As previously mentioned, corrosion of lead may result in a pH drop near the lead surface due to the liberation of H^+ ions. If the buffering capacity of the water is low (low alkalinity), pH decrease at the lead surface will be more prominent and may result in an overall reduction in pH of the water, which is highly unfavourable with respect to lead corrosion (as discussed previously). In waters of higher alkalinity, the pH drop as a result of lead corrosion is less pronounced due to buffering (Dudi and Edwards, 2004; Tang et al., 2006). Hozalski et al. (2005) reports that at alkalinities below 50 mg/L as $CaCO_3$, lead concentrations are highly sensitive to pH within the pH range of 7 – 8.5. On the other hand, at alkalinities above 100 mg/L as $CaCO_3$, lead release becomes insensitive to changes in pH. Edwards et al. (1999) suggests that an alkalinity of at least 30 mg/L as $CaCO_3$ is highly recommended for the reduction of lead release into the water and that exceeding the ``threshold`` level of alkalinity of 30 mg/L as $CaCO_3$ will not result in significant decrease in lead released into the water. These conclusions are consistent with experiments conducted by Edwards et al. (2002) on new vs. old pipes (shown in Figure 2-7). However, other researchers claim that increasing alkalinity does not always reduce lead release (Vasquez et al., 2006; Dudi and Edwards, 2004; Edwards et al., 1999).

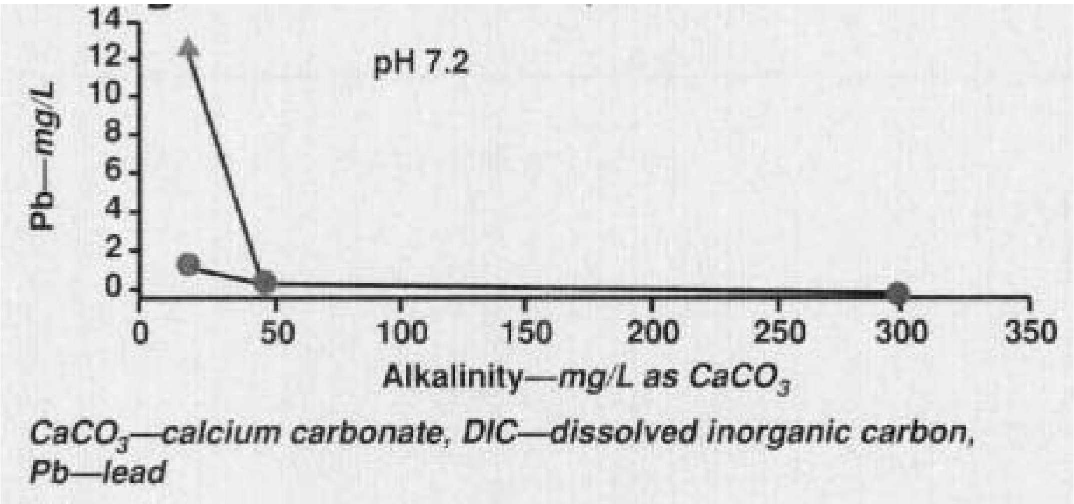


Figure 2-7: Effect of alkalinity on lead release in old (O) vs. new (Δ) pipes

(Reprinted by permission of the American Water Works Association, from "Effect of phosphate inhibitors on lead release from pipes", by Edwards, M., and McNeill, L. (2002), AWWA Vol. 94, No. 1)

In addition to its ability to buffer pH, alkalinity is important because carbonate species can react with lead to form insoluble lead carbonate ($PbCO_3$) which may be a component of the lead scale layer. Hozalski et al. (2005) noted that surface morphology of the scale present on the inner lining of a lead service line indeed showed the presence of lead carbonate ($PbCO_3$) among other compounds.

2.4.4.2.3 Oxidation-reduction potential

A glance at Figure 2-4 shows that aside from its dependence on pH, lead speciation is a function of the oxidation-reduction potential (ORP) of the water. Recently, this factor has been given prominent attention in light of the elevated lead levels of up to 48,000 µg/L that were reported in Washington, D.C. in response to a seemingly innocuous switch in disinfectant type from free chlorine to chloramine originally aimed to address DBP problems (Renner, 2006). While chloramines exhibit greater stability in water and reduce the chance of DBP formation in comparison with free chlorine, their use may have a detrimental effect on metal release in the water due to changes in redox conditions (ORP) of the water, which consequently affect the lead species controlling lead solubility hence lead scale formation. The theoretical redox potential required to transform Pb (II) to Pb (IV) is high relative to the potential required to transform iron from its low-oxidation state (ferrous - Fe(II)) to high oxidation state (ferric – Fe(III)). In drinking water, the only agents capable of increasing the redox potential to the extent required for Pb (IV) formation are free chlorine and chlorine dioxide (Boyd et al., 2008)

Edwards and Dudi (2004) demonstrated that lead release from lead-containing solder samples exposed to chloramines could be higher than samples exposed to free chlorine by a factor that could be as high as 10. Edwards and Dudi (2004) suggested that chloramination enhanced galvanic corrosion of lead in comparison with chlorination. Chloramines significantly increased the lead content of the waters by attacking lead-containing brass. On the contrary, lead leaching of pure lead samples was reported to be lower with chloramines than with free chlorine in the pH range of 7.2 – 8.5. These results contradicted with results by Switzer et al. (2006) where pure lead films immersed in disinfectant solutions showed greater decrease in mass in chloramine solutions in comparison with free chlorine.

Free chlorine (HOCl and OCl^-) is a stronger oxidant than mono-chloramine (NH_2Cl) (Vasquez et al., 2006; Snoeyink and Jenkins, 1980). This is illustrated in Figure 2-8 where the ORP of HOCl and OCl^- is seen to be higher than that for NH_2Cl at any pH. This diagram also illustrates that at a pH above the pKa of HOCl of 7.4, free chlorine is predominantly present in the form of OCl^- (Switzer et al., 2006).

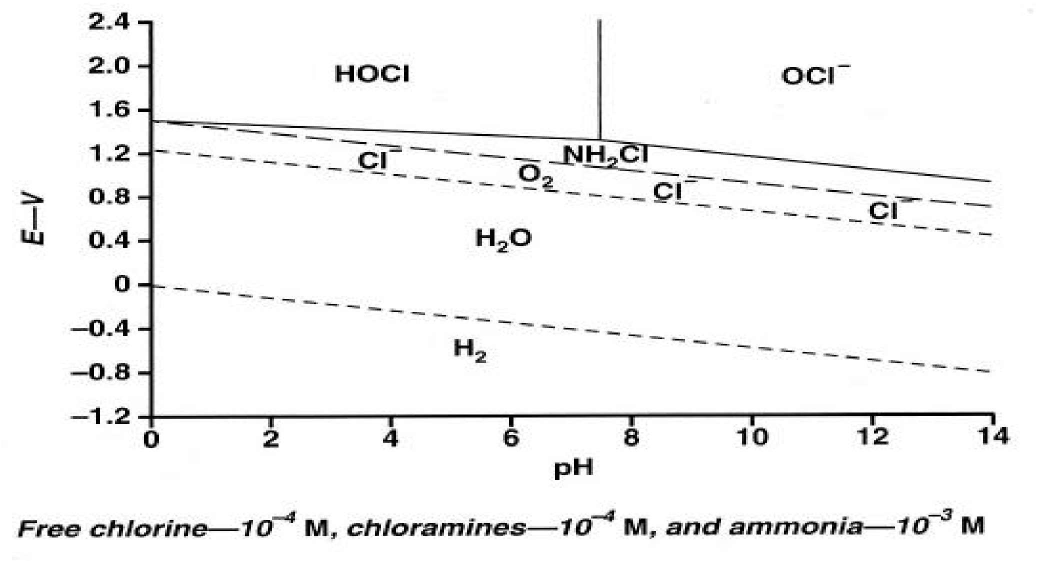


Figure 2-8: ORP of free chlorine vs. chloramines at 25 °C

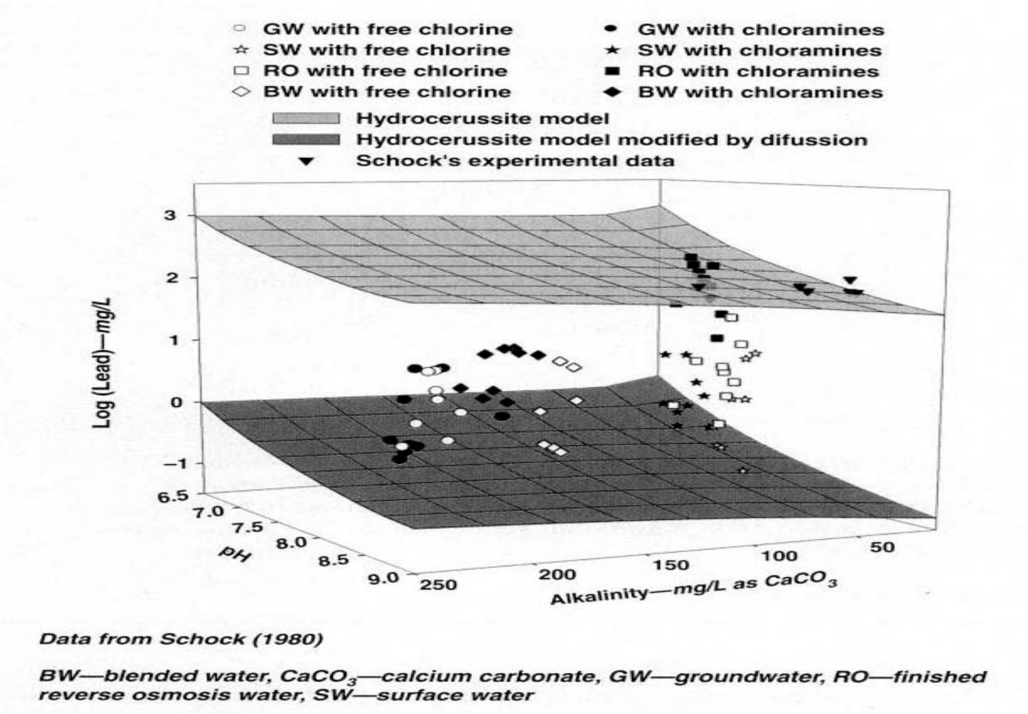
(Reprinted by permission of the American Water Works Association, from "Effect of free chlorine and chloramines on lead release in a distribution system", by Vasquez, F., Heaviside, R., Tang, Z., And Taylor, J. (2006), AWWA Vol. 98, No. 2)

The use of free chlorine in water could therefore result in high ORPs, which could lead to the formation of the tetravalent lead compound lead dioxide (PbO_2(s)). Being relatively insoluble, PbO_2 will consequently contribute to the passivity of lead thereby reducing lead release into the water. A switch from free chlorine to mono-chloramine will therefore reduce ORP and result in the conversion of PbO_2 (s) to soluble species which could deteriorate the water quality (Edwards and Dudi, 2004; Switzer et al., 2006; Vasquez et al., 2006).

Additional factors that can result in increased ORP include:

1. *Low NOM presence in the water* which results in a low oxidant demand in the water thereby causing an immediate increase in ORP of the water upon the addition of a disinfectant (oxidant) (Lytle and Schock, 2005)
2. *Low corrosion of other metals* such as iron and copper. Passivation of these metals in the water system will result in a reduced oxidant demand (Lytle and Schock, 2005)
3. *Treatment methods such as filtration* will reduce the oxidant demand in the waters (Lytle and Schock, 2005)

Vasquez et al. (2006) constructed an interesting plot (Figure 2-9) to illustrate the combined effects of pH, alkalinity, and disinfection method on the solubility of lead in the water based on data from previous literature. Based on their data, lead solubility decreases with increasing pH, the use of free chlorine (denoted by the clear symbols on Figure 2-9), and at low alkalinities.



Data from Schock (1980)

BW—blended water, $CaCO_3$—calcium carbonate, GW—groundwater, RO—finished reverse osmosis water, SW—surface water

Figure 2-9: Solubility as a function of pH, alkalinity, and disinfectant type

(Reprinted by permission of the American Water Works Association, from “Effect of free chlorine and chloramines on lead release in a distribution system”, by Vasquez, F., Heaviside, R., Tang, Z., And Taylor, J. (2006), AWWA Vol. 98, No. 2)

2.4.4.2.4 Chloride-to-sulfate mass ratio

Examination of lead release data from utilities in the US showed that the relative ratio of chloride ions (Cl^-) to sulfate ions (SO_4^{2-}) in the water had an effect on the 90th percentile lead concentrations in the resulting water. Virtually all the utilities that had a chloride-to-sulfate ratio below 0.58 met the USEPA action limit for lead of 15 µg/L while only 36% of the utilities with higher chloride-to-sulfate ratios met the lead action level. This was also consistent with anecdotal evidence from some water utilities (Edwards and Triantafyllidou, 2007; Edwards et al., 1999).

Previous studies suggested that chlorides can attack lead in the presence of a galvanic connection to the more cathodic metal copper (Dudi, 2004). However, chlorides tend to protect lead when not in contact with copper (Oliphant, 1983). Lead corrosion occurs due to lead oxidation (anodic reaction) and oxygen reduction (cathodic reaction) in the water (Zhang and Edwards, 2006). This reaction is proceeds as follows:

$$\text{Pb (s)} \leftrightarrow \text{Pb}^{2+} + 2\ \text{e}^- \qquad \text{(anodic reaction)}$$

$$\text{O}_2\ \text{(aq)} + 4\ \text{e}^- + 2\ \text{H}_2\text{O} \leftrightarrow 4\ \text{OH}^- \qquad \text{(cathodic reaction)}$$

The liberation of H^+ ions during the anodic reaction may result in pH decrease at the lead surface, especially during water stagnation (Dudi, 2004). In the absence of a galvanic connection, both reactions occur at the lead surface in close proximity. On the other hand, the presence of a galvanic connection to another metal such as copper results in separation of both reactions, with the anodic reaction occurring at the lead surface and cathodic at the copper surface.

Contrary to chloride presence, sulfates were found to inhibit attack on lead both in pure form and in the presence of galvanic connection to copper. Sulfates are believed to form a corrosion product layer which serves to protect lead from further corrosion. As such, this protective layer counters the detrimental effects of chloride presence on lead release (Oliphant, 1983).

Given the observed opposite effects of chloride and sulfate presence on lead release in galvanic settings, Gregory (1985) developed a ratio known as the chloride-to-sulfate mass ratio (CSMR), which is calculated as follows:

$$CSMR = \frac{[mg/L\,Cl^{-}]}{[mg/L\,SO_4^{2-}]}$$

Previous literature suggests that CSMR values above 0.5 can increase the galvanic corrosion of lead in connection with copper (Gregory, 1985; Oliphant, 1983). The target CSMR believed to be of influence in a survey of water utilities in the US was 0.58 (Edwards et al., 1999). It should be recalled though that the Ontario standard for lead is 10 µg/L which may require a lower CSMR. Changes in coagulants may influence the chloride and/or sulfate content of the water and hence CSMR, for example, polyaluminum chloride (PACl) adds chloride to the water thereby increasing CSMR while alum adds sulfate to the water thereby decreasing CSMR (Dudi, 2004; Dudi and Edwards, 2004; Edwards and Triantafyllidou, 2007).

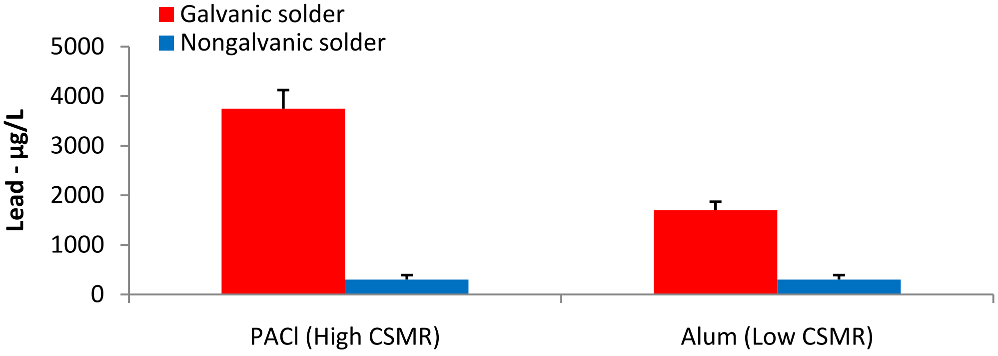
CSMR is believed to have an influence on the conductivity of the water (the conductor - one of the four main factors necessary for corrosion to occur); where a high CSMR may cause an increase in water conductivity thereby increasing the rate of galvanic lead corrosion (Edwards and Triantafyllidou, 2007). A different angle of looking into CSMR is to examine the “transfer number” or the percentage of anionic corrosion currents carried by the chlorides (Edwards et al., 1999). This is illustrated by the following equation:

% Current carried by Cl^- present = $[Cl^-]\{Cl^- + 1.04 \times 2 \times [SO_4^{2-}] + 0.58 \times [HCO_3^-] + 2.5 \times [OH^-]\}^{-1}$

where concentrations of species are expressed in moles/L

A high % value indicates that a high fraction of the galvanic current is carried by the chloride ions present in the water, which is likely to increase lead release in the water and vice versa.

Figure 2-10 illustrates the effect of coagulant choice (hence CSMR) on lead release from galvanized vs. non-galvanized solders in bench-scale coupon tests conducted on coagulated water for a duration of 11 weeks (Edwards and Triantafyllidou, 2007). Consistent with research by Gregory (1990, 1985), the presence of galvanic connections increased Pb release with both coagulants. It was also observed that the use of alum (a sulfate contributor) as a coagulant resulted in an overall lower CSMR and hence lower lead release in comparison with polyaluminum chloride (a chloride contributor) (Edwards and Triantafyllidou, 2007). However, the sensitivity of lead release to CSMR values and its specificity to water type was not investigated.



CSMR – chloride-to-sulfate mass ratio, PACl – polyaluminum chloride
The values reported represent averages. Error bars represent 95% confidence intervals

Figure 2-10: Effect of galvanic connection on Pb release from solder in PACl and alum treated waters

(Reprinted by permission of the American Water Works Association, from “Chloride-to-sulfate mass ratio and lead leaching to water”, by Edwards, M., and Triantafyllidou, S. (2007), AWWA Vol. 99, No. 7)

2.4.4.2.5 Additional factors

In addition to the factors discussed above, other factors influencing lead release in pipes include:

Presence of NOM: A recent study showed that the presence of NOM in the water reduced the formation of Pb (IV) species (Korshin, 2005). NOM removal by coagulation, on the other hand, tended to suppress the reduction of Pb (IV) species in the water. Reactions between NOM and disinfectants as well as NOM interaction with the metal surface are thought to affect Pb (IV) stability in the water (Boyd et al., 2008).

Stagnation time: Long periods of stagnation can result in acid formation on the anode surface thereby hindering passivation (Dudi and Edwards, 2004). A constant water flow rate eliminates the build up of acidic pH on the surface of the anode (Edwards and Triantafyllidou, 2007).

Temperature: Hozalski et al. (2005) observed a positive correlation between the influent water temperature and lead release into the water with corrosion being accelerated in warmer water.

Pipe age: Concentrations of soluble lead species were observed to decrease significantly with aging (Edwards et al., 2002).

Chapter 3 MATERIALS & METHODS

This section describes raw water sampling and collection, the equipment used to measure parameters of concern, as well as chemical preparation and dose calculations. For reasons of clarity, experimental designs are included in the results section.

While a comparison of different commercially available products is incorporated in this research, the author does not necessarily endorse any of the products mentioned and comparisons were made for the sole purpose of research.

This research involved testing of two source waters, Lake Ontario water (Part I) and Grand River water (Part II).

3.1 Lake Ontario Water

The Woodward Avenue Water Treatment Plant (WTP), located in Hamilton, Ontario, treats raw water from Lake Ontario. It has a rated capacity of 909,000 m^3/day and a gross capacity estimated at 926,000 m^3/day and normally operates at one-third to one-half of its capacity. It supplies drinking water to the majority of the City of Hamilton, Stoney Creek, Dundas, Ancaster, and Waterdown. In addition, parts of Flamborough, Glanbrook, Caledonia, York, and Cayuga are also served by Woodward Avenue WTP (Hargrave and Burdick, 2001; City of Hamilton, 2008).

Treatment at Woodward Ave. WTP includes screening, pre-chlorination for Zebra Mussel control, conventional coagulation involving rapid mixing ($G = 523\ s^{-1}$) of polyaluminum chloride (1.0 – 5.8 mg/L) with a detention time of 29 seconds (at gross design flow) (Acres & Associated, 2003), followed by a two stage tapered flocculation consisting of slow mixing at a velocity gradient (G) of 60 for 13 minutes (primary flocculation), then mixing at G = 40 for an additional 13 minutes (secondary flocculation). This is followed by sedimentation in tanks at a surface loading rate of 3.5 m/h. Filtration involves the use of 24 dual media rapid rate filters providing a filter area of 131.9 m^2 per filter. The filters consist of sand (150 mm) and granular activated carbon (740 mm) for the removal of seasonal taste and odour. Disinfection involves chlorination (liquid chlorine and calcium hypochlorite) and chloramination (anhydrous ammonia and ammonium sulfate) to maintain a total chlorine residual of 0.8 – 1.4 mg/L. Hydrofluosilicic acid is also used to provide fluoride for dental health (Hargrave and Burdick, 2001; City of Hamilton, 2008). Figure 3-1 shows a process schematic for treatment processes at Woodward Avenue WTP.

Raw, non-chlorinated Lake Ontario water was collected in 20 – 25 L Nalgene containers at the intake to Woodward Ave WTP near the low lift pumping station. The water was then transported to the University of Waterloo where it was refrigerated until it was needed for experimentation. Prior to each experiment, the water was brought to room temperature by allowing the water to sit outside the fridge for 24 – 48 hours in a large container containing a mix of waters from the different containers continuously being stirred. When cold water was analysed for the experiments, the water was obtained directly from the fridge and used in the experiments. The measured temperature of cold raw water during experimentation was 8 °C.

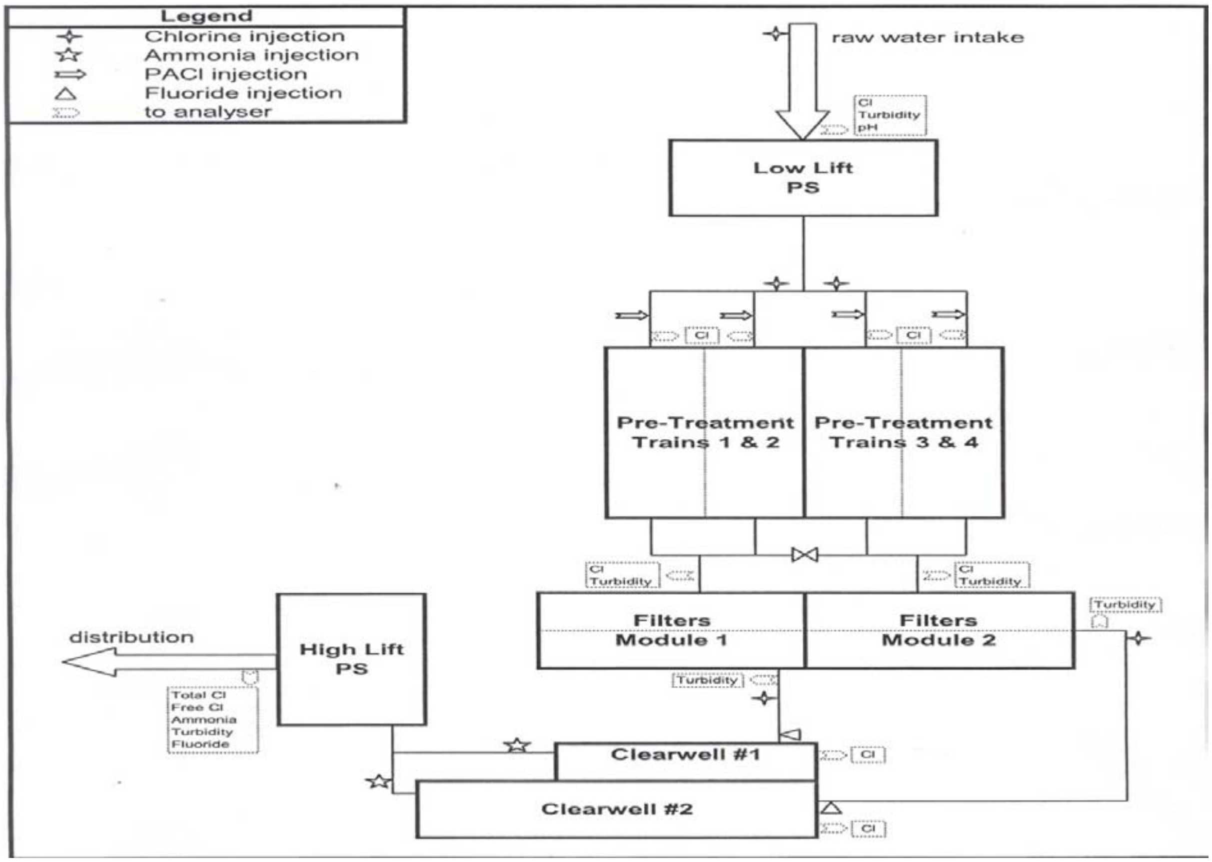


Figure 3-1: Process schematic for Woodward Avenue WTP (City of Hamilton, 2008)

Lake Ontario studies spanned three stages of jar testing. The first two stages involved the use of coagulants aluminum sulfate (alum) and polyaluminum chloride (PACl). Additionally, a newly formulated silica based polymer, cationic activated silica (CAS), was also used. The third stage of jar testing with Lake Ontario water involved the use of four coagulants: ferric sulfate, aluminum chlorohydrate (PAX-XL 1900), pre-hydroxylated aluminum sulfate (PHAS), and polyaluminum silicate sulfate (PASS 100) in addition alum and PACl. All the coagulants used in this study were supplied by Kemira Water Solutions (Brantford, ON). Parameters monitored during the course of this study included temperature, pH, turbidity, UV absorbance (254 nm), total organic carbon (TOC), dissolved organic carbon (DOC), chloride (Cl^-), sulfate (SO_4^{2-}), and simulated distribution system trihalomethanes (SDS THMs).

3.2 Grand River Water

The Brantford Water Treatment Plant (WTP), located in Brantford, treats raw water taken from the Grand River, at Holmedale Canal. It produces water volumes up to 100 ML/d to supply the City of Brantford’s population of about 90,000 (City of Brantford, 2008; Statistics Canada, 2006).

Treatment at the Brantford WTP consists of screening, followed by pre-treatment through the use of an upflow sand-ballasted clarification process known as Actiflo® (Veolia Water Solutions and Technologies, Saint Maurice, France) for the coagulation and flocculation of the water. Polyaluminum chloride is employed as the primary coagulant at doses ranging from 15 to 30 mg/L in the winter and 30 to 50 mg/L in the summer. Actiflo at Brantford employs anionic activated silica, a polymer (Magnafloc LT27A, Ciba Canada Ltd, Trois-Riviéres, Québec), previously dried hydrocyclone micro-sand (Veolia Water Solutions and Technologies, Saint Maurice, France), and the coagulant polyaluminum chloride (Kemira Water Solutions, Brantford, ON). Pre-treatment is followed by chlorination for primary disinfection, followed by the use of ammonia gas with chlorine (chloramination) for secondary disinfection. Filtration includes the use of granular activated carbon (GAC) for taste and odour control. In addition, sodium silicofluoride is used for fluoridation to prevent tooth decay (MOE, 2007). Figure 3-2 shows a process schematic for treatment processes at the Brantford WTP.

Raw, non-chlorinated Grand River water was tested in Part II of this research. Water was collected from a tap in the Brantford WTP lab and the experiments were conducted with University of Waterloo jar testing apparatus on-site. All water quality parameters were analysed twice a day (morning and afternoon) to ensure consistent water quality throughout the experiments. Raw water was occasionally sampled directly from the Grand River and was analysed and compared with raw water collected within the lab. This helped ensure that the sample water used for experiments was representative of the raw water directly obtained from the Grand River. Occasionally, the turbidity of the water collected through the line was lower than the real turbidity in the raw water directly sampled from the river. In such cases, the lines were flushed and the water was allowed to run for 2 hours after which the turbidity was re-measured and compared with turbidities from both Grand River and the SCADA system to ensure consistency.

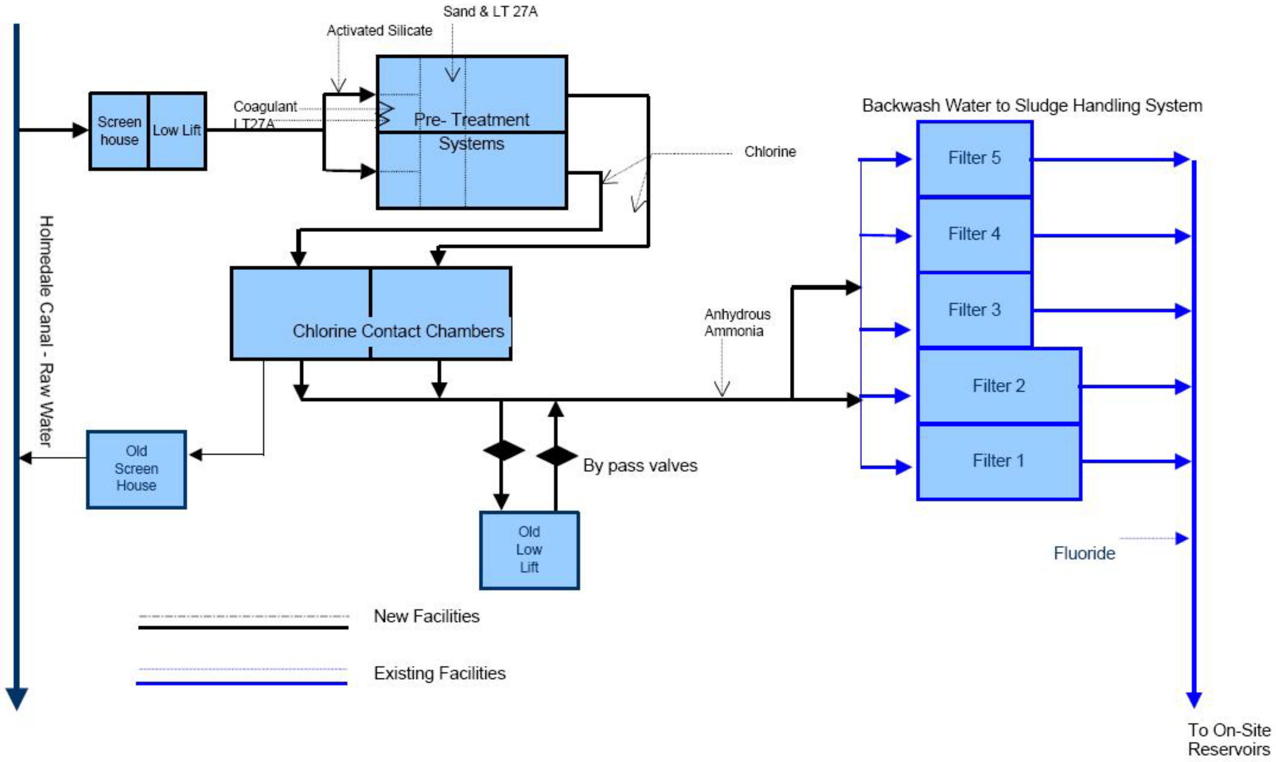


Figure 3-2: Process schematic for Holmedale (Brantford) WTP (City of Brantford, 1999)

Grand River studies spanned three phases of jar testing. The first phase involved the use of the six coagulants aluminum sulfate (alum), polyaluminum chloride (PACl), ferric sulfate, aluminum chlorohydrate (PAX-XL 1900), pre-hydroxylated aluminum sulfate (PHAS), and polyaluminum silicate sulfate (PASS 100). The second and third phases involved the use of coagulants alum and PACl along with micro-sand, commercially available polymer Magna-floc LT 27A (Ciba Canada Ltd, Trois-Riviéres, Québec), and anionic activated silica (AAS) which was prepared on-site in WTP tanks. Coagulants used in this study were supplied by Kemira Water Solutions (Brantford, ON) except for polyaluminum chloride which was obtained fresh each day from the plant's supply of chemicals. Parameters monitored during the course of this study included temperature, pH, turbidity, UV absorbance (254 nm), total organic carbon (TOC), dissolved organic carbon (DOC), dissolved oxygen (DO), chloride (Cl^-), and sulfate (SO_4^{2-}).

3.3 Analytical Methods

Parameters that were monitored throughout this research include pH, turbidity, total organic carbon (TOC), dissolved organic carbon (DOC), UV absorbance (254 nm), dissolved oxygen (DO), temperature, simulated distribution system trihalomethanes (SDS THMs), and chlorides and sulfates.

pH

pH was measured using ORION model 420A pH meter (Pollard Water, New Hyde Park, NY) and IQ Scientific (IQ 125) portable pH meter with silicon chip sensor (IQ Scientific Instruments, Carlsbad, CA). 3 point calibration was conducted prior to use of each of the pH meters. All pH measurements were conducted in duplicates to ensure consistency.

Total/dissolved organic carbon (TOC/DOC)

Total organic carbon (TOC) was measured using O/I Analytical model 1010 wet oxidation TOC analyzer (Graden Instruments, Oakville, ON) by total organic carbon heated-persulfate oxidation method described in section 5310 C in Standard Methods (APHA, AWWA, WEF, 2005).

Dissolved organic carbon analysis involved filtering the water samples through 0.45 µm mixed cellulose membrane filter (Pall Life Sciences, Ann Arbor, Michigan) following a filter rinse conducted by passing approximately 500 mL of ultra-pure Milli-Q water through the filter to remove any filter residues. In addition, the initial 40 mL of sample filtrate was wasted prior to filtered sample collection as recommended by Karanfil et al. (2003) to reduce the chances of contamination and interferences.

All TOC/DOC measurements were conducted in triplicate and the values were averaged. The instrument was checked for consistency through the inclusion of 1, 6, and 10 mg/L organic carbon solutions in each run and observing the instrument readings. In addition, blank TOC and DOC samples were prepared with ultra-pure Milli-Q water and analysed in all runs.

UV absorbance

The correlation between the UV absorbance of waters at wavelengths near 250 nm and the presence of aromatic content has been well documented (Karanfil et al., 2003; Chin et al., 1994; Traina et al., 1990). UV absorbance was measured at a wavelength of 254 nm using a Hewlett-Packard 8453 UV-Visible Spectrophotometer (Agilent Technologies Canada Inc, Mississauga, ON) and Real UVT portable UV absorbance/transmittance analyser (Real Tech Inc, Whitby, ON). The samples were filtered through Milli-Q rinsed 0.45 µm mixed cellulose membrane filters and were placed in quartz cells prior to UV absorbance analysis. Analysis was conducted as per section 5910 B in Standard Methods (APHA, AWWA, WEF, 2005).

Specific UV absorbance (SUVA)

Specific UV absorbance (SUVA) is defined as UV_{254} normalized with respect to DOC (Archer and Singer, 2006). It provides a quantitative measure of the aromatic content present per unit concentration of dissolved organic carbon (DOC) (Karanfil et al., 2003; USEPA, 2005). SUVA is reported in units of L/mg.m and was calculated based on the following equation:

$$SUVA\ (L/mg.m) = \frac{UV_{254}\,(cm^{-1})}{DOC\ (mg/L)} \times \frac{100\ cm}{m}$$

Research also suggests that SUVA may be used as a surrogate predictive tool for the effectiveness of coagulation, specifically enhanced coagulation, in removing TOC and UV absorbing substances. High SUVA waters are more amenable to NOM removal by enhanced coagulation and vice versa for low SUVA waters (Archer and Singer, 2006; White et al., 1997; Edzwald, 1993).

Simulated Distribution System Trihalomethanes (SDS-THM)

SDS-THM is a method which utilizes bench-scale testing techniques to simulate the effect of disinfection and distribution system conditions on the formation of trihalomethanes (THMs). THMs were measured at Woodward Environmental Laboratory (700 Woodward Avenue, Hamilton, ON) after chlorine was dosed at 5 mg/L and the sample incubated at a temperature of 20°C for a duration of 5 days. The chosen chlorine dose was representative of chlorination practices at Woodward Avenue WTP and the incubation temperature and duration was chosen as a worst case scenario for THM formation in the distribution system (high temperature and retention time will result in the highest THM concentrations). SDS-THM analysis was conducted as per section 5710 C in Standard Methods (APHA, AWWA, WEF, 2005).

Table 3-1 summarizes the parameters, instruments, and analysis methods employed in this study.

3.4 Coagulants

Dilutions were prepared for all the coagulants with the exception of PASS 100 which was dosed directly from the original solution as per instructions on material safety data sheet (MSDS) for the chemical. Relevant chemical properties of the six coagulants used in this research are shown in Table 3-2. A sample calculation for alum dosing is shown following the table.

Table 3-1: Summary of parameters analysed and methods followed

Parameter	Instrument	Supplier	Method	Standard Methods (APHA, AWWA, WEF 2005)
pH	▪ ORION model 420A pH meter ▪ IQ 125 portable pH meter with silicon chip sensor	▪ Pollard Water, New Hyde Park, NY ▪ IQ Scientific Instruments, Carlsbad, CA	Electrometric Method	4500-H^+ B
Turbidity	Portable Hach 2100P turbidimeter	Hach Company, Loveland, CO	Nephelometric Method	2130 B
TOC	O/I Analytical model 1010 wet oxidation TOC analyzer	Graden Instruments, Oakville, ON	Persulfate – Ultraviolet or Heated-persulfate Oxidation Method	5310 C
DOC	▪ 0.45 µm mixed cellulose membrane filter ▪ O/I Analytical model 1010 wet oxidation TOC analyzer (Graden instruments)	▪ Pall Life Sciences, Ann Arbor, Michigan ▪ Graden Instruments, Oakville, ON	Persulfate – Ultraviolet or Heated-persulfate Oxidation Method	5310 C

UV absorbance (UV_{254})	▪ HP 8453 UV-Visible Spectrophotometer ▪ Real UVT portable analyser; 0.45 µm mixed cellulose membrane filter	▪ Agilent Technologies Canada Inc, Mississauga, ON ▪ Real Tech Inc, Whitby, ON	Ultraviolet Absorption Method	5910 B
Temperature	Digital Stem Thermometer with stainless steel probe	General Brand	-	2550 B
DO	ORION pH/Dissolved Oxygen Meter	Thermo Fisher Scientific Inc, Waltham, MA	Membrane Electrode Method	4500-O G
Chlorides[1,2]	-	-	Ion Chromatography	4110
Sulfates[1,2]	-	-	Ion Chromatography	4110
SDS-THMs[1]	-	-	-	5710 C

1 – Analysis conducted at Woodward Environmental laboratory (700 Woodward Ave, Hamilton, ON) (not performed by author)

2 – Analysis conducted at SGS Lakefield Research Ltd Environmental & Minerals laboratory (185 Concession Street, Lakefield, ON). Method Detection Limit for Cl^-: 0.03 mg/L; SO_4^{2-} : 0.06 mg/L (not performed by author)

Table 3-2: Information of interest for the coagulants tested

Product name		Aluminum sulfate	Polyaluminum chloride	Ferric sulfate	Aluminum chlorohydrate	Pre-hydroxylated aluminum sulfate	Polyaluminum silicate sulfate
Commercial/trade name		Alum	SternPAC	Ferric sulfate	PAX-XL 1900	PHAS	PASS 100
Chemical formula		$Al_2(SO_4)_3$	$Al_{13}(OH)_{20}(SO_4)_2Cl_{15}$	$Fe_2(SO_4)_3.9H_2O$	$Al_2(OH)_5Cl.2H_2O$	$Al_2(SO_4)_3$	-
Concentration	As supplied	48 – 50 % as $Al_2(SO_4)_3.14H_2O$	15 – 40% as $Al_{13}(OH)_{20}(SO_4)_2Cl_{15}$	50 – 66 % as $Fe_2(SO_4)_3.9H_2O$	30 – 60 % as $Al_2(OH)_5Cl.2H_2O$	25 – 35 % as aluminum hydroxide sulfate	37 % as polyaluminum silicate sulfate; 5.25 % as aluminum
	Used	**49 %**	33 %	58 %	45 %	30 %	37 %
Specific gravity (20°C)	As supplied	1.2 – 1.35	1.205 +/- 0.003	1.38 – 1.59	1.34 +/- 0.1	1.26	1.26 – 1.35
	Used	1.2	1.205	1.485	1.34	1.26	1.305
pH as is		< 2.5	2.6 +/- 0.3	< 2.0	4.0 – 4.4	3.0	3.0 – 3.8
Product uses		Paper production, water/waste-water treatment	Paper production, water/waste-water treatment	Water/waste-water treatment, odour removal	Water treatment	-	Industrial waste-water treatment

Dosage calculation

A sample dosing calculation for alum is shown below. Similar calculations for the other chemicals were done in a similar fashion.

Alum

Active concentration: 48 – 50 % as $Al_2(SO_4)_3.14H_2O$ [use 49%]

Specific gravity: 1.2 – 1.35 [use 1.2]

For dilutions, $C_1V_1 = C_2V_2$

Want to prepare a stock solution such that adding 1 mL of the stock solution to a 2 L jar would result in 4 mg/L of Alum:

To determine the desired strength of stock solution:

$C_1V_1 = C_2V_2$

Where, C_1 = Desired strength of stock solution (unknown) (mg/L)

C_2 = Target alum concentration in 1 mL of stock solution (4 mg/L)

V_1 = Desired pipetting volume (1 mL)

V_2 = Volume of jar (2 L)

Solving for C_1: C_1 = 8 mg/mL (Desired concentration of stock solution)

Alum concentration = 49 x (g-alum / 100 g- solution) x (1.2 g-solution / 1 mL-solution)x(1000 mL/L)

Alum concentration = 588 g-alum/L (588 mg/mL)

Want to prepare 250 mL of 8 mg/mL alum stock solution:

$C_1V_1 = C_2V_2$

Where, C_1 = Concentration of original alum solution (588 mg/mL)

C_2 = Target concentration of stock solution (8 mg/mL)

V_1 = Unknown volume of original alum to be added to 250 mL flask (mL)

V_2 = Desired volume of stock solution (250 mL)

Solving for V_1: $V_1 = 3.4$ mL

Therefore, **Add 3.4 mL of original alum to 246.6 mL of D.I. water (final volume = 250 mL)**

Preparation of cationic activated silica (CAS) involved adding 50 mL of sodium silicate solution (N sodium silicate) containing 37.5 % silicic acid and sodium salt (National Silicates, affiliate of PQ Corporation, Toronto, ON) to 925 mL of deionized water which was rapidly mixed. During the mixing process 96 % H_2SO_4 (BDH Inc, Toronto, ON) was added to drop the pH to between 7 and 8. Once the desired pH range was achieved, the solution was allowed to mix for 1 min after which additional 96 % H_2SO_4 was added to the water to drop the pH to between 1.5 – 2.25 mL of aluminum sulfate was then added to achieve 2 % CAS. 1 % CAS (containing 10,000 mg SiO_2/L) was then prepared by adding 1 L deionized water containing 1 mL 96 % H_2SO_4 to the solution and mixing.

Preparation of anionic activated silica (AAS) was done in the tanks at Brantford WTP. Fresh samples of AAS were obtained every day for the experiments since the solution gelation is fairly rapid. Silica activation was carried out using sulfuric acid. In general, preparation of AAS sodium silicate solution (pH ~ 12) at concentrations in excess of 2×10^{-3} M is neutralized with sulfuric acid to a pH below 9 to oversaturate the solution with amorphous silica thereby forming polymeric silicates. The polymerization reaction is then stopped by diluting the silicate solution to concentrations less than 2×10^{-3} M (Bratby, 2006). At Brantford WTP, the activation sequence carried out to form AAS can be described as follows (Halevy, 2008):

1. Add 9729 L of water to a tank
2. Add a 1:1 mixture of bulk sodium silicate and water = 1023 L (511 L of bulk sodium silicate)
3. Add 49 L of concentrated sulfuric acid
4. After 10 min reaction time, add 2864 L of water for quenching the reaction
5. Top up with an additional 6774 L of water.

The concentration of the active ingredient (sodium silicate) in the AAS solution used in the experiments was 13,150 mg/L (Halevy, 2008). The stock solution concentration of the commercially available polymer Magnafloc LT27A (Ciba Canada Ltd, Trois-Riviéres, Québec) tested during Actiflo experiments was 1250 mg/L (in terms of the active ingredient).

3.5 Jar testing

Bench scale jar testing was conducted at both test sites using Phipps and Bird PB-700 Six-Paddle Standard Jar Tester (Dalco International Inc, Richmond, VA). Figure 3-3 shows the jar tester used.

Figure 3-3: Phipps and Bird PB-700 Standard Jar Testers

Jar testing on Lake Ontario water involved rapid mixing at 200 rpm for 30 s in six 2 L acrylic type Phipps and Bird B-KER2 square jars (Dalco International Inc, Richmond, VA), tapered flocculation involving mixing at 60 rpm for 15 min (primary flocculation), followed by mixing at 40 rpm for an additional 15 min (secondary flocculation), and finally settling for a duration of 15 min after which the water samples were collected for analysis. Coagulant and activated silica dosing was carried out using HandyStep electronic repeating pipette (BrandTech Scientific, Essex, CT) with 12.5 mL BRAND PD-Tip syringe tips while that for PASS 100 was done using 10 – 100 µL VWR Single-Channel pipettor (VWR International, Mississauga, ON) since it was dosed directly from the factory supplied solution (with no stock solutions prepared). Immediately after starting the stopwatch the six beakers were dosed consecutively with the coagulant at 3 s intervals. When activated silica was also tested, it was injected during the flocculation stage 0 – 4 min into flocculation (details discussed in Chapter 4). Following settling, water samples were first sampled from the centre of the jar 7.3 cm below the water surface for turbidity analysis. Sampling was done from the center of the jar to obtain a representative turbidity sample and to avoid floc-breakage and accumulation that may be present in the collected water if the valves were used. Turbidity sampling was then followed by water collection through the valves for analysis of other parameters. The water was collected in 125 mL Redi-Pak Starline High Density Polyethylene (HDPE) wide mouth bottles (Wheaton Science Products, Millville, NJ) for chloride and sulfate analysis and in thoroughly washed and rinsed 240 mL Qorpak Amber Boston Round bottles (Qorpak division of ALL-PAK, Bridgeville, PA) for analysis of the remaining parameters.

Jar testing on Grand River water was conducted on-site in Brantford WTP with dosing assistance provided by two Brantford WTP employees. Coagulant and polymer (Magnafloc LT 27A) dosing was carried out using 1 – 3 mL BD Medical General-Purpose syringes (BD, Franklin Lakes, NJ) while activated silica and PASS 100 were dosed using VWR Single-Channel pipettors (VWR International, Mississauga, ON) for greater accuracy. For Actiflo experiments, Brantford WTP Phipps and Bird PB-700 Six-Paddle Standard Jar Tester was used (Dalco International Inc, Richmond, VA). The paddle blades were slightly twisted as it was suggested that this would provide a better representation of the blades used at the WTP. During the simulation, the micro-sand was dosed into the beakers by using a sand cup which holds 10 g of sand when full. During the experiments, chemicals were injected simultaneously into all the beakers with help from two Brantford WTP employees to achieve more accurate timings. A modified jar test protocol was developed by John Meunier Inc (St-Laurent, QC) for simulation of the Actiflo process at Brantford WTP and the steps are described as follows (John Meunier Inc, 2008):

1. Measure parameters of concern and prepare stock solutions
2. Weigh 5 g of previously dried hydrocyclone sand
3. Measure dosages of coagulant, coagulant aid (activated silica), polymer (split in half doses) in syringes for each beaker
4. Fill 2 L square beakers with water
5. Sit the beakers on the bench allowing the paddle to be 1 cm from the bottom of the beaker
6. Mix at a constant rpm throughout the test
7. Add activated silica
8. Add coagulant

9. Add 5 g of dried micro-sand at 2 min
10. Quickly add half the polymer dose
11. Add the other half of the polymer at 4 min
12. Allow mixing for an additional 6 min
13. At the end of 10 min turn the mixer off and allow the water to settle for 3 min
14. Begin sampling at the end of the 13 min mark

The actual jar testing procedure used for Actiflo simulation during experiments was slightly modified and is as follows:

1. Measure parameters of concern and prepare stock solutions
2. Weigh 5 g of previously dried hydrocyclone sand
3. Measure dosages of coagulant, coagulant aid (activated silica), polymer in syringes or pipettes for each beaker
4. Fill 1 L round bottom beakers with water
5. Sit the beakers on the bench allowing the paddle to be 1 cm from the bottom of the beaker
6. Mix at 150 rpm throughout the test
7. Inject the activated silica prior to start of the experiment
8. Inject the coagulants and immediately start the stopwatch
9. Add 5 g of dried micro-sand at 2 min
10. Add full polymer dose at 4 min
11. Allow mixing for an additional 6 min
12. At the end of 10 min turn the mixer off and allow the water to settle for 3 min
13. Begin sampling at the end of the 13 min mark

3.6 Quality Control

Measures were taken to ensure that the data collected during analytical procedures were defensible, consistent, and accurate. These measures included the following:

- Thorough rinsing and washing of all containers, vials, beakers, and pipettes both with Milli-Q water and sample water prior to use.
- pH and UV absorbance measurements were conducted in duplicate for all the samples, whereas turbidity values were recorded as the average of 10 consecutive readings to avoid potential fluctuations in the readings caused by the presence of particles in the sample waters.
- TOC/DOC measurements were conducted in triplicate, with reference to a calibration curve, standards (1, 6, and 10 mg/L), as well as TOC/DOC blanks in each run to ensure accuracy and consistency.
- When two different instruments were used to measure the same parameter, as in the case of turbidity, pH, and UV absorbance, readings were taken for several samples using both instruments, recorded and verified to not differ significantly.
- When the Brantford WTP on-site jar tester was used, its mixing speeds were verified to match with those of University of Waterloo’s jar tester using a VWR Digital Tachometer (VWR International, Mississauga, ON). The mixing speeds differed by less than 10 rpm at the five speeds tested (100, 125, 150, 175, and 200 rpm).

Chapter 4 EXPERIMENTS ON LAKE ONTARIO WATER

This chapter describes a series of jar test trials of different experimental designs which were conducted during the course of testing with Lake Ontario water. The objectives of this phase were three-fold:

1. To evaluate the performance of the new polymer cationic activated silica (CAS) as a primary coagulant for turbidity and TOC removal in comparison with conventional coagulants alum and polyaluminum chloride.

2. To evaluate the performance of cationic activated silica used as a flocculant aid in conjunction with conventionally used primary coagulants alum and polyaluminum chloride for the removal of DOC and control of SDS-THMs, and its effect on the chloride-to-sulfate mass ratio (CSMR).

3. To investigate the effect of six different coagulants on CSMR as it pertains to the galvanic corrosion of lead.

4.1 Raw water characteristics

Lake Ontario has the smallest surface area (19,000 km^2) of the five Great Lakes of North America although its volume of 1640 km^3 exceeds that of Lake Erie by three-fold. Lake Ontario receives 80% of its water from Lake Erie through the Niagara River. Additionally, Lake Ontario receives water from the Don, Genesee, Oswego, Black, Salmon, Trent, Cataraqui, and Humber rivers, and from precipitation. Ninety-three percent of the lake’s water flows out through the St. Lawrence River while the remainder is lost by evaporation. The average hydraulic residence time of the water in Lake Ontario is reported to be approximately six years. The Lake’s climate and soil type near its shores supports a variety of agricultural, urban, and industrial activities. Highly urbanized and industrialized areas near Lake Ontario include Metropolitan Toronto and Hamilton’s industrial centre near the Hamilton Harbour (MOE, 2008).

Inspection of certain raw quality parameters during sampling showed results similar to those typical for Lake Ontario water. Table 4-1 shows a comparison between historical data accumulated from various sources for Lake Ontario over the period from 1998 to 2003 versus measured values obtained during analysis of the raw water collected for experiments. Turbidity of the sampled water was typically low, averaging at 0.6 NTU. Such low recorded turbidities were below the average historical turbidity of 2.6 NTU. Lake Ontario has typically low turbidity ranging from 0.2 to 23.5 NTU with occasional spikes (>100 NTU) occurring between January and May resulting from storm events (Acres & Associated, 2003; Hargrave & Burdick, 2001). Low turbidities are expected in lake waters since lakes act as a natural coagulation and sedimentation basins due to their relatively high hydraulic residence times ranging from months to years (O’Melia, 1998). Additionally, the raw water intake at Woodward Ave. WTP is located at an average depth of 9 metres (Hargrave and Burdick, 2001), thereby reducing variability in the turbidity of the influent water due to a decreased influence from activity at the water surface. Similarly, historical and measured TOC concentrations were typically less than 3 mg/L, averaging 2.3 mg/L during sampling. Organics in Lake Ontario water may originate from natural sources (predominantly plant activity), agricultural sources (herbicides and insecticides), or from industrial sources (facility and wastewater discharge) which may contribute a wide array of synthetic organic compounds (SOCs) and trace organics such as polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PCHs) to the water (MOE, 1999). Pre-chlorination of the raw water prior to coagulation is implemented at Woodward Avenue WTP for Zebra Mussel control. However, Lake Ontario water tested throughout all the experiments in this research was non-chlorinated.

Table 4-1: Comparison between historical and measured raw water quality for Lake Ontario water

	Historical range (1998 – 2003)		Measured values[e] (2007 – 2008)	
	Average	**Range**	**Average**	**Range**
pH	8.1[a, b, c, f]	7.0 – 8.8[a,b,c]	8.0[f]	7.5 – 8.1
Turbidity (NTU)	2.6[a,b, g]	0.2 – 23.5[a,b, g]	0.6	0.3 – 1.3
Temperature (°C)	8[a]	1 – 22[a, c, d]	10	8 – 15
TOC (mg/L)	1.7[b,d]	1.4 – 3.0[b,d]	2.3	< 3
CSMR	0.92[a,b]	0.77 – 1.27[a,b]	0.91	0.83 – 1.03

a – Drinking Water Surveillance Program (2008) for years 2000 - 2003

b – Hargrave & Burdick (2001) for years 1998 - 2000

c – Acres & Associated (2003)

d – M. Ratajczak (2007)

e – Measured during experimentation from October 2007 – April 2008

f – Value represents the median

g – Turbidity values do not represent occasional spikes that may arise from storm events and on-shore winds – spikes as high as high as 500 NTU were documented (Hargrave & Burdick, 2001; Acres & Associated, 2003)

Lake Ontario water is slightly basic with a pH ranging from 7.5 to 8.1 at the time of sampling with a historical and measured median pH of 8.0 and 8.1 respectively. The pH of the water increases up to 8.8 between June and September (Acres & Associated, 2003). Water temperature at the plant intake varied seasonally with lowest recorded temperatures occurring in January and February (less than 4°C) and the highest between July and October (16 – 22°C) (Acres & Associated, 2003; DWSP, 2008; Ratajczak, 2005). Average water temperature between 2000 and 2003 was recorded as approximately 8°C (DWSP, 2008).

Inspection of historical chloride and sulfate data for the lake water from two sources (DWSP 2008; Hargrave and Burdick 2001) reveal that chloride concentrations ranged from 20 – 33 mg/L and sulfate ranged from 24 – 28 mg/L over the period from 1998 to 2003. Chloride originates predominantly from rock salt (sodium chloride). Being the most common de-icing salt used in southern Ontario, rock salt is classified as the largest single contributor of chlorides to Lake Ontario (MOE, 1999). Expectedly, highest chloride levels were observed in watersheds of highly urbanized areas such as the Greater Toronto area due to extensive use of road de-icing salts. In general, chloride levels have followed an increasing trend over the long term due to urbanization (MOE, 1999). Sulfates on the other hand may originate in natural waters from bacterial metabolism or from the leaching of minerals such as anhydrite ($CaSO_4$), gypsum ($CaSO_4H_2O$), or pyrite (FeS_2) (MWH, 2005). Sulfates in Lake Ontario water were observed to vary to a lesser extent than chlorides (DWSP, 2008; Hargrave and Burdick, 2001). Accordingly, the chloride-to-sulfate mass ratio (CSMR) of the water varied from 0.77 to 1.27 over a four year period, averaging at 0.9 both historically and analytically. It is therefore reasonable to assume that variations in raw water CSMR throughout the year are likely due to changes in chloride levels.

4.2 Treated water CSMR

Treated water sampled from the high lift pump discharge at Woodward Avenue WTP over the period from February 2002 until May 2007 showed that CSMR generally increased over the years (Figure 4-1), shifting away from Edwards and Triantafyllidou's (2007) and Edwards et al's (1999) suggested CSMR values of 0.5 and 0.58, respectively. Higher CSMR waters have been documented to be more aggressive to lead leaching in the presence of brass and solder-copper (galvanic) connections. Close inspection of the available chloride and sulfate data show that in a similar fashion to raw water, the chloride concentrations varied over a wider range (23.4 – 35 mg/L) than did sulfate (24.6 – 30.3 mg/L). At the Woodward Avenue WTP, the main contributor of chloride (and consequently high CSMR) is the use of the chloride-containing coagulant polyaluminum chloride. Additionally, chlorination can also contribute chlorides when hydrolysis products of chlorine (HOCl and OCl^-) are formed (MWH, 2005). In general, the use of sulfate-containing coagulants such as aluminum sulfate and ferric sulfate (Edwards and Triantafyllidou, 2007) or flocculant aids such as activated silica could be a major sulfate contributor to the treated water.

The effect of coagulant and flocculant aid choice on CSMR as it pertains to lead release in galvanic settings is therefore of significance. This is an objective which has been addressed during experiments.

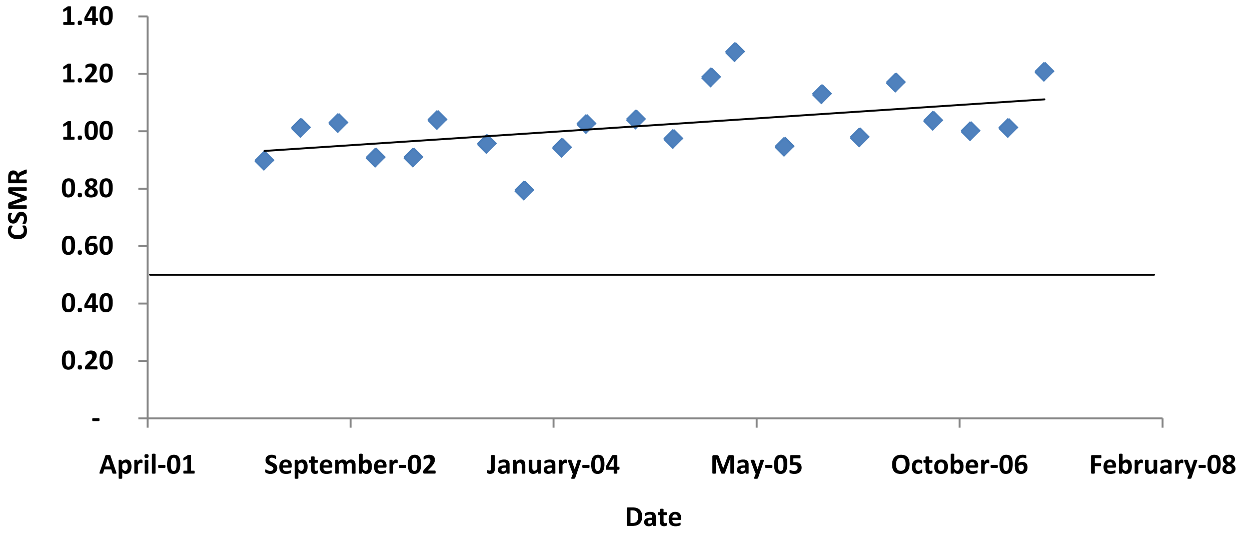


Figure 4-1: Historical treated water CSMR data for Woodward Avenue WTP (City of Hamilton, 2008)

4.3 Experimental approach

Experiments on Lake Ontario water were conducted in three distinct stages, namely the testing of cationic activated silica (CAS), aluminum sulfate, and polyaluminum chloride as primary coagulants (Stage I), testing of CAS as a flocculant aid with aluminum sulfate and polyaluminum chlorides as the primary coagulants (Stage II), and finally the testing of six alternative coagulants for their effect on certain water quality parameters (Stage III). Figure 4-2 shows a descriptive summary of the three stages of testing conducted on Lake Ontario water with the main parameters investigated at each stage.

Rapid mixing for all stages was performed at 200 rpm for 30 s to simulate by bench-scale jar testing the velocity gradient (G) of 523 s^{-1} and the plug flow retention time of 29 s (at gross design flow) at the Woodward Avenue WTP (Acres & Associated, 2003). Slow mixing (flocculation) was conducted in two stages, the first of which was mixing at 60 rpm for 15 min, followed by mixing at 40 rpm for an additional 15 min to simulate the two stage tapered flocculation at Woodward Avenue WTP consisting of slow mixing at velocity gradient (G) of 60 for 13 minutes (primary flocculation) followed by mixing at G = 40 for an additional 13 minutes (secondary flocculation) (Hargrave & Burdick, 2001). The surface loading rate and the calculated detention time of the water during sedimentation at Woodward Avenue WTP are 3.5 m/h (Hargrave & Burdick, 2001) and 1.2 h, respectively. If water was sampled in jar tests at 10 cm below the water surface, in order to simulate the surface loading rate of 3.5 m/h (or particle settling velocity of 5.83 cm/min) at the WTP, the water can only be allowed to settle for 1.7 min (10 cm / (5.83 cm/min)) after which samples should be collected to simulate performance of the sedimentation tank at the WTP. Such a theoretical sampling time is not practical in jar testing as there might be some residual fluid movement in the jars shortly after the mixers are turned off which is not accounted for in the calculation. A more practical sedimentation time that is standard to jar testing practice was therefore chosen as 15 min (AWWA, 2000).

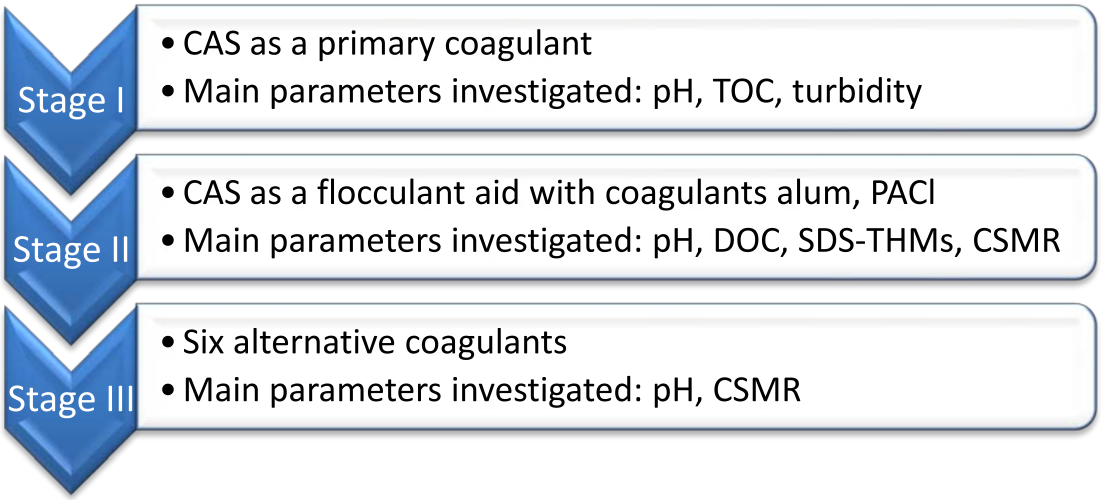


Figure 4-2: Experimental approach for Lake Ontario water

4.4 Stage I – Cationic activated silica as a primary coagulant

Cationic activated silica (CAS) is a newly formulated polymer. Although anecdotal evidence at a northern Ontario water treatment plant suggested its successful application as a flocculant aid, its application in drinking water treatment either as a primary coagulant or a flocculant aid has not been scientifically documented or considered. Because its properties as a potential primary coagulant are completely unknown, it was decided to test CAS as a primary coagulant for potential application in drinking water treatment in Stage I of this research, which aimed to address the following objectives:

1. To assess the performance of CAS as a primary coagulant in comparison with alum and polyaluminum chloride for the removal of turbidity.

2. To investigate the effect of CAS on additional water quality parameters such as TOC and pH.

Experiments for Stage I involved conducting three series of jar tests at room temperature, one with each of the coagulants alum, polyaluminum chloride, and CAS. In each run, five jars were dosed with the coagulant from 4 to 20 mg/L in increments of 4 mg/L. The sixth jar in each run contained raw water subjected to the same coagulation, flocculation, and sedimentation regime as the five other jars to act as a control. Dose ranges for alum and polyaluminum chloride were chosen based on previous research conducted on Lake Ontario water suggesting that the effective dose range for TOC removal is in the range of 10 – 20 mg/L of the active ingredient for both coagulants (Ratajczak, 2007). Coagulant doses below 10 mg/L were also included in the design to encompass the polyaluminum chloride dose range of 1 – 5.8 mg/L employed at Woodward Avenue WTP (Acres & Associated, 2003). With no previous research having been conducted on the application of CAS as a primary coagulant on any water, it was decided to dose the CAS within the same range as that used for the other two coagulants (4 – 20 mg/L of the active ingredient) for comparison purposes. Figure 4-3 shows a schematic of jar test trial conducted with a single coagulant.

Parameters monitored during this stage of experiments included turbidity, pH, TOC, UV_{254} absorbance, and temperature.

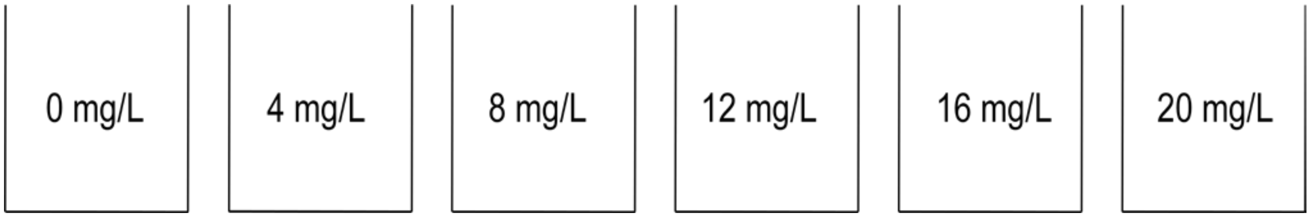


Figure 4-3: Schematic of a jar test trial for Stage I of testing on Lake Ontario water

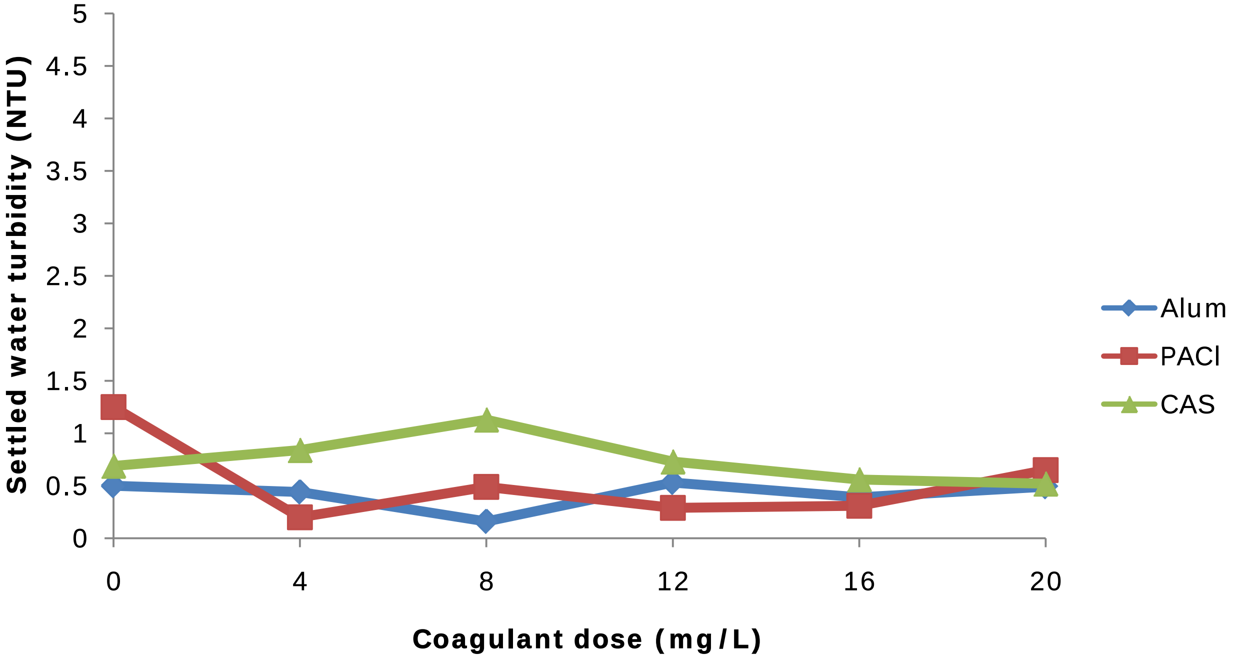
4.4.1 Stage I results

Turbidity profiles were obtained for the different coagulants by sampling at 0, 5, and 10 minutes of settling, as well as at the final settling time of 15 minutes and are shown in Appendix A (Figures A1 – A3). Settling times between 5 and 10 min seem to be optimal for turbidity removal, after which the turbidity either plateaus or decreases gradually. In some instances, as in the case of alum doses at 12 and 20 mg/L or in the case of PACl dose at 8 mg/L, it was observed that the turbidity increased with periods of prolonged settling (exceeding 10 min). Such anomalies might be attributed to floc breakage during sampling. In the case of CAS, turbidities decreased with settling time at all the doses tested with turbidity values generally tending to plateau beyond 5 min of settling time indicating rapid settling of CAS without its ability to adhere to colloids. Rapid settleability of CAS is not unexpected given the fact that CAS is a polymer with a relatively high molecular weight. Noteworthy about polymers in general is the fact that polymer addition beyond the optimum dose may contribute to water turbidity.

Turbidity at 15 minutes of settling represents the final or residual turbidity and is plotted as a function of coagulant dose in Figure 4-4. Since the starting turbidity of the waters varied slightly in each run (0.5, 1.25, and 0.69 NTU for runs with alum, PACl, and CAS respectively), inspection of percentage turbidity removals might provide a better means of comparison. Such a plot is shown in Figure 4-5. The highest turbidity removal of 84% was achieved with PACl at a low coagulant dose of 4 mg/L whereas alum removed 68% of the turbidity at a higher dose of 8 mg/L (Figures 4-4, 4-5). Beyond these doses the efficiency of the coagulants in removing turbidity is noticeably reduced. In the pH range of 7 – 8.1 measured during the experiments, the predominant aluminum species during alum coagulation are theoretically the negatively charged aluminum hydrolysis species $Al(OH)_4^{1-}$ as has been discussed in Chapter 2 (Figure 2-2) while those predominating during PACl coagulation are Al_{13}^{7+} polymers up to a pH of 7.5 and $Al(OH)_4^{1-}$ at higher pH (Figure 2-3). This suggests that colloid removal in this scenario occurs predominantly via colloid enmeshment in the case of alum and by bridging or charge neutralization from Al_{13}^{7+} polymers in the case of PACl. Colloid re-stabilization is apparent at doses exceeding 4 mg/L for PACl and 8 mg/L for alum. Turbidity reductions beyond these doses may also be attributed to experimental error.

Particularly for polyaluminum chloride, this may be a result of the adsorption of excess counter ions on the colloid surface causing charge reversal or from the excess adsorption of polymeric species on the colloid surface thereby blocking adsorption sites and preventing inter-particle bridging (Bratby, 2006).

Inspection of Figures 4-4 and 4-5 show that CAS contributed to the water turbidity under the conditions tested. This might be attributed to rapid gelation of the CAS solution immediately after preparation. Turbidity removal with CAS was only apparent at the high doses of 16 and 20 mg/L with the highest removal recorded of 25% at a 20 mg/L dose. This may suggest that the turbidity contribution from CAS at low doses is not attributed to exceeding the optimum polymer dose. The efficiency of CAS in removing turbidity is therefore inferior to that achieved with the other coagulants by 2 – 3 fold.



The three points shown on the plot at the 0 mg/L coagulant dose represent the initial or raw water turbidity in each run (1st jar)

Figure 4-4: Settled water turbidity vs. coagulant dose for alum, PACl, CAS

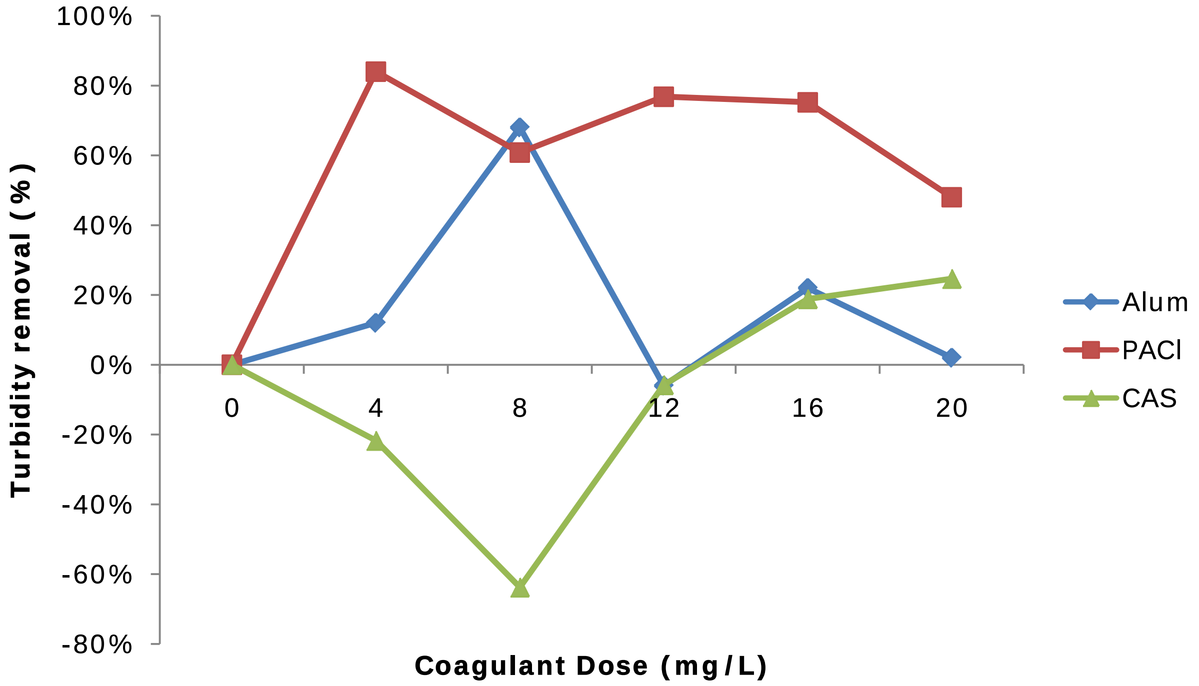


Figure 4-5: Percentage turbidity removal vs. coagulant dose, type

Figure 4-6 shows the effect of coagulant dose on pH and TOC removal. Initial TOC of the water was 2.3 mg/L while the initial pH ranged from 7.9 to 8.1. As apparent in the figure, PACl outperformed both alum and CAS with respect to TOC removal. The highest TOC removal achieved with PACl was 30% at a 16 mg/L dose, while that for alum was 18% at the same dose, followed by CAS, removing only 6% at the 16 mg/L dose. Those values are deemed to be the optimal with respect to TOC removal and are in agreement with previous literature for testing of alum and polyaluminum chloride on Lake Ontario water (Ratajczak, 2007). Organics removal mechanisms include the ones described previously for turbidity/colloid removal. Inspection of the effect of coagulant addition on pH shows that both coagulants alum and PACl resulted in similar reductions in pH (0.5 and 0.4 units respectively at the highest dose tested of 20 mg/L). The pH drop with PACl is less substantial due to the basic nature of the coagulant. The largest pH drop was obtained with the addition of CAS (0.9 units at 20 mg/L) and is attributed to the formulation of the chemical, remembering that concentrated sulfuric acid was used in its preparation. Enhanced coagulation for both alum and PACl was not achieved since the pH did not drop to the pH range of 6 to 7 (Sharp et al., 2006). The operating dose currently implemented at the Woodward Avenue WTP is shaded in Figure 4-6.

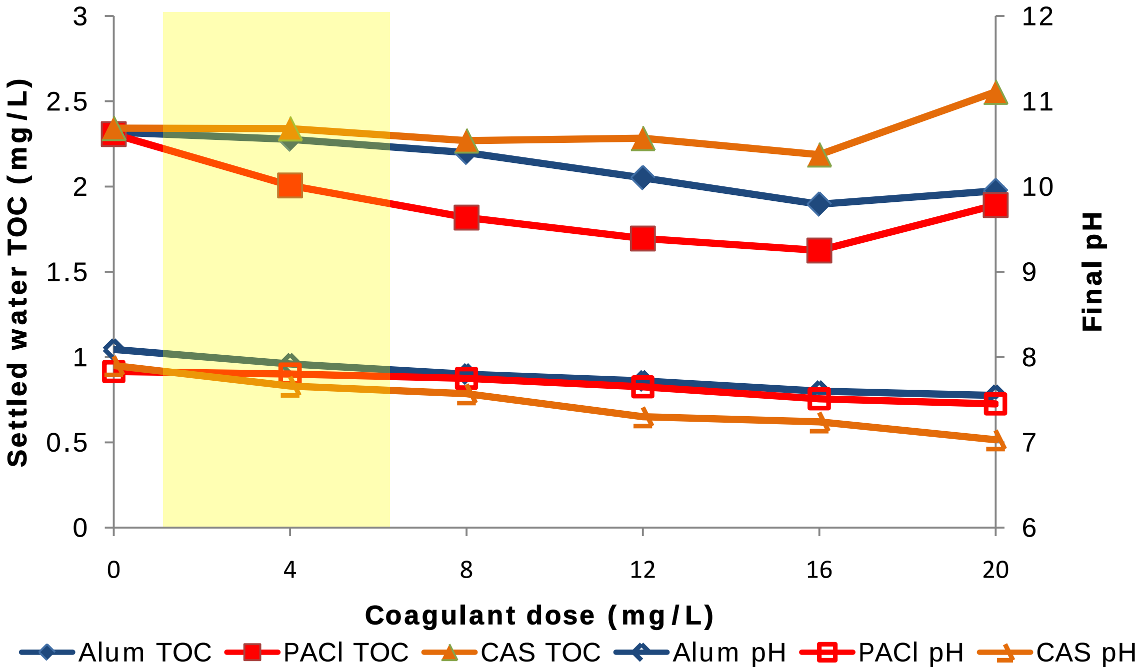


Figure 4-6: TOC and pH vs. coagulant dose for alum, PACl, CAS

It can therefore be deduced from this stage that PACl performed the best in terms of turbidity (84%) and TOC (30%) reduction at doses equal to or less than those of alum. In the dose range currently employed at Woodward Avenue WTP, polyaluminum chloride resulted in DOC removals in the range of 13 – 21% in comparison with 2 – 5% for alum and 1 – 3% for CAS. The performance of CAS as a primary coagulant therefore did not compare with that for alum or PACl. The polymeric nature of this chemical suggests its potential use as a flocculant aid; an objective which has been addressed in Stage II of testing.

Noteworthy is the fact that these experimental conditions were not replicated in this stage and as such, chances for analytical error are magnified. However, from the results that follow, it can be confirmed that the behaviour of alum and PACl is in agreement with the observations from this section.

4.5 Stage II – Cationic activated silica as a flocculant aid

Further testing of CAS was conducted in this stage to test the ability of the polymer to perform in its intended context - as a flocculant aid. As previously mentioned, anecdotal evidence from an Ontario water treatment utility suggested that it may have a value as a flocculant aid. Accordingly, the following objectives of this stage were set:

1. To test the effectiveness of CAS as a flocculant aid in reducing settled water dissolved organic carbon (DOC) and simulated distribution system trihalomethanes (SDS-THMs) formation.

2. To test the influence of CAS on the chloride-to-sulfate mass ratio (CSMR); a parameter which pertains to lead release in galvanic settings.

Testing during this stage of research was conducted in two distinct phases, the first of which was a series of control and optimization experiments (Stage II A) to provide a baseline for comparison when CAS was tested (Stage II B). Experiments were conducted in February, 2008. Parameters monitored during this stage include turbidity, pH, DOC, UV_{254} absorbance, SDS-THMs, CSMR, and temperature.

4.5.1 Stage II A – Alum & PACl alone

During this phase, alum and PACl were tested using Lake Ontario water at two different temperatures at the same dose range employed in Stage I (0 – 20 mg/L). The objectives of this phase were to:

1. Serve as control experiments thereby providing a baseline for comparison when CAS was tested on Lake Ontario water in Stage II B of this research.

2. Replicate and validate results from Stage I pertaining to the optimal coagulant dose for turbidity and organics removal.

3. Determine the effects of temperature on coagulant performance.

4. Determine the optimal coagulant dose for DOC removal from Lake Ontario water during the period over which Stage II was conducted (February, 2008). This dose will serve as the backbone for the design of Stage II B of this research.

Experiments for Stage II A involved conducting two runs of jar test trials, one with each of the coagulants alum and PACl. In each of the runs, five jars were injected with a coagulant dose of 3, 5, 10, 15, and 20 mg/L at 20°C. Doses were chosen to bracket the coagulant dose range currently implemented at Woodward Avenue WTP (1 – 5.8 mg/L PACl) as well as the optimum dose for turbidity and organics removal, determined from Stage I and from previous research (Ratajczak, 2007). The sixth jar was meant to imitate the coagulant dose (5 mg/L PACl) and water temperature (10°C) at Woodward Avenue WTP at the time of experiments and to assess whether a change in the raw water temperature will affect coagulant performance. This was accomplished by comparing results at 10°C and 20°C at a coagulant dose of 5 mg/L, when all the other water quality parameters were unaltered. Figure 4-7 shows a summary of the experimental design for Stage II A with a single coagulant.

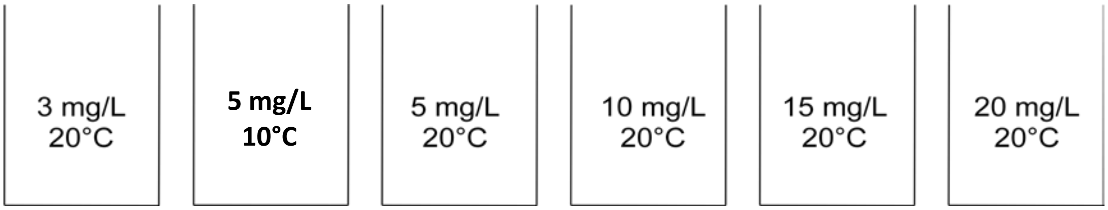


Figure 4-7: Schematic of a jar test trial for Stage II A of testing on Lake Ontario water

4.5.1.1 Stage II A results - Organics

Plots pertaining to residual turbidity, % DOC removal, and UV absorbance as a function of coagulant dose are shown in Appendix A (Figures A5 – A7). Alum achieved its highest turbidity removal (34%) at a coagulant dose of 5 mg/L and at room temperature while PACl removed 41% of the turbidity at the 15 mg/L dose also at ambient temperature (Figure A5). However, it should be noted that both the initial and final turbidity of the water were very low (0.17 – 0.32 NTU) making turbidity highly sensitive to the sampling technique as well as any analytical and instrumental errors. This is evident from the fact that the residual turbidity both at an alum dose of 3 mg/L (at 20°C) and a polyaluminum dose of 5 mg/L (at 5°C) was higher than the initial turbidity.

The relationship between coagulant dose and pH as well as DOC removal is illustrated in Figure 4-8. Inspection of Figures 4-8 and A6 show that DOC removal generally increased with the addition of alum up to the highest dose tested of 20 mg/L, which resulted in 27% removal. The optimum dose for DOC removal with alum appears to have exceeded the dose range tested (3 – 20 mg/L) and therefore cannot be determined. In the case of PACl the optimum dose for DOC removal was within the dose range of 10 – 15 mg/L resulting in 28 – 29% removal. At a constant coagulant dose of 5 mg/L, the performance of alum at 5°C was better than at 20°C with respect to DOC removal (16 and 12% respectively) suggesting a slightly improved performance at cold water temperatures. Re-inspection of the lower plot in Figure 2-2 (Chapter 2) showing Al speciation in colder waters provides possible explanation for this phenomenon: colder waters shifted the predominant Al species from those with low positive or negative charge ($Al(OH)_2^{1+}$ and $Al(OH)_4^{1-}$ respectively) to those of higher positive charge ($Al(OH)^{2+}$ and Al^{3+}) at the given pH which essentially enhanced DOC removal even at a lower coagulant dose since charge neutralization may now be possible (although colloid enmeshment is still believed to predominate) (Pernitsky and Edzwald, 2003; Bratby, 2006). However, the difference in removal is small enough that it may be due to experimental error. In the case of PACl, DOC removal at 5°C (10%) was degraded in comparison with removal at 20°C (18%) at the 5 mg/L dose. This might be attributed to analytical error since the highly charged Al_{13}^{7+} polymer is expected to be present in higher concentrations in colder waters at a given pH thereby enhancing colloid enmeshment and polymer bridging. Results for UV_{254}

absorbance as a function of coagulant dose are shown in the appendix (Figure A7). UV_{254} was decreased with an increased coagulant dose, with the relatively rapid decrease at lower coagulant doses (3 – 10 mg/L) and a gradual decrease at higher doses. At colder water temperatures, the performance of alum was similar to that observed at room temperature while that of PACl seemed to be different (higher UV_{254} in cold water) suggesting potential experimental error. In general, the aromatic content of the water indicated by inspection of UV_{254} decreased with an increased coagulant dose.

Coagulant addition resulted in a smaller pH drop at the intermediate coagulant doses of 3 – 15 mg/L. However, the final pH at the highest dose tested for both coagulants was similar (pH 7.7 at 20 mg/L coagulant dose). Temperature did not have an effect on the final pH. The operating dose currently implemented at the Woodward Avenue WTP is shaded in Figure 4-8.

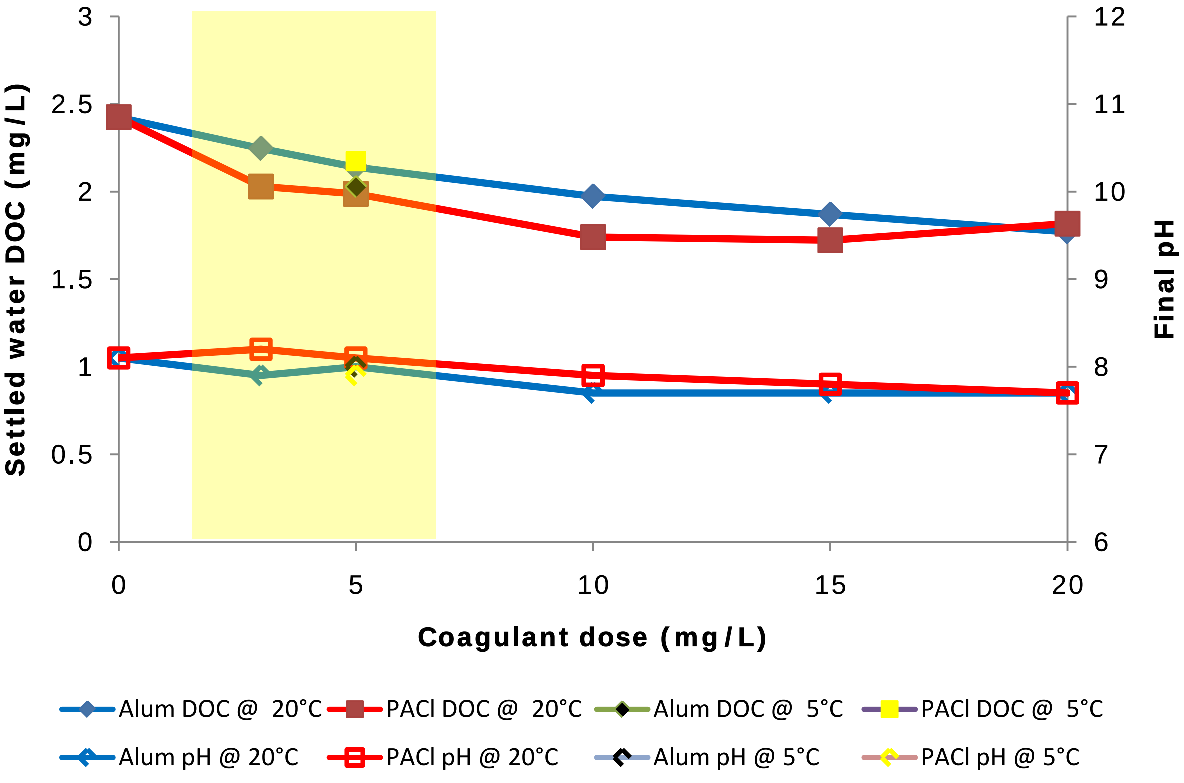


Figure 4-8: DOC, pH vs. coagulant dose for alum, PACl at two temperatures

Figure 4-9 shows the effect of increasing coagulant dose on total trihalomethanes (TTHMs) at the end of a 5 day incubation period at 20°C. As previously mentioned, the SDS-THM method aimed to simulate disinfection practices at Woodward Avenue WTP by dosing the sample waters with 5 mg/L of free chlorine and incubating the samples for 5 days at 20°C to obtain a worst case scenario representing the highest THM concentrations possible. Residual chlorine at the end of the incubation period was analysed and was found to lie within the range of 3.3 to 4.3 mg/L Cl_2. The Woodward Avenue WTP aims to maintain a combined chlorine residual of approximately 1.3 mg/L in the treated water (City of Hamilton, 2008). However, SDS-THM conditions in this scenario were not purely representative of disinfection at the WTP since ammonium hydroxide is also added to form a chloramine residual for secondary disinfection. This was not accounted for during SDS-THM experiments since these experiments were conducted to assume worst case scenario conditions without the use of chloramines for secondary disinfection.

The 5 day chlorine demand plotted as a function of coagulant dose is shown in Figure A8 (Appendix A). The lowest 5 day chlorine demand achieved with both coagulants was 0.8 mg/L Cl_2. This was achieved with PACl at a low dose (3 mg/L) compared with alum (15 mg/L). Examination of Figure 4-9 clearly shows that the DBP precursor removal is dependent on coagulant dose. Total SDS-THM in the raw water was 80 µg/L; a value that is lower than the regulatory limit of 100 µg/L to start with. TTHM formation decreased with higher coagulant doses with both coagulants, with the rate of decrease being more pronounced at low coagulant doses (below 5 mg/L) and gradual at higher doses. No noticeable difference was observed between coagulants with respect to SDS-THM formation at the doses tested. Temperature did not seem to have an influence on coagulant performance with respect to SDS-THM formation.

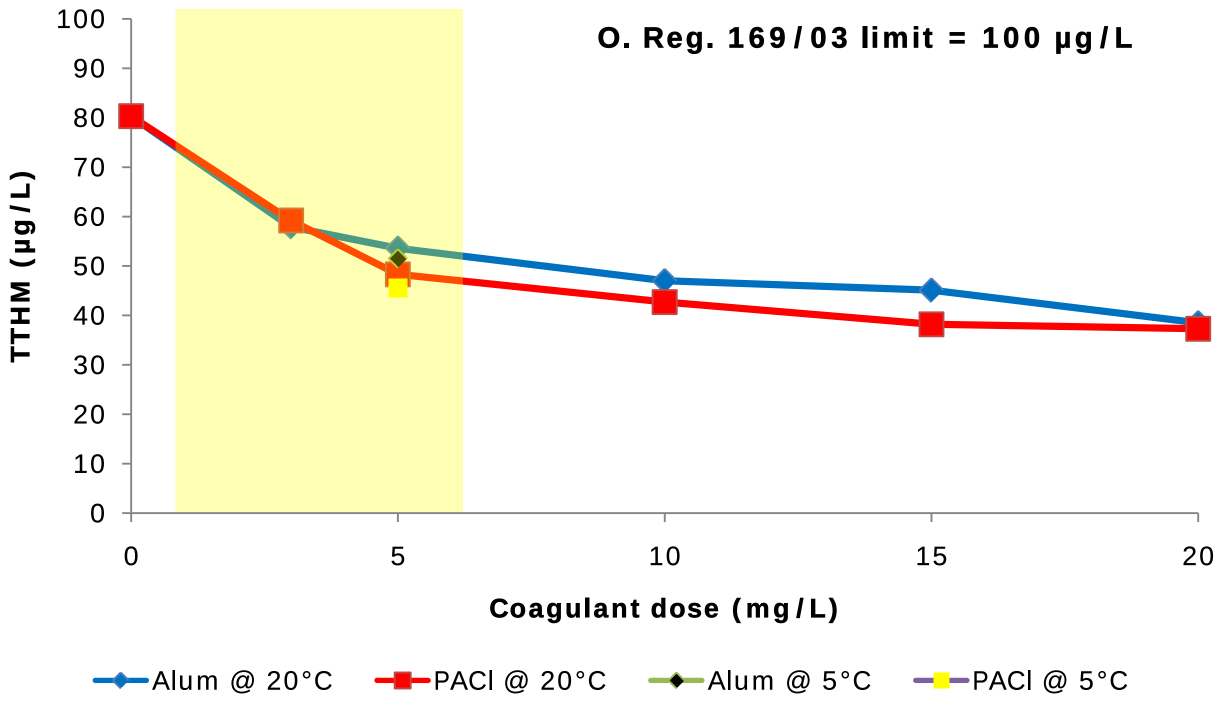


Figure 4-9: SDS-THM vs. coagulant dose for alum, PACl

4.5.1.2 Stage II A results – CSMR adjustment for controlling galvanic lead corrosion

For alum and PACl, the effect of coagulant dose and type on the chloride-to-sulfate mass ratio CSMR is shown in Figure 4-10. Non-chlorinated raw water was used throughout all the experiments and had a CSMR of 0.87 (23.9 mg/L Cl^- and 27.6 mg/L SO_4^{2-}). Noteworthy is the fact that pre-chlorination (with approximately 2.5 mg/L Cl_2) increased the CSMR of the raw water from 0.87 to 1.15 (32.5 mg/L Cl^- and 28.3 mg/L SO_4^{2-}). While attention has been focused on the contribution of chloride from coagulants, it is important to note that chlorine (Cl_2) degrades to chloride thereby contributing to additional chloride levels in the water. Projected CSMR values for both coagulants if the water tested had been pre-chlorinated (increasing CSMR by 0.28 at all coagulant doses tested) is shown by the two dashed sloping lines in the upper portion of Figure 4-10.

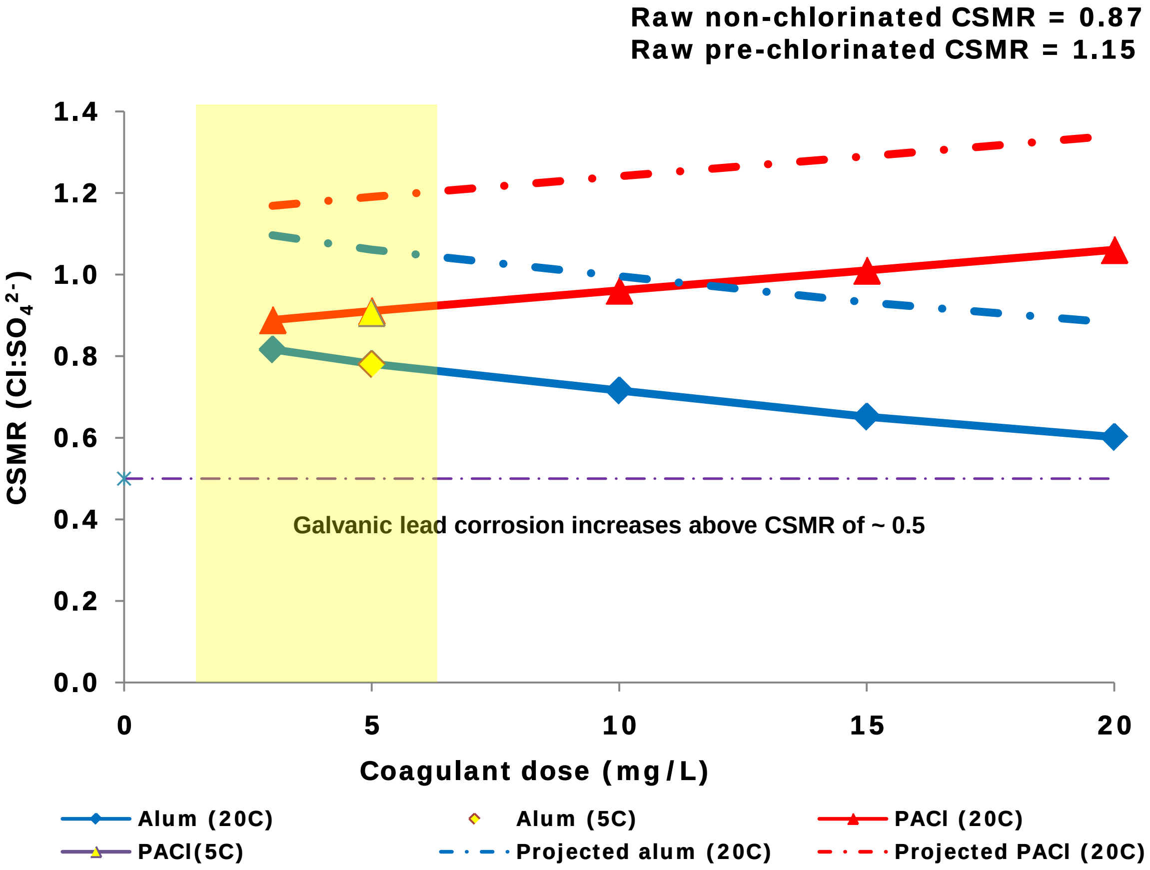


Figure 4-10: CSMR vs. coagulant dose for alum, PACl

It can clearly be seen from Figure 4-10 that alum and PACl have opposite effects on CSMR, as would be expected. Chloride-containing coagulant PACl contributed chloride to the water thereby increasing CSMR. Chloride contribution per mg/L of PACl was an average of 0.3 mg/L. PACl addition therefore drifted CSMR away from the optimal suggested CSMR value of 0.5 above which lead release from brass and solder connections can increase (Edwards and Triantafyllidou, 2007). A target CSMR value of 0.5 is represented in the figure by the dashed horizontal line. Alum on the other hand contributed favourably to CSMR by reducing the values with further addition of the coagulant. This is attributed to sulfate contribution at an average of 0.5 mg/L per mg/L of the coagulant. The lowest CSMR was achieved with alum (0.60) at the highest dose tested of 20 mg/L. However, the target CSMR of 0.5 was never reached. As can be expected, temperature did not have an influence on CSMR and cold water conditions acted as replicas of warm water conditions at the same coagulant dose. The operating coagulant dose currently employed at Woodward Avenue WTP is again represented in Figure 4-10 by the shaded region. At the upper end of this range, CSMR of alum and PACl differed by 0.1 (0.8 for alum and 0.9 for PACl at 20°C).

4.5.2 Stage II B – CAS as a flocculant aid

During this phase, the synthetic cationic polymer CAS was tested as a flocculant aid in conjunction with primary coagulants alum and PACl. The objectives of this phase were to:

1. Test the applicability of CAS as a flocculant aid in the removal of DOC and DBP precursors (using SDS-THM as a surrogate). Additional parameters investigated included pH, turbidity and UV_{254} absorbance.

2. Test the effect of CAS use on CSMR as it pertains to lead release in galvanic settings.

Ideally, a good flocculant aid would increase floc size and enhance particle settleability by bridging between the coagulated particles or through the mechanism of electrostatic patch adsorption (discussed in Chapter 2). Consequently, good polymers could also result in coagulant reductions thereby reducing the overall cost for a water utility. The evaluation and optimization of a polymer as a flocculant aid necessitates an investigation of a number of factors. In the evaluation of CAS, three factors were considered, namely the dose of the primary coagulant, the coagulant-to-polymer ratio, and the time of polymer addition.

The effect of the three factors aforementioned on the responses DOC, SDS-THM, CSMR, and pH (among others) was investigated at two levels for each factor, namely low (denoted by "-") and high (denoted by "+") levels. A 2^3 full factorial design was selected for this scenario since the effect of all possible combinations of the factor levels on the responses under concern can be investigated. A factorial design therefore also takes into account any interactions that may take occur between the factors considered. In order to account for potential curvatures in the response functions (2^{nd} order effects), the design was augmented by the addition of 3 center-point replicates at the design center. Center-point replicates therefore represented the intermediate or average of the two levels for each of factors considered; calculated for each factor by the simple equation of (low level + high level)/2 (Montgomery, 2005). Center-points in the CAS experiments corresponded to what was believed to be the optimum conditions for the performance of CAS and the coagulants.

In summary, a 2^3 factorial experiment with 3 center-point replicates was performed for each of the coagulants, resulting in 11 trials per coagulant in total (2^3 = 8 trials + 3 center-points = 11 trials) as shown in Table 4-2. The low and high levels for the first factor, coagulant dose (factor A) were chosen as 5 and 15 mg/L, respectively, and the center-point replicates were therefore conducted at a coagulant dose of 10 mg/L. The logical explanation underlying the choice of these levels can be extracted from the results for Stage II A; where the optimum PACl dose for DOC removal was in the range of 10 – 15 mg/L. The 5 mg/L coagulant dose was chosen as the low level in order to incorporate the dosing practices at Woodward Avenue WTP at the time the experiments were conducted into the design. The center-point values for the other two factors, coagulant:polymer (CAS) ratio (factor B, center-point value of 10:1), and time of polymer (CAS) addition (factor C, center-point value of 2 min) were assigned based on recommendations of what were believed to be the optimum conditions for CAS performance from anecdotal testing of the polymer at a northern Ontario water treatment plant (Robles, 2007). Low and high levels were then chosen to bracket the center-point values for factors B and C (5:1 and 15:1 respectively for factor B; 0 min and 4 min respectively for factor C) to determine if optimization was possible. Table 4-2 shows a summary of the low, high, and center-point values for the three factors considered and the accompanying table (Table 4-3) shows the factorial design. The order in which each of the runs were conducted was randomized to avoid bias. However, the 3 center-point replicates were run in a non-random order with one being conducted at the beginning, middle, and end of the experiments. Center-points were deliberately scattered out in order to check for the stability of the process (Montgomery, 2005). The actual order in which the experiments were conducted is shown in Appendix A (Figure A9) along with the measured responses. The experimental design was not replicated.

Table 4-2: Low, high, and center-point values for three factors investigated in CAS evaluation

Level	Factor		
	Coagulant Dose [mg/L] (A)	**Liquid Coagulant : CAS (SiO_2) ratio (B)**	**Time (after rapid mix) of CAS addition [min] (C)**
Low (-)	5	5:1	0
High (+)	15	15:1	4
Center-point	10	10:1	2

Table 4-3: Experimental design for runs conducted with each of alum, PACl

Run	Factor		
	A	**B**	**C**
1	-	-	-
2	+	-	-
3	-	+	-
4	+	+	-
5	-	-	+
6	+	-	+
7	-	+	+
8	+	+	+
9	Center-point	Center-point	Center-point
10	Center-point	Center-point	Center-point
11	Center-point	Center-point	Center-point

4.5.2.1 Stage II B results

Initial subjective evaluation of the effect of the individual factors (with no account for any interactions) on the responses investigated showed apparent trends with respect to coagulant dose and CSMR, DOC, UV_{254} absorbance, pH, and SDS-THM for both coagulants. Table 4-4 shows the magnitude and direction of correlations between each of the three factors and the responses considered. As can be seen, the strongest correlations exist between the coagulant dose and CSMR (99% and 98%, respectively), being negative in the case of alum addition due to sulfate contribution, and positive in the case of PACl addition due to chloride contribution. The coagulant dose is also correlated with pH to a noticeable extent (83% and 75% respectively for alum and PACl) indicating that coagulant addition would drop pH with both coagulants. Also noteworthy is the negative strong correlation (70 – 91%) between coagulant addition and DOC as well as UV254 absorbance. Graphical representations of the correlations between coagulant dose and CSMR, DOC, UV_{254} absorbance and pH for each of PACl and alum are shown in Appendix A (Figures A10 – A16). It is important to mention that correlation is subjective tool and should not be used for complete evaluation of a factorial design. An in-depth analysis of the factorial experiment follows.

Table 4-4: Correlation between experimental variables and responses with no account for any interactions

Factor	Response	Correlation (%)	
		Alum	PACl
Coagulant dose	CSMR	- 99	+ 98
	DOC	- 70	- 86
	UV_{254} absorbance	- 86	- 91
	pH	- 83	- 75
	SDS-THM	- 72	- 93
	Turbidity	- 52	+ 35
Coagulant:CAS	CSMR	0	+ 14
	DOC	0	- 18
	UV_{254} absorbance	0	0
	pH	+ 28	- 38
	SDS-THM	+ 18	- 16
	turbidity	- 36	- 35
Time of CAS addition	CSMR	0	0
	DOC	0	0
	UV_{254} absorbance	0	0
	pH	0	0
	SDS-THM	0	0
	turbidity	0	0

Observations from a factorial experiment can be more accurately analysed through statistical analysis to account for the main effects and any two or three-factor interactions that may influence the responses considered. Pictorially, one can get a feeling of the significance of factors and interactions with respect to a response by examining a normal or a half-normal plot. Half-normal plots are generally easier to interpret. Half-normal plots show the absolute values of all the effects in a model as a function of their cumulative normal probabilities (Montgomery, 2005). Examples of half-normal plots showing the significance of the effects with respect to CSMR for both PACl and alum are represented in Figures 4-11 and 4-12, respectively. Similar figures for DOC and SDS-THMs are shown in Appendix A (Figures

A17 – A22) with two figures in each page representing PACl (top figures) and alum (bottom figures) experiments.

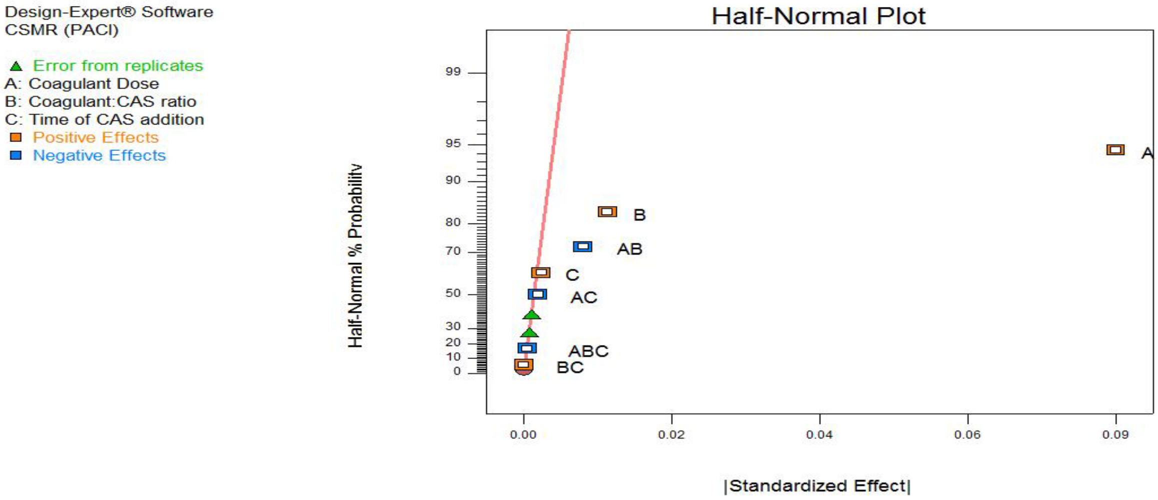


Figure 4-11: Half-normal plot for the significance of effects on CSMR with PACl

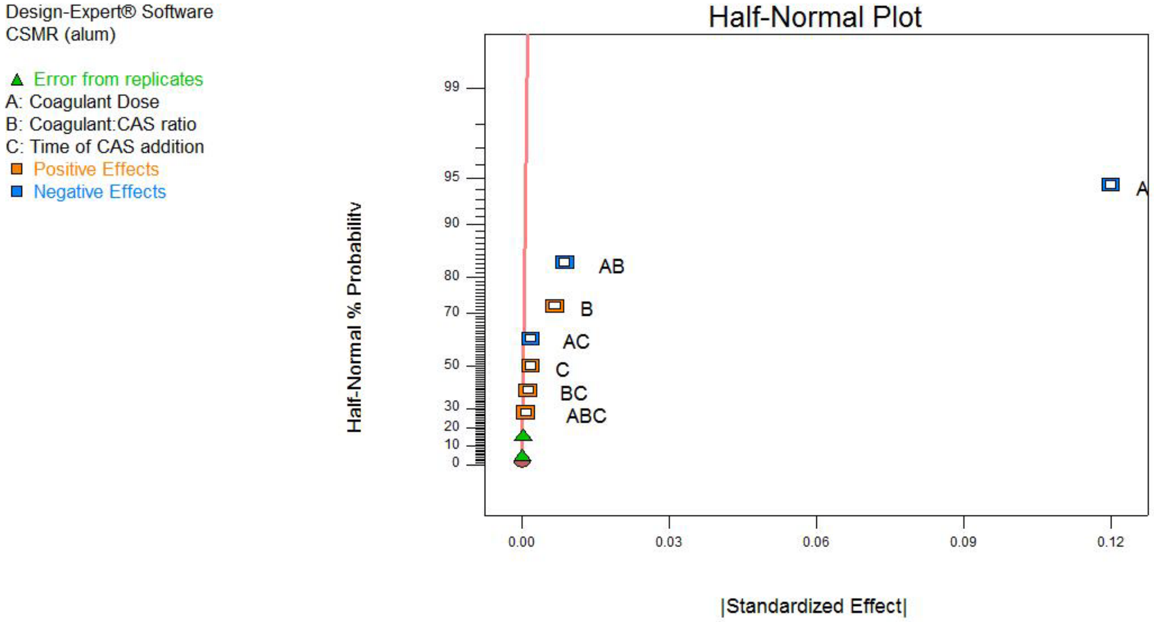


Figure 4-12: Half-normal plot for the significance of effects on CSMR with alum

Analysis of variance (ANOVA) tables at 95 % confidence levels are shown in Appendix A (Figures A23 – A34) for CSMR, turbidity, DOC, UV_{254} absorbance, pH, and SDS-THM for both coagulants. Of relevance with respect to model evaluation are the F-values and the p-values which are represented as the last two columns in the ANOVA tables. F-values compare the model variance with the residual variance and are calculated by dividing the Mean Square for the model or term by the Mean Square for the error (MS_{model}/MS_{error}). A large F-value for the model indicates that the variance can be explained by the model, and a large F-value for a term relative to other terms in the model implies that the term contributes more to the model relative to other terms. Inferences about the significance of a model or a term are incomplete without looking at the p-values; these are probabilities associated with the F-values at the 95 % confidence level. A p-value that is less than 0.05 would therefore indicate that the model/term under investigation is significant (Montgomery, 2005). These concepts are used in the analysis of the observations from the factorial design.

CSMR: The ANOVA tables for CSMR with PACl and alum (Figures A23, A24 respectively) show that some terms are significant at the 95% confidence level for both coagulants (model $p\text{-values} < 0.05$). Investigation of the individual effects of each of the terms in the models show that both coagulant dose (factor A) and coagulant:CAS ratio (factor B) have significant effects on CSMR with both coagulants (term $p\text{-values} < 0.05$). While both factors have a significant effect, coagulant dose (factor A) is the major contributor to CSMR in comparison with coagulant:CAS ratio (factor B). This can be deduced by comparing between the F-values for both significant factors (F-value for coagulant dose is much higher than that for coagulant:CAS ratio with both coagulants). In the case of PACl, two and three-factor interactions do not contribute significantly to CSMR while with alum, the two-factor interaction (alum dose with coagulant dose:CAS ratio) is a significant contributor (p-value = 0.0022). Logical interpretation of the observed results is that the coagulants contribute chlorides (in the case of PACl) and sulfates (in the case of alum) when added to the water. Additionally, CAS contributes sulfates as well since it has been formulated by the incorporation of sulfuric acid ($H_2\mathbf{SO_4}$) with alum ($Al_2(\mathbf{SO_4})_3$).

DOC and UV254 absorbance: The complete ANOVA models for both DOC (Figures A25, A26) and UV_{254} absorbance (A27, A28) are consistent and are not significant at the 95% confidence level (p-values > 0.05). However, closer inspection of the significance of the individual terms shows that PACl dose has a significant effect on DOC removal (and UV_{254} reduction). Alum did not have a significant effect on DOC removal at the 95% confidence level. The effect of alum dose on UV_{254} however, hinted that its dose might have an effect on UV_{254} but a solid conclusion at the 95% confidence level cannot be deduced since the p-value was standing at 0.05. Interpretation of these results indicates that in this water PACl is more effective than alum in removing DOC. This is consistent with results from stages I and II A.

pH: ANOVA analysis for pH is shown for PACl and alum in Figures A29 and A30, respectively. Not unexpectedly, coagulant dose has a significant effect on pH with both coagulants. In the case of PACl, coagulant:CAS ratio is also a significant contributor to pH. All the other parameters and interactions between them did not have any significant effects on pH. The addition of coagulant drops the pH and consumes alkalinity. The addition of CAS with PACl consumed even more alkalinity since CAS is acidic (pH dropped below 2 at the time of preparation).

SDS-THMs: ANOVA tables for SDS-THMs for both coagulants are represented in Figures A31 and A32. Coagulant dose was the only significant contributor to THM formation reduction with both coagulants. DBP precursors were therefore affected by coagulant addition only and the ratio of coagulant:CAS and the time of CAS addition did not affect precursor removal.

Turbidity: ANOVA tables for turbidity for both coagulants are shown in the appendix (Figures A33, A34). In experiments with PACl as the primary coagulant, none of the main effects or multiple factor interactions had a significant effect on turbidity removal. In alum experiments, different results were observed; both the alum dose and alum:CAS ratio affected turbidity to a significant extent and the ANOVA model was significant. Additionally, interactions between alum:CAS ratio and the time of CAS addition had a significant effect on turbidity removal at the 95% confidence level. CAS in this scenario might enhance turbidity removal depending on the ratio and time of its addition. The magnitude of contribution of the two-factor interaction (BC) was similar to that of the main effect, coagulant dose. This might be attributed to experimental conditions (low starting turbidity) and further research is warranted. This hint might explain and agree with the anecdotal evidence from CAS testing in an Ontario WTP. Turbidity was probably the main parameter monitored during CAS testing with alum at the WTP.

The relative importance of each term investigated in the experiments can be more easily demonstrated by looking at the percentage contribution of each of the factors to the parameters analyzed (percent contribution of each model term to the total sum of squares). A summary of these values is presented in Table 4-5. In general, it is apparent the contribution of coagulant dose to the parameters investigated is the most important (higher values relative to other values in the same column. Results from this table are in agreement with previous interpretations from the ANOVA tables.

Table 4-5: Percent contribution of compared factors to CSMR, DOC, turbidity and pH reduction and to SDS-THM formation

Factor	CSMR		DOC		pH		SDS-THM		Turbidity	
	PACl	Alum	PACl	Alum	PACl	Alum	PACl	Alum	PACl	Alum
A: Coagulant dose	96.6	98.1	74.4	49.3	56.4	68.8	87.2	52.3	12.2	27.5
B: Coagulant:CAS ratio	1.9	0.3	3.3	0.3	14.1	7.6	2.7	3.3	12.2	13.2
C: Time of CAS addition	0.1	0	0.3	26.9	0	0.9	3.7	4.7	2.0	4.1
AB	1.0	0.5	0.7	8.1	14.1	7.6	0.4	6.4	0.5	4.1
AC	0.1	0	8.0	0	0	0.9	3.3	2.1	0	4.1
BC	0	0	1.8	0	0	7.6	0.8	1.2	17.6	27.5
ABC	0	0	2.8	4.1	0	0.9	0	6.4	7.8	7.8

A comparison between results from stages II A (testing of coagulants alone) and II B (testing of coagulants with CAS) is useful for determining the overall contribution of CAS to observed coagulant performance enhancement. CSMR, DOC, and SDS-THMs were examined. The designs for both stages were different, however, a coagulant dose range common to both stages was 5 – 15 mg/L. Average results in a fixed dose range can therefore be compared. This was computed from Stage II B by fixing the coagulant dose at a certain value and averaging the responses at that value. Bar charts comparing the results from both stages II A and II B are shown in Appendix A.

Average values obtained for CSMR with the coagulants alone (red bars) in comparison with the coagulants with CAS (blue bars) at each dose are shown in Appendix A (Figures A35 – A37). CAS generally improved CSMR values by up to 14%. This was expected given that CAS contains sulfates both from alum and sulfuric acid. CAS improved DOC removal by 2 – 15% (Figures A38 – A40). This could have been attributed to the alum content of CAS or to the polymer itself. Finally, CAS improved the removal of DBP precursors (tested by SDS-THM) by 2 – 11% (Figures A41 – A43). This could have also been attributed to the extra alum added to the water consequent to CAS addition or to the associated drop in pH.

CAS addition therefore resulted in slight improvements in the main parameters of concern. However, being of a small magnitude (<15%), those improvements would have to be carefully considered before switching to the use of CAS as a flocculant aid on a large scale since the observed small improvements could be due to experimental and analytical error. In addition, CAS use would trigger an increase in chemical cost which may not be commensurate with the observed improvements.

From the results discussed to-date it is clear that polyaluminum chloride (which is used at full-scale) was contributing to unfavourable CSMRs thereby likely increasing galvanic-induced lead dissolution into the water. Alum on the other hand, while able to reduce CSMR, could not get it to a sufficiently low value at dosages which could be reasonably applied at the Woodward Avenue WTP. Given so, it became apparent that an investigation of the effect of different coagulants on CSMR would be of merit. This was therefore investigated in the following stage.

4.6 Stage III – Investigation of alternative coagulants

Following the evaluation of CAS as a flocculant aid, it became evident that an investigation of alternative coagulants was necessary. The following six coagulants were tested during experimentation which was conducted in March and April 2008:

1. Aluminum sulfate (alum)
2. Polyaluminum chloride (PACl)
3. Ferric sulfate
4. Pre-hydroxylated aluminum sulfate (PHAS)
5. Aluminum chlorohydrate (PAX-XL 1900)
6. Polyaluminum silicate sulfate (PASS 100)

Testing of the six aforementioned coagulants was carried out in order to address the following two objectives:

1. To evaluate the effect of coagulant type and dose on CSMR as it pertains to the galvanic corrosion of lead in drinking water.

2. To evaluate the effect of coagulant type and dose on DOC removal as well as pH since it also has an influence on the solubility and speciation of lead in brass, solders, and fittings.

Experiments for Stage III involved conducting six runs of jar test trials at room temperature, one with each of the coagulants considered. The temperature of the water at the time of collection was 8°C. As was shown in Table 3-2 (Chapter 3), the application of the two coagulants PAX-XL 1900 and PASS 100 as coagulants in drinking water treatment is not as widespread in comparison with the four other coagulants. Given so, no previous literature was available to be used as a guide in the selection of the dose range to be considered in the experiments. A relatively wide dose range of 5 – 30 mg/L was therefore chosen in order to bracket what could be the optimum dose for organics removal. The six jars were therefore dosed from 5 to 30 mg/L (of the coagulant active ingredient) in increments of 5 mg/L. Figure 4-13 shows a schematic of a sample run conducted with an individual coagulant.

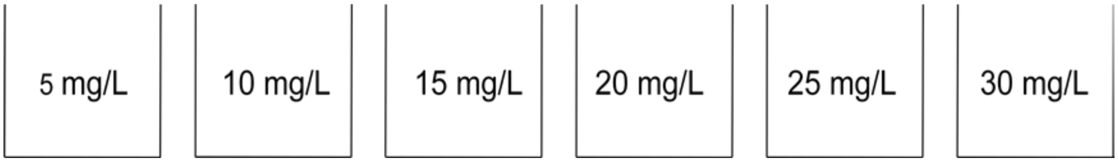


Figure 4-13: Schematic of a jar test trial for Stage III of testing on Lake Ontario water

Parameters monitored during this stage of experimentation included CSMR, DOC, pH, turbidity, UV_{254} absorbance, and temperature.

4.6.1 Stage III results

The effect of coagulant dose and type on the chloride-to-sulfate mass ratio CSMR is shown in Figure 4-14. Non-chlorinated raw water was used throughout all the experiments and had an initial CSMR of 1.03 (29.8 mg/L Cl^- and 28.9 mg/L SO_4^{2-}). As previously discussed, it has to be emphasized that the chloride in the tested water is under-estimated since pre-chlorination (as is practiced at full-scale) would increase its levels in the water. CSMR for pre-chlorinated water can be projected if it is analyzed for raw pre-pre-chlorinated water samples as was illustrated in Figure 4-10. Analysis of a pre-chlorinated water sample in Stage II A showed that CSMR increased by 0.28 as a result of pre-chlorination. Chlorine contribution to CSMR therefore cannot be neglected. Chlorine can be added for primary and secondary disinfection.

The linear correlation between coagulant addition and CSMR is clearly apparent for all coagulants considered. While the chloride and sulfate contents of the coagulants were not provided by the supplier, it can be determined from the data available that the chloride contribution per unit dose of PACl is higher than that of aluminum chlorohydrate (PAX-XL 1900). Both coagulants are formulations of polyaluminum chloride and for that reason contributed positively to CSMR. These two coagulants are represented in Figure 11 as the top two sloping lines with the positive slopes. On average, aluminum chlorohydrate contributed 0.93 mg/L Cl^- per 5 mg/L dose, while PACl contributed 1.14 mg/L Cl^- per 5 mg/L dose. Both coagulants therefore shifted CSMR away from the suggested CSMR for galvanic lead corrosion of 0.5 or less. In total, 30 mg/L of PACl increased the CSMR by 0.18 while aluminum chlorohydrate increased the CSMR by 0.25. The final CSMR with PACl at the highest dose tested of 30 mg/L was 1.21 while that for aluminum chlorohydrate was 1.29.

From Figure 4-14 it can also be seen that the four remaining coagulants all reduced the CSMR due to sulfate contribution. The average sulfate contributions per 5 mg/L dose for each of alum, ferric sulfate, pre-hydroxylated aluminum sulfate (PHAS), and polyaluminum silicate sulfate (PASS 100) were 2.80, 3.06, 3.20, and 2.47 mg SO_4^{2-}/L respectively. Ferric sulfate and pre-hydroxylated aluminum sulfate were therefore the highest sulfate contributors from all the coagulants tested. In that respect, their use might be favourable. Indeed they both achieved the lowest CSMR values of all the coagulants (CSMR of 0.6 at 30 mg/L of coagulants). However, the target CSMR value of 0.5 was never reached. It has to be emphasized that their effect on pH was not yet accounted for; a parameter that could greatly influence lead release in the water (discussed later). The dose range employed at Woodward Avenue WTP throughout the year is represented by the shaded areas in Figures 4-14 through 4-16.

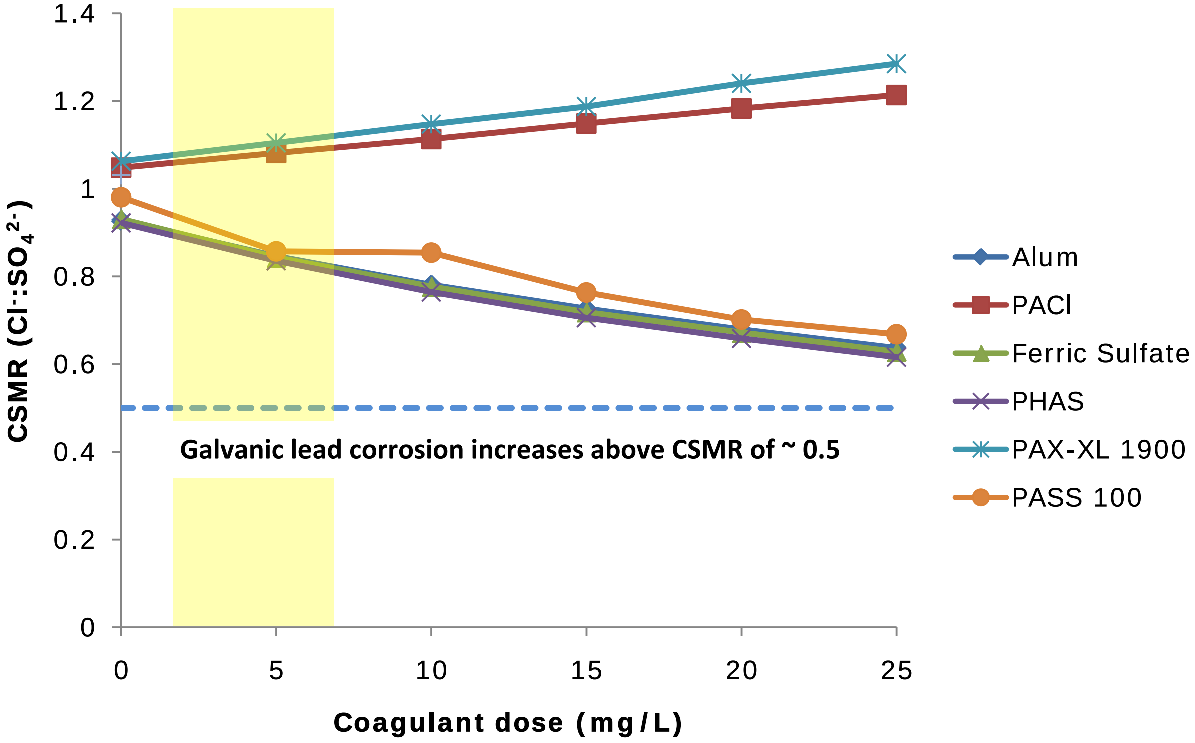


Figure 4-14: CSMR vs. coagulant type and dose

Alum, PACl, and PAX-XL 1900, and PASS 100 dropped the pH by up to the same extent (drop in pH of 0.5) at the highest doses tested (Figure 4-15). Ferric sulfate resulted in a greater drop in pH (0.7) and pH drop as a result of PHAS addition was most pronounced, dropping the pH by 0.9 units at the highest dose tested. Therefore with respect to pH, the addition of PHAS could potentially have the most detrimental effect on lead release in the water, followed by ferric sulfate.

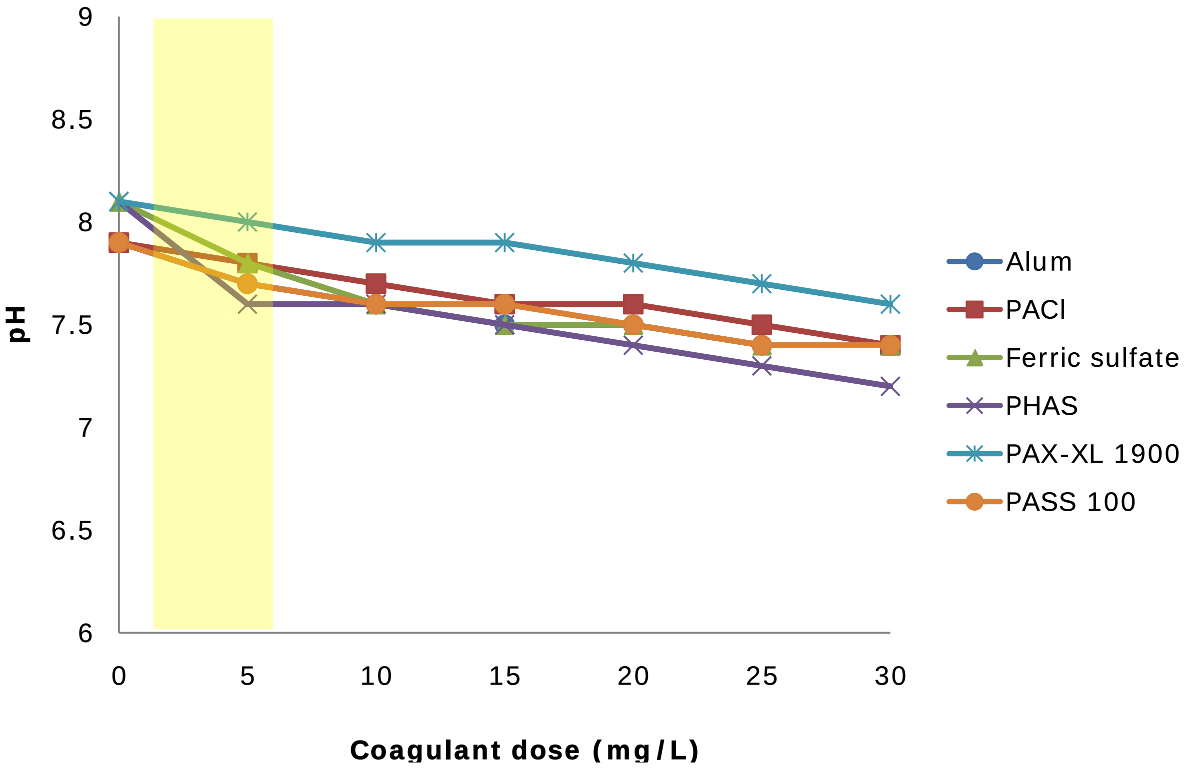


Figure 4-15: pH vs. coagulant type and dose

The effect of each of the coagulants on the DOC concentration in the water is shown in Figure 4-16. An alternate representation is shown in Appendix A (Figure A44) as percentage removal. The highest DOC removals (~36%) were achieved with both chloride-containing coagulants polyaluminum chlorides PACl and aluminum chlorohydrate (PAX-XL 1900). However, PAX-XL 1900 was more efficient since it removed DOC by up to the same extent as PACl but at half the dose (15 mg/L). The highest DOC removals achieved by the remaining coagulants were 30% for PHAS (30 mg/L), 29% for alum (30 mg/L), 27% for PASS 100 (25 mg/L), and 22% for ferric sulfate (30 mg/L).

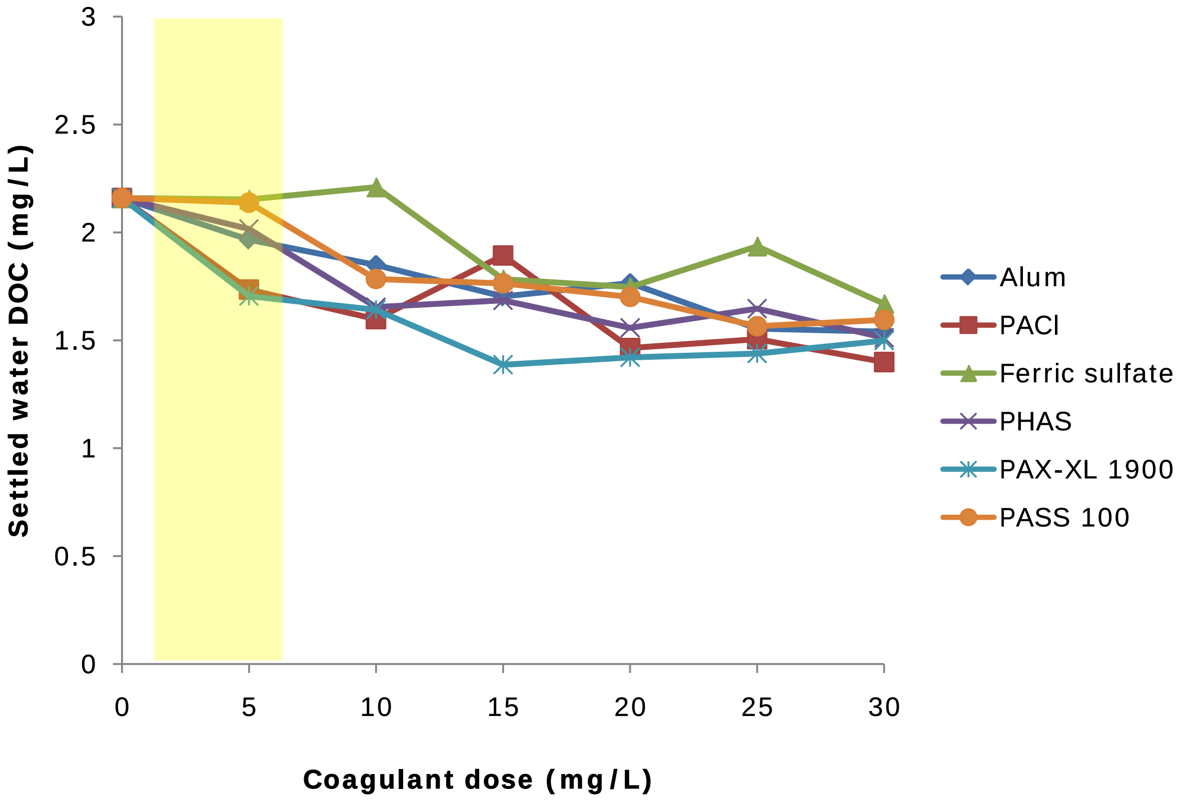


Figure 4-16: Settled water DOC vs. coagulant type and dose

The lowest UV_{254} values were achieved with PACl indicating that it is the most efficient in removing the humic content of the water (Figure A45). UV_{254} values obtained for ferric sulfate show an anomaly which is likely attributed to experimental error. The performance of the remainder of the coagulants with respect to humics removal was about the same.

Investigation of percentage turbidity removal as a function of coagulant dose is illustrated in Appendix A (Figure A46). PACl outperformed all the coagulants with respect to turbidity removal (89% removal at 10 mg/L) followed by alum (84% at 10 mg/L), pre-hydroxylated aluminum sulfate (PHAS) (75% at 5 mg/L), ferric sulfate (70% at 20 mg/L), aluminum chlorohydrate (PAX-XL 1900) (57% at 30 mg/L), and finally polyaluminum silicate sulfate (PASS 100), removing 39% at 5 mg/L. These doses represent the optimum for turbidity removal. For all the coagulants, increasing the dose beyond the optimum results in decreased removal efficiencies due to colloid re-stabilization. Four of the doses tested with PASS 100 contributed to turbidity.

From this stage it can be deduced that the addition of polyaluminum chloride coagulants PACl and PAX-XL 1900 has an unfavourable effect on CSMR since it increases it. On the other hand, ferric sulfate and PHAS reduced CSMR to the greatest extent. Although, the use of PHAS improved CSMR values, its addition resulted in the most substantial pH drop which may have a negative influence on lead release. Its use for CSMR adjustment would therefore not be recommended. If only pH and CSMR effects on lead release were considered, the best suited coagulant in that respect would be alum since it results in relatively small drops in pH and at the same time reduces CSMR. Polyaluminum silicate sulfate (PASS 100) also shows potential, followed by ferric sulfate.

A different approach towards measuring the effect of coagulant choice on CSMR could have been achieved by measuring the chloride and sulfate concentrations directly in the additive solutions then projecting the resulting chloride and sulfate concentrations based on coagulant dose and the background concentrations of the two parameters in the raw water. Similar results would have been achieved. However, in order to ensure that the direct effect of coagulant addition on chlorides and sulfates in the water is accounted for, and to verify the integrity of the calculations pertaining to coagulant dose, actual concentrations were measured in each of the coagulated waters.

Chapter 5 EXPERIMENTS ON GRAND RIVER WATER

This chapter begins with a comparative analysis of historical and measured raw water parameters. This is followed by a discussion of the experimental approach undertaken for testing of Grand River water. Designs and results for each of the experimental phases involved are then presented. Testing on Grand River water was conducted at Brantford WTP during the months of July and August 2008 through a series of jar test trials. The main objectives of these experiments were as follows:

1. To investigate the effect of six different coagulants on CSMR and organics removal in Grand River water, among other parameters.

2. To evaluate the performance of the polymer anionic activated silica (AAS) as a flocculant aid with respect to CSMR reduction and organics removal.

3. To validate standard jar test procedures by comparing to a bench scale jar-test apparatus that was designed to simulate the performance of a high-rate sand-ballasted clarification process for the coagulation/flocculation of water.

5.1 Raw water characteristics

Encompassing a water-shed area of approximately 68,000 km^2, the Grand River constitutes the largest river in southern Ontario. It flows through Kitchener, Waterloo, Cambridge, Brantford, Paris, Caledonia, Grand Valley, Fergus, Elora, and Cayuga and has numerous tributaries such as the Nith, Eramosa, Speed, and Conestogo rivers. The Grand River flows a distance of 280 km towards the southern Ontario where it empties into Lake Eerie. Having a fairly large watershed size, the Grand River spans a number of climate and forest zones. The river’s climate and the soil type in its watershed support a variety of agricultural and urban activities. Currently, it is estimated that a human population of approximately 925,000 inhabits the water-shed, with the central region being the most densely populated (GRCA, 2008).

Table 5-1 shows a comparison between historical and measured raw water parameters from the Grand River and Figures B1 – B4 (Appendix B) show variations in turbidity, dissolved oxygen, TOC, and UV_{254} absorbance measured throughout the duration of the experiments. Turbidity of the water collected averaged 13 NTU. Turbidity variations of approximately 10 NTU were encountered. The lowest recorded turbidity was encountered on August 5th, and the highest turbidity was recorded on the consecutive day, August 6th due to an overnight rain event (Figure B1). Over the period from 2000 – 2003, turbidity data obtained from the Drinking Water Surveillance Program (DWSP, 2008) showed an average of 5.1 NTU. Based on the turbidity range obtained from DWSP, spikes in turbidity resulting from storm events were not accounted from DWSP data since sampling was conducted every 3 – 4 months. Turbidity of Grand River water was generally the highest between the months of April and June, and lowest during late December / early January.

Table 5-1: Comparison between historical and measured raw water quality for Grand River water

	Historical range[a] (2000 – 2003)		**Measured values[b] (2008)**	
	Average	**Range**	**Average**	**Range**
pH	8.3[c]	8.1 – 8.4	7.8[c]	7.6 – 7.9
Turbidity (NTU)	5.1	1.0 – 14.2	13.0	6.6 – 16.7
Temperature (°C)	8.0	0.1 – 27.6	22.4	19.9 – 23.5
DOC (mg/L)	5.0	4.1 – 6.5	6.0	5.2 – 7.6
CSMR	1.2	0.8 – 1.5	1.6	1.3 – 1.9
Dissolved oxygen (mg/L)	-	-	7.1	6.2 – 8.4

a – Data obtained from Drinking Water Surveillance Program (2008) for years 2000 - 2003

b – Measured during experimentation from October 2007 – April 2008

c – Value represents the median

TOC, DOC and UV_{254} absorbance of the raw water were also monitored. Figure 5-1 shows DOC levels in the raw water at the time of experiments. Sampling dates on the graph denoted by the letter “A” indicate that the samples were collected and analyzed in the afternoon. DOC levels ranged from 5.2 to 7.6 mg/L, averaging at 6 mg/L. As can be seen from Table 5-1, such DOC levels are fairly typical of the Grand River. The predominant sources of organics in Grand River water could be either natural (aquatic plants) or agricultural (use of insecticides and pesticides) since the water-shed supports heavy agriculture (GRCA, 2008). Industrial sources may also be possible. TOC and UV_{254} absorbance trends of the sampled water agreed with those for DOC and the plots are shown in Appendix B (Figures B3, B4). Examination of Specific UV absorbance (Figure 5-2) shows that with the exception of one day, the water had SUVA values above 3 throughout the duration of the experiments, suggesting a tendency towards high aromatic content and amenability to NOM removal by enhanced coagulation. SUVA of the water dropped noticeably on the afternoon of August 1st. However, this may have been due to experimental error since the SUVA of a water sample collected in the morning of the same day was higher and consistent with SUVA measured on the other days.

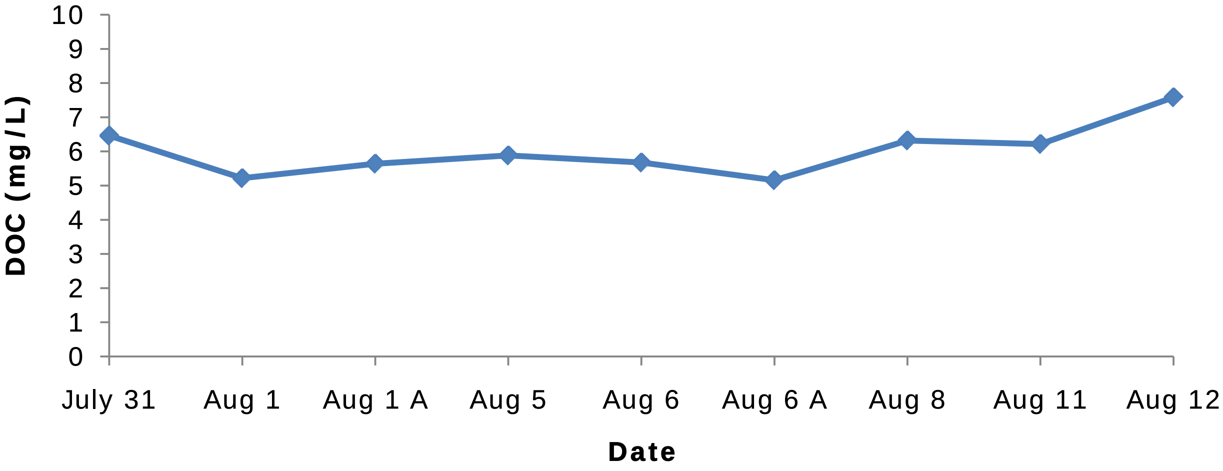


Figure 5-1: Variations in DOC levels of Grand River water during experiments

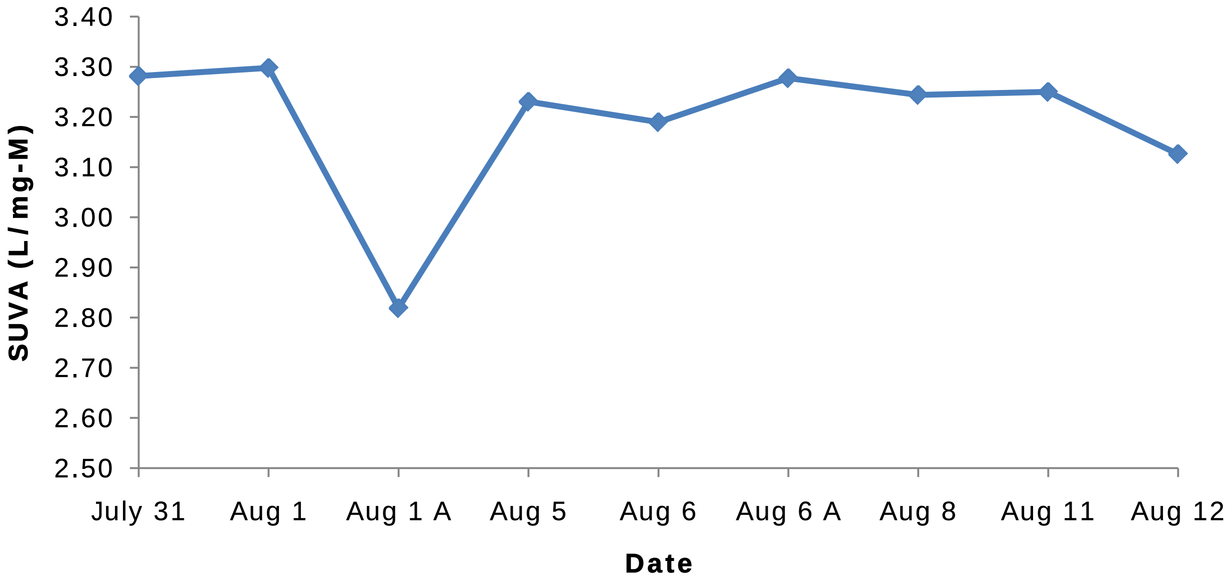


Figure 5-2: Variations in SUVA of Grand River water during experiments

Grand River water is typically basic with a pH ranging from 8.1 to 8.4 throughout the year. The median historical pH is at 8.3. The pH of the sampled water at the time of collection was lower (Figure 5-3), ranging from 7.6 – 7.9 with a median of 7.8. The recorded pH was a bit low for that time of the year and did not fall within the historical range obtained from DWSP. The river water temperature in July and August was in the high range, averaging at approximately 22°C. The average yearly temperature of Grand River water is 8°C.

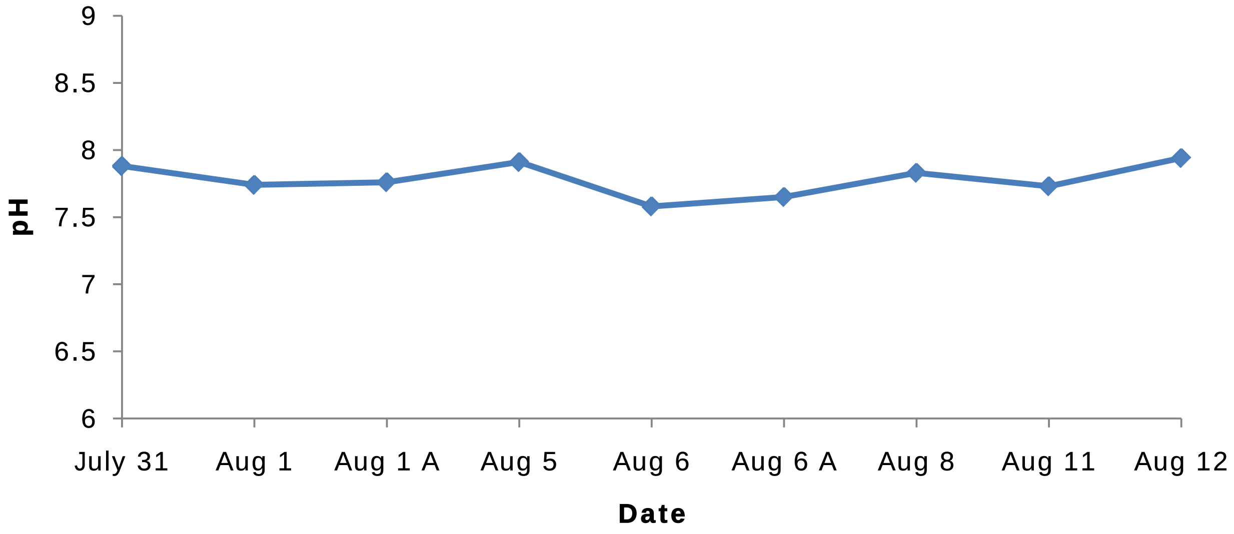


Figure 5-3: Variations in pH of Grand River water during experiments

Inspection of historical chloride and sulfate data in river water between 2000 and 2003 show large variations in the levels of both chlorides (47 – 160 mg/L) and sulfates (32 – 134 mg/L). Variations in the river water chloride levels are strongly correlated with the season and time of the year, with lowest chloride values recorded during the spring and summer seasons, and the highest levels recorded between October and March. This is clearly attributed to the use of road de-icing salts as previously discussed. Although bacterial activity may contribute sulfates to the water, such large variations in the sulfate levels of the river water throughout the year are more than likely attributable to an anthropogenic origin such as wastewater treatment plant discharge.

Figure 5-4 shows variations in CSMRs throughout the duration of the experiments with a portrayal of the contribution of its individual constituents (chloride, sulfate) also represented. The CSMR averaged 1.6, ranging from 1.3 to 1.9. The highest peak in CSMR was recorded on August 6th. Further investigation attributed the spike to a sharp drop in the sulfate level on that day (50% sulfate reduction). Sulfate levels were consistently low following August 6th, and although chloride levels were relatively low during that period, an apparent increase in CSMR was still observed due to the large drop in the sulfates. Sudden drops in the sulfate levels of the water of such magnitude are not likely attributable to natural sources and are probably a result of human activities.

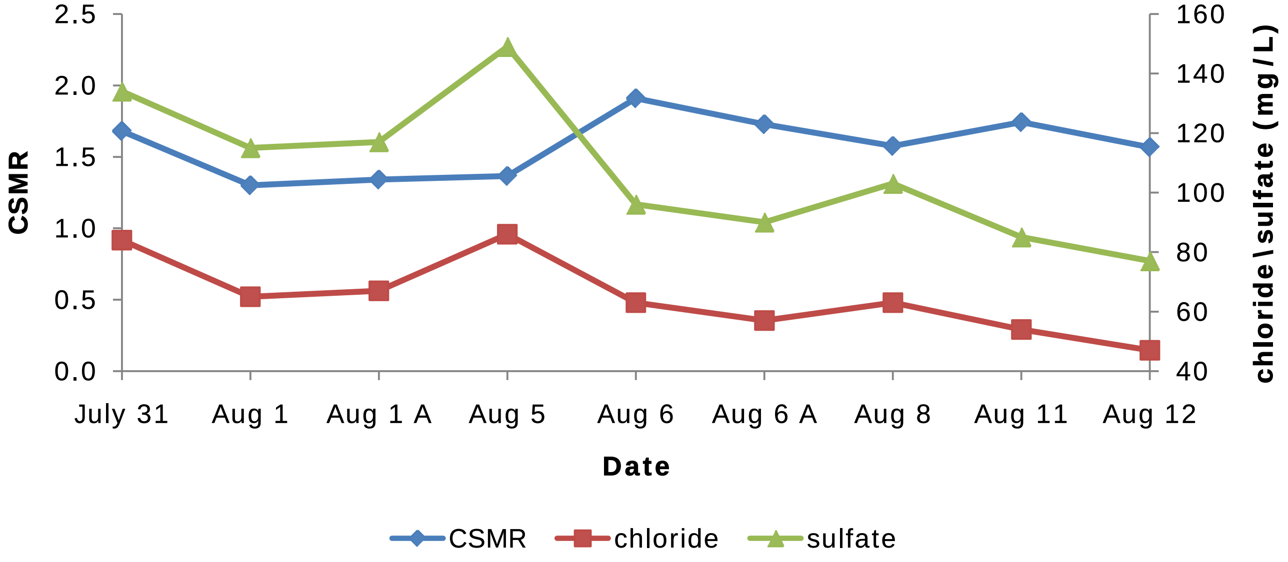


Figure 5-4: Variations in CSMR of Grand River water during experiments

5.2 Treated water CSMR

Two year's worth of data pertaining to CSMR of the treated water from Brantford WTP (DWSP, 2008) is plotted in Figure 5-5. A general increasing trend in CSMR is evident. It was especially apparent that the CSMR increased noticeably in the period between April and November 2001 suggesting potential grouping of the data. Further investigation into the issue showed that a coagulant switch from alum to polyaluminum chloride was implemented during that period. A coagulant switch from alum not only reduced the sulfate contribution to the water, but it also resulted in a chloride contribution from the polyaluminum chloride coagulant. This in turn increased CSMR values, shifting them away from Edwards and Triantafyllidou's (2007) recommended CSMR of 0.5 to reduce lead release from brass and solder-copper connections.

Inspection of Figure 5 therefore warranted further investigation into the effect of coagulant choice on CSMR as it pertains to lead release in galvanic settings. This was one of the primary objectives of the experiments on Grand River water.

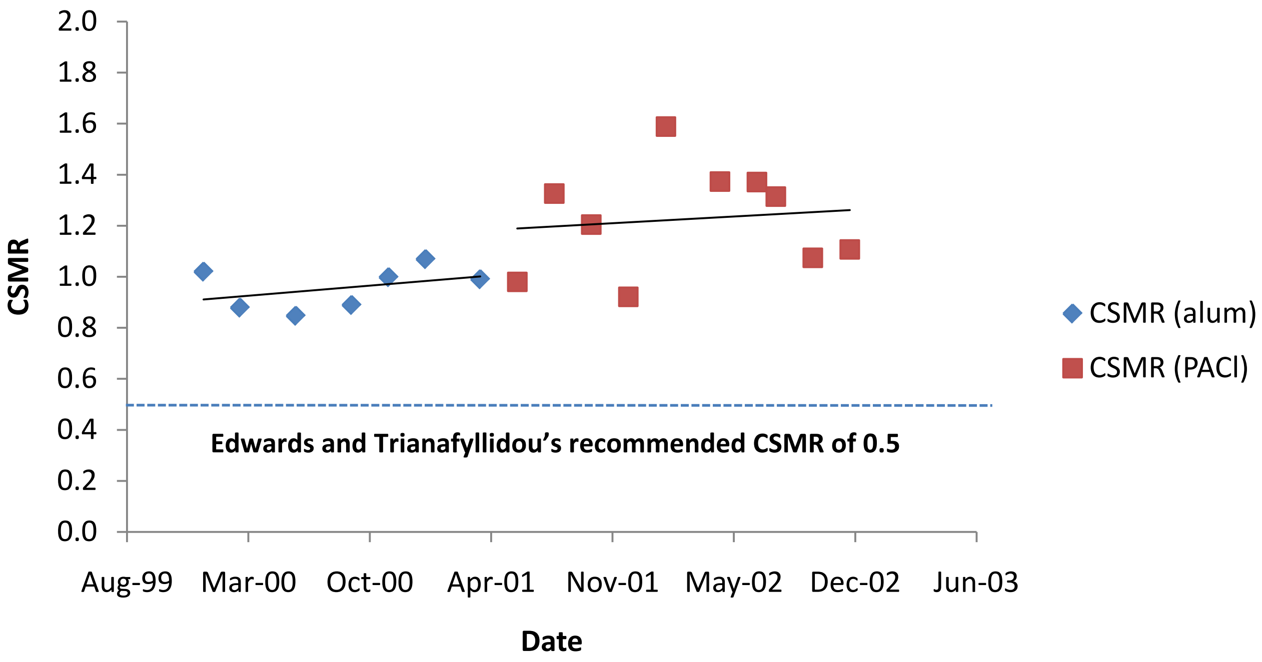


Figure 5-5: Treated water CSMR data for Brantford WTP (DWSP 2008)

5.3 Experimental approach

Experiments on Grand River water were conducted in two phases; the first of which incorporated a test of six alternative coagulants (Phase I A) and the use of anionic activated silica as a flocculant aid in conventional treatment (Phase I B). In Phase II, simulated sand-ballasted coagulation/flocculation (Actiflo) was compared to traditional jar test apparatus for selected parameters. Figure 5-6 shows a summary of the approach taken towards the testing of Grand River water.

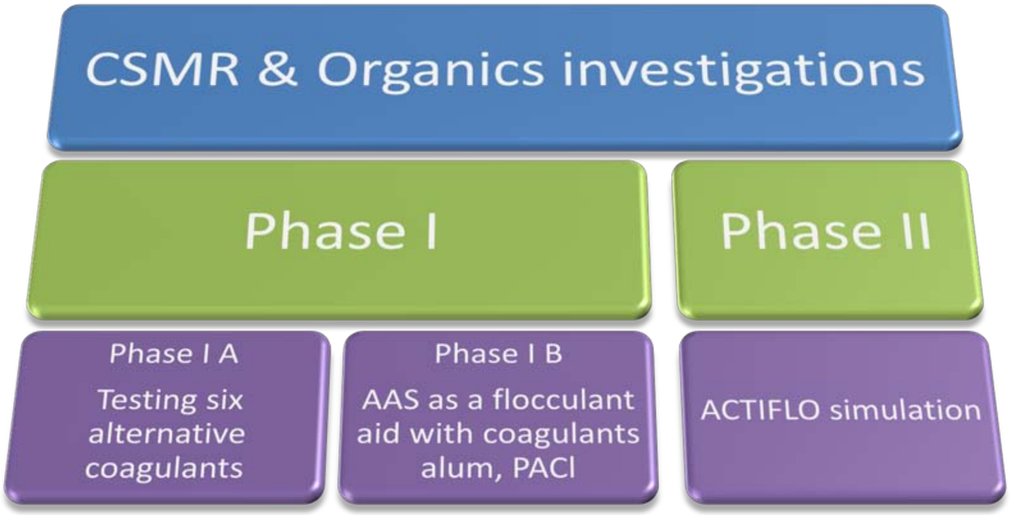


Figure 5-6: Experimental approach for Grand River water

5.4 Phase I

Experiments conducted in this phase were designed with one primary objective in mind, that is, to obtain results from a different source water that could be compared with results from testing on Lake Ontario water (investigated in Chapter 4). This phase was divided into two subsections, namely Phase I A for coagulant testing and Phase I B for flocculant aid testing.

In order to obtain comparable results to Lake Ontario water, similar coagulation, flocculation, and sedimentation conditions were assigned with only the coagulant dosage being increased. Rapid mixing was therefore performed at 200 rpm for 30 s, followed by a two-stage tapered flocculation, consisting of slow mixing at 60 rpm for 15 min, followed by mixing at 40 rpm for an additional 15 min. Finally, the water was allowed to settle for 15 min after which the water samples were collected and analysed.

Parameters investigated during this phase include CSMR, TOC, DOC, pH, turbidity, UV_{254} absorbance, dissolved oxygen and temperature.

5.4.1 Phase I A – Alternative coagulants for CSMR modification

During this phase, the six coagulants previously investigated on Lake Ontario water (Chapter 4, Stage III) were tested on Grand River water through the implementation of six jar trials. As a reminder, the six coagulants tested were

1. Aluminum sulfate (alum)
2. Polyaluminum chloride (PACl)
3. Ferric sulfate
4. Pre-hydroxylated aluminum sulfate (PHAS)
5. Aluminum chlorohydrate (PAX-XL 1900)
6. Polyaluminum silicate sulfate (PASS 100)

The six coagulants were investigated in this stage in order to satisfy the following two objectives:

1. To gain a better understanding of the behaviour of the coagulants with respect to CSMR, pH, and organics removal in a different type water; a river water. Additional parameters were also considered.

2. To obtain coagulant performance results from Grand River water that could potentially be compared with those obtained from testing Lake Ontario water.

Experiments for Phase I A involved conducting six runs of jar test trials at room temperature. Brantford WTP coagulates the water with polyaluminum chloride at a dose range of 15 to 50 mg/L depending on the season. The coagulant dose employed at the WTP at the time of experiments was 35 mg/L. In order to incorporate the WTP dosing practice into the design, the doses tested were in the range of 10 – 60 mg/L of the coagulant in increments of 10 mg/L. Each run was conducted with the six coagulants at a fixed coagulant dose. This was different from the approach taken for Stage III of testing on Lake Ontario water where the coagulant type was fixed and the dose altered over a single run. The logic for conducting the runs on Grand River water in such a way lies in the fact that the experiments spanned several days over which variations in water quality could have been a potential concern. It was therefore more desirable to conduct each single run with the six coagulants at a fixed dose in order to compare between the performance of the six coagulants on the same water at a given dose.

Experiments were conducted on-site at the Brantford WTP with the same jar testing apparatus used for Lake Ontario trials. Fresh, raw, non-chlorinated water was collected from the raw water line on each day of experimentation.

Coagulation, flocculation, and sedimentation conditions employed were as mentioned previously. Figure 5-7 shows a schematic of a single run conducted at a fixed coagulant dose of 10 mg/L.

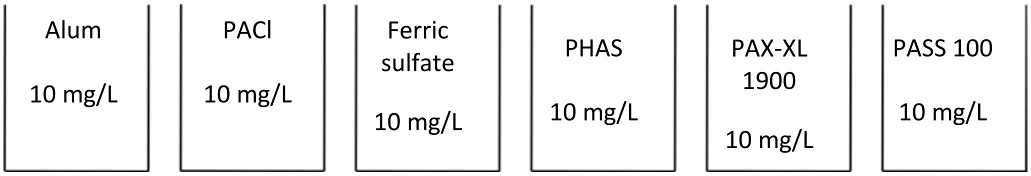


Figure 5-7: Schematic of a jar test trial for Phase I A of testing on Grand River water

5.4.1.1 Phase I A results

Figure 5-8 shows a plot of CSMR as a function of coagulant type at the different doses tested. The two lines on the plot show the effect of coagulant type on CSMR at the lowest and highest doses tested of 10 and 60 mg/L, respectively. Each line on the plot also pertains to a single run of jar tests conducted at a fixed coagulant dose with the different coagulants. Since the raw water quality varied for each coagulant dose/run, a more plausible way of presenting the data was by relating the performance of the different coagulants at a single dose as shown in the figure. CSMR values for each run were joined in the plot for clarity.

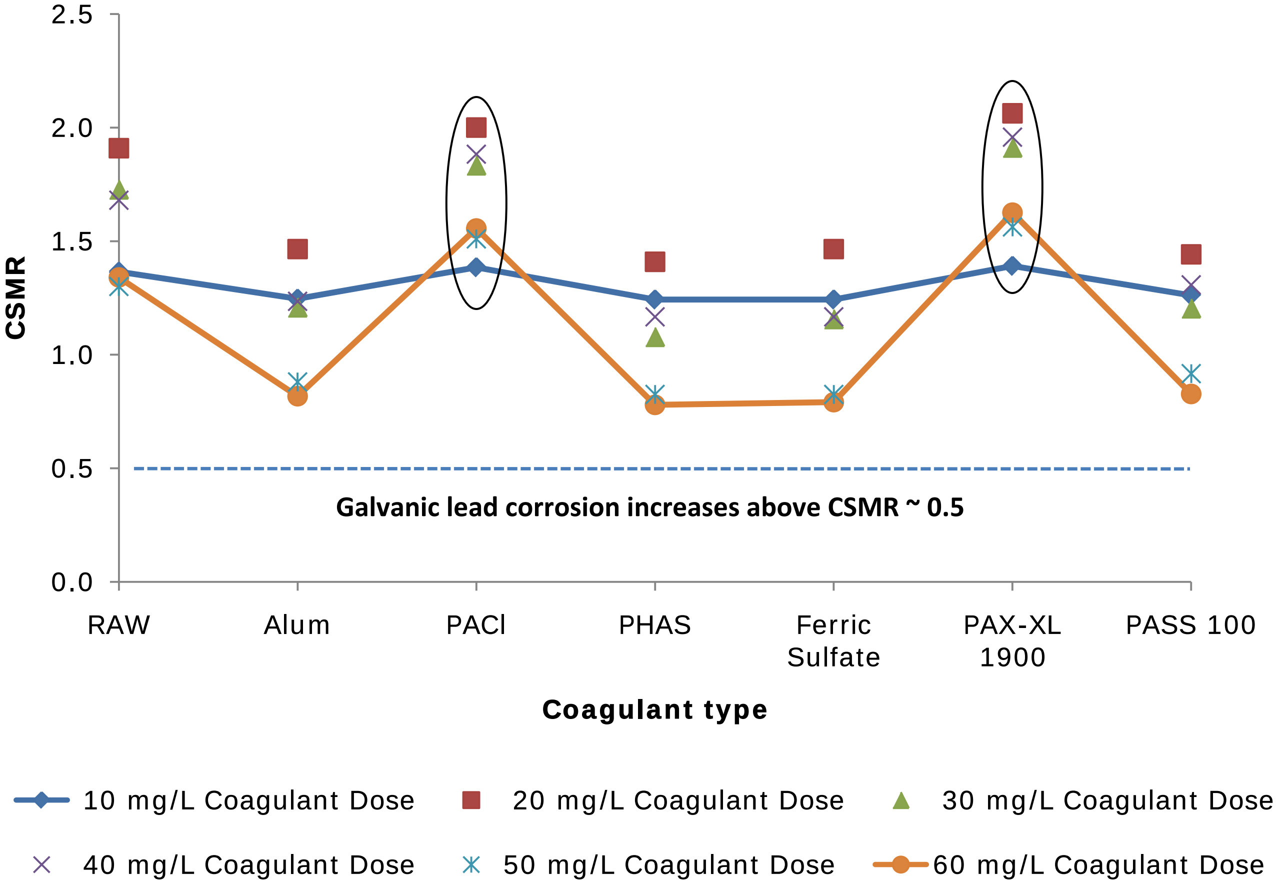


Figure 5-8: CSMR vs. coagulant type, dose

Raw water CSMR was in the range of 1.30 – 1.91 during the experiments with values in the high range noted in the water when the three runs at 20, 30, and 40 mg/L were conducted (CSMR values of 1.91, 1.73, and 1.68 respectively). CSMR of the raw water was fairly steady when the remainder of the runs were conducted (1.30 – 1.37). Consistent with observations from testing on Lake Ontario water, it can be seen from Figure 5-8 that the two chloride-containing coagulants PACl and aluminum chlorohydrate increased CSMR in the water relative to all the other coagulants tested. This is shown in the figure by the two ovals. Peaks obtained at the 10 mg/L dose were less pronounced due to low chloride contribution relative to the sulfate. Even at a low coagulant dose of 20 mg/L, chloride-containing coagulants resulted in CSMR values as high as 2.0 and 2.1 (PACl and aluminum chlorohydrate respectively). The highest values were recorded at the low coagulant dose of 20 mg/L because the initial CSMR of the water was high relative to the other runs. PACl contributed more chloride to the water than aluminum chlorohydrate at comparable coagulant doses. The average chloride contributions per 10 mg/L of PACl and aluminum chlorohydrate were 3.06 and 2.17 mg-Cl^-/L respectively. Bearing in mind that the water tested was non-chlorinated, CSMR levels approaching 2.5 in the treated water are possible when both chlorination and polyaluminum chloride doses in the high Brantford WTP operating range of 30 – 50 mg/L are taken into consideration. Actual CSMR values of post-filtration and post-reservoir water sampled on two days at the WTP are shown in Appendix B (Figure B5). Noteworthy is the sulfate increase in the water resulting from water retention in the reservoir which is likely attributable to the residence time in the reservoir (which was not taken into account when samples were taken). Other parameters measured are also included in the figure.

The four remaining coagulants tested in the experiments all resulted in CSMR reductions relative to the raw water due to sulfate contribution as shown in Figure 5-8. The average sulfate contribution per 10 mg/L dose of each of alum, ferric sulfate, pre-hydroxylated aluminum sulfate (PHAS), and polyaluminum silicate sulfate (PASS 100) was 5.14, 5.92, 6.00, and 4.94 mg SO_4^{2-}/L respectively. Ferric sulfate and pre-hydroxylated aluminum sulfate were therefore still the highest sulfate contributors of all the coagulants tested which is favourable in terms of reducing CSMR values for lead control in galvanic settings. Indeed they both achieved the lowest CSMR values of all the coagulants at any dose tested. The lowest CSMR values that were achieved were 0.78 and 0.79 for ferric sulfate and pre-hydroxylated aluminum sulfate respectively at the 60 mg/L dose. Alum's role in reducing CSMR was also comparable to the two coagulants resulting in CSMR of 0.82 at the 60 mg/L dose. The target CSMR value of 0.5 was still never reached and neither pre- nor post-chlorination were accounted for.

DOC removal (%) as a function of coagulant dose for the different coagulants tested is shown in Figure 5-9. As previously mentioned, with different starting DOC values of the raw waters, normalization of the data was necessary and expression in terms of % removal relative to the raw water DOC was deemed as the best representation of the available data. A look at percentage removal provides means for relatively comparing between the performance of the coagulants despite variations in the raw water DOC.

From Figure 5-9 it can be seen that aluminum chlorohydrate (PAX-XL 1900) was superior relative to all the other coagulants with respect to DOC removal at all the doses tested. The optimum dose for DOC removal with that coagulant lies in the neighbourhood of 20 mg/L (43% removal). This can be deduced from the almost linear increase in DOC removal as the coagulant dose is increased from 0 to 20 mg/L, after which the increase in DOC removal is gradual and less pronounced with an increase by only 10% achieved when the coagulant dose was increased from 20 to 60 mg/L. PACl was the second-best in terms of DOC removal, achieving 47% removal at the highest dose tested of 60 mg/L. The performance of the other coagulants was also comparable, with a 40%, 39%, 41%, and 34% removals achieved with the coagulants alum, ferric sulfate, pre-hydroxylated aluminum sulfate (PHAS), and polyaluminum silicate sulfate (PASS 100), respectively. The yearly operating dose range of 15 – 50 mg/L employed at Brantford WTP is represented in Figure 9 by the shaded area. Figures B6 – B9 in Appendix B show additional plots for DOC, UV absorbance, and TOC and their trends generally agree with those obtained with DOC removal.

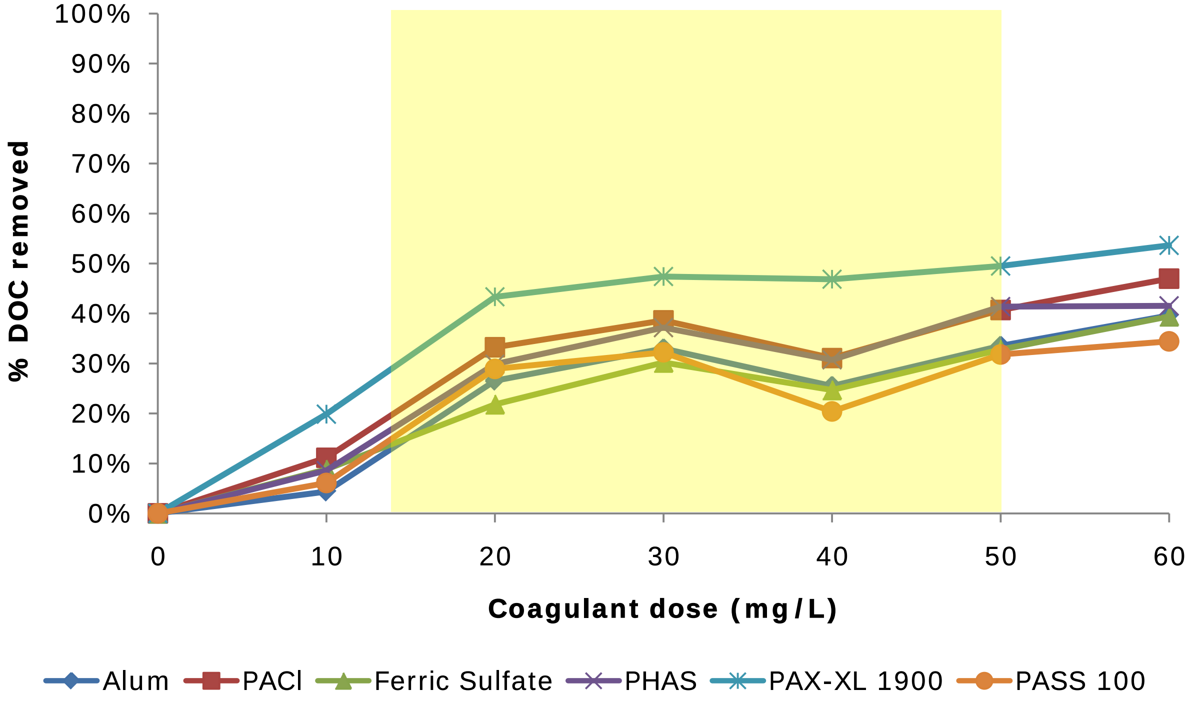


Figure 5-9: DOC removal vs. coagulant dose and type

The effect of coagulant addition on pH is shown in Figure 5-10. Again, the starting pH of the raw waters was different and as such a plot of the different coagulants at a single dose is represented. The effect of coagulant addition on pH is more prominent at the highest coagulant dose tested of 60 mg/L, where pH drops as a result of alum and ferric sulfate addition were the most substantial relative to the other coagulants. Starting with a raw water pH of 7.76, alum dropped the pH by 0.69 units to 7.07 at 60 mg/L while ferric sulfate dropped the pH by 0.64 resulting in a final pH of 7.12 at the same dose. Aluminum chlorohydrate on the other hand dropped the pH by the least extent (0.28) at 60 mg/L due to its high basicity relative to PACl which dropped the pH by 0.36 at the highest tested dose. Less substantial drops in pH as a result of coagulant addition are generally favoured in full scale since it eliminates the need for pH readjustment at the WTP from the perspective of lead corrosion.

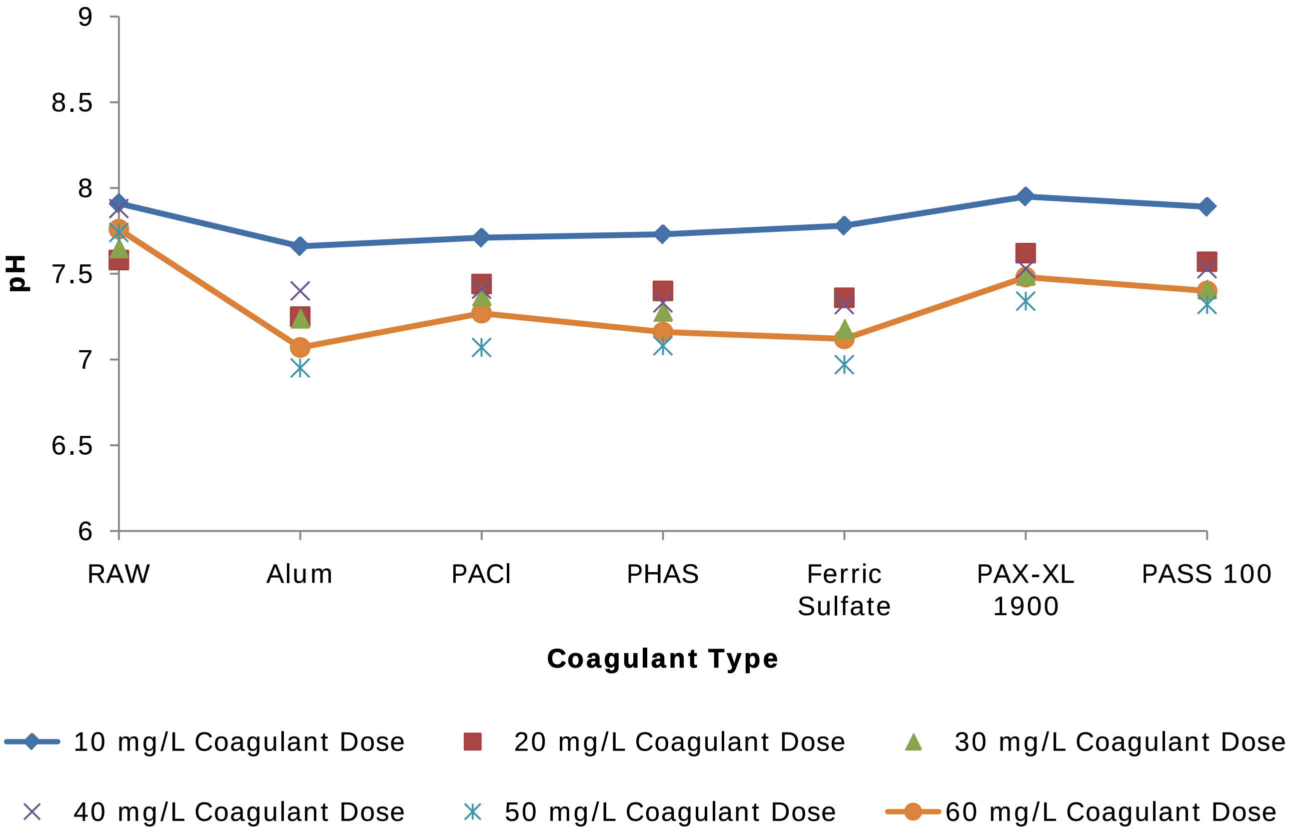


Figure 5-10: pH vs. coagulant type, dose

Turbidity removal (%) as a function of coagulant dose is plotted in Figure 5-11. Residual turbidity is shown in the appendix (Figure B10). Interesting are the results obtained with PACl, which resulted in the highest turbidity removal (97%) at a relatively low coagulant dose of 20 mg/L. This dose is believed to be the optimum dose for turbidity removal. Colloid destabilization in this scenario and at the pH given could be via polymer bridging and colloid enmeshment. Polyaluminum silicate sulfate (PASS 100) achieved the second highest turbidity removal (94%) at a 30 mg/L dose. The performance of the remainder of the coagulants was very similar with alum, ferric sulfate, pre-hydroxylated aluminum sulfate (PHAS), and aluminum chlorohydrate (PAX-XL 1900) achieving their highest removals of 87%, 90%, 90%, and 87% at doses of 30, 50, 30, and 30 mg/L of the coagulants, respectively. PACl therefore performed the best in terms of turbidity removal when both the optimum coagulant dose and % removal are taken into consideration. The shaded area in Figure 11 indicates that Brantford WTP is operating at the optimum PACl for turbidity removal at their current dosing practices.

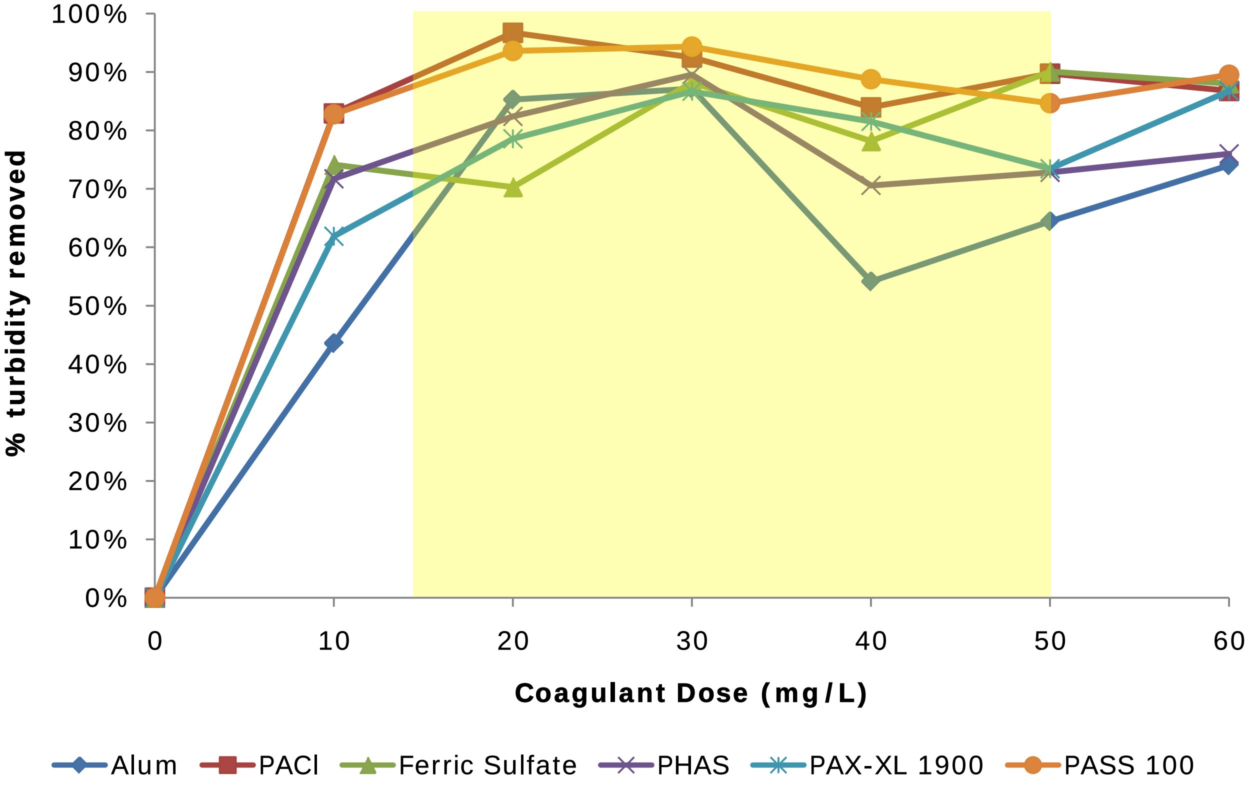


Figure 5-11: Turbidity removal vs. coagulant dose, type

5.4.2 Phase I B – Testing of anionic activated silica

In this phase, alum and PACl were tested on Grand River water in conjunction with anionic activated silica (AAS) as a flocculant aid. The objectives of this phase were as follows:

1. To test the effect of AAS use on CSMR as it pertains to lead release in galvanic settings.

2. To test the effectiveness of anionic activated silica (AAS) as a flocculant aid in the removal of organics (DOC) and turbidity. Additional parameters investigated included pH, TOC, and UV_{254} absorbance.

Brantford WTP currently uses sulfuric acid activated anionic activated silica as a flocculant aid. The flocculant aid is injected into the water prior to coagulant addition. A coagulant-to-AAS ratio of 3:1 is generally maintained at the WTP (AAS expressed in terms of the active ingredient). The experiments in this stage were designed in such a way that coagulant dosing range as well as the dosing ratio and time of injection of AAS at Brantford WTP were simulated. The coagulant dose range employed in the experiments for each of alum and PACl was as before (10 – 60 mg/L) in increments of 10 mg/L and the experiments were conducted by testing each of the individual coagulants at the six doses per single run (two runs in total). Experiments were conducted at room temperature. AAS was injected into the jars prior to coagulant addition and the mixing and sedimentation conditions followed were as described before.

The AAS dose targeted in the experiments was to satisfy the coagulant dose to AAS ratio of 3:1. Initially, information pertaining to the concentration of the active ingredient in AAS was provided by Brantford WTP as 10 g/L and the experiments were designed based on the provided information. However, it was determined later that there was a slight discrepancy in the information provided and that the actual concentration of the active ingredient in AAS was 13.15 g/L. This meant that the actual coagulant:AAS dose employed in the experiments was 2.3:1 as opposed to the initially targeted ratio of 3:1. The initial design of the experiment aimed to maintain the coagulant dose to AAS ratio in the first 4 jars only and holding the same AAS dose in the last two jars as in the jar with 40 mg/L coagulant dose. This was done in order to maintain the AAS level below the maximum dry sodium silicate concentration recommended by the NSF/ANSI Standard 60 of 16 mg/L (NSF International 2008). However, after the discrepancy in AAS concentration was determined, the NSF limit for sodium silicate was slightly exceeded in the three upper dose ranges of 40, 50, and 60 mg/L. A summary of the experimental design is shown in Table 5-2.

Table 5-2: Design of experiments for Phase I B

Coagulant dose (mg/L)	10	20	30	40	50	60
AAS dose (2.3:1)	4.4	8.8	13.2	17.5*	17.5*	17.5*

* NSF/ANSI Standard 60 limit of 16 mg/L (dry sodium silicate) exceeded.

5.4.2.1 Phase I B results

Figure 5-12 shows the effect of coagulant addition on CSMR in the presence of AAS at a coagulant-to-AAS ratio of 2.3:1. It can be observed that increases in CSMR normally brought about by PACl addition are not seen in the presence of AAS. This can be attributed to the sulfate contribution by AAS, remembering that AAS is sulfuric acid-activated. The highest CSMR value reached was 1.71, from a starting raw water CSMR of 1.58. AAS presence in the water was therefore favoured with respect to its effect on keeping CSMR from increasing in the case of PACl. When alum was used as the primary coagulant, CSMR dropped sharply due to sulfate contribution from both alum and AAS. CSMR dropped from 1.58 to 0.84 at the highest tested alum dose of 60 mg/L and at an AAS dose of 17.5 mg/L. However, it has to be kept in mind that the NSF limit of 16 mg/L for dry sodium silicate was exceeded.

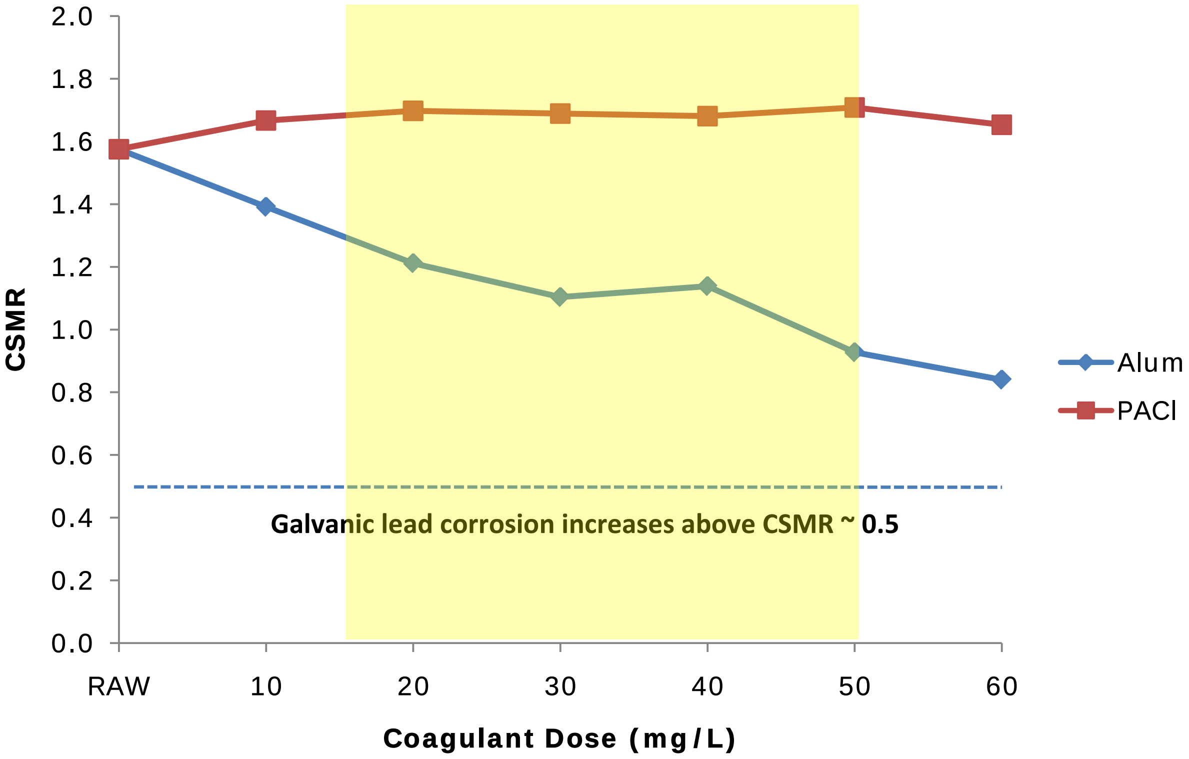


Figure 5-12: Final CSMR vs. coagulant dose for Phase I A

The effect of coagulant addition in the presence of AAS on DOC and pH is shown in Figure 5-13. DOC decreased almost linearly as the coagulant dose was increased. The combination of PACl with AAS achieved better DOC removals at all the doses tested in comparison with alum. The optimum dose for DOC removal with both the coagulants would have to be determined by taking into account other operational and economic considerations. PACl and alum achieved their highest DOC removal (39% and 27% respectively) at the highest coagulant dose tested of 60 mg/L. TOC and UV absorbance plots are also presented in the Appendix B (Figures B11, B12).

pH decreases in the presence of AAS with alum were in close resemblance with those achieved with the coagulant alone (Figure 5-13). With a starting pH of 7.83, pH drop in the presence of alum as the primary coagulant was 0.71 at the highest dose tested of 60 mg/L. pH drop with PACl and AAS was more pronounced than with PACl alone, resulting in a pH drop by 0.62 units. This is attributed to the acidity of AAS which is prepared with concentrated sulfuric acid.

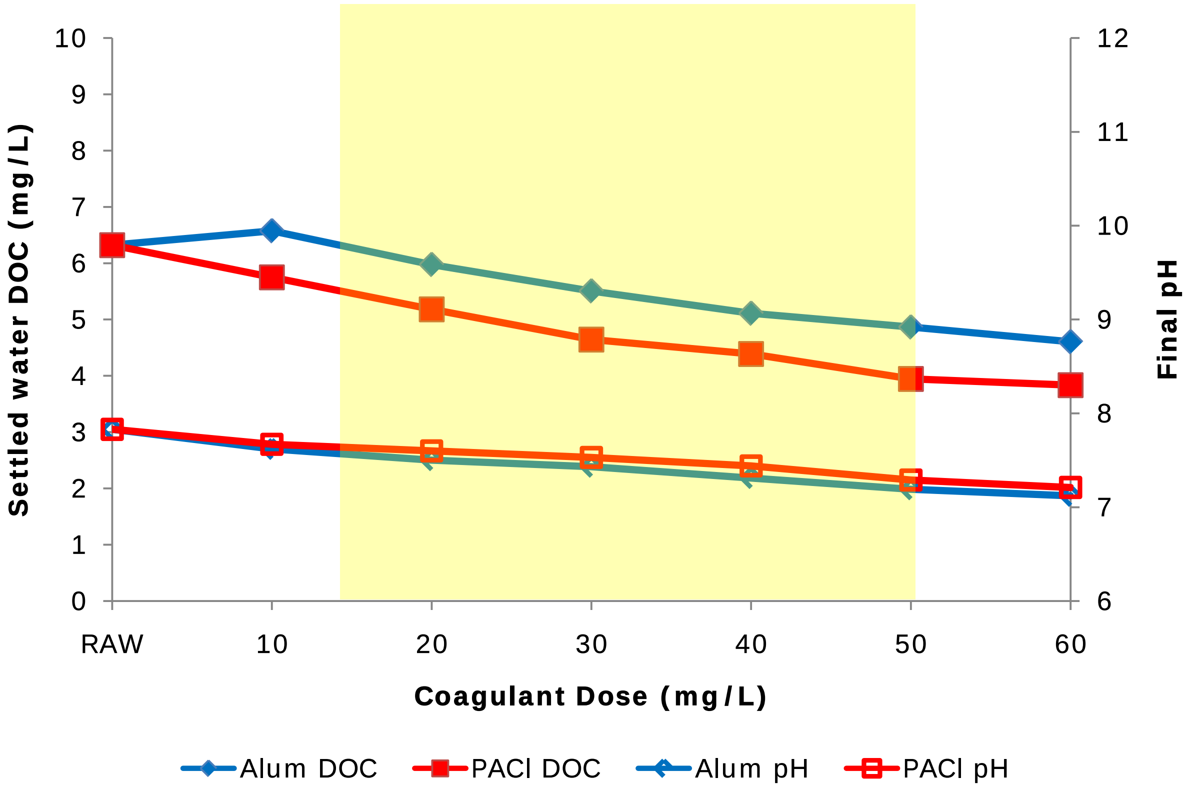


Figure 5-13: Settled water DOC, pH vs. coagulant dose

The enhancement of AAS presence as a flocculant aid with respect to turbidity removal is prominent from Figure 5-14. High turbidity removals (94% with alum and 93% with PACl) were achieved at low coagulant doses of 10 mg/L in the presence of AAS. The

AS dose in that condition was approximately 4 mg/L. This suggests that AAS was effective in enhancing colloid removal by polymer bridging and electrostatic patch mechanism. The presence of AAS reduced the optimum coagulant dose required to remove turbidity to a reasonable extent, remembering that the optimum doses for turbidity removal with PACl and alum alone were higher at 20 mg/L and 30 mg/L respectively, as determined from Phase I A.

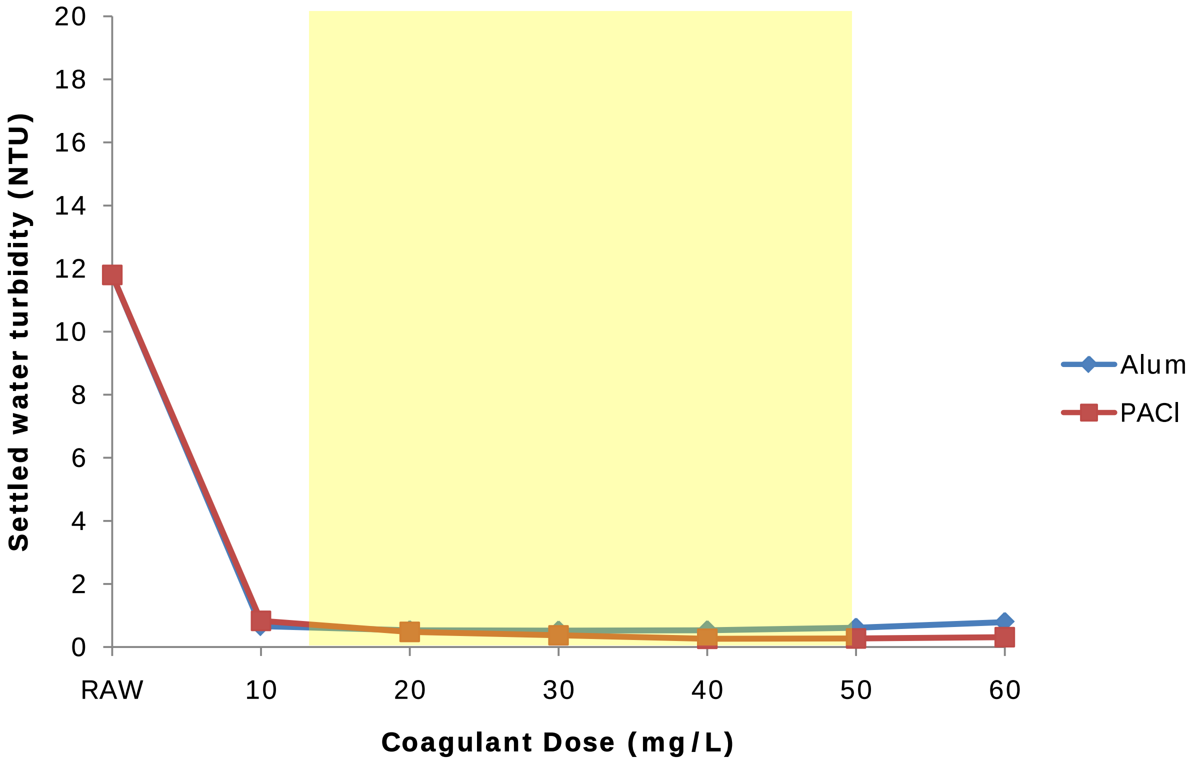


Figure 5-14: Settled water turbidity vs. coagulant dose

5.5 Phase II – Actiflo simulation

In this stage, alum and PACl were tested with flocculant aid anionic activated silica (AAS), micro-sand, and a commercially available polymer (LT 27AG) to satisfy the following objectives:

1. To simulate the high-rate clarification process Actiflo currently employed at Brantford WTP for coagulation/flocculation on a bench-scale level in order to observe its effect on organics removal as well as CSMR.

2. To determine the effect of coagulant choice on the performance of the Actiflo process with respect to the aforementioned parameters

4. To validate standard jar test procedures by comparing to a bench scale jar-test apparatus that was designed to simulate the performance of a high-rate sand-ballasted clarification process for the coagulation/flocculation of water.

This phase involved conducting two jar test trials (one with each of alum and PACl) using the jar testing apparatus available at the Brantford WTP lab in 1 L round beakers. The jar tester was similar to the one employed for all the other experiments with the exception of the mixing blades, which were manually twisted to simulate the blade design at the WTP.

Coagulant and AAS dosing in the six jars was similar to Phase I B and is shown in Table 5-3. Polymer LT 27AG was also added to the jars at a dose of 0.1 mg/L. Additionally, patented micro-sand (Actisand) was added at a dose of 5 g/L during the experiments. The detailed procedure for Actiflo simulation is discussed in Chapter 3. In summary, constant mixing speed of 150 rpm was attained after which AAS and coagulant were injected. The stopwatch was then started, sand added at 2 min, and polymer LT 27AG at 4 min. At 10 min the mixing was stopped and the water was allowed to settle for 3 min after which it was collected for sampling. The chosen doses of polymer LT 27AG, micro-sand simulated Actiflo conditions at Brantford.

Table 5-3: Design of experiments for Phase II

Coagulant dose (mg/L)	10	20	30	40	50	60
AAS dose (2.3:1)	4.39	8.77	13.16	17.54*	17.54*	17.54*
Polymer dose (mg/L)	0.1	0.1	0.1	0.1	0.1	0.1
Sand dose (g/L)	5	5	5	5	5	5

* NSF/ANSI Standard 60 limit of 16 mg/L (dry sodium silicate) exceeded.

5.5.1 Phase II results

The effect of Actiflo simulation with alum and PACl on CSMR is represented in Figure 5-15. When PACl was used as the primary coagulant, CSMR was not only held from increasing, but it was also reduced slightly to a lowest value of 1.51 at the 40 mg/L dose (from a raw water CSMR of 1.74). Since a constant coagulant:AAS ratio of 2.3:1 in Stage I B only held PACl from increasing, this suggests that there is a sulfate contribution from another ingredient which resulted in the CSMR drop. It is probable that the polymer LT 27AG was the contributor as this was the only parameter that was changed (other than the addition of micro-sand). In the case of alum as the primary coagulant, CSMR dropped sharply as more coagulant was added. The lowest achieved CSMR value was 0.67 at a 60 mg/L coagulant dose (raw water CSMR was 1.57). This verifies the potential sulfate contribution from a new source. Noteworthy is the fact that the target CSMR value of 0.5 believed to be critical for galvanic corrosion of lead was still never achieved.

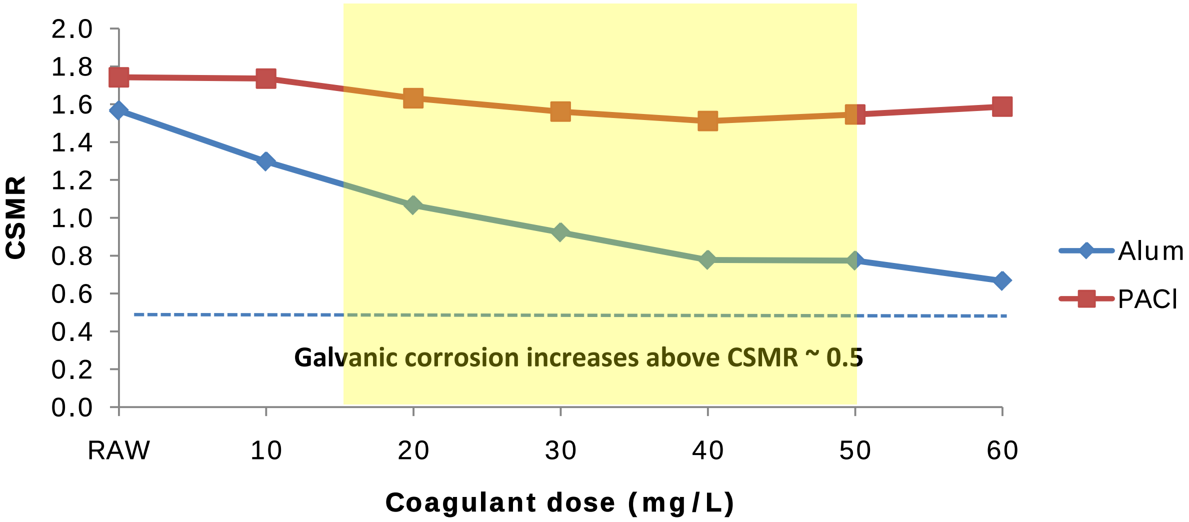


Figure 5-15: CSMR vs. coagulant dose for Phase II

Figure 5-16 shows DOC percentage removal as a function of coagulant dose. PACl achieved higher DOC removals than alum suggesting that it's a better candidate than alum in that respect. The highest DOC removal achieved with PACl was 37% at the 50 mg/L dose while that for alum (32%) was achieved at the highest tested dose of 60 mg/L. The shaded area in the figure shows that the WTP is operating near the optimum dose for DOC removal when coagulant doses in the high range are employed. DOC removals using Actiflo therefore are comparable to removals with conventional coagulation (39% and 27% for PACl and alum respectively from Phase I B). Appendix B Figures B13 and B14 show plots for UV absorbance and % TOC removal, respectively.

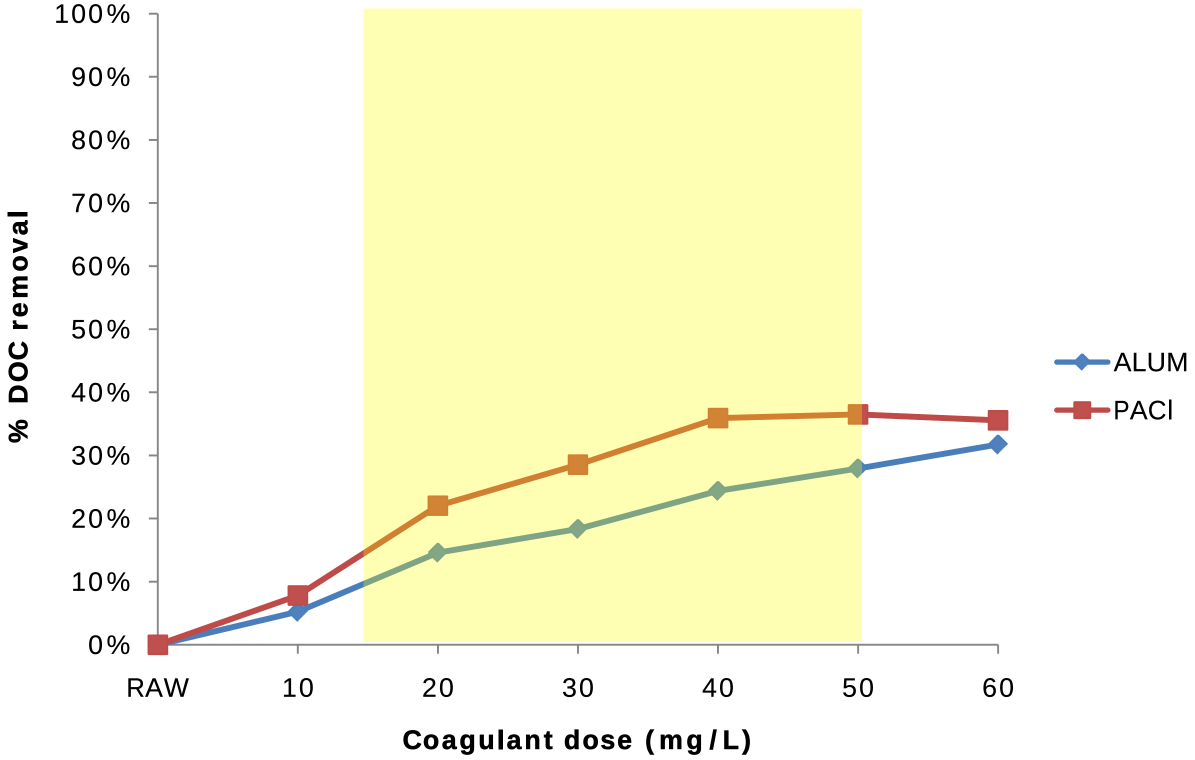


Figure 5-16: DOC removal vs. coagulant dose

pH reductions during the Actiflo process are shown in Figure 5-17. At the highest dose tested, alum dropped the pH by 0.66 while PACl dropped it by 0.41. pH drop as a result of alum use was similar to results from Phase I B with AAS alone with the coagulant. pH drop with PACl was less substantial in comparison with Phase I B (dropped by 0.62 units at the highest dose tested).

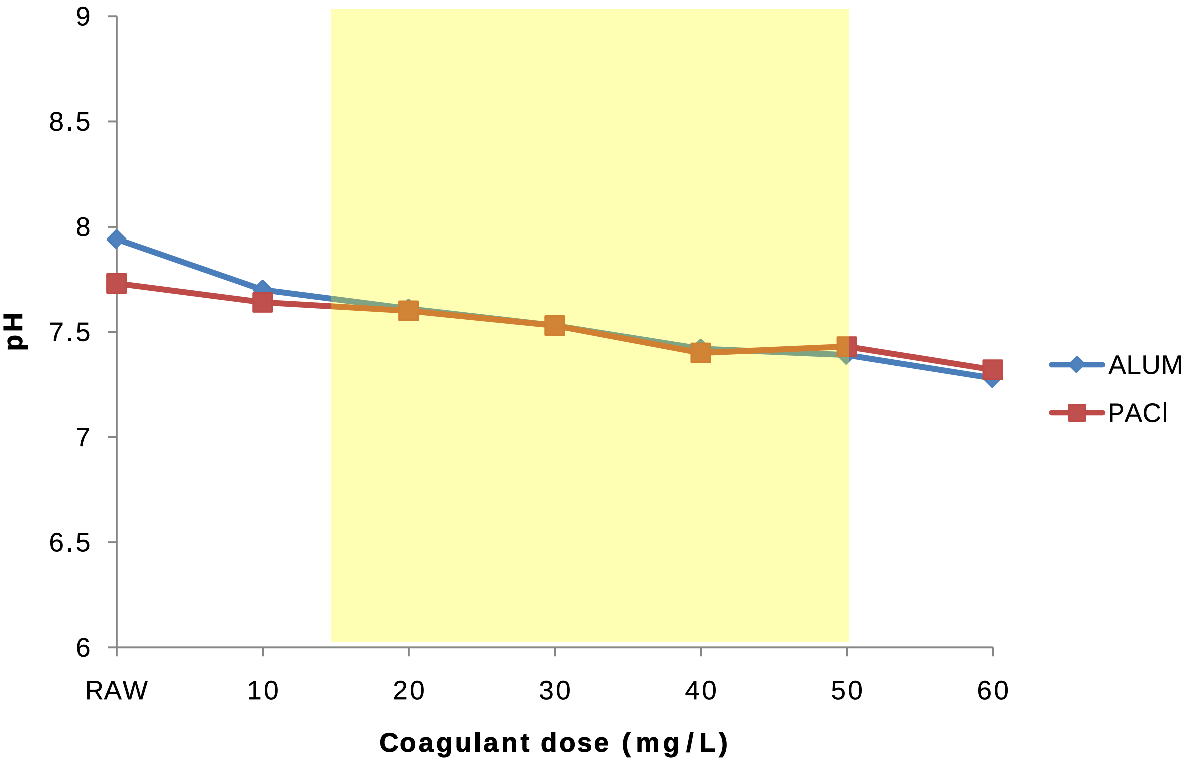


Figure 5-17: pH vs. coagulant dose

Results pertaining to turbidity removal were similar to those obtained in Phase I B (Figure 5-18). The seemingly optimum dose for turbidity removal with both the coagulants with Actiflo simulation is in the neighbourhood of 10 mg/L of the coagulant. At that dose removals of removals of 87% and 83% were recorded for alum and PACl respectively. Such removals were slightly lower than those achieved with conventional coagulation (94% with alum and 93% with PACl) but are still comparable. This suggests that the Actiflo has efficiencies comparable to those achieved with conventional coagulation. Degradations in water turbidity as a result of excess polymer addition did not occur. With comparatively lower water retention times required for turbidity and DOC removal in Actiflo, it presents advantages compared to conventional coagulation.

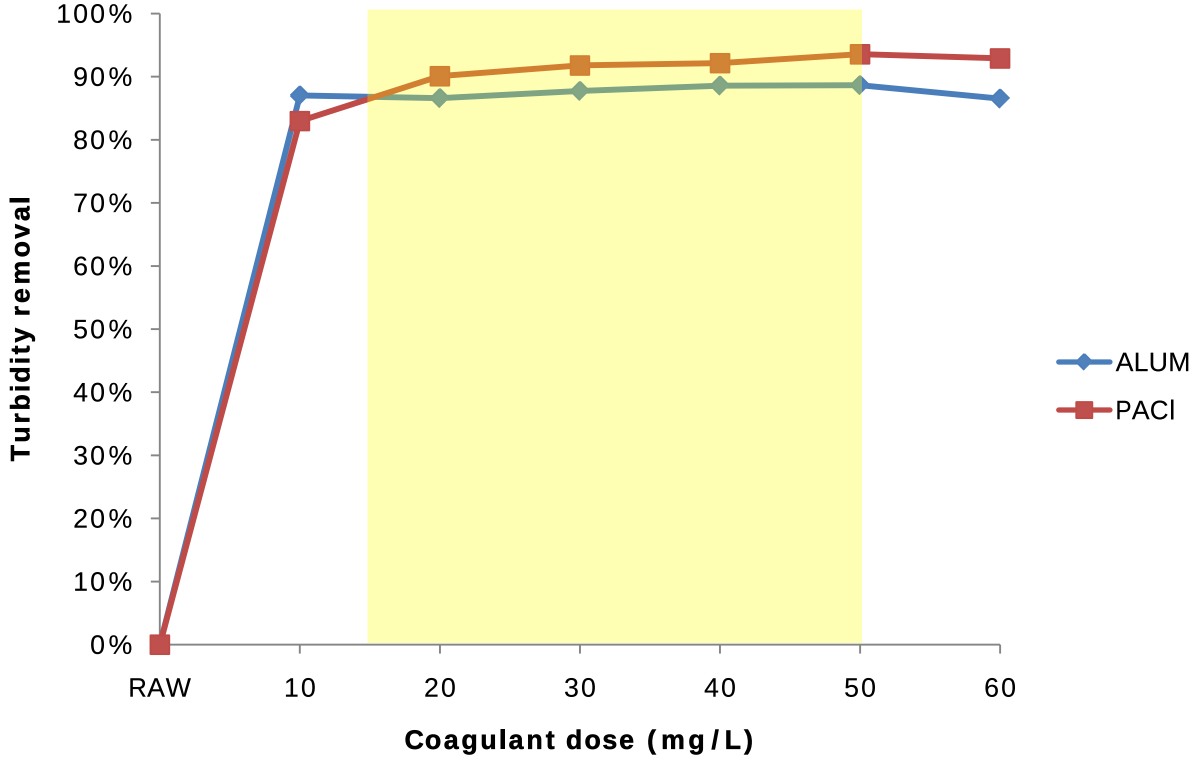


Figure 5-18: Turbidity removal vs. coagulant dose

Chapter 6 COMPARISON OF THE TWO WATERS

This chapter compares the analysed raw water qualities of the two water sources, Lake Ontario and Grand River. This is followed by a hypothesization of possible combinations of chloride and sulfate concentrations in both raw waters and a link with coagulant contributions to the hypothesized CSMR scenarios in the waters. A comparison of coagulant performance with respect to organics and turbidity removal for the two waters is then discussed. These two parameters were chosen as means of comparison because their data can be normalized and compared in terms of percent removals. Additionally, turbidity removal is the basis for coagulant selection both at Woodward Avenue and Brantford water treatment plants. Coagulant performance can also be judged with respect to organics removal in large scale applications.

6.1 Raw water

Investigation of the two water sources shows that their qualities differ substantially (Table 6-1). Lake Ontario is slightly basic with a pH of approximately 8.0, typically has low turbidity (0.6 NTU) and DOC content (2.3 mg/L). The CSMR of Lake Ontario water averaged at 0.9 at the time of sampling. The Grand River on the other hand, is less basic (pH of 7.8) and typically has higher turbidity (13 NTU) and DOC (6 mg/L). The CSMR of Grand River water was also higher, averaging 1.6. The difference in raw water qualities with respect to turbidity and organics concentrations are attributable to a number of factors. The first factor is the difference in hydraulic conditions between a lake and a river. A lake has a relatively high water retention time and acts as a natural coagulation/sedimentation basin thereby removing some of the colloids and organics. Rivers on the other hand incorporate a mix of laminar and turbulent flows and as such colloid settling is not achieved thereby resulting in higher turbidity and organic content. Secondly, dilution plays a role in reducing the variability in lake concentration levels and also lowering organics and turbidity levels. Seasonal variations in raw water quality were also influential to the differences observed since the raw waters for both sources were collected at different seasons as shown in the footnote in Table 6-1. Finally, the depth of raw water collection is relevant. At Woodward Avenue WTP, the water is collected at a 9 metre depth, this eliminated large variabilities in raw water quality during sampling in comparison with water collected at Brantford WTP, which was obtained relatively close to the water surface.

Variations in raw water CSMR are believed to be dependent upon the proximity of the sampling point to urban, industrial, and agricultural areas.

Table 6-1: Characteristics of the two raw water sources

	Lake Ontario[a]		Grand River[b]	
	Average	**Range**	**Average**	**Range**
pH	8.0[c]	7.5 – 8.1	7.8[a]	7.6 – 7.9
Turbidity (NTU)	0.6	0.3 – 1.3	13.0	6.6 – 16.7
Temperature (°C)	10	8 – 15	22.4	19.9 – 23.5
DOC (mg/L)	2.3	2.2 – 2.4	6.0	5.2 – 7.6
CSMR	0.9	0.8 – 1.0	1.6	1.3 – 1.9

a – Measured during experimentation from October 2007 – April 2008

b – Measured during experimentation from July 2008 – August 2008

c – Value represents the median

6.2 Coagulant performance

In this section, coagulants are compared first on the basis of CSMR contribution to the two source waters followed by a performance comparison with respect to turbidity and organics removal.

6.2.1 Effect on CSMR

Historical chloride and sulfate data pertaining to both waters can be obtained from the Drinking Water Surveillance program (DWSP, 2008). While the data is only available for two years, it can be usefully applied to potential comparisons between the coagulants with respect to CSMR. This may then be used as a useful predictive tool for water utilities for the effect of coagulant dose and type on CSMR in the water.

The 25th, 50th, and 75th percentiles as well as the average chloride and sulfate concentrations were determined for the two source waters based on the historical data available and are shown in Table 6-2. It is known from Chapters 4 and 5 that the only chloride-contributing coagulants in the variety of coagulants tested were polyaluminum chloride and aluminum chlorohydrate (PAX-XL 1900). With that in mind, a hypothetical water scenario at the different percentile levels as well as the average level for chloride can be compared to the average levels of sulfate (which is not altered since its concentration is not affected by the two chloride-containing coagulants). Similarly, sulfate concentrations for both waters can be altered and chloride levels fixed to test the effect of the remaining sulfate-contributing coagulants on sulfate levels and consequently CSMR. Table 6-2 shows the percentile and average values of chloride and sulfate concentrations in the two waters.

Table 6-2: Percentile and average chloride and sulfate levels in the two source waters

	Grand River		Lake Ontario	
	chloride (mg/L)	sulfate (mg/L)	chloride (mg/L)	sulfate (mg/L)
25th percentile	69.6	64.3	21.7	25.5
50th percentile	86.0	80.8	22.0	26.4
75th percentile	93.4	85.0	23.4	27.0
average	85.9	77.6	23.1	26.1

From this data, a range of CSMR values can be generated for each water if the concentration of the unaltered parameter was fixed at the historical average and the percentile and average historical values of the other parameter are considered. The parameter to remain unaltered is dependent upon the coagulant used and is the one that is not contributed to by coagulant addition. As an example, if alum, a sulfate contributor, is being investigated, the unaltered parameter would be the chloride average and the range of sulfate concentrations can e represented at the 4 values (25th, 50th, 75th percentiles and average) thereby generating a range of possible CSMR values for the coagulant. This is shown in Table 6-3.

Table 6-3: Hypothesized CSMR values for the two source waters

	Grand River			Lake Ontario		
Chloride-contributing coagulants						
	chloride average / percentile (mg/L)	sulfate average / percentile (mg/L)	CSMR	chloride average / percentile (mg/L)	sulfate average / percentile (mg/L)	CSMR
25th percentile	69.6	77.6	0.9	21.7	26.1	0.8
50th percentile	86.0		1.1	22.0		0.8
75th percentile	93.4		1.2	23.4		0.9
average	85.9		1.1	23.1		0.9
Sulfate-contributing coagulants						
25th percentile	85.9	64.3	1.3	23.1	25.5	0.9
50th percentile		80.8	1.1		26.4	0.9
75th percentile		85.0	1.0		27.0	0.9
average		77.6	1.1		26.1	0.9

Ranges and averages of chloride and sulfate contributions per 10 mg/L dose for each of the coagulants tested on both waters (Chapter 4 – Stage III and Chapter 5 – Phase I A) are shown in Table 6-4. These values were determined based on 12 samples per parameter. Sulfate-contributing coagulants are shaded in yellow.

Table 6-4: Coagulant contributions to chloride and sulfate per unit dose

	Contribution per 10 mg/L			
	chloride (mg/L)		sulfate (mg/L)	
	Range	Average	Range	Average
Alum	-	-	4.5 – 6.0	5.4
PACl	1.6 – 4.0	2.7	0.25 – 2.0	0.75
Ferric sulfate	-	-	5.0 – 7.0	6.0
PHAS	-	-	5.5 – 7.0	6.2
PAX-XL 1900	1.5 – 3.0	2.0	-	-
PASS 100	-	-	3.4 – 6.1	4.9

Information from both Tables 6-3 and 6-4 can then be applied to simulate practical scenarios that may be possible at a both water treatment plants. For example, if Woodward Avenue WTP employed a polyaluminum chloride dose in their upper range (approximately 6 mg/L), the top half of Table 6-3 for Lake Ontario water can be combined with information pertaining to the average chloride contribution by PACl obtained from Table 6-4, resulting in predicted coagulated water CSMRs as shown in Table 6-5. Noteworthy especially with the coagulant polyaluminum chloride is the minimal sulfate contribution by the coagulant. Although relatively small, such contributions may affect CSMR especially if the background chloride and sulfate concentrations are relatively small. In the scenario hypothesized in Table 6-5, the sulfate contribution by PACl was neglected.

Table 6-5: Raw vs. coagulated water CSMR for a hypothetical scenario at Woodward Ave. WTP

Lake Ontario						
	Raw water			**PACl at 6 mg/L dose**		
	Initial chloride levels (mg/L)	Initial average sulfate level (mg/L)	**Initial raw water CSMR**	Final chloride levels (mg/L)	Final average sulfate levels (mg/L)	**Coagulated water CSMR**
25th percentile	21.7	26.1	**0.8**	23.3	26.1	**0.9**
50th percentile	22.0		**0.8**	23.6		**0.9**
75th percentile	23.4		**0.9**	25.0		**1.0**
average	23.1		**0.9**	24.7		**0.9**

If a water treatment utility is considering switching coagulants to alter treated water CSMRs for lead control, information of the sort presented in table 6-5 is useful. It helps evaluate the changes in CSMR as a result of the addition of a particular coagulant at a fixed dose. In the scenario in Table 6-5, we observe an increase in CSMR values of 0.1 at all percentile levels when PACl is added to the water only at a 6 mg/L dose.

A similar hypothetical scenario could also be established for Grand River water. For example, at the time experiments were conducted at Brantford WTP the coagulant (polyaluminum chloride) dose employed was approximately 40 mg/L. If the utility is considering switching to alum for the sole purpose of CSMR improvement, and assuming that the same dose of 40 mg/L is to be used, coagulated water CSMR values can be predicted as shown in Table 6-6.

Table 6-6: Raw vs. coagulated water CSMR for a hypothetical scenario at Brantford WTP

Grand River						
	Raw water			**Alum at 40 mg/L dose**		
	Initial average chloride level (mg/L)	Initial sulfate levels (mg/L)	**Initial raw water CSMR**	Final average chloride level (mg/L)	Final sulfate levels (mg/L)	**Coagulated water CSMR**
25th percentile	85.9	64.3	**1.3**	85.9	85.9	**1.0**
50th percentile		80.8	**1.1**		102.4	**0.8**
75th percentile		85.0	**1.0**		106.6	**0.8**
average		77.6	**1.1**		99.2	**0.9**

In that scenario, a switch to alum for coagulation would bring about CSMR reductions in the order of 0.2 – 0.3 which is favourable with respect to galvanic corrosion control.

Generic equations pertaining to the chloride and sulfate contributions by the different coagulants tested could therefore be developed from the information in Table 6-4 and potential CSMR values resulting from the use of a particular coagulant could be obtained. Such equations may be used by water utilities if the raw water chloride and sulfate concentrations are known.

For the major sulfate-contributing coagulants alum, ferric sulfate, pre-hydroxylated aluminum sulfate, and polyaluminum silicate sulfate, equations pertaining to sulfate contribution are as follows:

Alum: $\text{Final SO}_4^{2-}\text{ (mg/L)} = \text{Initial SO}_4^{2-}\text{ (mg/L)} + (0.54 \times \text{dose})$

Ferric sulfate: $\text{Final SO}_4^{2-}\text{ (mg/L)} = \text{Initial SO}_4^{2-}\text{ (mg/L)} + (0.60 \times \text{dose})$

PHAS: $\text{Final SO}_4^{2-}\text{ (mg/L)} = \text{Initial SO}_4^{2-}\text{ (mg/L)} + (0.62 \times \text{dose})$

PASS 100: Final SO_4^{2-} (mg/L) = Initial SO_4^{2-} (mg/L) + (0.49 x dose)

Noteworthy is also the fact that polyaluminum chloride, a major chloride contributor, results in sulfate contribution to the water which although minor, should not be neglected. Average sulfate contribution by polyaluminum chloride can be represented by the equation:

PACl: Final SO_4^{2-} (mg/L) = Initial SO_4^{2-} (mg/L) + (0.075 x dose)

In the above equations, initial SO_4^{2-} represents the background sulfate concentration in the raw water, whereas final SO_4^{2-} represents the sulfate concentration in the coagulated water resulting from coagulant addition. The dose represents the coagulant dose in mg/L expressed in terms of the active ingredient (shown in Table 3-2).

Similarly, for the major chloride-contributing coagulants polyaluminum chloride and aluminum chlorohydrate, equations pertaining to chloride contribution are as follows:

PACl: Final Cl^- (mg/L) = Initial Cl^- (mg/L) + (0.27 x dose)

PAX-XL 1900: Final Cl^- (mg/L) = Initial Cl^- (mg/L) + (0.20 x dose)

In the above equations, initial Cl^- represents the background chloride concentration in the raw water, whereas final Cl^- represents the chloride concentration in the coagulated water resulting from coagulant addition. The dose represents the coagulant dose in mg/L expressed in terms of the active ingredient (shown in Table 3-2).

In the case of polyaluminum chloride, both chloride and sulfate contribution equations should be applied to get as close an estimate as possible to the final concentrations of both parameters in the coagulated water resulting from coagulant addition.

With respect to the hypothesized examples discussed above, two remarks are important. The first is the fact that shifts in CSMR resulting from a coagulant switch could be prominent in waters with low background (initial) chloride and sulfate concentrations. This is consistent with findings by Edwards and Triantafyllidou (2007). Secondly, it is important to note that other water treatment processes contributing chloride and sulfate to the water were not accounted for in this model. Examples of such processes include chloride contribution by processes such as anion exchange and chlorination, and sulfate contribution by processes such as the use of ammonium sulfate for secondary disinfection.

6.2.2 Turbidity and organics removal

A comparison between the performance of the six coagulants on the two waters tested can be achieved to some extent by normalization of turbidity and DOC data. Stage III of testing on Lake Ontario water employed a coagulant dose within the range of 5 – 30 mg/L while Stage I of testing on Grand River water employed a dose range of 10 – 60 mg/L. Three common coagulant doses of 10, 20, and 30 mg/L can therefore be compared between the two waters.

Table 6-7 shows percent DOC removal for the six coagulants tested on the two waters in the common dose range of 10 – 30 mg/L. The highest removal achieved at each dose is represented by the bold font. A pictorial plot of the data is shown in Appendix C (Figure C1). At a 10 mg/L coagulant dose, PACl achieved the highest DOC removal (26%) in Lake Ontario water despite its relatively low organic content. At the 10mg/L dose, percentage DOC removal for all the coagulants, with the exception of ferric sulfate, was higher in Lake Ontario water. Bearing in mind that coagulation, flocculation, and sedimentation conditions assigned during the experiments were primarily chosen to simulate conditions at Woodward Avenue WTP for the treatment of Lake Ontario water, such results were not unexpected. Additionally, initial DOC in Grand River water was higher to start with. At higher coagulant doses of 20 and 30 mg/L in Lake Ontario water, there are diminishing returns as coagulant dose is increased. This can be illustrated by the fact that a dose increase on Lake Ontario water did not bring about substantial improvements in DOC removals relative to the 10 mg/L dose. On the other hand, the optimum coagulant dose for DOC removal from Grand River water seem to be approached at 20 - 30 mg/L which is shown by the prominent increase in removal efficiencies as the coagulant dose is increased from 10 to 20 mg/L on Grand River water. This could be due to the fact that the DOC content of Grand River water is higher to start with, so the coagulant demand is higher. At both high doses of 20 and 30 mg/L, the highest removals were achieved with aluminum chlorohydrate (PAX-XL 1900) at 43% and 47% respectively.

From the results shown in Table 6-7 it can be observed that the performance of chloride-containing coagulants with respect to DOC removal was superior to that achieved with sulfate-contributing coagulants at all the doses tested. Aluminum chlorohydrate especially performed better with respect to DOC removal at virtually all the conditions and waters tested.

Higher DOC removals associated with the coagulants in Grand River water are also attributed to higher specific UV absorbance of the Grand River water (average 3.2 L/mg.m) compared to Lake Ontario water (average 0.99 L/mg.m). These results are consistent with previous findings indicating that higher SUVA waters are more amenable to NOM removal by coagulation (Archer and Singer, 2006; White et al., 1997; Edzwald, 1993). In this scenario, Grand River water had higher aromatic content and was therefore more amenable to coagulation.

Table 6-7: Percent DOC removals for the two waters at selected coagulant doses

	% DOC removal					
	10 mg/L		20 mg/L		30 mg/L	
	Lake ON	Grand River	Lake ON	Grand River	Lake ON	Grand River
Alum	14	4	18	27	29	33
PACl	**26**	11	32	33	35	39
Ferric sulfate	-2	9	19	22	23	30
PHAS	23	9	28	30	30	37
PAX-XL 1900	24	**20**	**34**	**43**	**31**	**47**
PASS 100	17	6	21	29	26	32

Table 6-8 shows similar representation of percent turbidity removal for the six coagulants from the two waters tested. A pictorial plot of the data is shown in Appendix C (Figure C2). Similar trends with respect to the optimums were noticed, with the highest turbidity % removal achieved at 10 mg/L dose being on Lake Ontario with PACl (89%). However, in this case, turbidity removals of the coagulants on Grand River water were comparable, even exceeding those achieved in Lake Ontario water with coagulants ferric sulfate, aluminum chlorohydrate (PAX-XL 1900), and PASS 100. The negative removals in Table 6-8 only occurred in Lake Ontario water and are attributed to the reduced accuracy of the lab turbidimeter in reading low turbidities (< 1 NTU) on Lake Ontario water. Similar to DOC removal, the highest turbidity removals at the 20 and 30 mg/L doses were achieved in Grand River water, in this case with the coagulant polyaluminum chloride, achieving removals of 97% and 92% respectively. At both higher doses, all coagulants performed better in Grand River water. Again, this may imply that the optimum doses for turbidity removal from Grand River water are being approached at the higher dose ranges. This is attributed to higher starting turbidity in Grand River waters. Such results are in general agreement with other research (Pernitsky and Edzwald, 2006).

Table 6-8: Percent turbidity removals for the two waters at selected coagulant doses

	% turbidity removal					
	10 mg/L		20 mg/L		30 mg/L	
	Lake ON	Grand River	Lake ON	Grand River	Lake ON	Grand River
Alum	84	44	76	85	65	87
PACl	**89**	83	87	**97**	77	**92**
Ferric sulfate	57	74	70	70	50	88
PHAS	75	72	52	82	15	90
PAX-XL 1900	0	62	14	79	57	87
PASS 100	-63	83	21	94	-34	94

In the research conducted on both source waters, it is imperative to mention the fact that consequent to limited lab time and budget considerations, it was decided that broadening the range of coagulant dose in each of the waters tested to account for as many conditions as possible was of more relevance in comparison with the replication of selected conditions in work illustrated in Chapter 4 (Stages I, IIA, and III) and Chapter 5 (Phases I and II). While such an approach detracted from the ability to measure data variability, more information was obtained as to the effect of the different coagulants and flocculant aids on the two source waters at a number of varying conditions.

Chapter 7 CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

Six coagulants were tested on two surface waters for their effect on dissolved organic carbon (DOC) removal and the chloride-to-sulfate mass ratio (CSMR) which is pertinent to lead corrosion in galvanic settings. Two polymers were also investigated for their effectiveness in improving coagulation performance. Testing was conducted through the utilization of bench-scale techniques to best simulate pre-treatment conditions at both utilities. On average, based on values measured during this study, Lake Ontario water has low turbidities (less than 1.5 NTU), relatively low organics (DOC < 2.5 mg/L), and CSMR of 0.9 while Grand River water has higher turbidities (~15 NTU), organics (DOC = ~6 mg/L), and CSMR of approximately 1.6.

From the research conducted, the following conclusions can be deduced:

1. The type and dose of coagulant had a significant impact on CSMR in the treated water which is expected given the chemical compositions of the different coagulants.

2. As would be anticipated, the effect of coagulant switch on CSMR is more prominent in waters with low initial chloride and sulfate concentrations.

3. Cationic activated silica (CAS), being a polymer of relatively high molecular weight, was not effective as a primary coagulant. The efficiency of CAS in removing turbidity and organics was inferior to that achieved with conventional coagulants by 2 – 3 and 3 – 5 fold, respectively. The drop in pH resulting from CAS addition was relatively substantial due the presence of sulfuric acid as a CAS activating agent.

4. Highest DOC removals were achieved with the chloride-containing coagulants in both waters (35 – 50%) with aluminum chlorohydrate showing superiority in that respect. Removals with sulfate-containing coagulants were less, generally in the range of 22 – 41%.

5. The optimum dose for DOC removal in Lake Ontario water for alum and polyaluminum chloride was approximately 30 mg/L and 20 mg/L, respectively. On the other hand, the optimum dose for DOC removal from Grand River water for both coagulants was approximately 40 mg/L.

6. As can be expected, the use of CAS as a flocculant aid produced slight reductions in CSMR due to sulfate contribution from its constituents, alum and sulfuric acid.

7. Coagulant dose was the main parameter affecting DOC removal and THM formation control with both coagulants. The ratio of coagulant dose to CAS had less than a 4 % impact on the removal of the two parameters aforementioned.

8. The use of anionic activated silica (AAS) at a constant coagulant-to-silicate ratio on Grand River water held CSMR from increasing when the coagulant polyaluminum chloride was used. In the case of alum, its addition resulted in more pronounced reductions in CSMR.

9. A linear relationship exists between coagulant dose and CSMR which is to be expected from a chemical perspective. Polyaluminum chloride and aluminum chlorohydrate contributed chlorides to the water thereby increasing CSMR, while the sulfate-containing coagulants aluminum sulfate, pre-hydroxylated aluminum sulfate, ferric sulfate, and polyaluminum silicate sulfate resulted in reductions in CSMR in proportion to the dose added.

10. Of the coagulants tested, polyaluminum chloride was the highest chloride contributor (2.7 mg Cl^-/L per 10 mg/L) and pre-hydroxylated aluminum sulfate was the highest sulfate contributor (6.2 mg SO_4^{2}/L^- per 10 mg/L).

11. The lowest CSMR achieved for Lake Ontario water was 0.6 with the coagulants aluminum sulfate, pre-hydroxylated aluminum sulfate, and ferric sulfate at the highest dose tested of 30 mg/L. The lowest CSMR achieved in Grand River water was 0.8

with the three coagulants aforementioned in addition to polyaluminum silicate sulfate at the highest dose tested of 60 mg/L. Recommended critical CSMR values below 0.58 for controlling lead release in water (Edwards and Triantafyllidou, 2007) were never achieved at doses practical to a water treatment plant operation.

12. Simulation of upflow sand-ballasted clarification on Grand River water with polyaluminum chloride reduced turbidity by up to 94% and organics DOC by up to 37% at the high range of coagulant dosing employed at Brantford WTP of 50 mg/L.

13. While a high dose of any of the sulfate-containing coagulants may bring about reductions in CSMR, such doses will also bring about reductions in pH which is detrimental with respect to lead corrosion. High coagulant doses are also technically and operationally unfeasible due to cost considerations such as high sludge handling and disposal costs as well as the need for pH readjustment. High coagulant doses may also exceed the optimums for turbidity and DOC removal.

7.2 Recommendations

Beyond the scope of this research, but meriting further investigation are the following:

1. The relationship between the water source/type and the critical CSMR value affecting lead corrosion: The general critical CSMR value suggested by researchers beyond which lead leaching is thought to increase in galvanic settings is in the range of 0.5 to 0.58. This value could be a site-specific guideline based on limited testing and its specificity to water type and chemistry should be further investigated.

2. Interactions between CSMR and other factors affecting lead corrosion: Factors affecting lead release interact simultaneously in a given water system. The effect of interactions between CSMR and other main parameters affecting lead corrosion such as pH, alkalinity, temperature, and inhibitors needs to be examined.

3. Long term effects of process changes for CSMR reduction on lead leaching: experiments conducted by Edwards and Triantafyllidou (2007) investigating the effect of CSMR level on lead leaching only spanned several weeks. While a sudden switch in coagulant or disinfectant type may trigger lead release in the short term, its effect on lead corrosion in long term has not been thoroughly investigated. Additionally, the effect of sustaining consistent high or low CSMR values for long periods needs to be further studied.

4. Influence of CAS on subsequent water treatment processes: The effect of CAS use as a flocculant aid on filter and membrane performance needs to be studied. It is unknown whether the use of this polymer would bring about changes in filter run time and the type of membrane fouling. This warrants further investigation into the issue.

5. The potential wider applicability of polyaluminum silicate sulfate in drinking water treatment: The addition of this coagulant to the water results in less substantial drops in pH as well as CSMR reductions. This is favourable with respect to lead control. Further research needs to be conducted to determine the practicality of facilitating more widespread use of this chemical in treating potable water.

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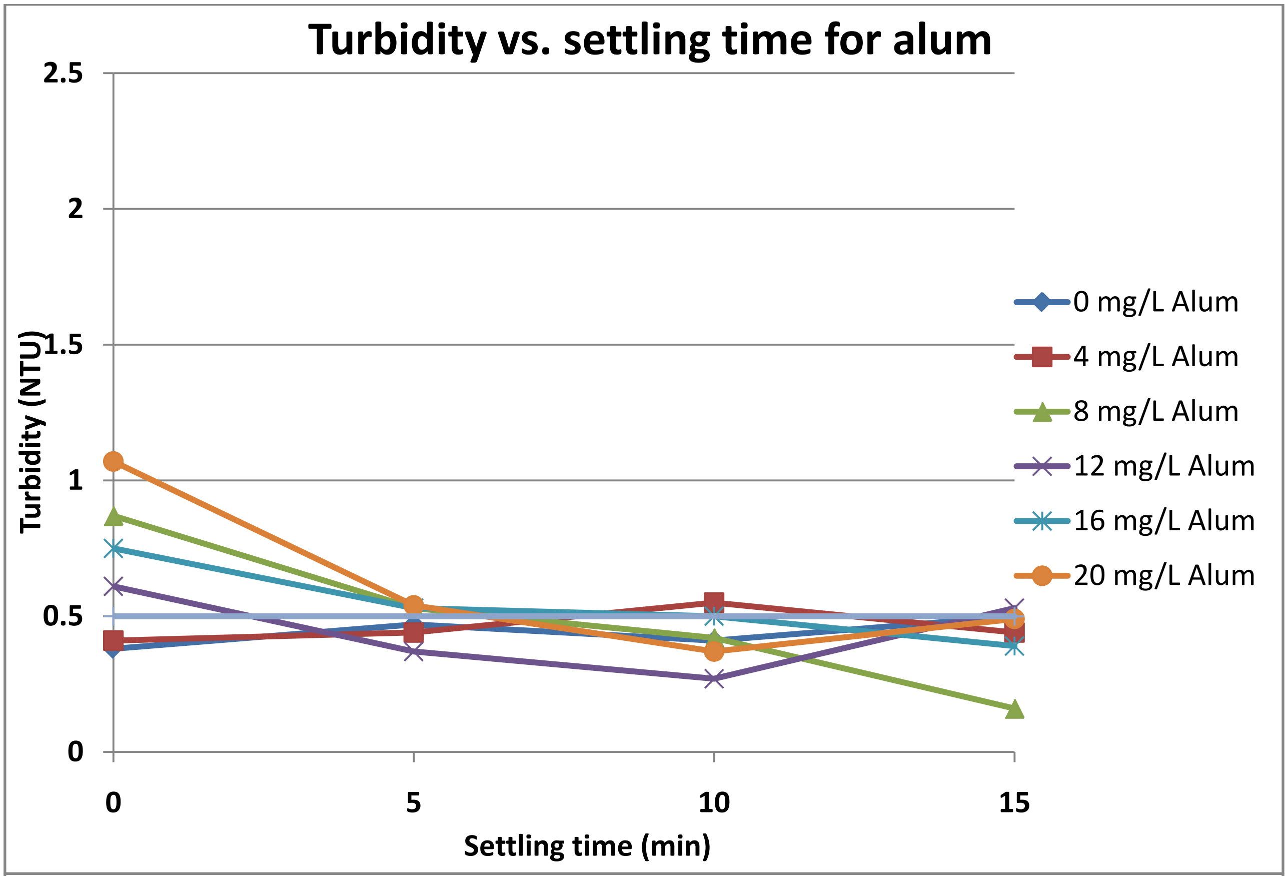
Appendices

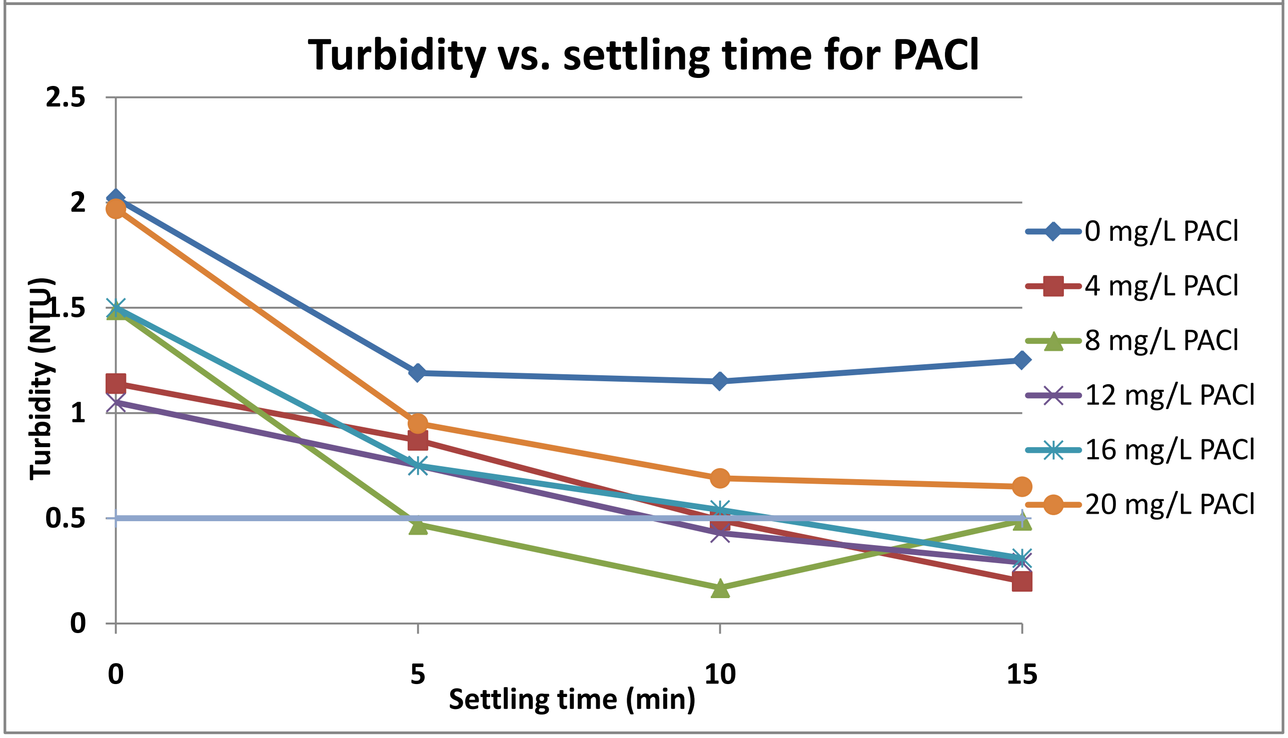
Appendix A: Summary plots for Lake Ontario water

Figures A1 – A4

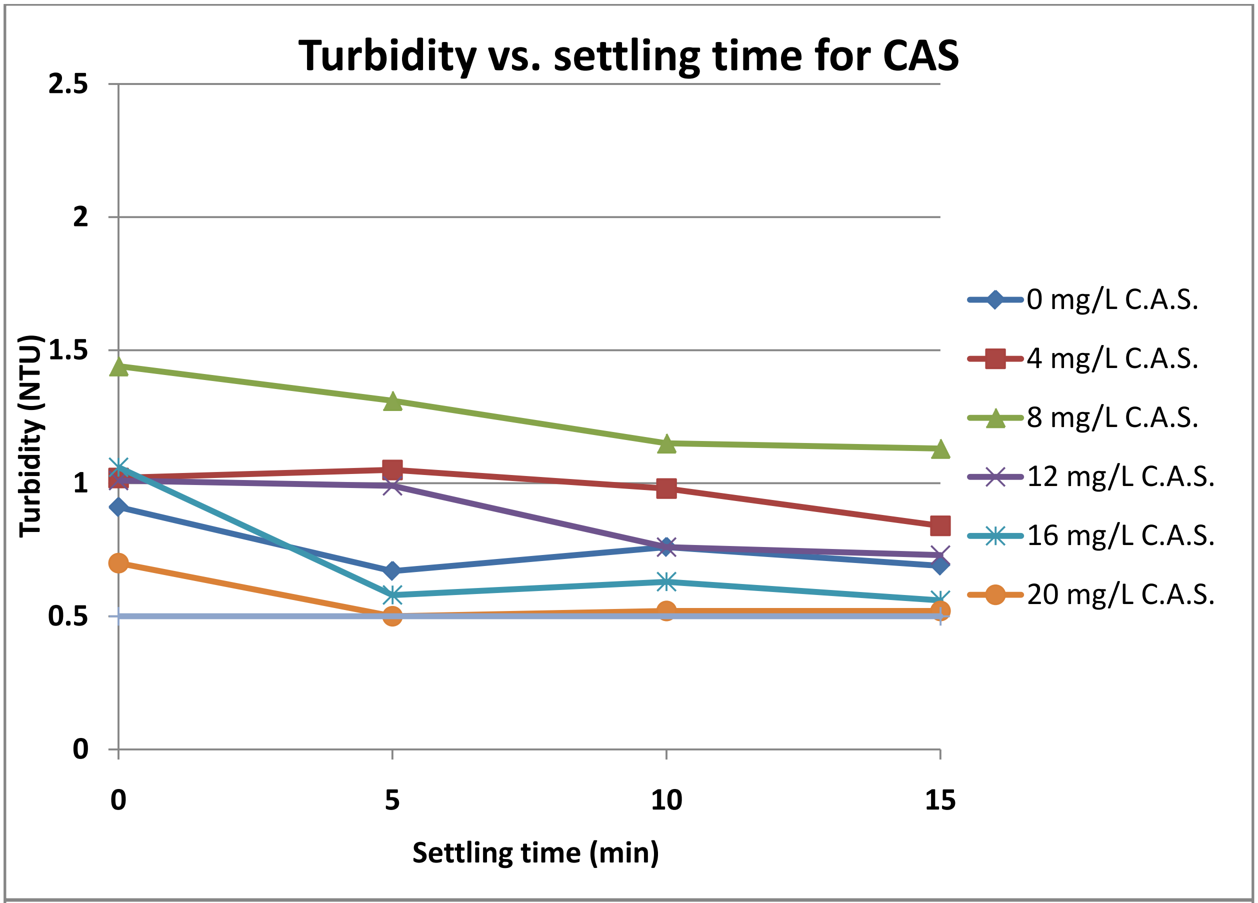
Summary plots for Stage I

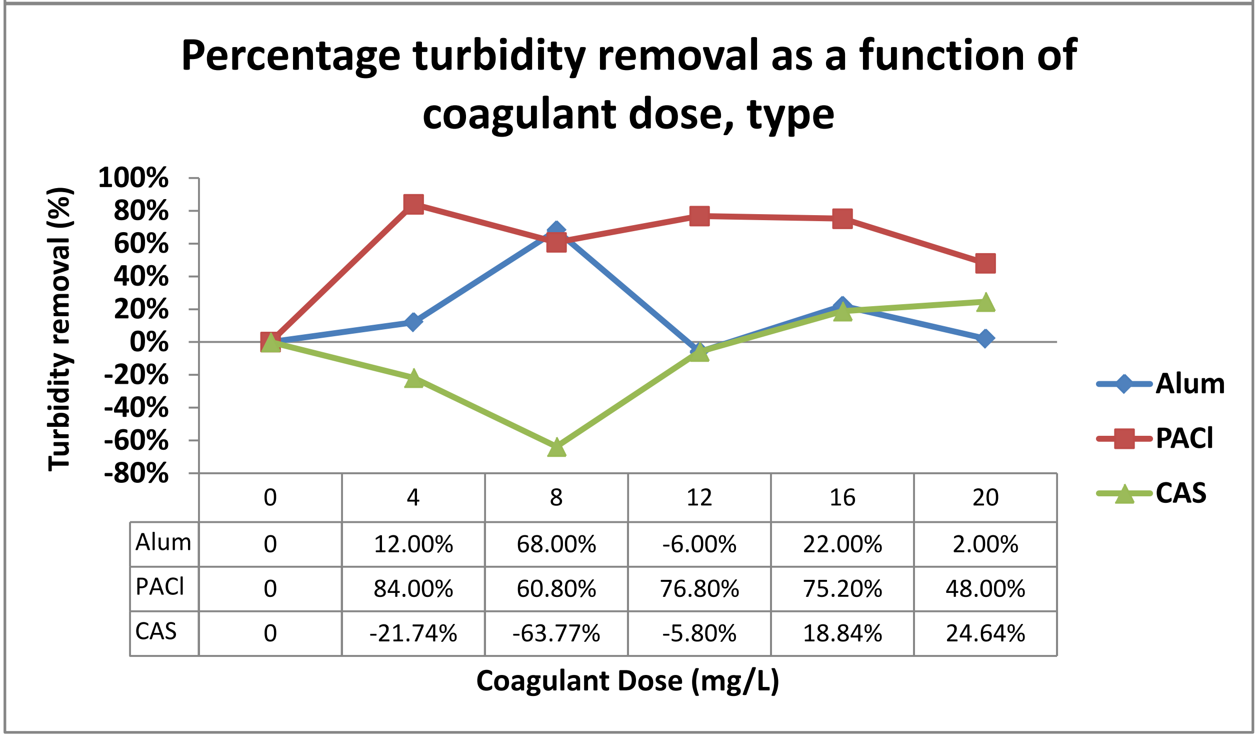
Figures A1, A2





Figures A3, A4



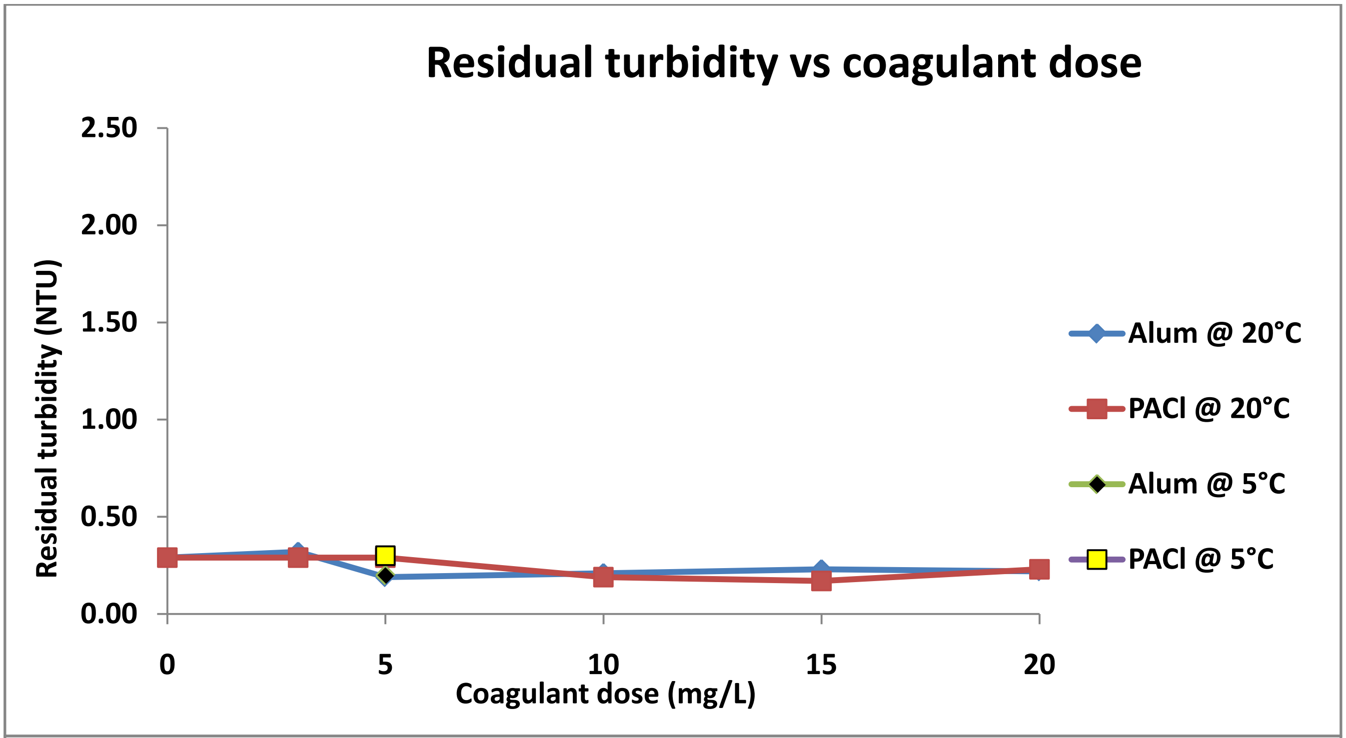


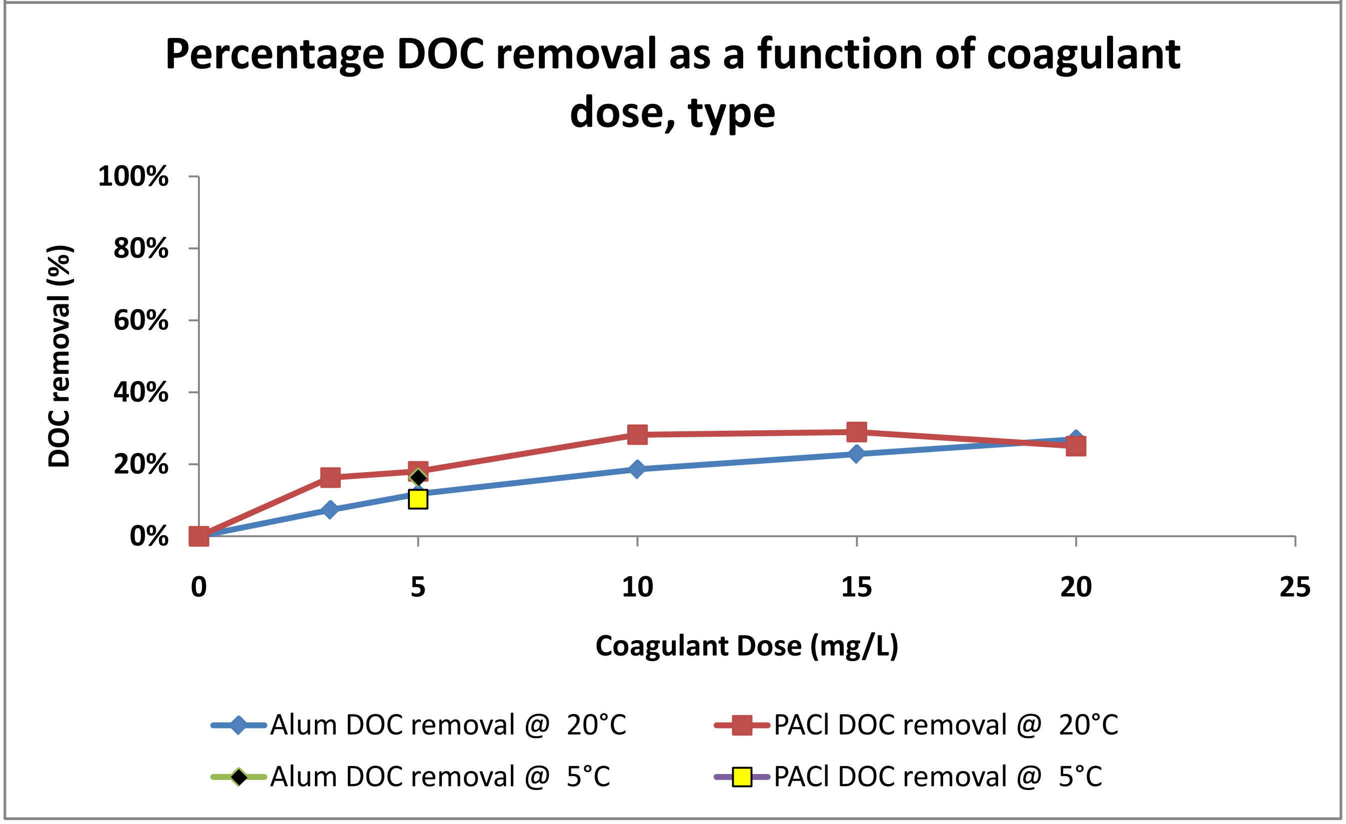
	0	4	8	12	16	20
Alum	0	12.00%	68.00%	-6.00%	22.00%	2.00%
PACl	0	84.00%	60.80%	76.80%	75.20%	48.00%
CAS	0	-21.74%	-63.77%	-5.80%	18.84%	24.64%

Figures A5 – A43

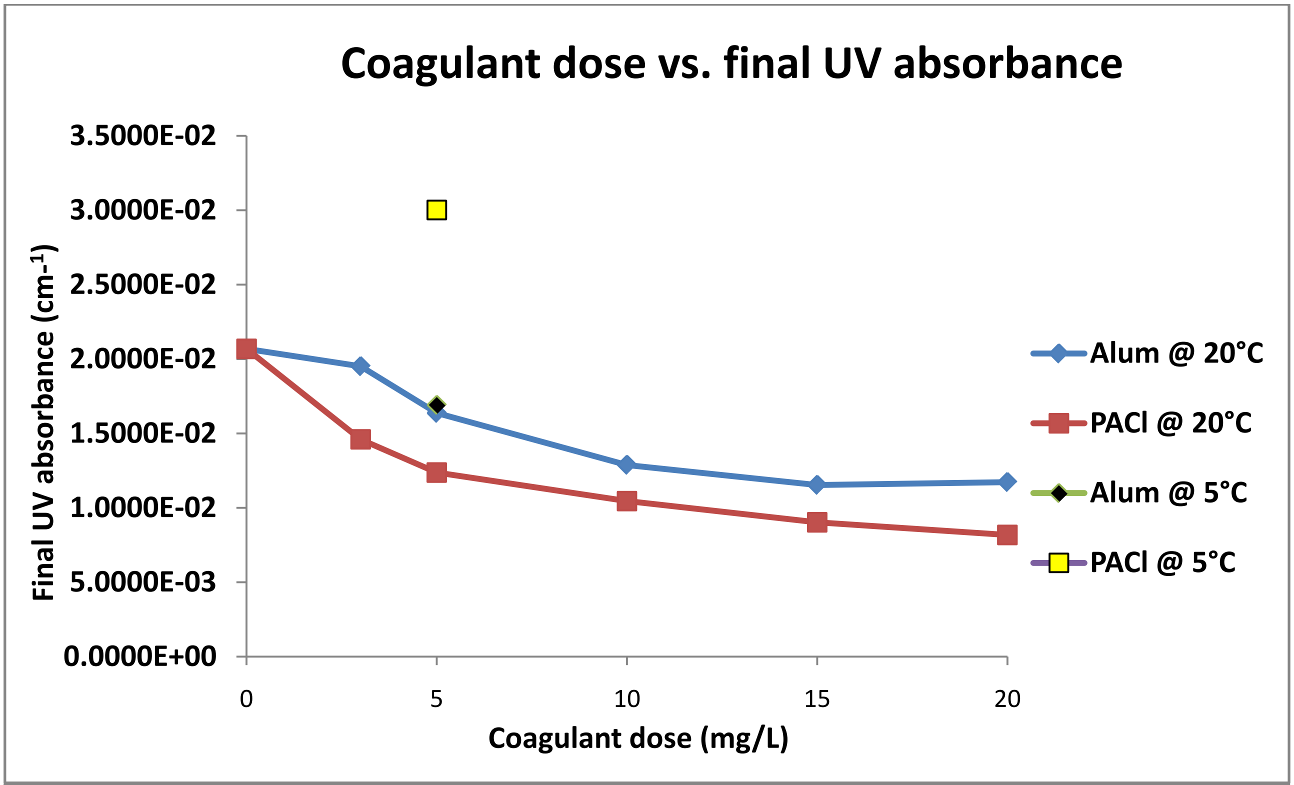
Summary plots for Stage II

Figures A5, A6





Figures A7, A8



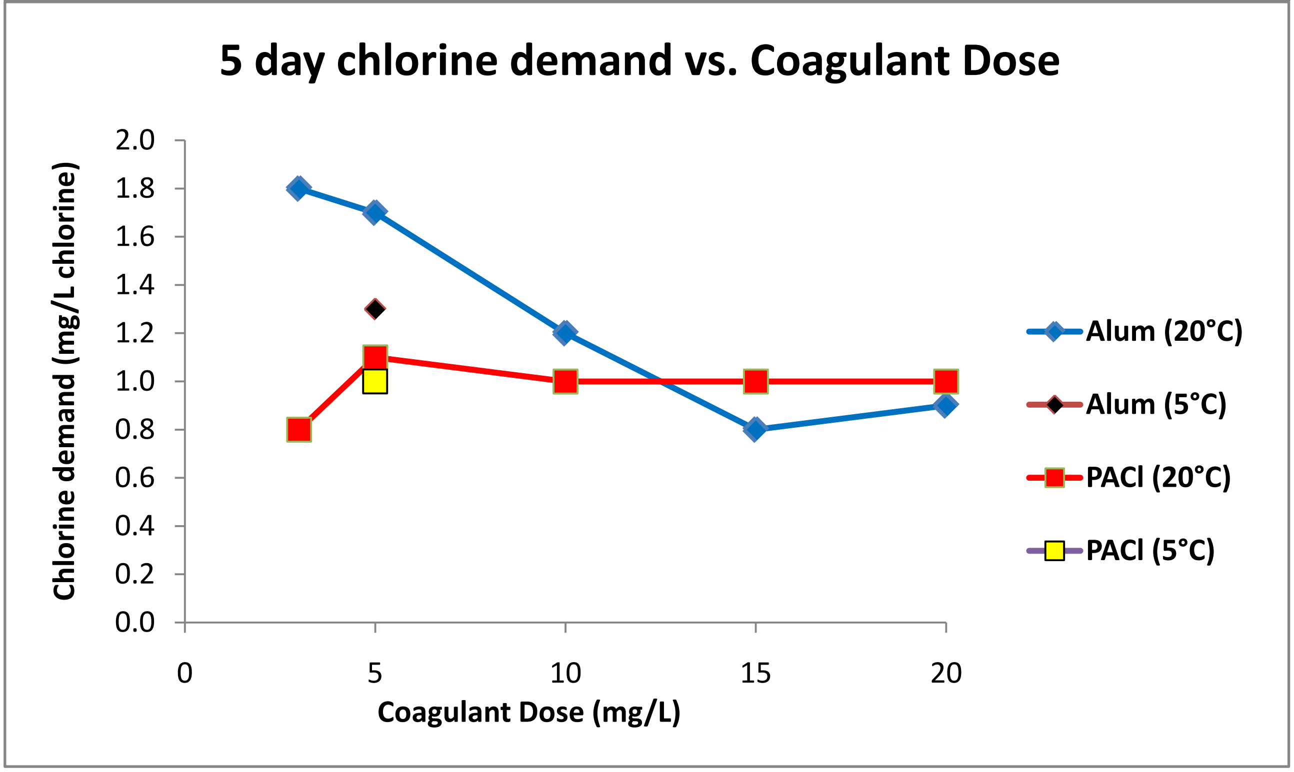
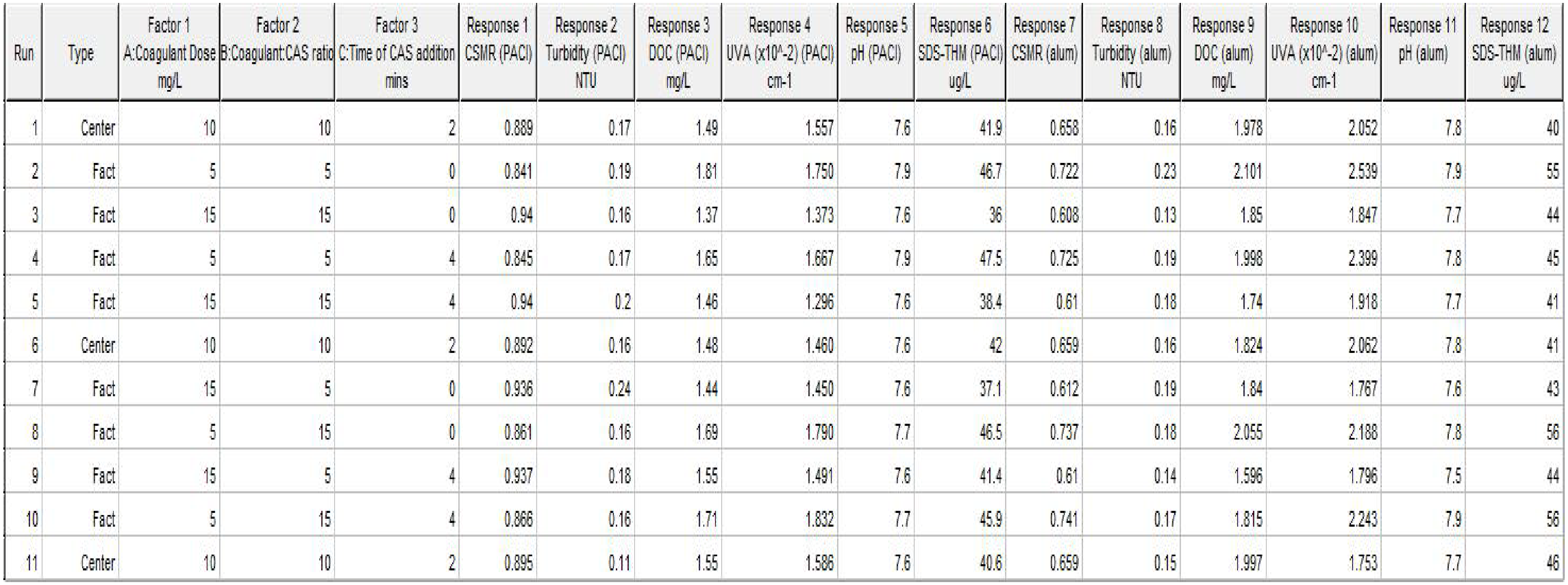


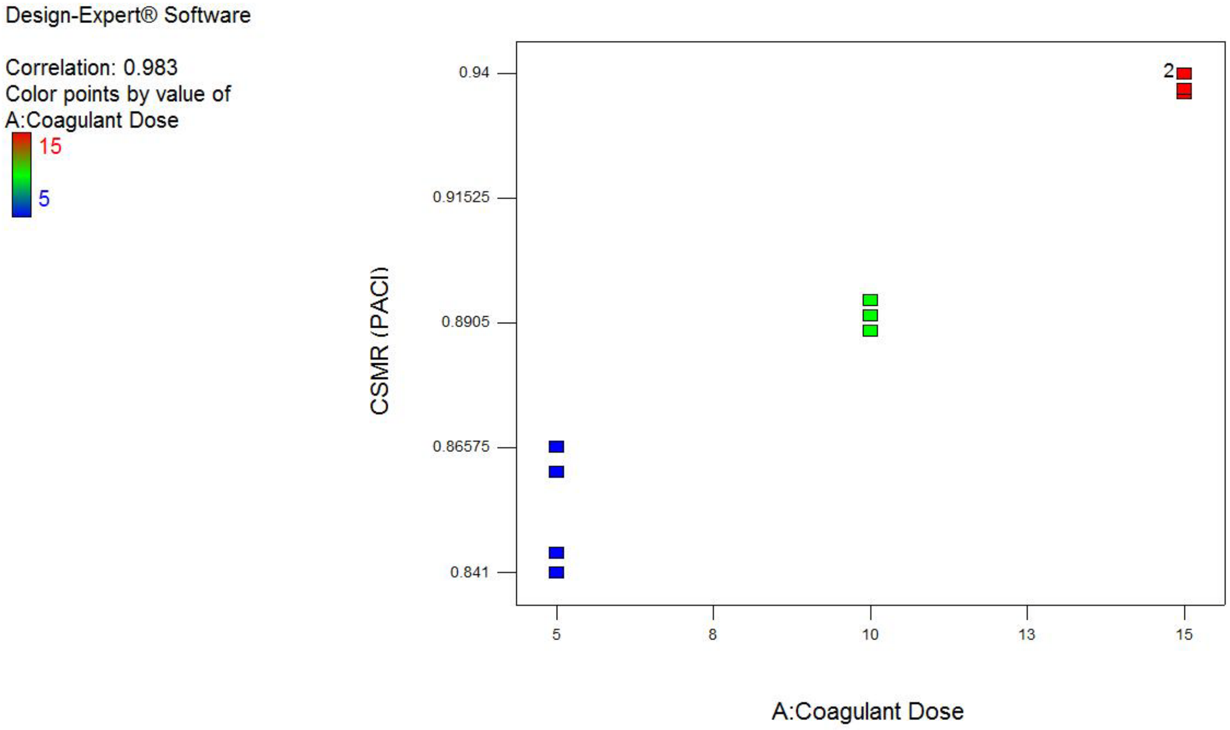
Figure A9

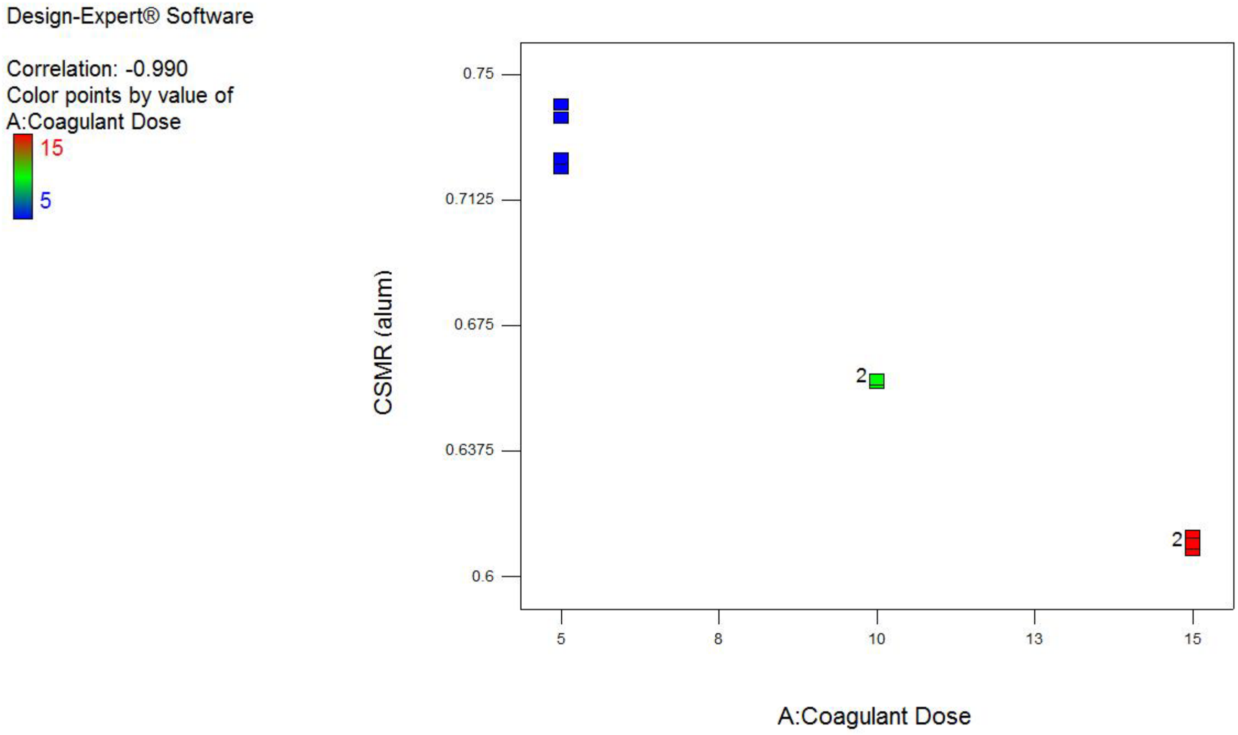
Summary of design and results from CAS experiments (generated by Design Expert 7, Stat-Ease Inc)



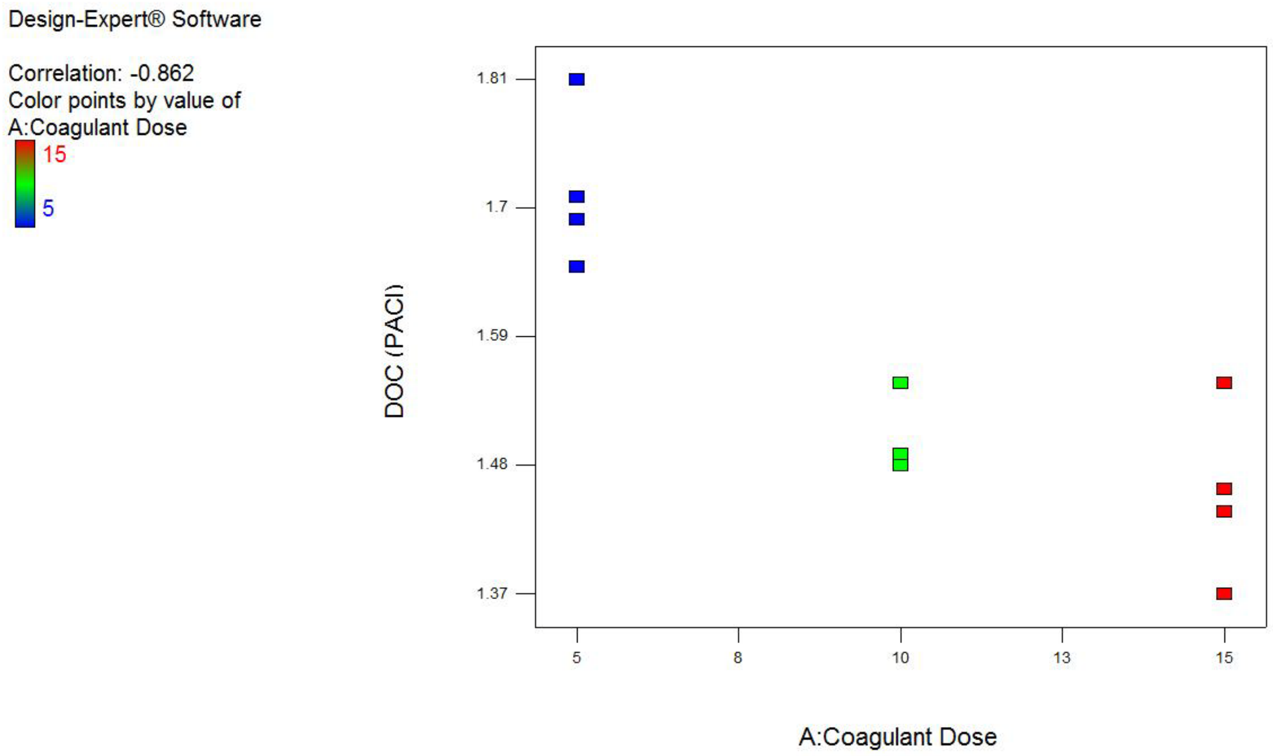
Run	Type	Factor 1 A:Coagulant Dose mg/L	Factor 2 B:Coagulant:CAS ratio	Factor 3 C:Time of CAS addition mins	Response 1 CSMR (PACl)	Response 2 Turbidity (PACl) NTU	Response 3 DOC (PACl) mg/L	Response 4 UVA (x10^-2) (PACl) cm-1	Response 5 pH (PACl)	Response 6 SDS-THM (PACl) ug/L	Response 7 CSMR (alum)	Response 8 Turbidity (alum) NTU	Response 9 DOC (alum) mg/L	Response 10 UVA (x10^-2) (alum) cm-1	Response 11 pH (alum)	Response 12 SDS-THM (alum) ug/L
1	Center	10	10	2	0.889	0.17	1.49	1.557	7.6	41.9	0.658	0.16	1.978	2.052	7.8	40
2	Fact	5	5	0	0.841	0.19	1.81	1.750	7.9	46.7	0.722	0.23	2.101	2.539	7.9	55
3	Fact	15	15	0	0.94	0.16	1.37	1.373	7.6	36	0.608	0.13	1.85	1.847	7.7	44
4	Fact	5	5	4	0.845	0.17	1.65	1.667	7.9	47.5	0.725	0.19	1.998	2.399	7.8	45
5	Fact	15	15	4	0.94	0.2	1.46	1.296	7.6	38.4	0.61	0.18	1.74	1.918	7.7	41
6	Center	10	10	2	0.892	0.16	1.48	1.460	7.6	42	0.659	0.16	1.824	2.062	7.8	41
7	Fact	15	5	0	0.936	0.24	1.44	1.450	7.6	37.1	0.612	0.19	1.84	1.767	7.6	43
8	Fact	5	15	0	0.861	0.16	1.69	1.790	7.7	46.5	0.737	0.18	2.055	2.188	7.8	56
9	Fact	15	5	4	0.937	0.18	1.55	1.491	7.6	41.4	0.61	0.14	1.596	1.796	7.5	44
10	Fact	5	15	4	0.866	0.16	1.71	1.832	7.7	45.9	0.741	0.17	1.815	2.243	7.9	56
11	Center	10	10	2	0.895	0.11	1.55	1.586	7.6	40.6	0.659	0.15	1.997	1.753	7.7	46

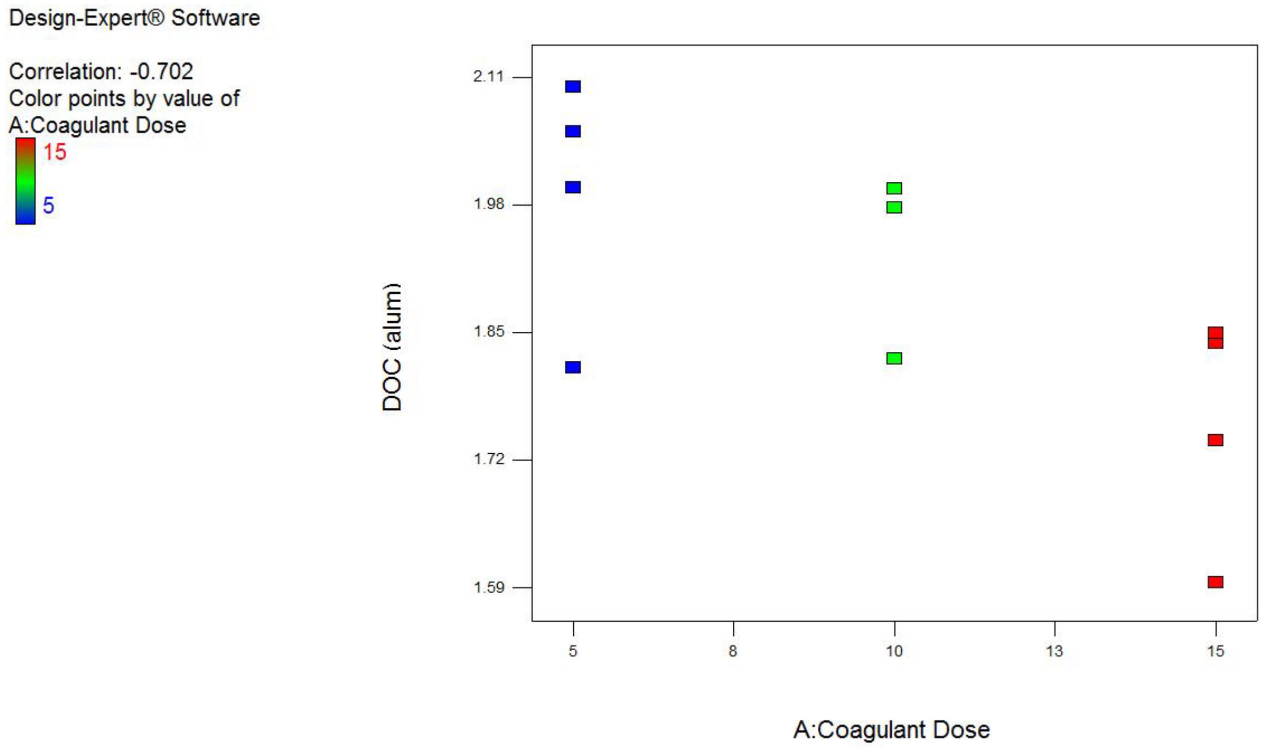
Figures A10, A11 (CSMR)



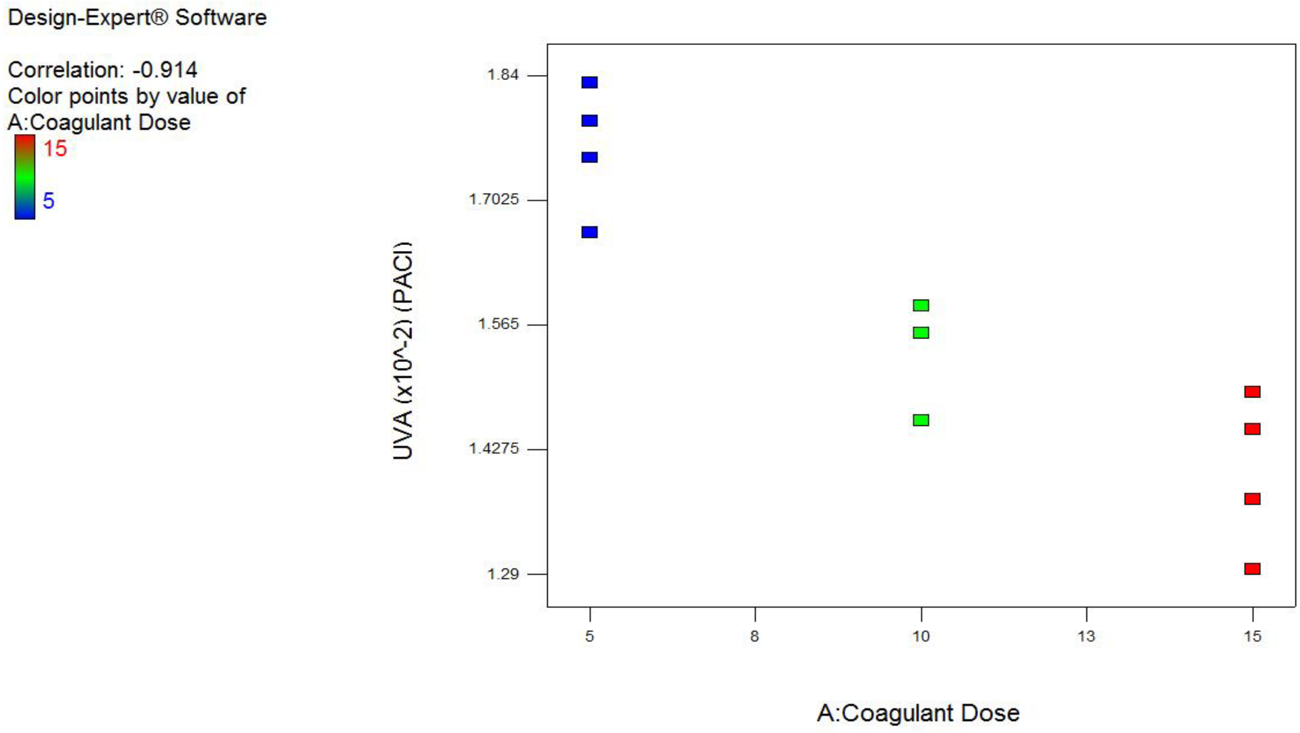


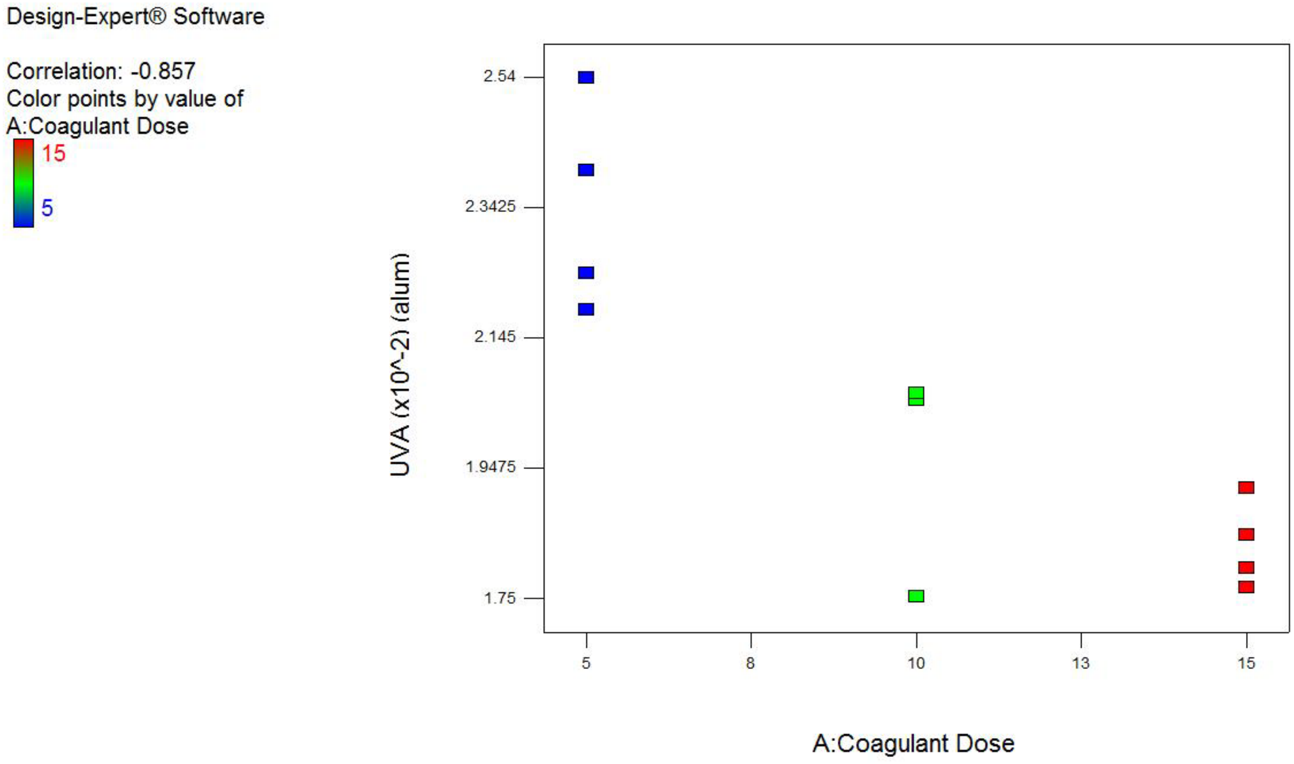
Figures A11, A12 (DOC)



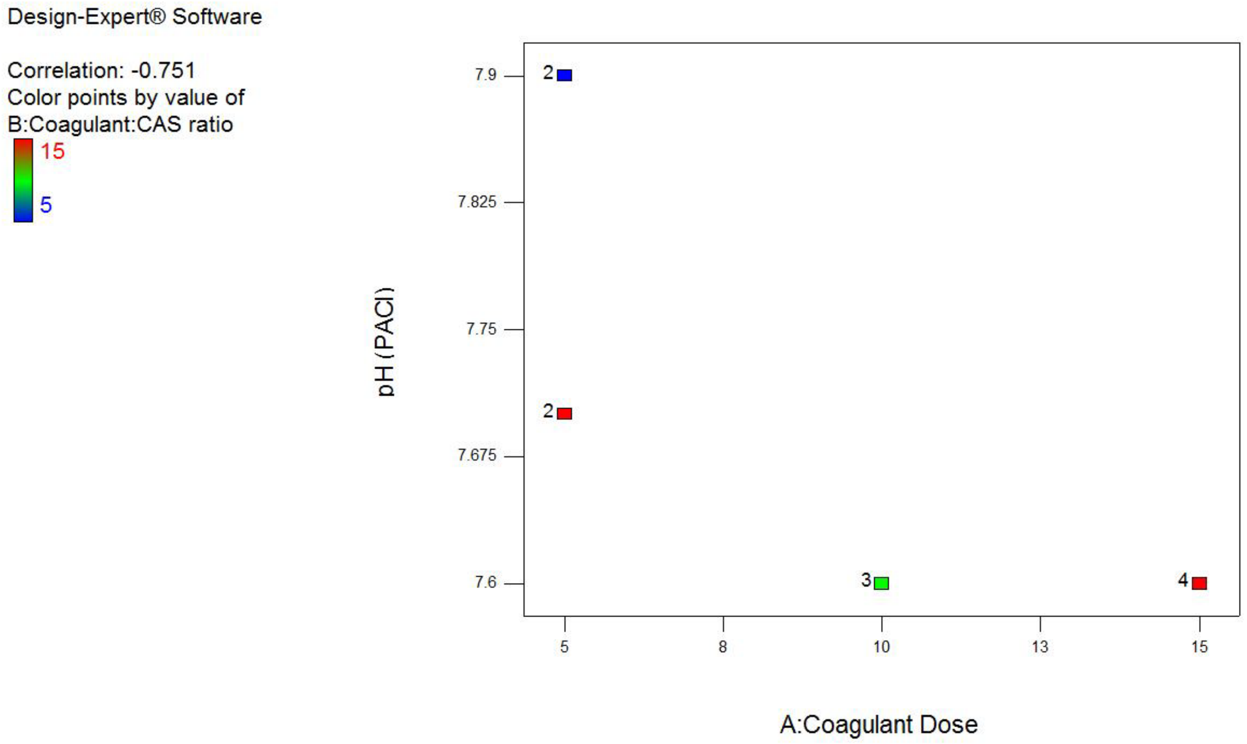


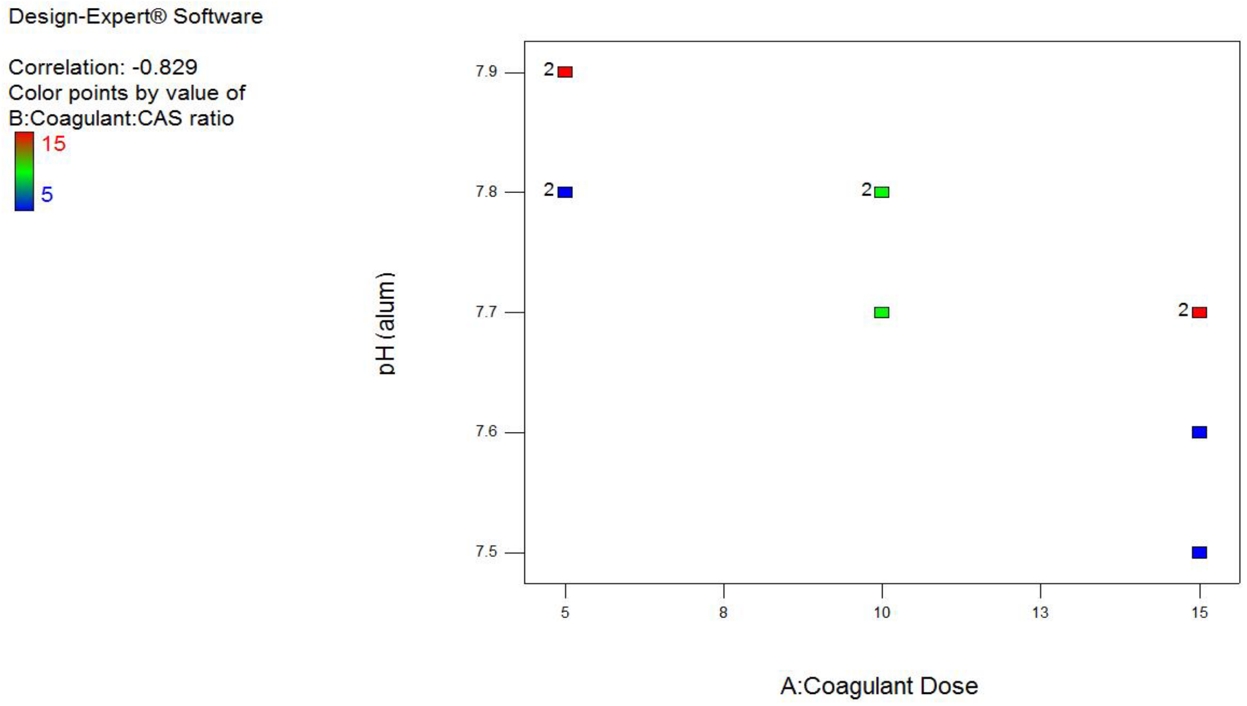
Figures A13, A14 (UV254)



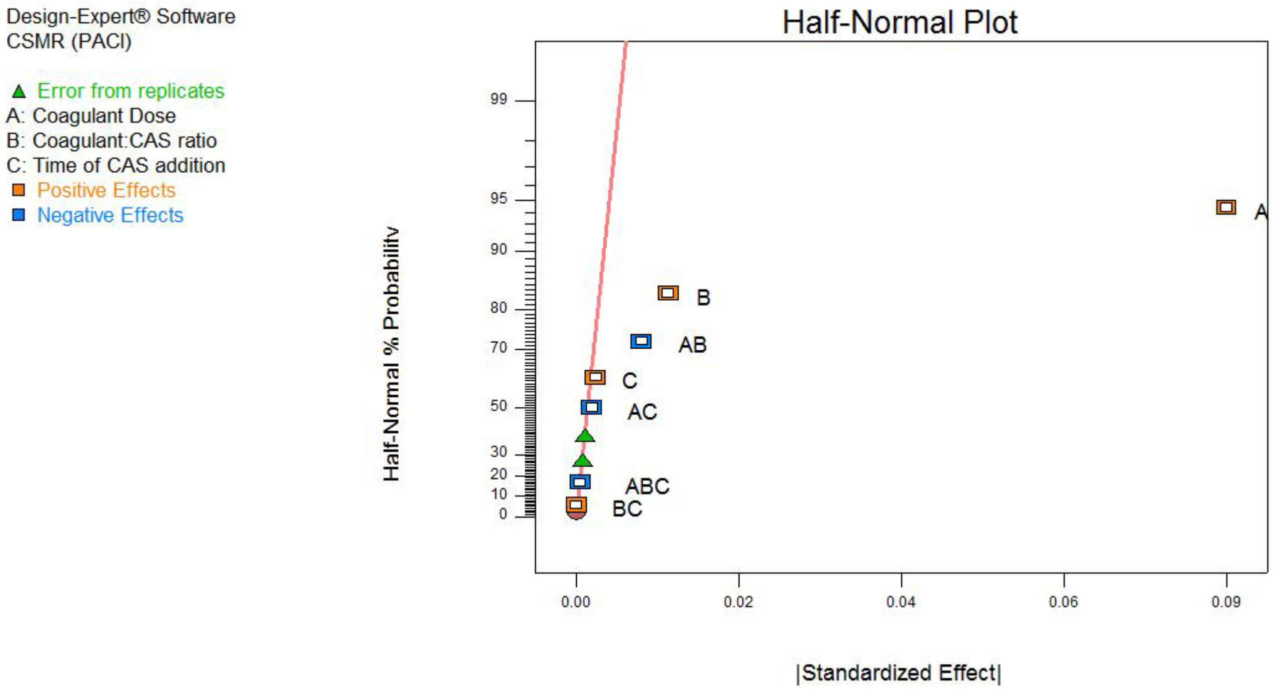


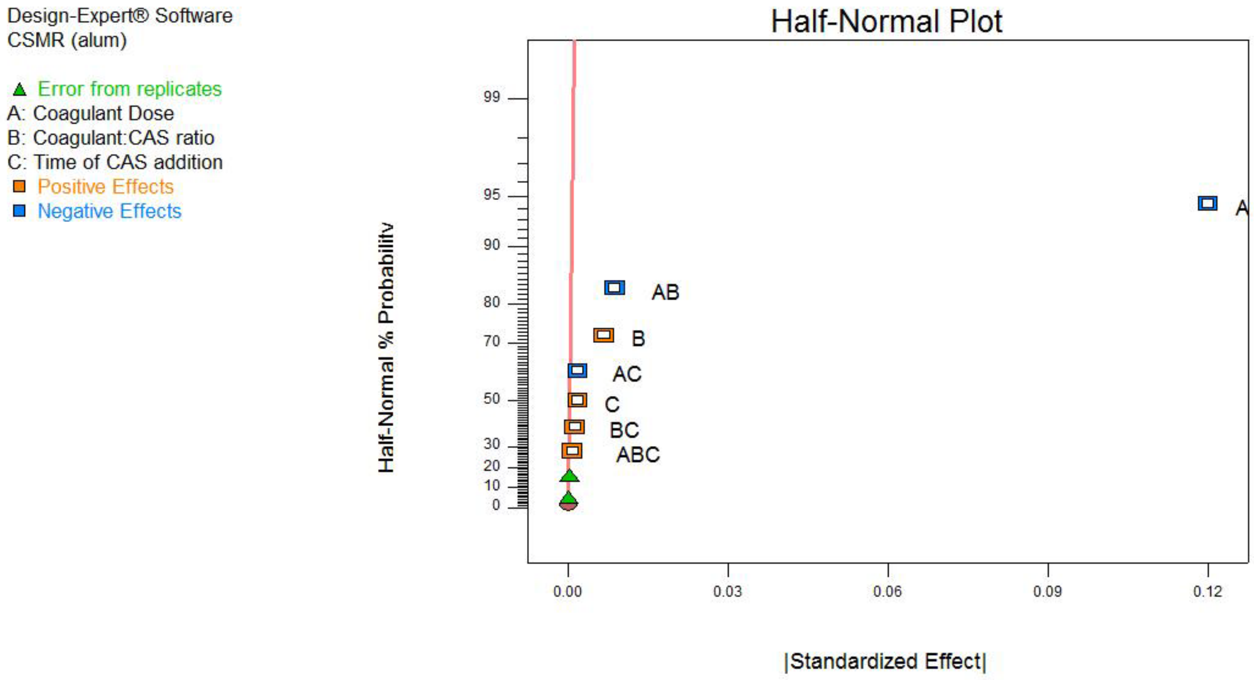
Figures A15, A16 (pH)



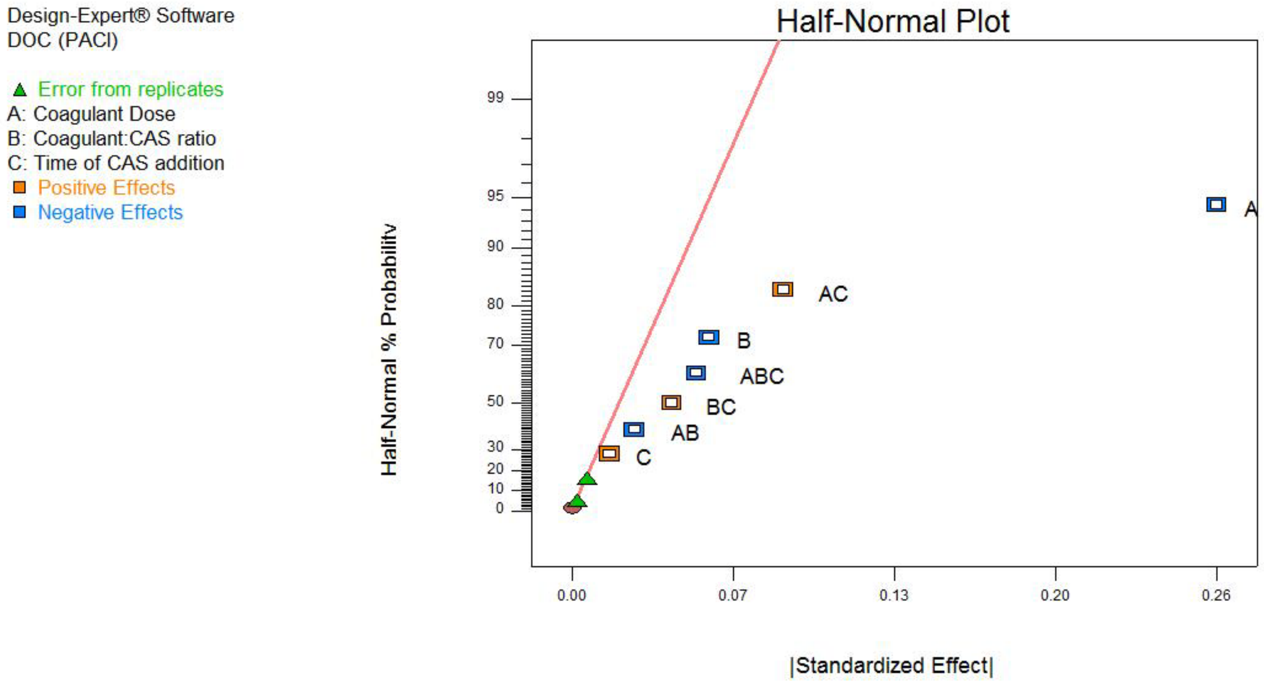


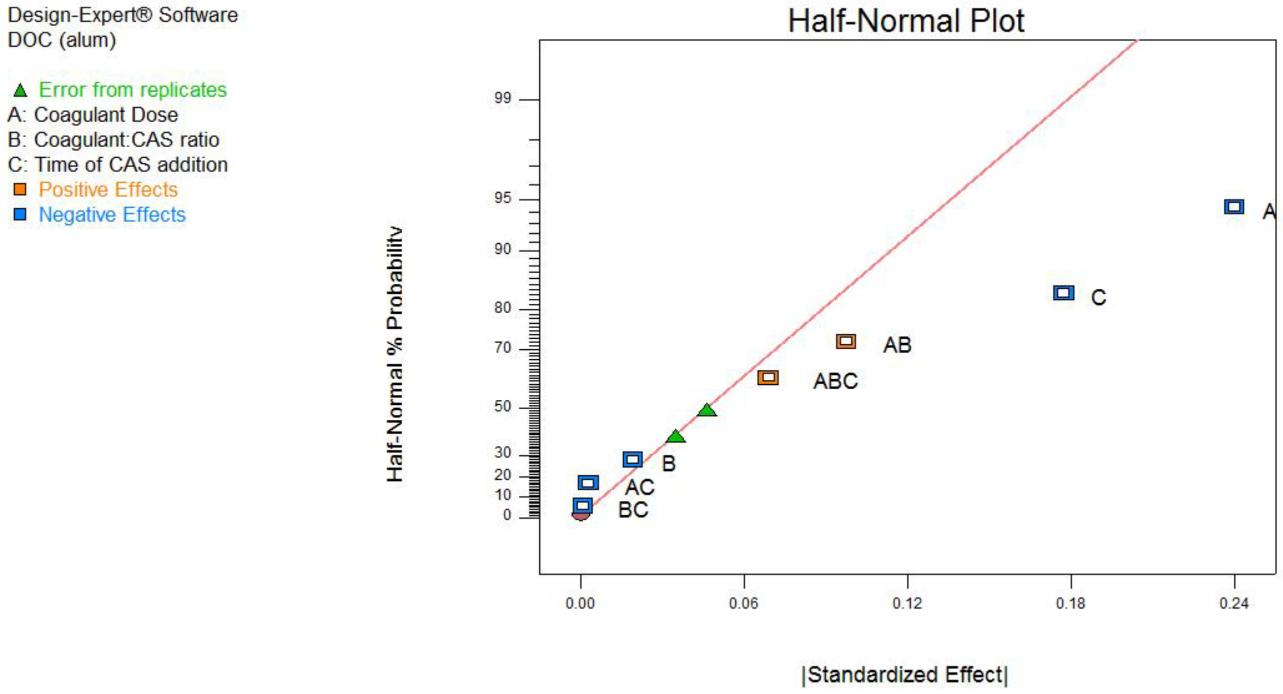
Figures A17, A18 (CSMR)



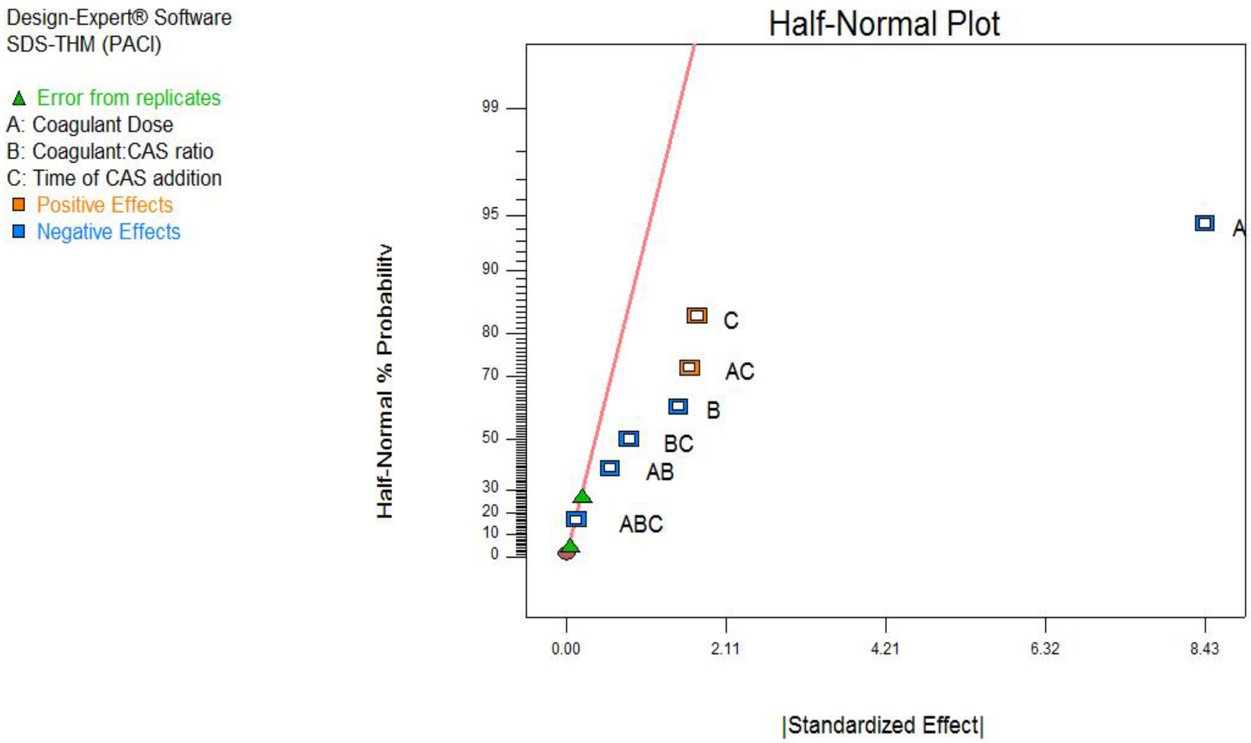


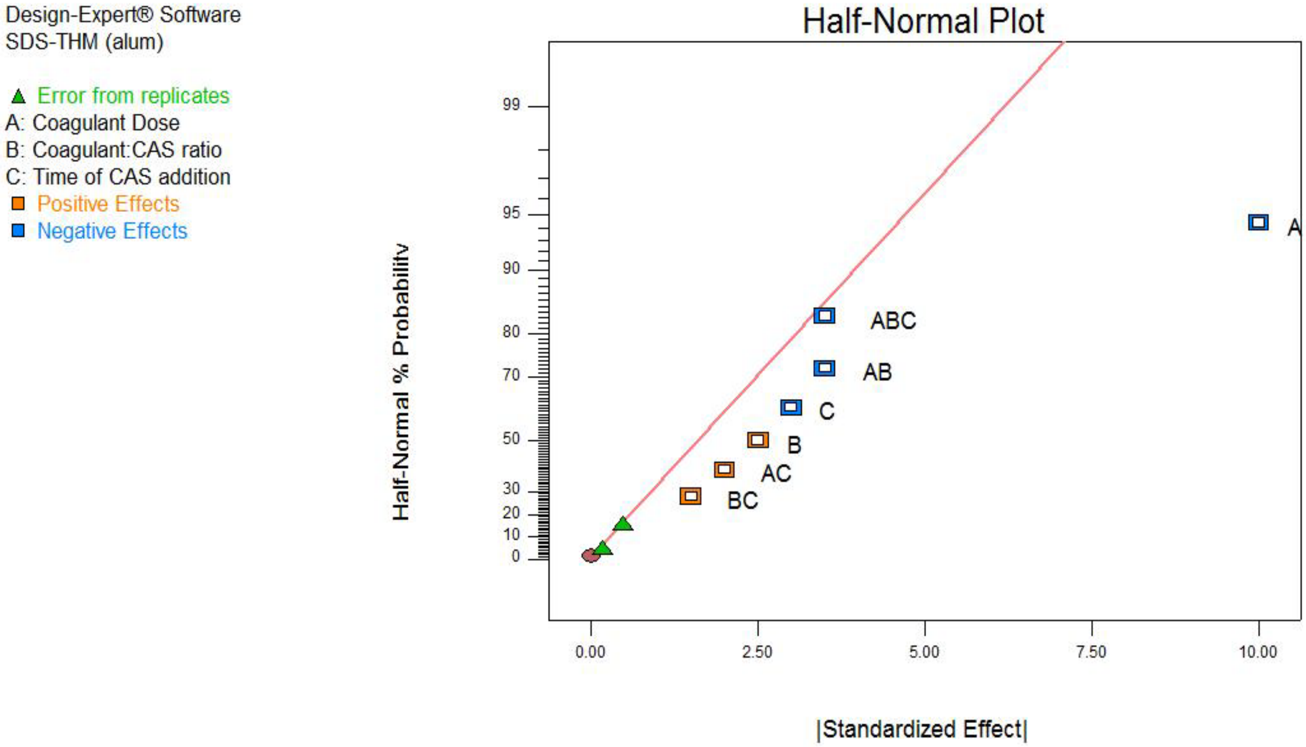
Figures A19, A20 (DOC)



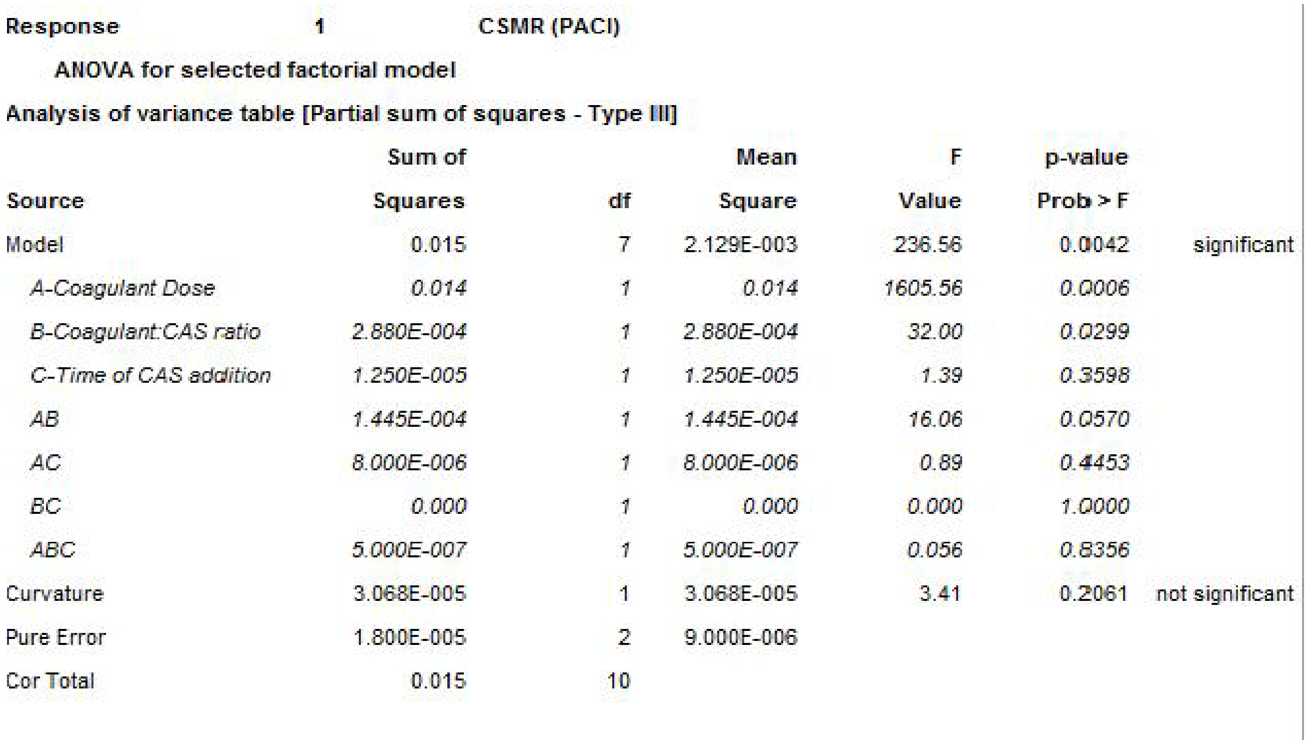


Figures A21, A22 (SDS-THM)





Figures A23, A24 (ANOVA – CSMR)

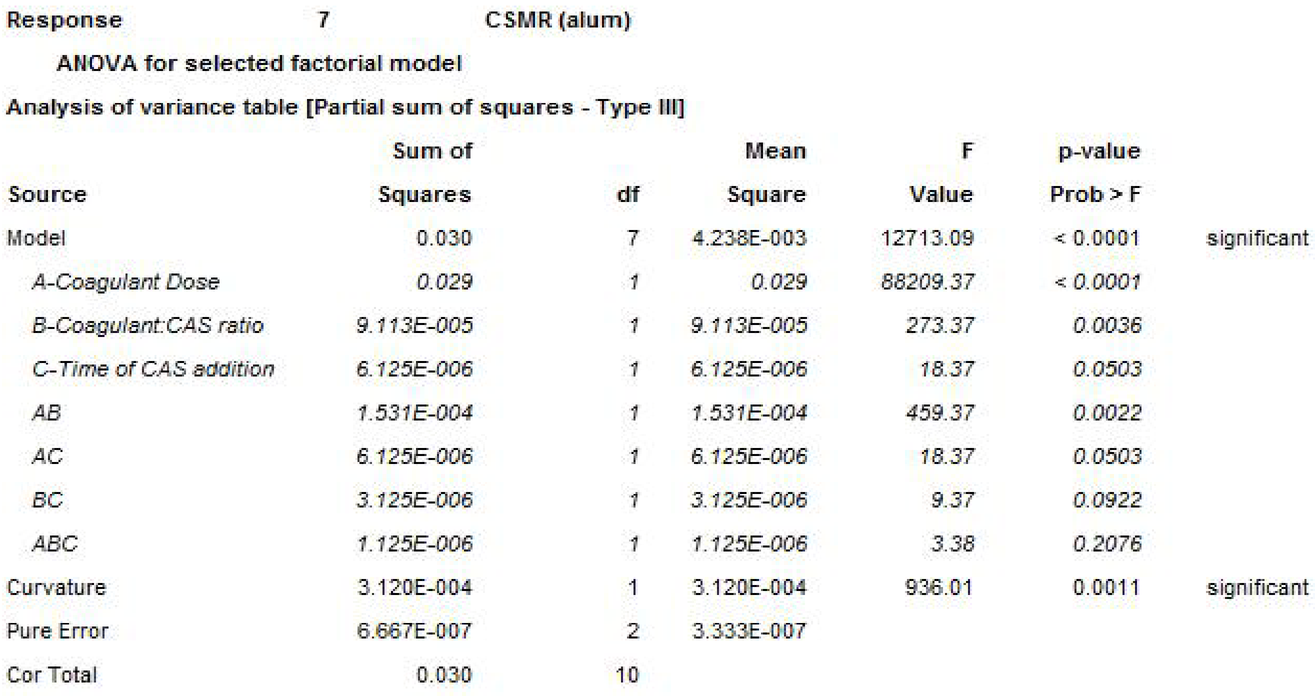


Response **1** **CSMR (PACl)**

ANOVA for selected factorial model

Analysis of variance table [Partial sum of squares - Type III]

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	0.015	7	2.129E-003	236.56	0.0042	significant
A-Coagulant Dose	*0.014*	*1*	*0.014*	*1605.56*	*0.0006*	
B-Coagulant:CAS ratio	*2.880E-004*	*1*	*2.880E-004*	*32.00*	*0.0299*	
C-Time of CAS addition	*1.250E-005*	*1*	*1.250E-005*	*1.39*	*0.3598*	
AB	*1.445E-004*	*1*	*1.445E-004*	*16.06*	*0.0570*	
AC	*8.000E-006*	*1*	*8.000E-006*	*0.89*	*0.4453*	
BC	*0.000*	*1*	*0.000*	*0.000*	*1.0000*	
ABC	*5.000E-007*	*1*	*5.000E-007*	*0.056*	*0.8356*	
Curvature	3.068E-005	1	3.068E-005	3.41	0.2061	not significant
Pure Error	1.800E-005	2	9.000E-006			
Cor Total	0.015	10				



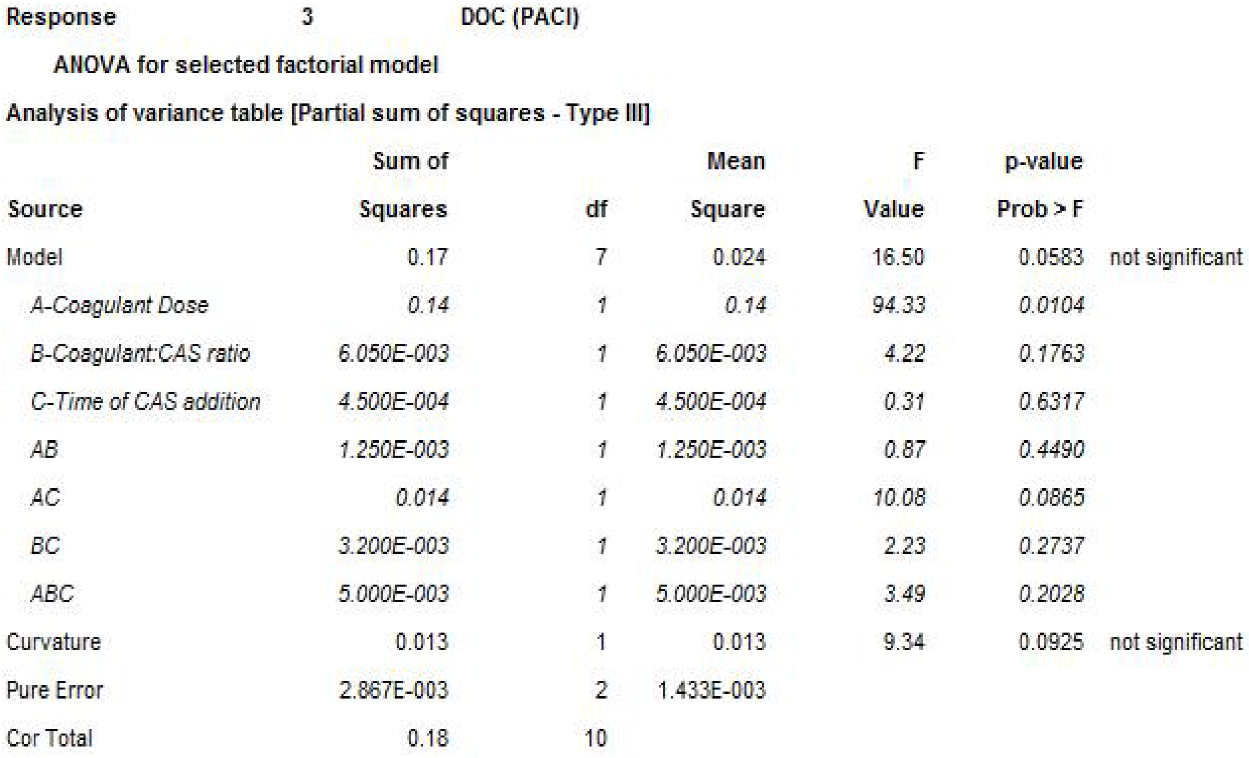
Response **7** **CSMR (alum)**

ANOVA for selected factorial model

Analysis of variance table [Partial sum of squares - Type III]

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	0.030	7	4.238E-003	12713.09	< 0.0001	significant
A-Coagulant Dose	*0.029*	*1*	*0.029*	*88209.37*	*< 0.0001*	
B-Coagulant:CAS ratio	*9.113E-005*	*1*	*9.113E-005*	*273.37*	*0.0036*	
C-Time of CAS addition	*6.125E-006*	*1*	*6.125E-006*	*18.37*	*0.0503*	
AB	*1.531E-004*	*1*	*1.531E-004*	*459.37*	*0.0022*	
AC	*6.125E-006*	*1*	*6.125E-006*	*18.37*	*0.0503*	
BC	*3.125E-006*	*1*	*3.125E-006*	*9.37*	*0.0922*	
ABC	*1.125E-006*	*1*	*1.125E-006*	*3.38*	*0.2076*	
Curvature	3.120E-004	1	3.120E-004	936.01	0.0011	significant
Pure Error	6.667E-007	2	3.333E-007			
Cor Total	0.030	10				

Figures A25, A26 (ANOVA – DOC)

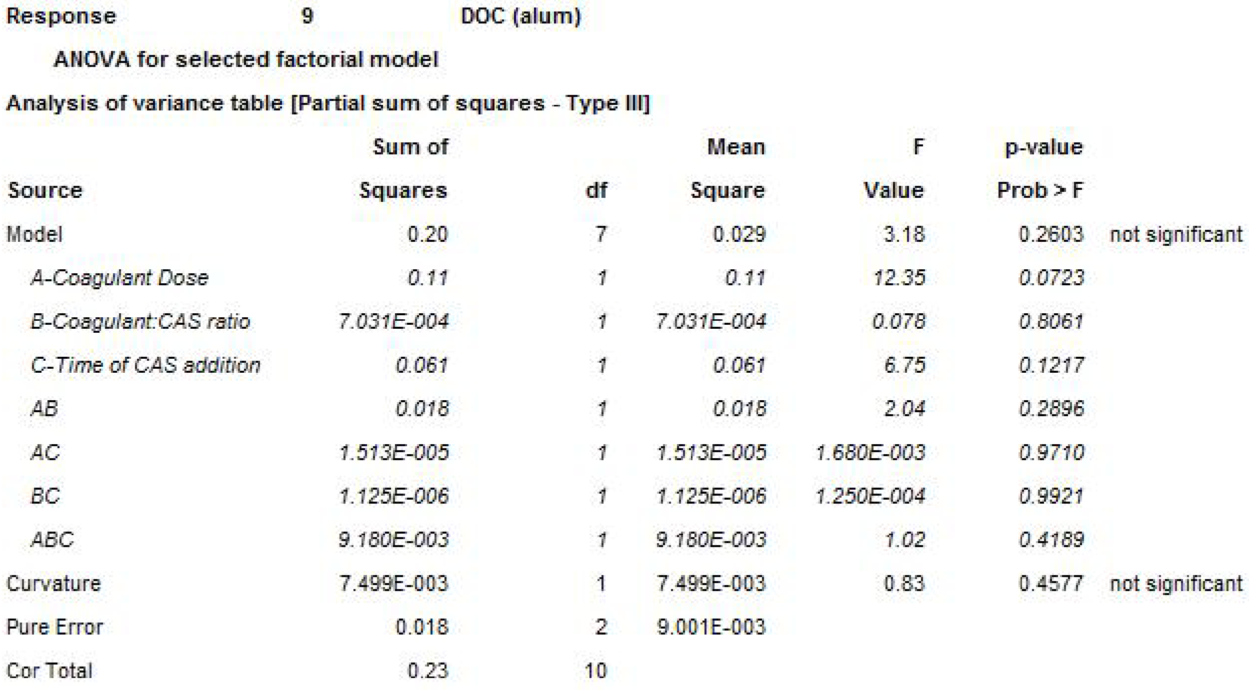


Response 3 DOC (PACl)

ANOVA for selected factorial model

Analysis of variance table [Partial sum of squares - Type III]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	0.17	7	0.024	16.50	0.0583	not significant
A-Coagulant Dose	*0.14*	*1*	*0.14*	*94.33*	*0.0104*	
B-Coagulant:CAS ratio	*6.050E-003*	*1*	*6.050E-003*	*4.22*	*0.1763*	
C-Time of CAS addition	*4.500E-004*	*1*	*4.500E-004*	*0.31*	*0.6317*	
AB	*1.250E-003*	*1*	*1.250E-003*	*0.87*	*0.4490*	
AC	*0.014*	*1*	*0.014*	*10.08*	*0.0865*	
BC	*3.200E-003*	*1*	*3.200E-003*	*2.23*	*0.2737*	
ABC	*5.000E-003*	*1*	*5.000E-003*	*3.49*	*0.2028*	
Curvature	0.013	1	0.013	9.34	0.0925	not significant
Pure Error	2.867E-003	2	1.433E-003			
Cor Total	0.18	10				



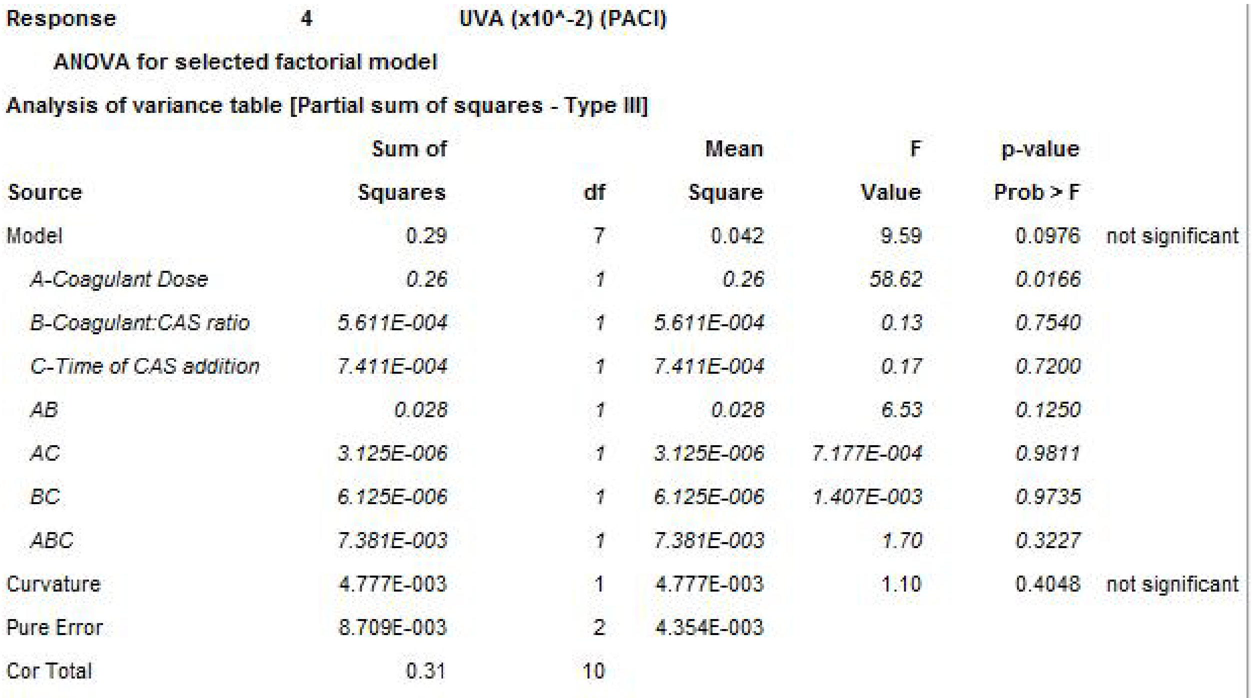
Response 9 DOC (alum)

ANOVA for selected factorial model

Analysis of variance table [Partial sum of squares - Type III]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	0.20	7	0.029	3.18	0.2603	not significant
A-Coagulant Dose	*0.11*	*1*	*0.11*	*12.35*	*0.0723*	
B-Coagulant:CAS ratio	*7.031E-004*	*1*	*7.031E-004*	*0.078*	*0.8061*	
C-Time of CAS addition	*0.061*	*1*	*0.061*	*6.75*	*0.1217*	
AB	*0.018*	*1*	*0.018*	*2.04*	*0.2896*	
AC	*1.513E-005*	*1*	*1.513E-005*	*1.680E-003*	*0.9710*	
BC	*1.125E-006*	*1*	*1.125E-006*	*1.250E-004*	*0.9921*	
ABC	*9.180E-003*	*1*	*9.180E-003*	*1.02*	*0.4189*	
Curvature	7.499E-003	1	7.499E-003	0.83	0.4577	not significant
Pure Error	0.018	2	9.001E-003			
Cor Total	0.23	10				

Figures A27, A28 (ANOVA – UV254)

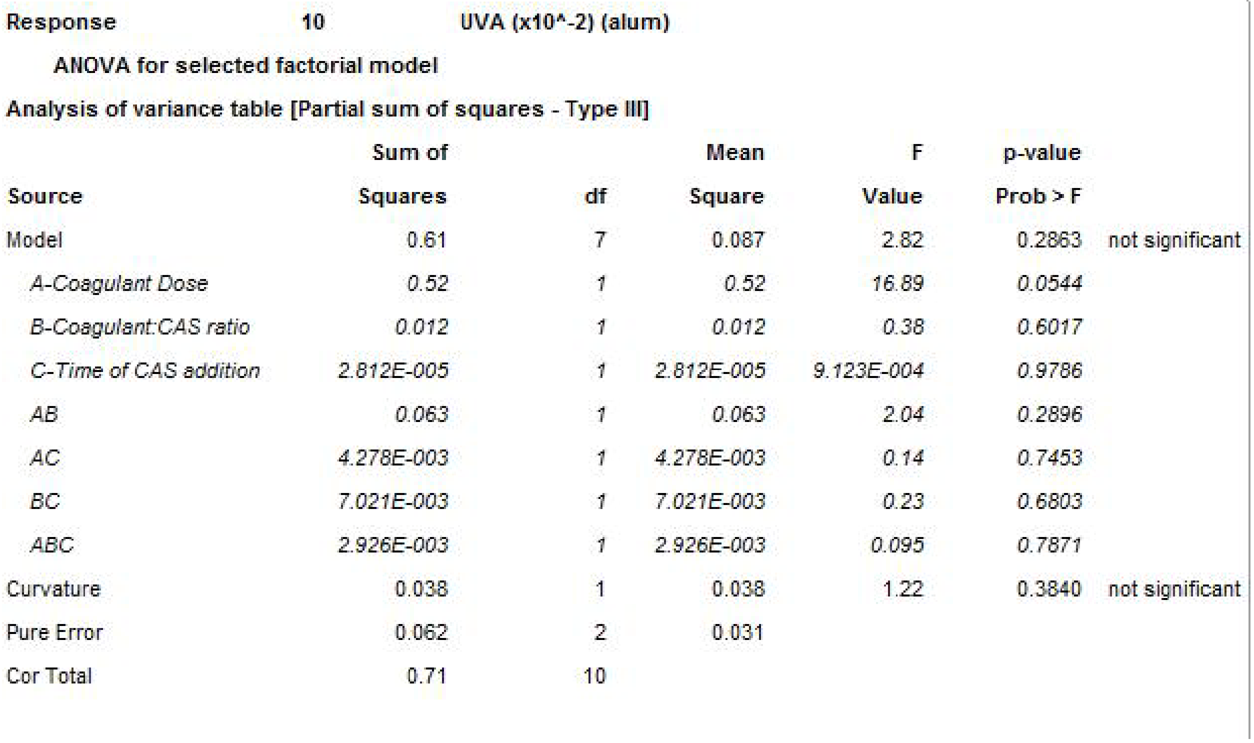


Response 4 **UVA (x10^-2) (PACl)**

ANOVA for selected factorial model

Analysis of variance table [Partial sum of squares - Type III]

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	0.29	7	0.042	9.59	0.0976	not significant
A-Coagulant Dose	*0.26*	*1*	*0.26*	*58.62*	*0.0166*	
B-Coagulant:CAS ratio	*5.611E-004*	*1*	*5.611E-004*	*0.13*	*0.7540*	
C-Time of CAS addition	*7.411E-004*	*1*	*7.411E-004*	*0.17*	*0.7200*	
AB	*0.028*	*1*	*0.028*	*6.53*	*0.1250*	
AC	*3.125E-006*	*1*	*3.125E-006*	*7.177E-004*	*0.9811*	
BC	*6.125E-006*	*1*	*6.125E-006*	*1.407E-003*	*0.9735*	
ABC	*7.381E-003*	*1*	*7.381E-003*	*1.70*	*0.3227*	
Curvature	4.777E-003	1	4.777E-003	1.10	0.4048	not significant
Pure Error	8.709E-003	2	4.354E-003			
Cor Total	0.31	10				



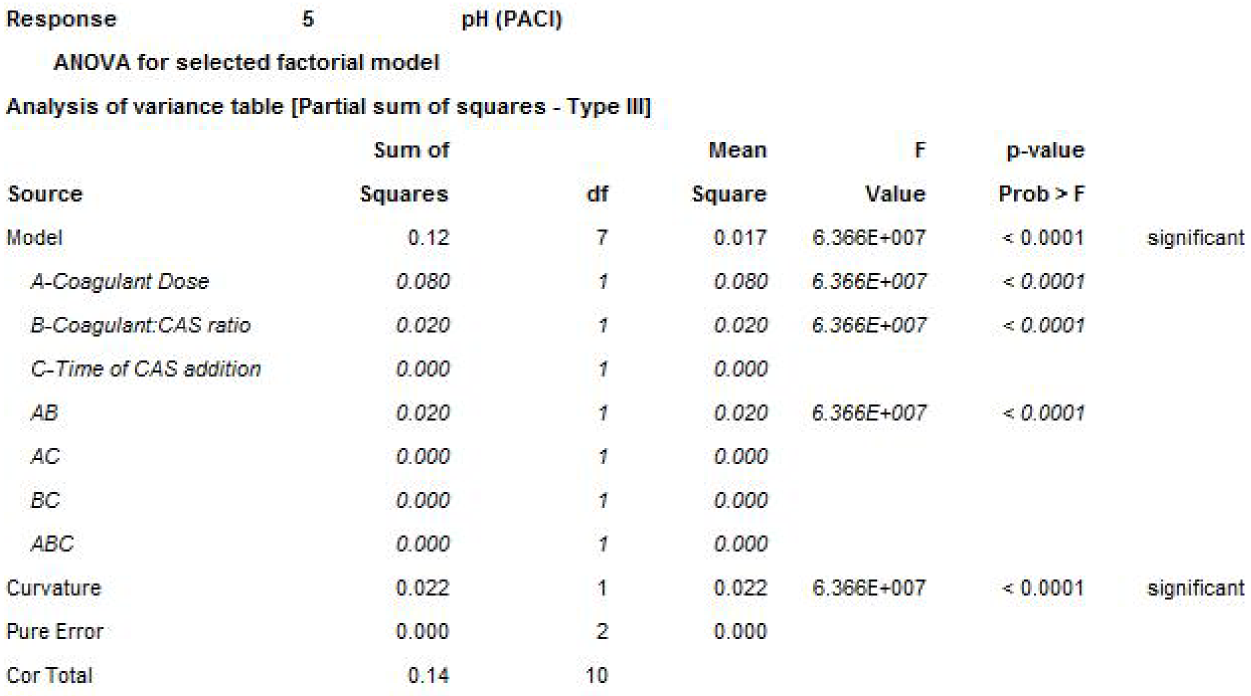
Response 10 **UVA (x10^-2) (alum)**

ANOVA for selected factorial model

Analysis of variance table [Partial sum of squares - Type III]

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	0.61	7	0.087	2.82	0.2863	not significant
A-Coagulant Dose	*0.52*	*1*	*0.52*	*16.89*	*0.0544*	
B-Coagulant:CAS ratio	*0.012*	*1*	*0.012*	*0.38*	*0.6017*	
C-Time of CAS addition	*2.812E-005*	*1*	*2.812E-005*	*9.123E-004*	*0.9786*	
AB	*0.063*	*1*	*0.063*	*2.04*	*0.2896*	
AC	*4.278E-003*	*1*	*4.278E-003*	*0.14*	*0.7453*	
BC	*7.021E-003*	*1*	*7.021E-003*	*0.23*	*0.6803*	
ABC	*2.926E-003*	*1*	*2.926E-003*	*0.095*	*0.7871*	
Curvature	0.038	1	0.038	1.22	0.3840	not significant
Pure Error	0.062	2	0.031			
Cor Total	0.71	10				

Figures A29, A30 (ANOVA – pH)

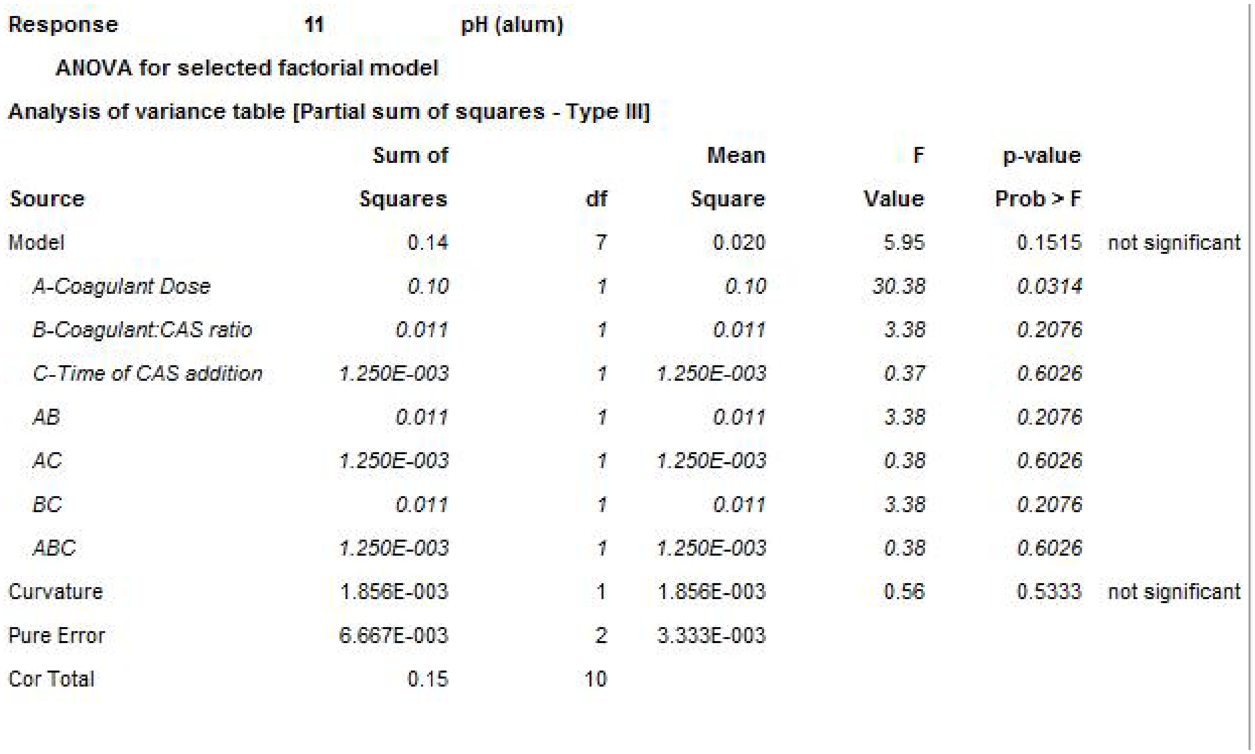


Response **5** **pH (PACl)**

ANOVA for selected factorial model

Analysis of variance table [Partial sum of squares - Type III]

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	0.12	7	0.017	6.366E+007	< 0.0001	significant
A-Coagulant Dose	*0.080*	*1*	*0.080*	*6.366E+007*	*< 0.0001*	
B-Coagulant:CAS ratio	*0.020*	*1*	*0.020*	*6.366E+007*	*< 0.0001*	
C-Time of CAS addition	*0.000*	*1*	*0.000*			
AB	*0.020*	*1*	*0.020*	*6.366E+007*	*< 0.0001*	
AC	*0.000*	*1*	*0.000*			
BC	*0.000*	*1*	*0.000*			
ABC	*0.000*	*1*	*0.000*			
Curvature	0.022	1	0.022	6.366E+007	< 0.0001	significant
Pure Error	0.000	2	0.000			
Cor Total	0.14	10				



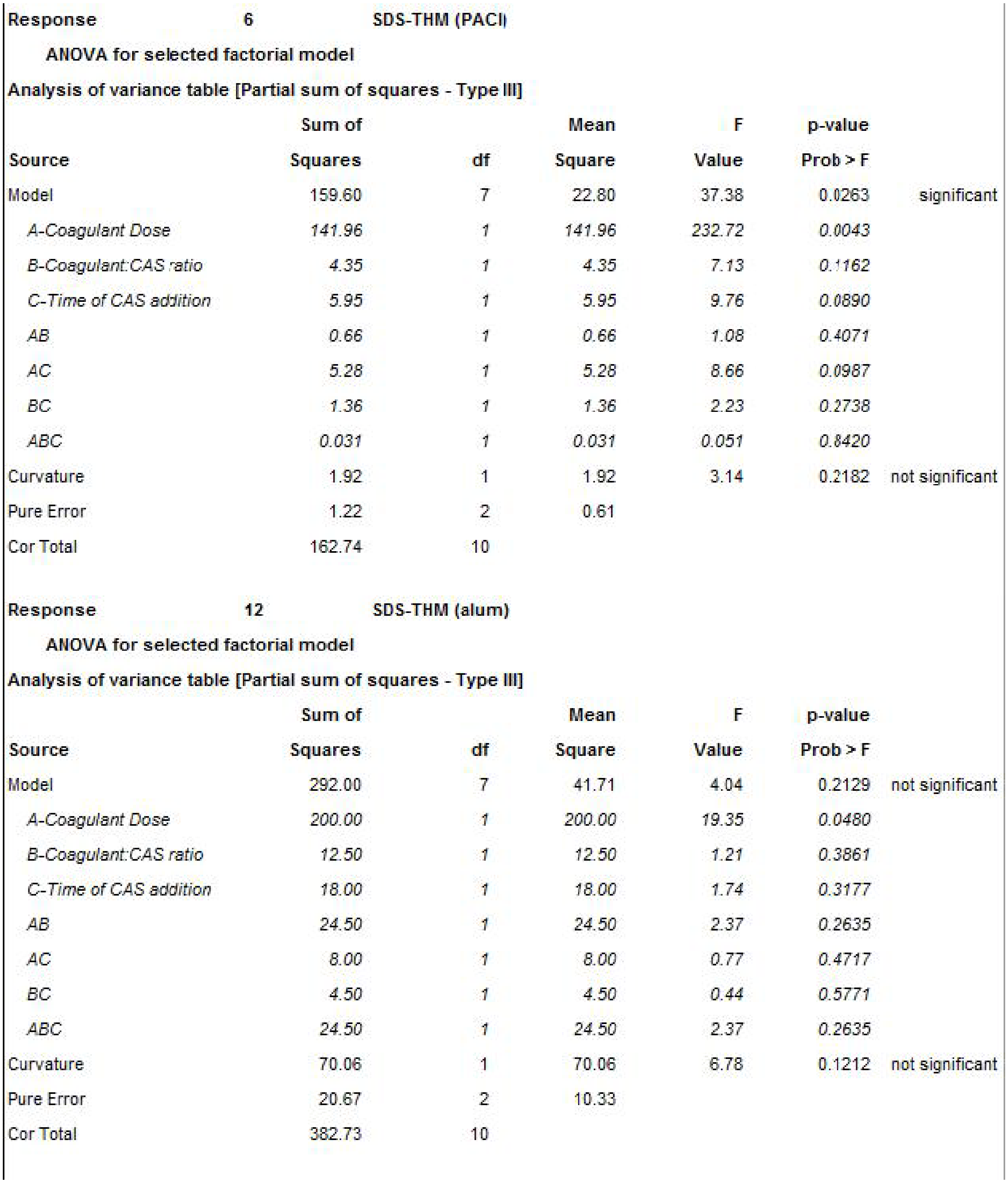
Response **11** **pH (alum)**

ANOVA for selected factorial model

Analysis of variance table [Partial sum of squares - Type III]

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	0.14	7	0.020	5.95	0.1515	not significant
A-Coagulant Dose	*0.10*	*1*	*0.10*	*30.38*	*0.0314*	
B-Coagulant:CAS ratio	*0.011*	*1*	*0.011*	*3.38*	*0.2076*	
C-Time of CAS addition	*1.250E-003*	*1*	*1.250E-003*	*0.37*	*0.6026*	
AB	*0.011*	*1*	*0.011*	*3.38*	*0.2076*	
AC	*1.250E-003*	*1*	*1.250E-003*	*0.38*	*0.6026*	
BC	*0.011*	*1*	*0.011*	*3.38*	*0.2076*	
ABC	*1.250E-003*	*1*	*1.250E-003*	*0.38*	*0.6026*	
Curvature	1.856E-003	1	1.856E-003	0.56	0.5333	not significant
Pure Error	6.667E-003	2	3.333E-003			
Cor Total	0.15	10				

Figures A31, A32 (ANOVA – SDS-THM)



Response **6** **SDS-THM (PACl)**

ANOVA for selected factorial model

Analysis of variance table [Partial sum of squares - Type III]

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	159.60	7	22.80	37.38	0.0263	significant
A-Coagulant Dose	*141.96*	*1*	*141.96*	*232.72*	*0.0043*	
B-Coagulant:CAS ratio	*4.35*	*1*	*4.35*	*7.13*	*0.1162*	
C-Time of CAS addition	*5.95*	*1*	*5.95*	*9.76*	*0.0890*	
AB	*0.66*	*1*	*0.66*	*1.08*	*0.4071*	
AC	*5.28*	*1*	*5.28*	*8.66*	*0.0987*	
BC	*1.36*	*1*	*1.36*	*2.23*	*0.2738*	
ABC	*0.031*	*1*	*0.031*	*0.051*	*0.8420*	
Curvature	1.92	1	1.92	3.14	0.2182	not significant
Pure Error	1.22	2	0.61			
Cor Total	162.74	10				

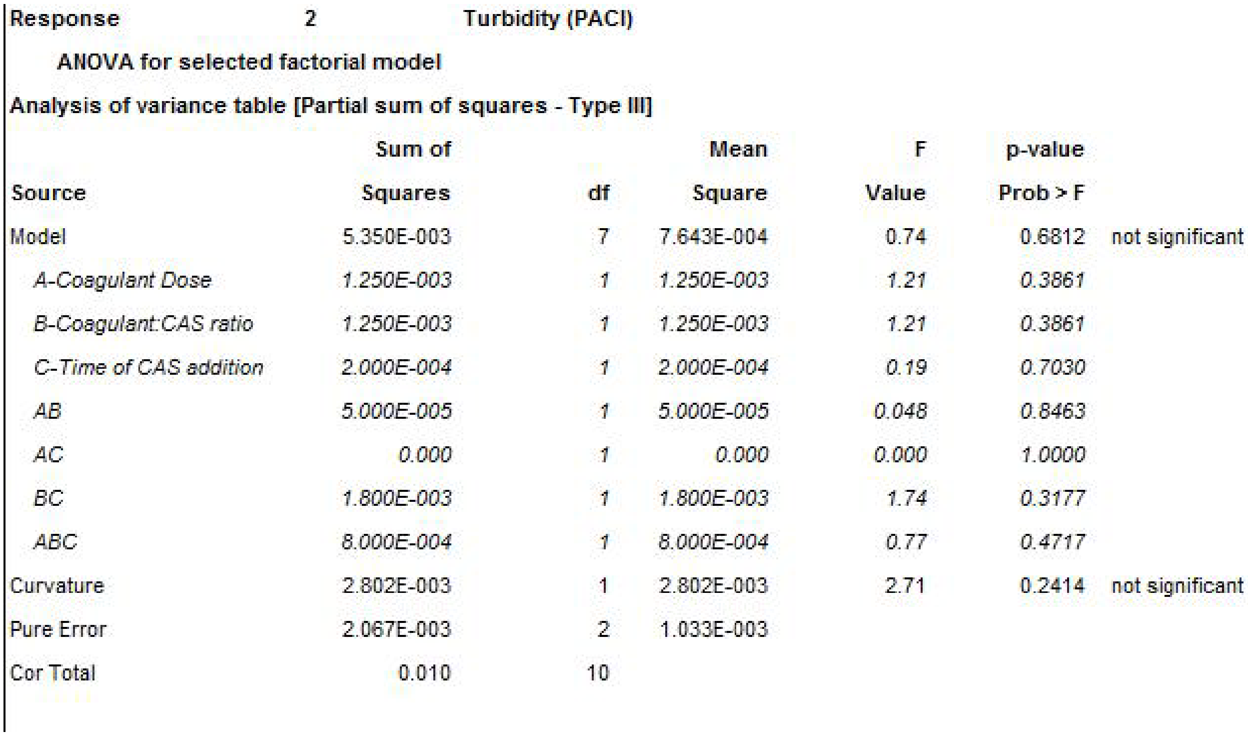
Response **12** **SDS-THM (alum)**

ANOVA for selected factorial model

Analysis of variance table [Partial sum of squares - Type III]

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	292.00	7	41.71	4.04	0.2129	not significant
A-Coagulant Dose	*200.00*	*1*	*200.00*	*19.35*	*0.0480*	
B-Coagulant:CAS ratio	*12.50*	*1*	*12.50*	*1.21*	*0.3861*	
C-Time of CAS addition	*18.00*	*1*	*18.00*	*1.74*	*0.3177*	
AB	*24.50*	*1*	*24.50*	*2.37*	*0.2635*	
AC	*8.00*	*1*	*8.00*	*0.77*	*0.4717*	
BC	*4.50*	*1*	*4.50*	*0.44*	*0.5771*	
ABC	*24.50*	*1*	*24.50*	*2.37*	*0.2635*	
Curvature	70.06	1	70.06	6.78	0.1212	not significant
Pure Error	20.67	2	10.33			
Cor Total	382.73	10				

Figures A33, A34 (ANOVA – Turbidity)

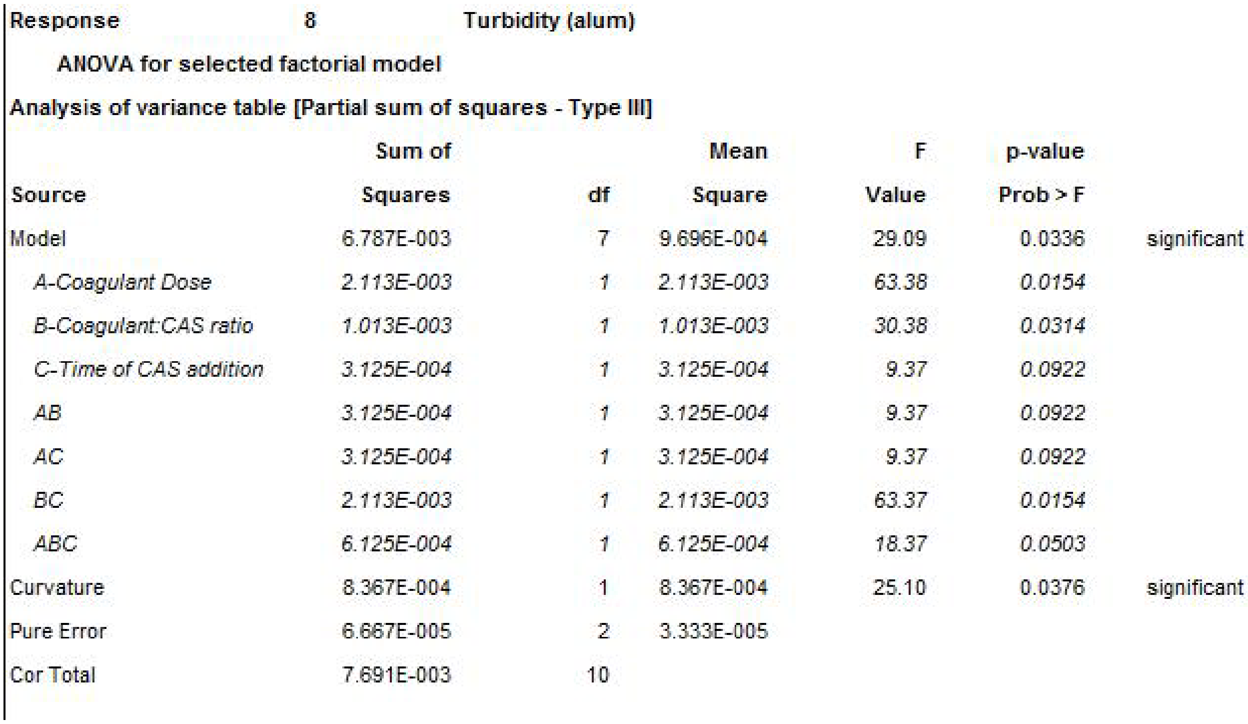


Response **2** **Turbidity (PACl)**

ANOVA for selected factorial model

Analysis of variance table [Partial sum of squares - Type III]

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	5.350E-003	7	7.643E-004	0.74	0.6812	not significant
A-Coagulant Dose	*1.250E-003*	*1*	*1.250E-003*	*1.21*	*0.3861*	
B-Coagulant:CAS ratio	*1.250E-003*	*1*	*1.250E-003*	*1.21*	*0.3861*	
C-Time of CAS addition	*2.000E-004*	*1*	*2.000E-004*	*0.19*	*0.7030*	
AB	*5.000E-005*	*1*	*5.000E-005*	*0.048*	*0.8463*	
AC	*0.000*	*1*	*0.000*	*0.000*	*1.0000*	
BC	*1.800E-003*	*1*	*1.800E-003*	*1.74*	*0.3177*	
ABC	*8.000E-004*	*1*	*8.000E-004*	*0.77*	*0.4717*	
Curvature	2.802E-003	1	2.802E-003	2.71	0.2414	not significant
Pure Error	2.067E-003	2	1.033E-003			
Cor Total	0.010	10				



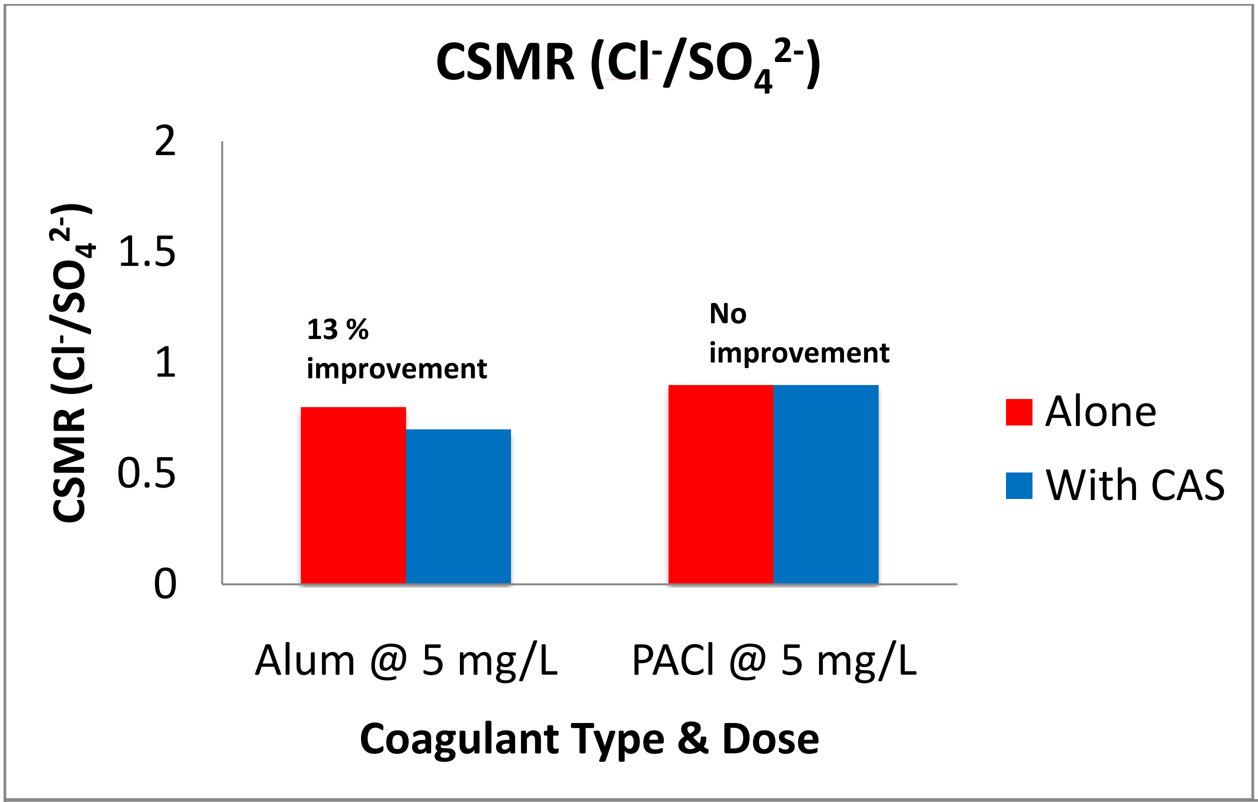
Response **8** **Turbidity (alum)**

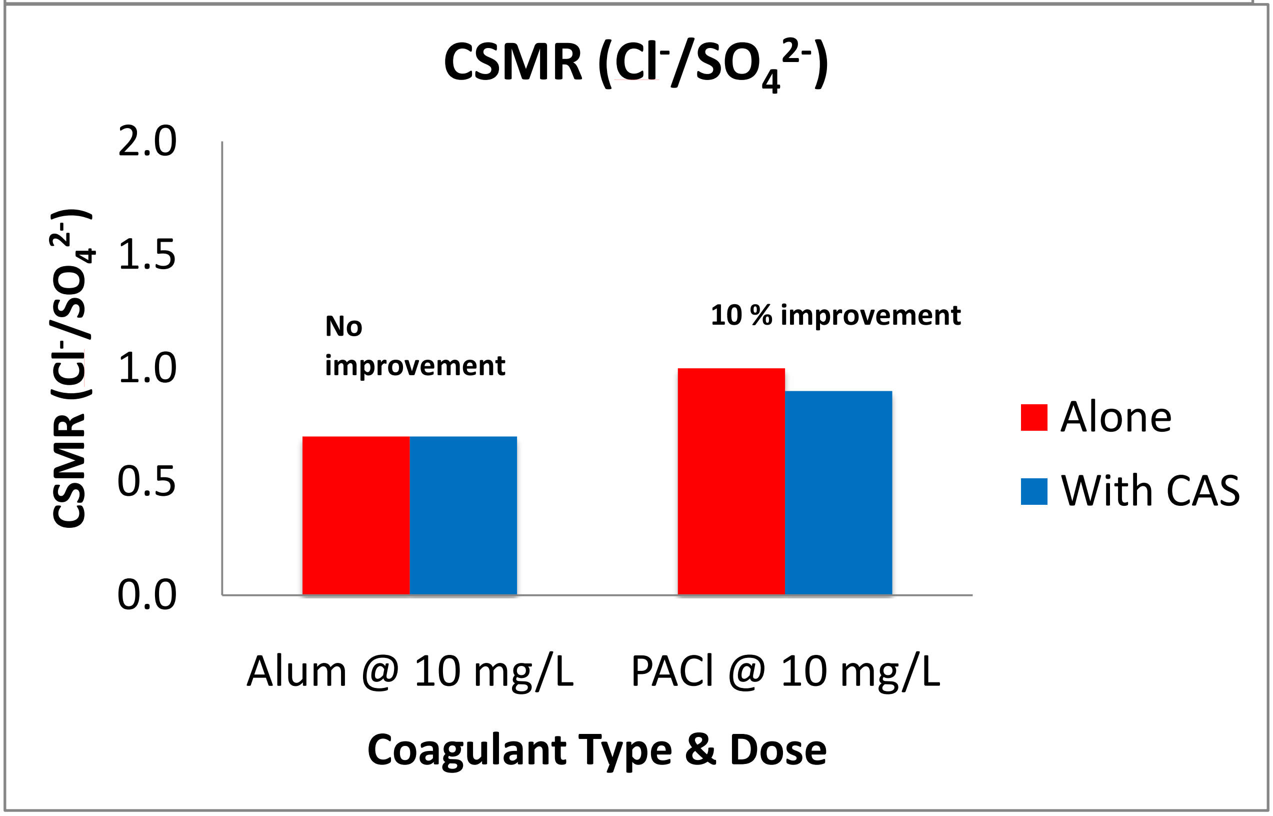
ANOVA for selected factorial model

Analysis of variance table [Partial sum of squares - Type III]

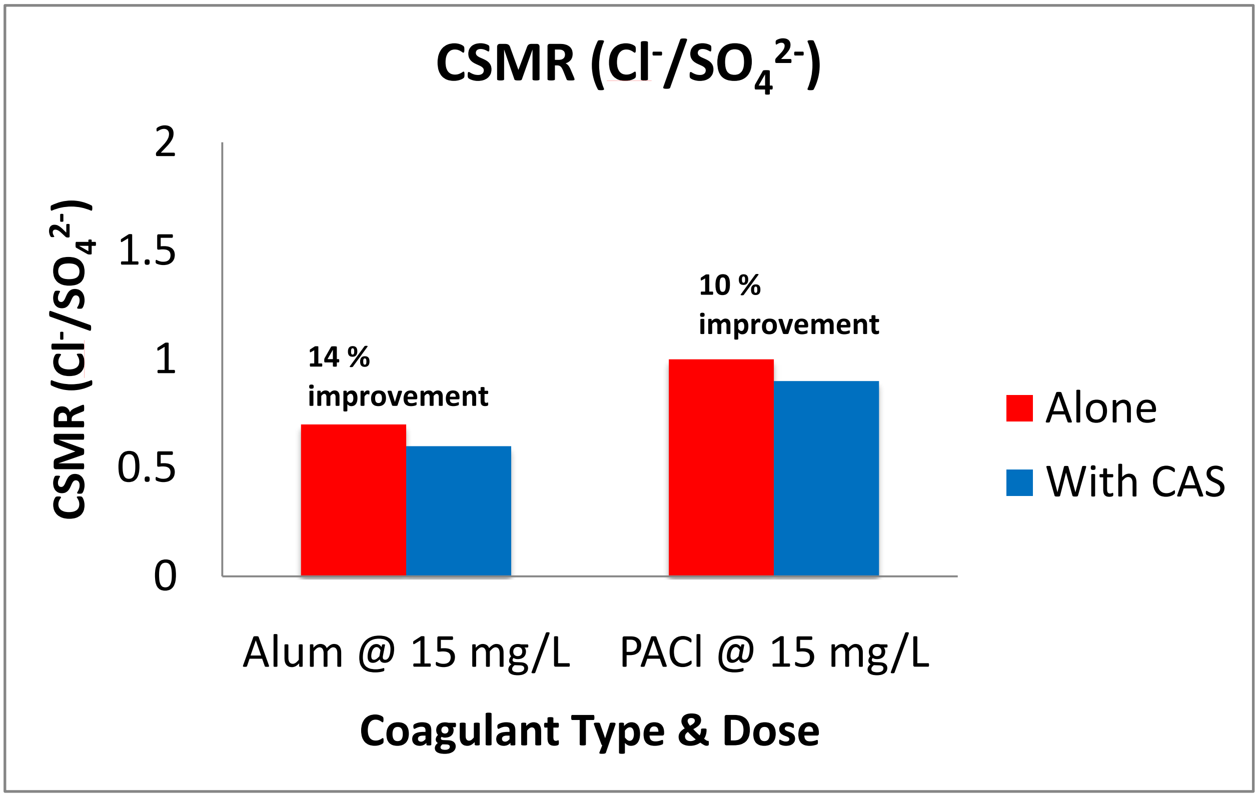
Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	6.787E-003	7	9.696E-004	29.09	0.0336	significant
A-Coagulant Dose	*2.113E-003*	*1*	*2.113E-003*	*63.38*	*0.0154*	
B-Coagulant:CAS ratio	*1.013E-003*	*1*	*1.013E-003*	*30.38*	*0.0314*	
C-Time of CAS addition	*3.125E-004*	*1*	*3.125E-004*	*9.37*	*0.0922*	
AB	*3.125E-004*	*1*	*3.125E-004*	*9.37*	*0.0922*	
AC	*3.125E-004*	*1*	*3.125E-004*	*9.37*	*0.0922*	
BC	*2.113E-003*	*1*	*2.113E-003*	*63.37*	*0.0154*	
ABC	*6.125E-004*	*1*	*6.125E-004*	*18.37*	*0.0503*	
Curvature	8.367E-004	1	8.367E-004	25.10	0.0376	significant
Pure Error	6.667E-005	2	3.333E-005			
Cor Total	7.691E-003	10				

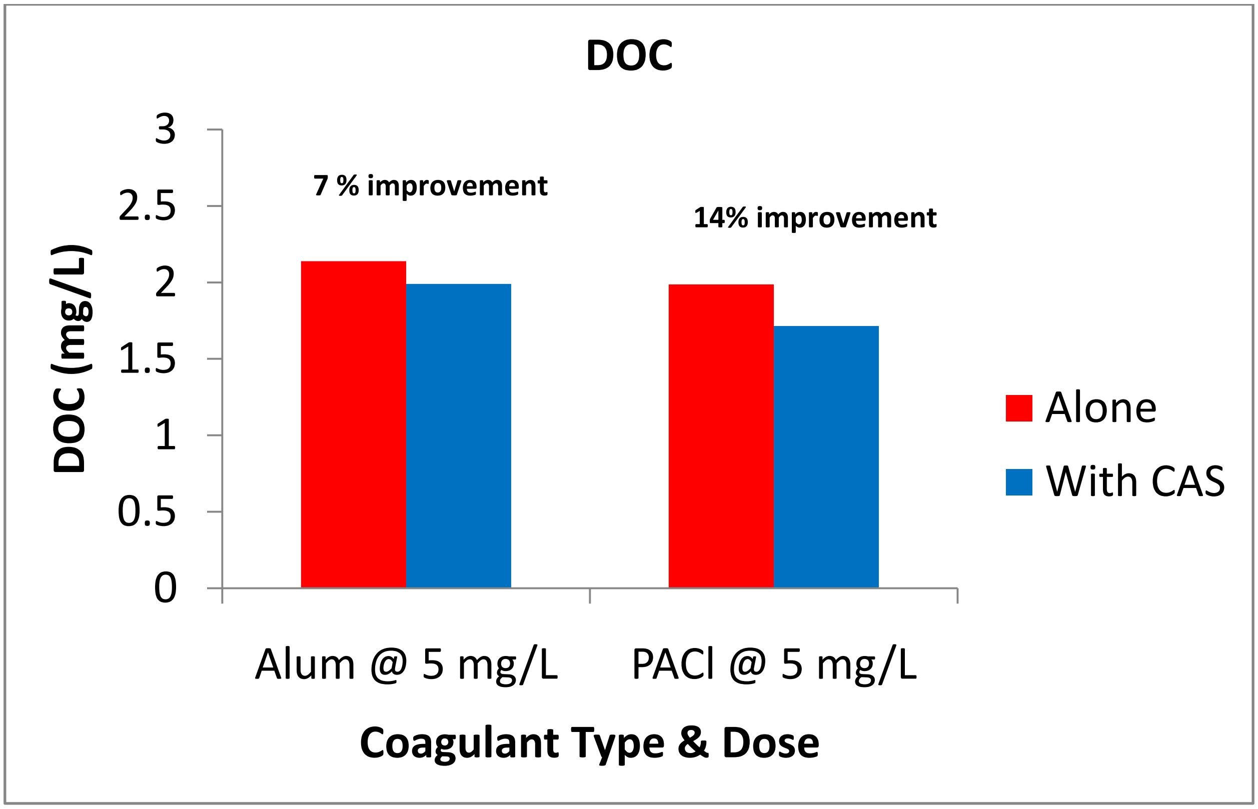
Figures A35, A36



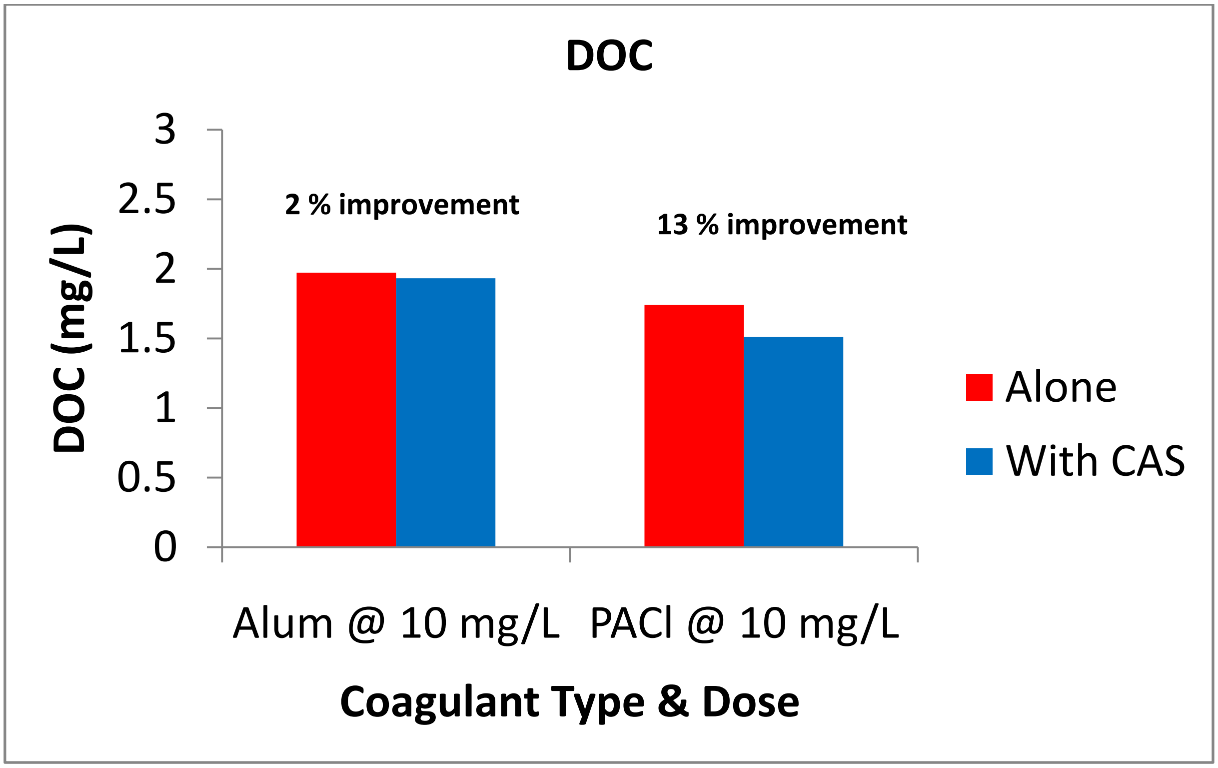


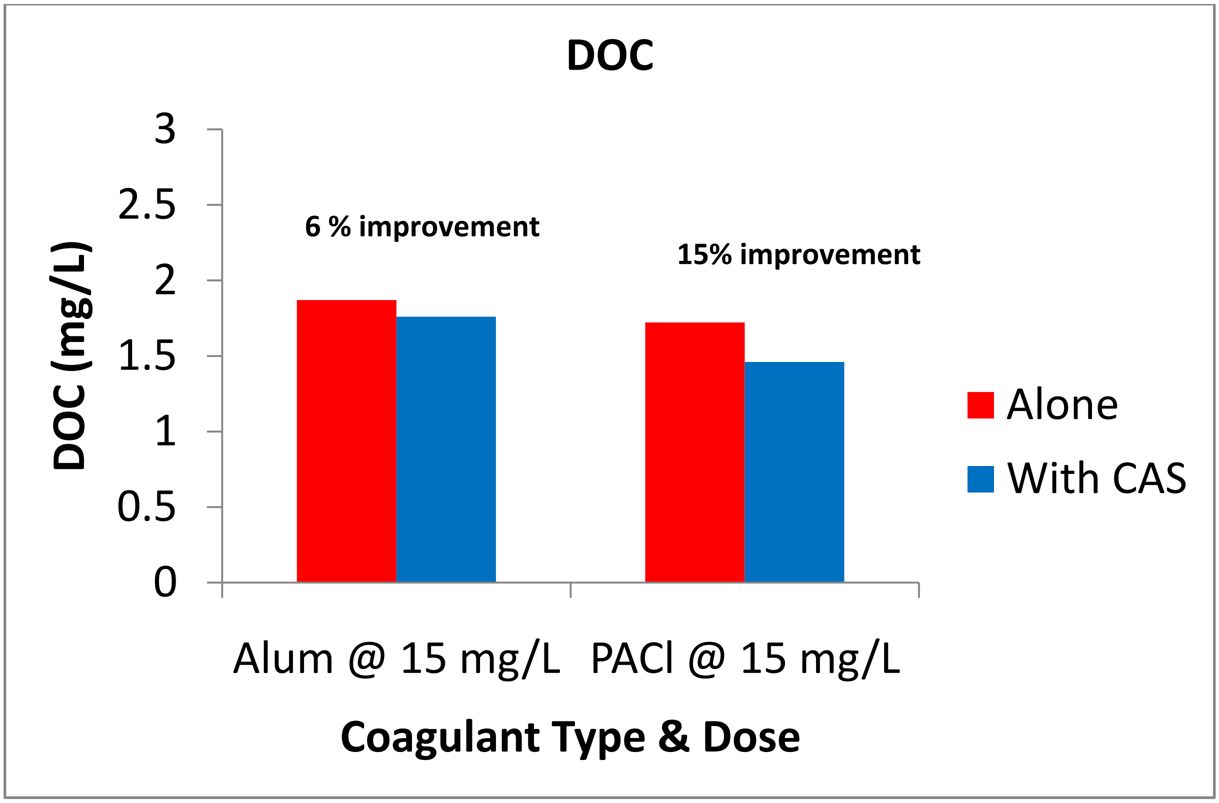
Figures A37, A38



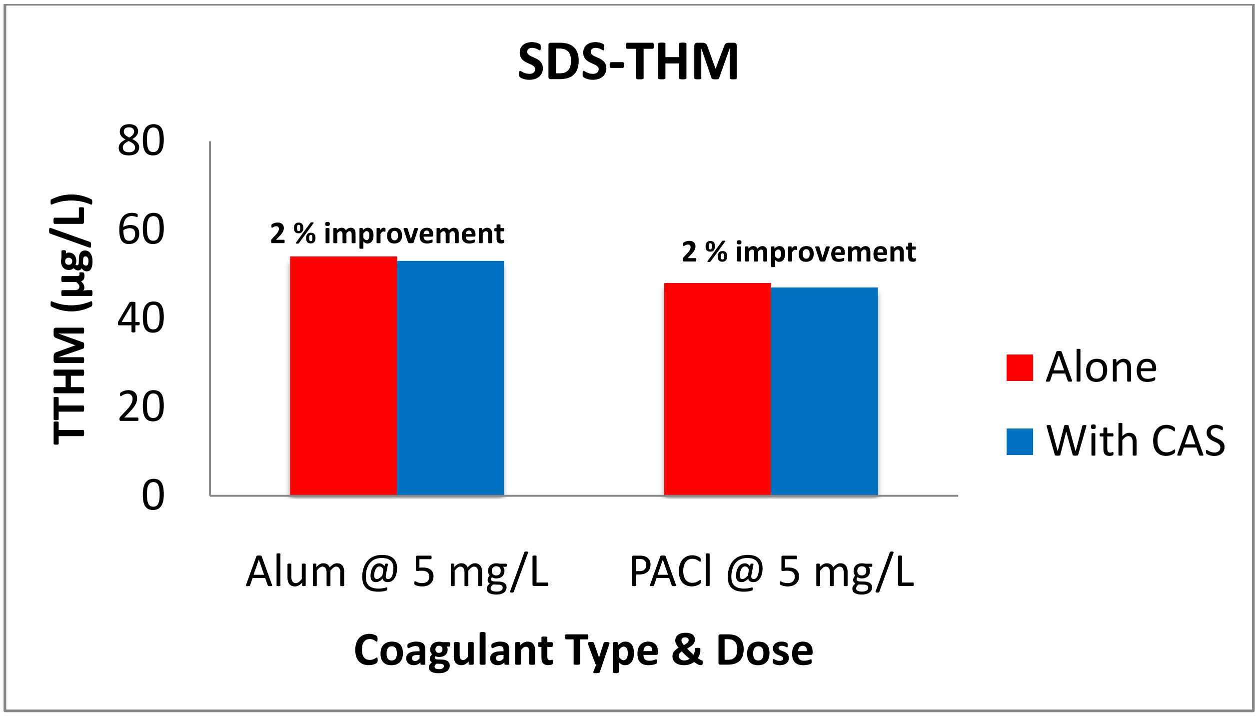


Figures A39, A40





Figures A41, A42



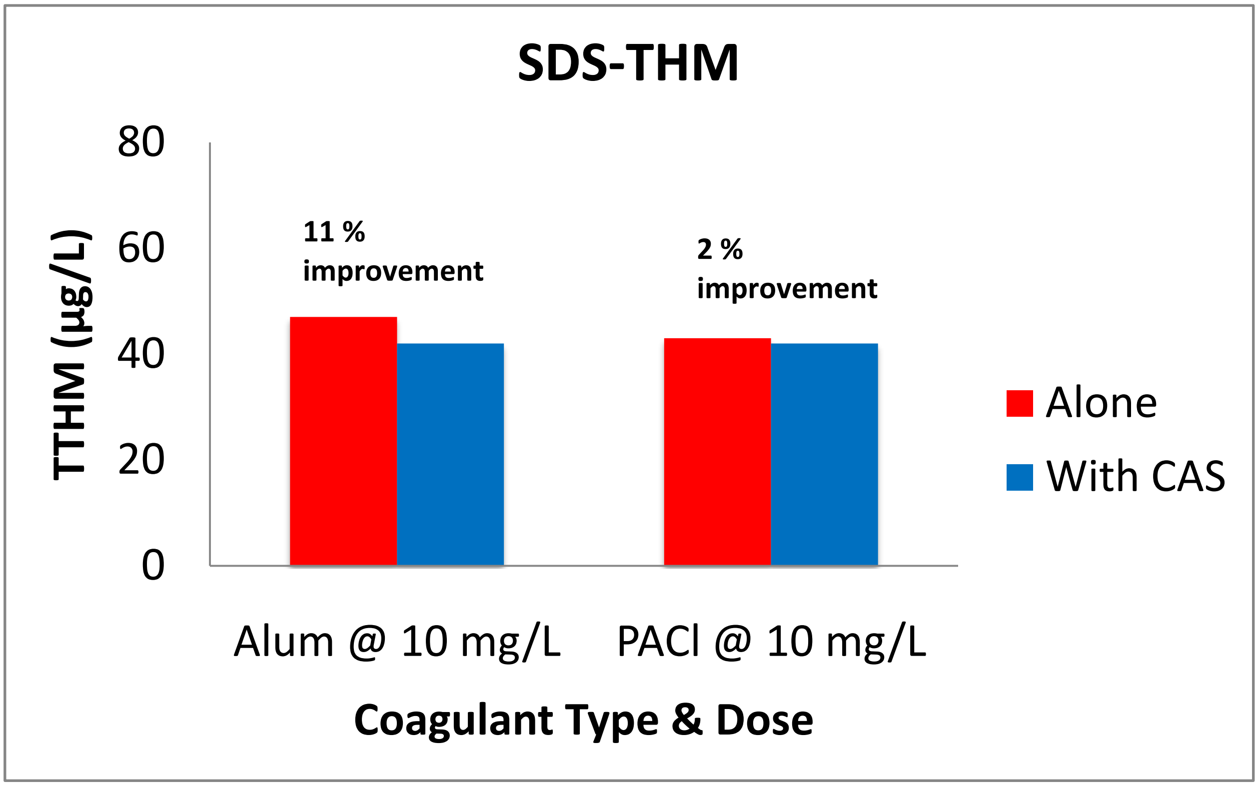
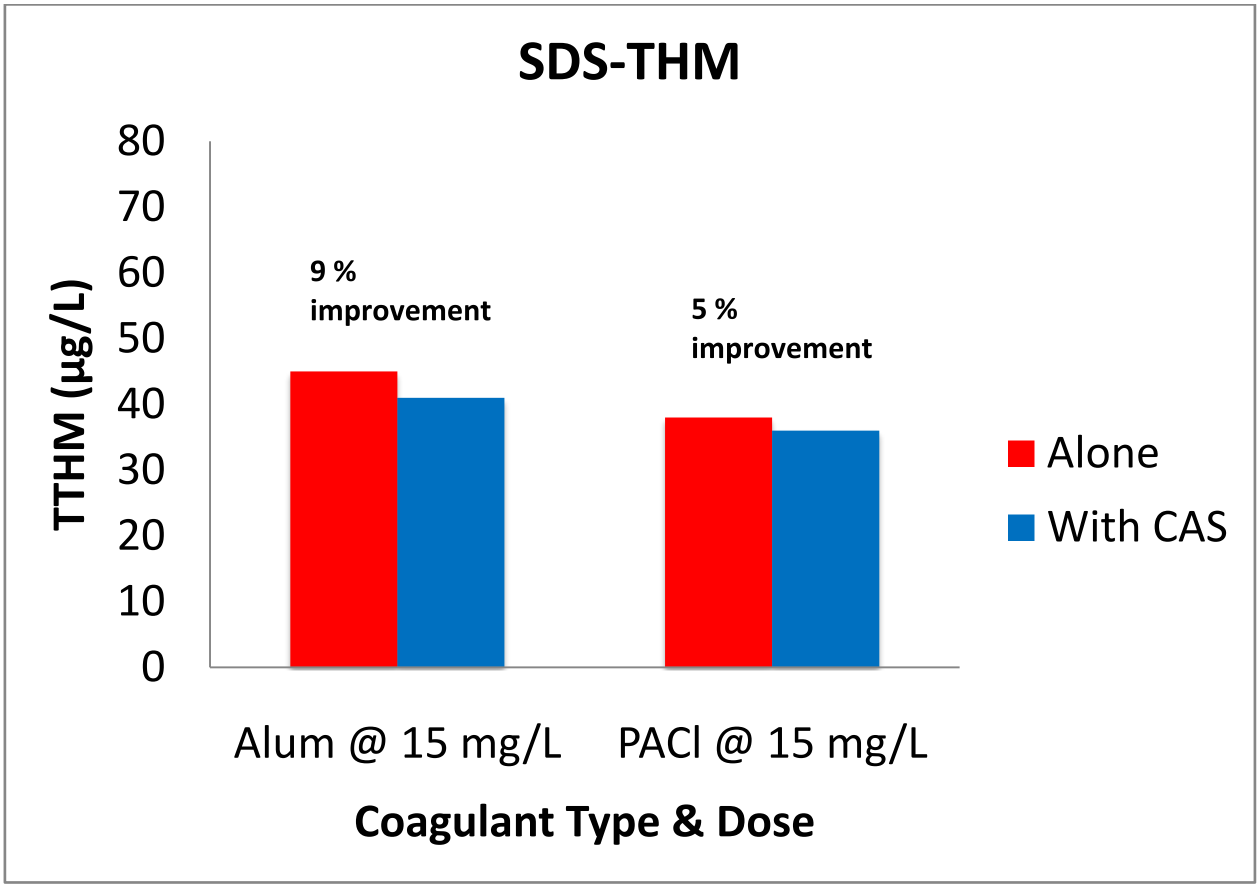


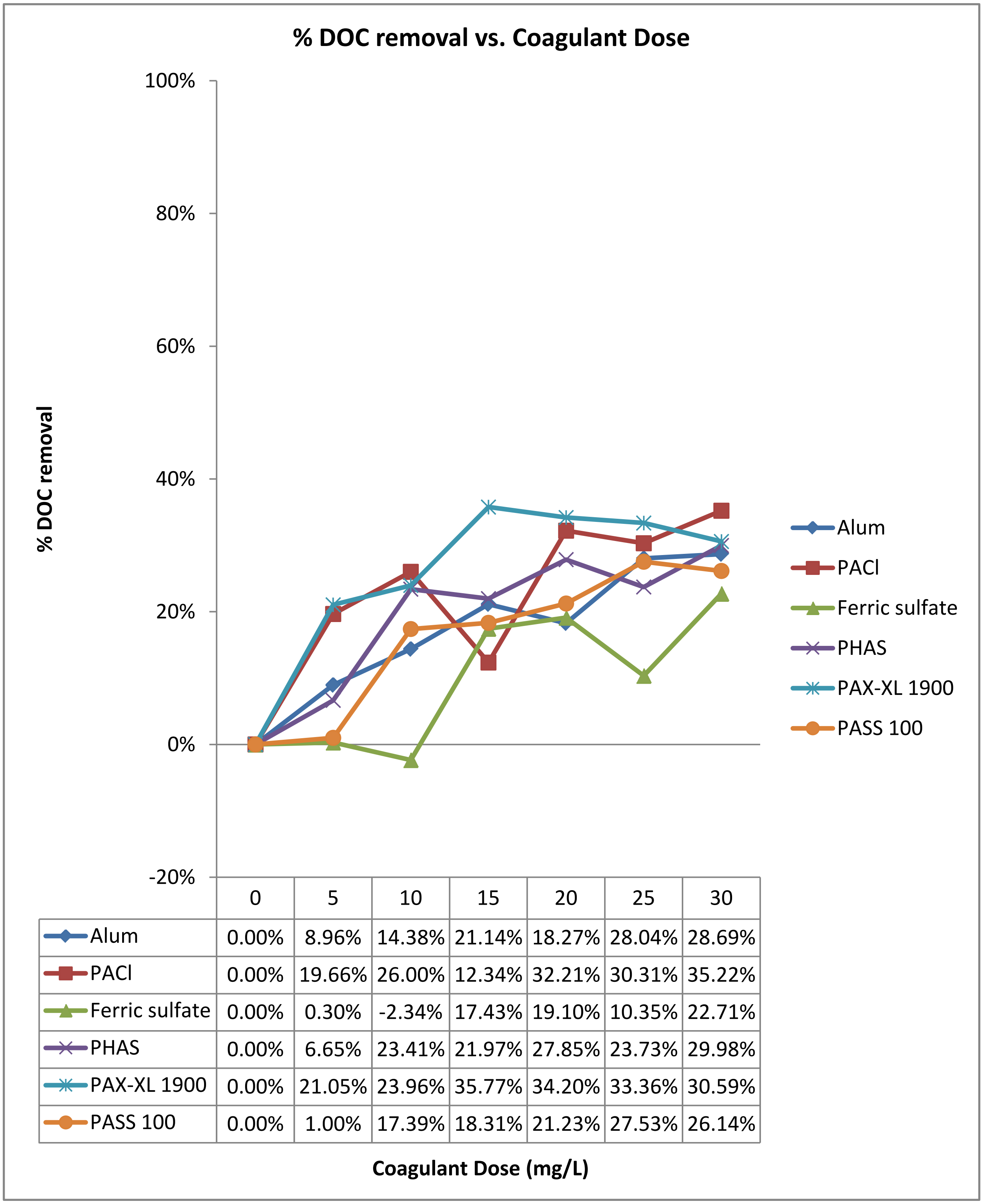
Figure A43


SDS-THM
TTHM (µg/L)
80
70
60
50
40
30
20
10
0
9 % improvement
5 % improvement
Alum @ 15 mg/L
PACl @ 15 mg/L
Coagulant Type & Dose
Alone
With CAS

Figures A44 – A46

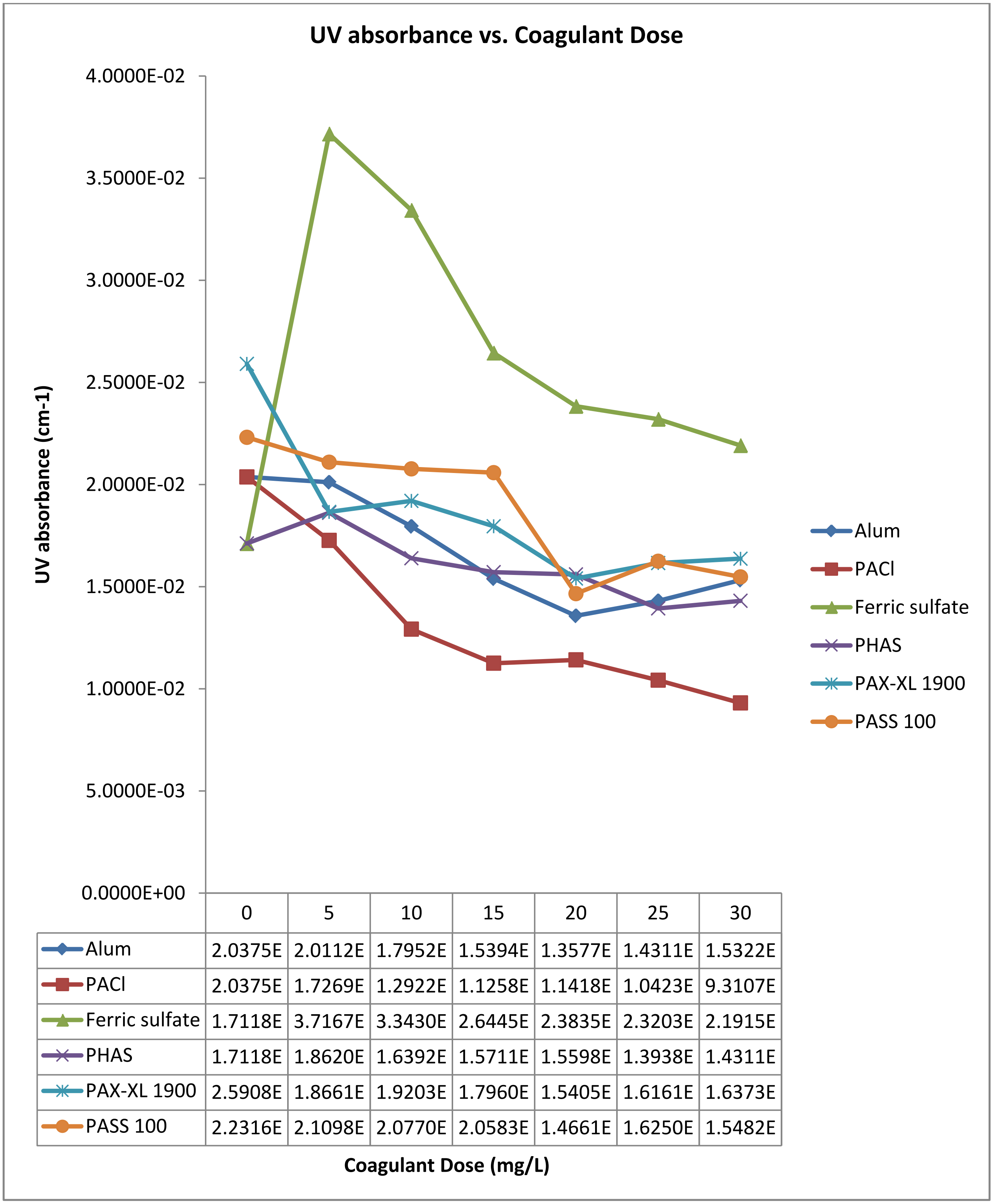
Summary plots for Stage III

Figure A44



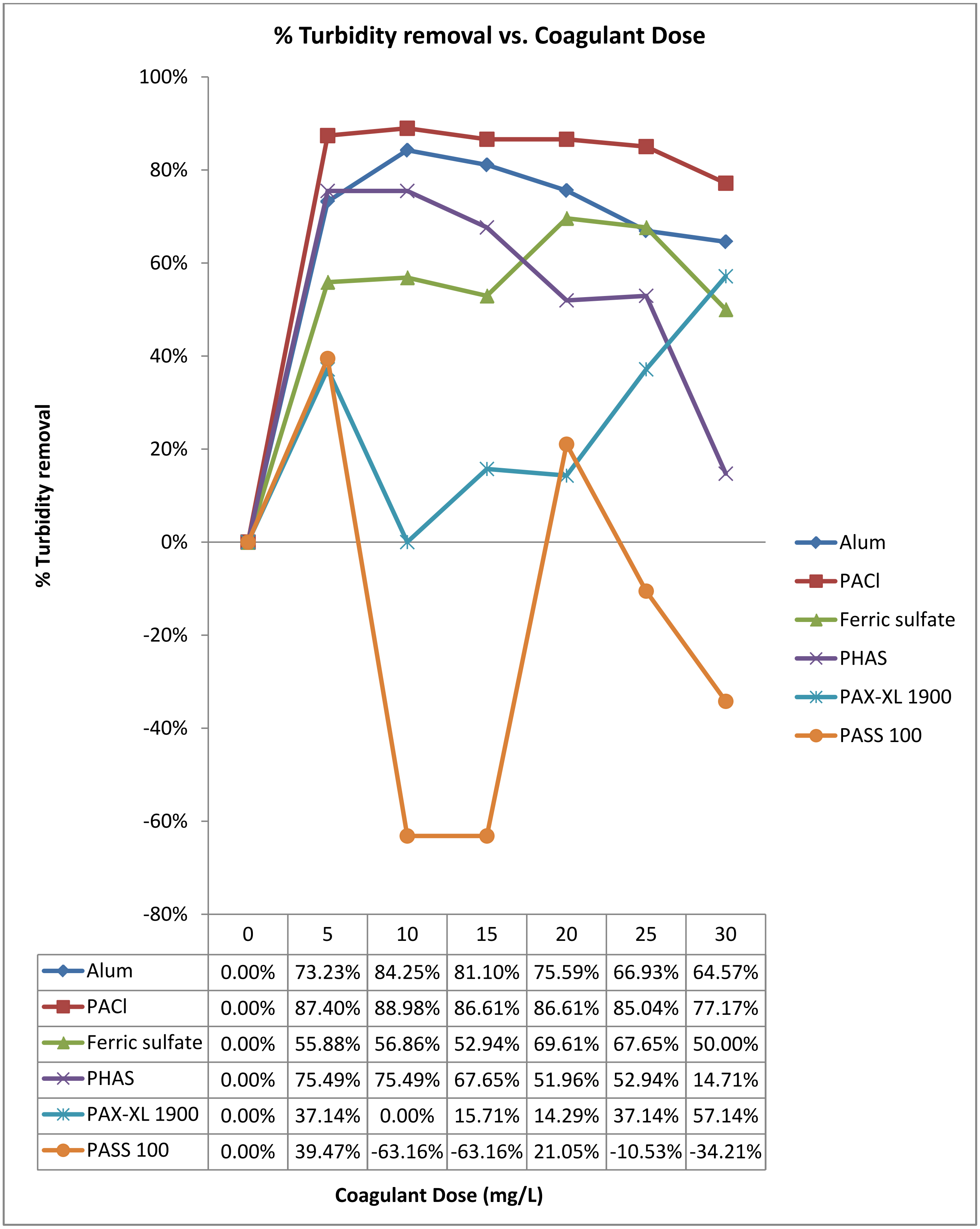
	0	5	10	15	20	25	30
Alum	0.00%	8.96%	14.38%	21.14%	18.27%	28.04%	28.69%
PACl	0.00%	19.66%	26.00%	12.34%	32.21%	30.31%	35.22%
Ferric sulfate	0.00%	0.30%	-2.34%	17.43%	19.10%	10.35%	22.71%
PHAS	0.00%	6.65%	23.41%	21.97%	27.85%	23.73%	29.98%
PAX-XL 1900	0.00%	21.05%	23.96%	35.77%	34.20%	33.36%	30.59%
PASS 100	0.00%	1.00%	17.39%	18.31%	21.23%	27.53%	26.14%

Figure A45



	0	5	10	15	20	25	30
Alum	2.0375E	2.0112E	1.7952E	1.5394E	1.3577E	1.4311E	1.5322E
PACl	2.0375E	1.7269E	1.2922E	1.1258E	1.1418E	1.0423E	9.3107E
Ferric sulfate	1.7118E	3.7167E	3.3430E	2.6445E	2.3835E	2.3203E	2.1915E
PHAS	1.7118E	1.8620E	1.6392E	1.5711E	1.5598E	1.3938E	1.4311E
PAX-XL 1900	2.5908E	1.8661E	1.9203E	1.7960E	1.5405E	1.6161E	1.6373E
PASS 100	2.2316E	2.1098E	2.0770E	2.0583E	1.4661E	1.6250E	1.5482E

Figure A46


% Turbidity removal vs. Coagulant Dose

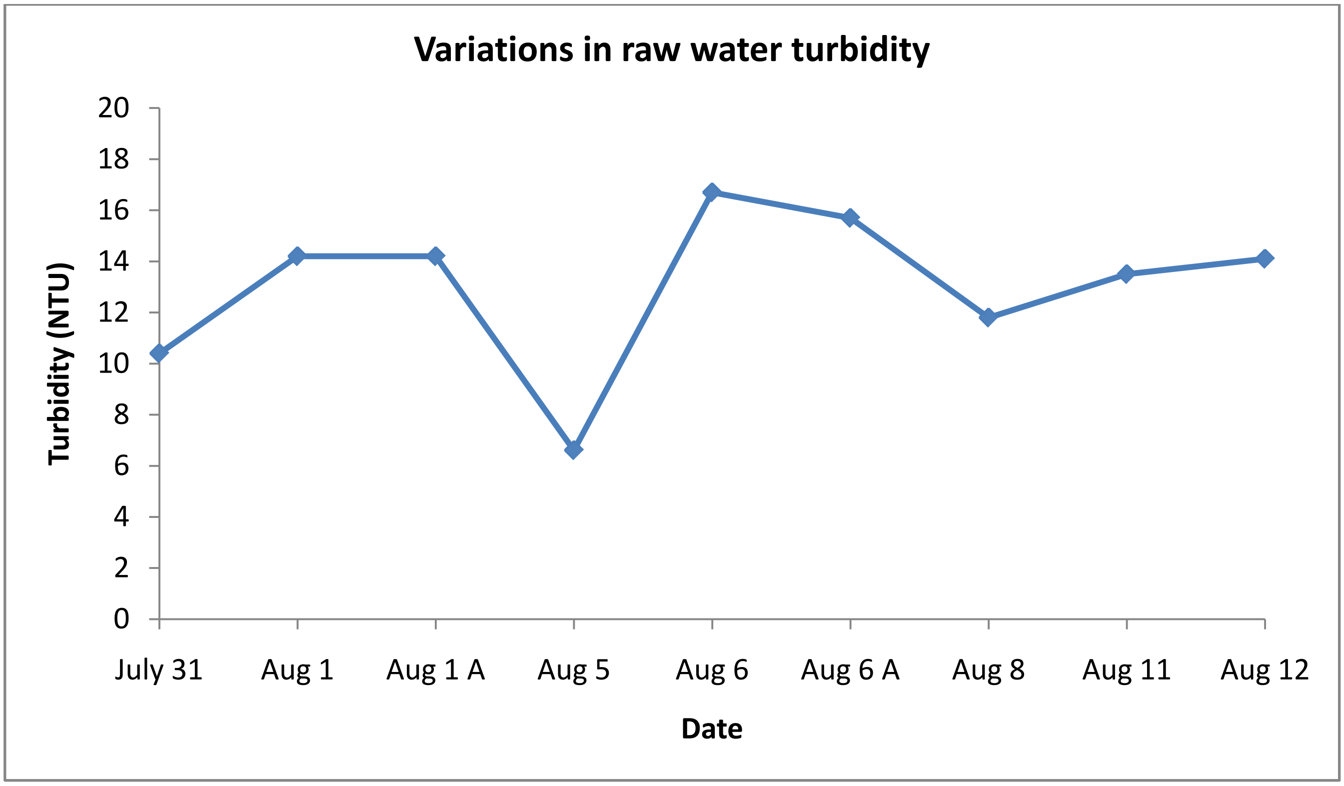
	0	5	10	15	20	25	30
Alum	0.00%	73.23%	84.25%	81.10%	75.59%	66.93%	64.57%
PACl	0.00%	87.40%	88.98%	86.61%	86.61%	85.04%	77.17%
Ferric sulfate	0.00%	55.88%	56.86%	52.94%	69.61%	67.65%	50.00%
PHAS	0.00%	75.49%	75.49%	67.65%	51.96%	52.94%	14.71%
PAX-XL 1900	0.00%	37.14%	0.00%	15.71%	14.29%	37.14%	57.14%
PASS 100	0.00%	39.47%	-63.16%	-63.16%	21.05%	-10.53%	-34.21%

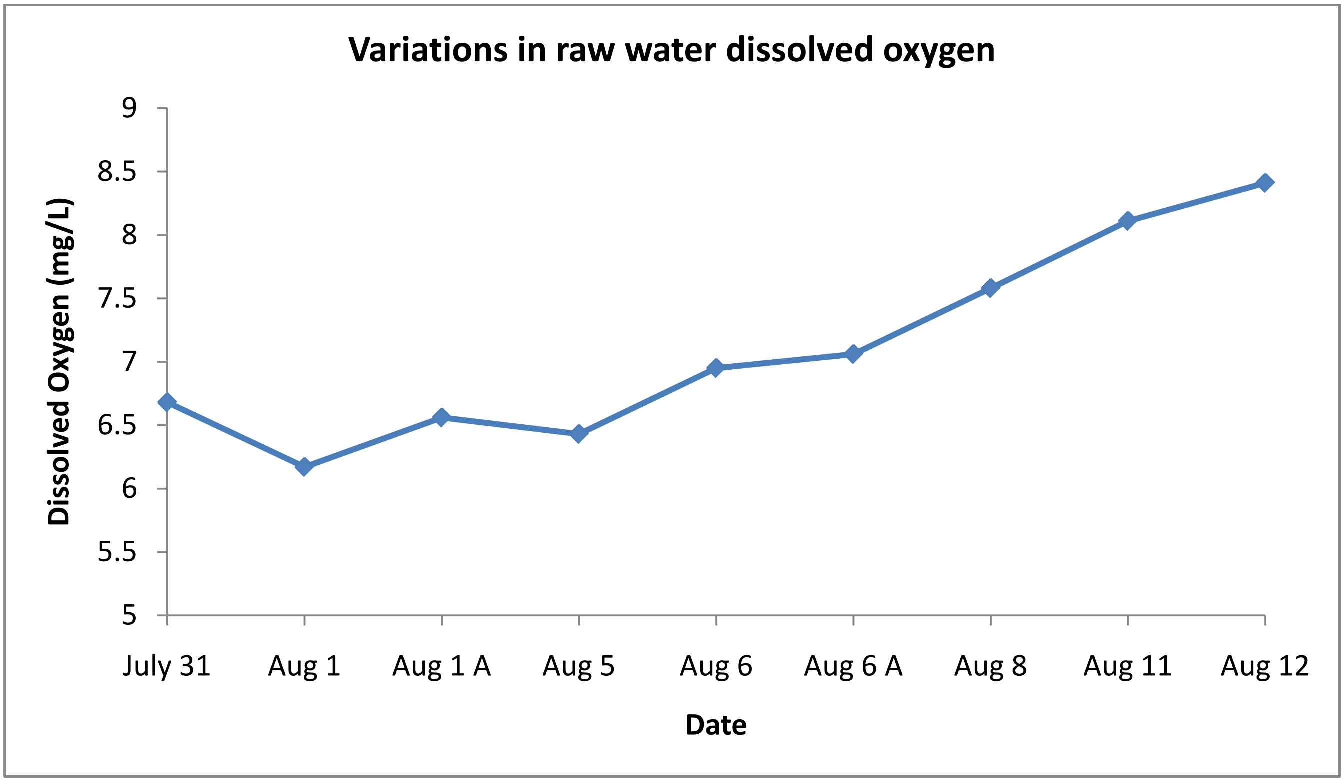
Appendix B: Summary plots for Grand River water

Figures B1 – B4

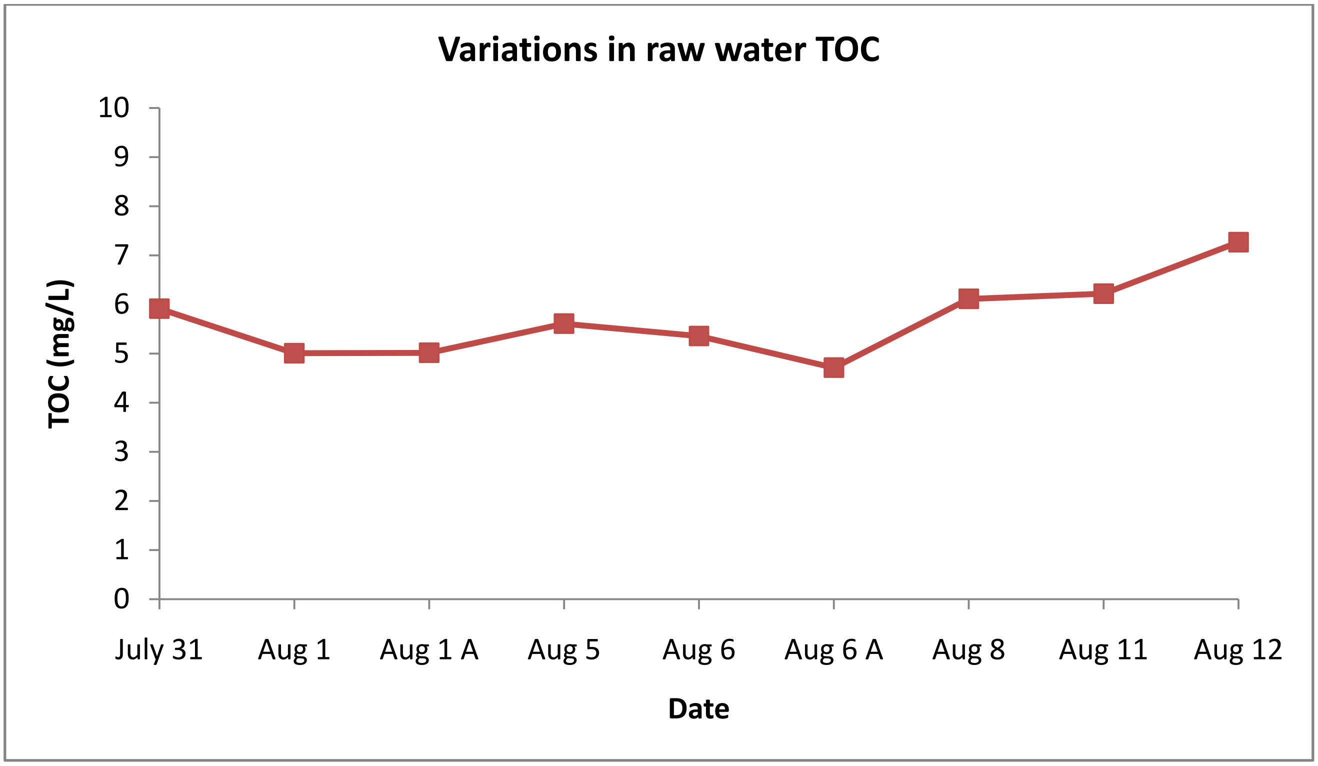
Summary plots for raw water

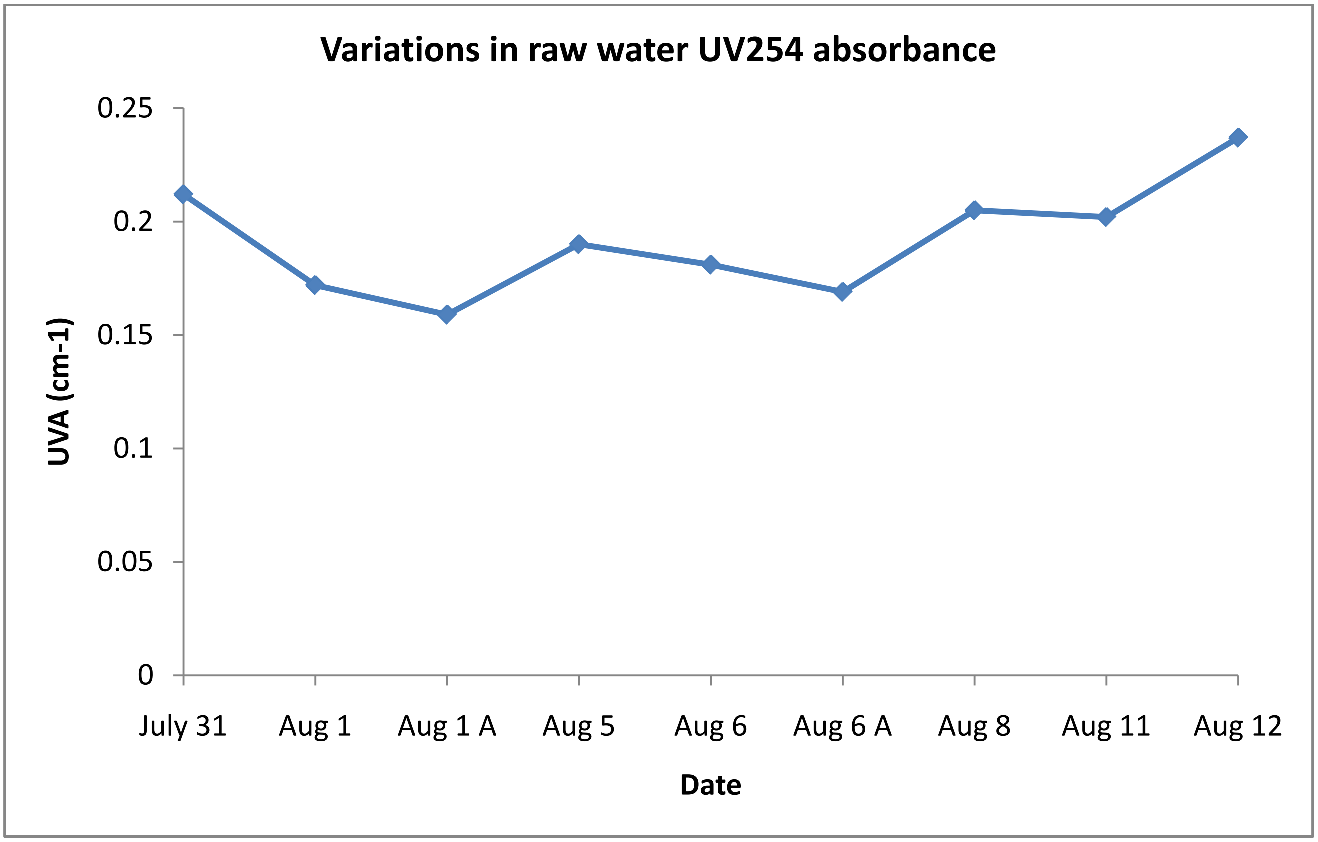
Figures B1, B2





Figures B3, B4





Figures B5 – B12

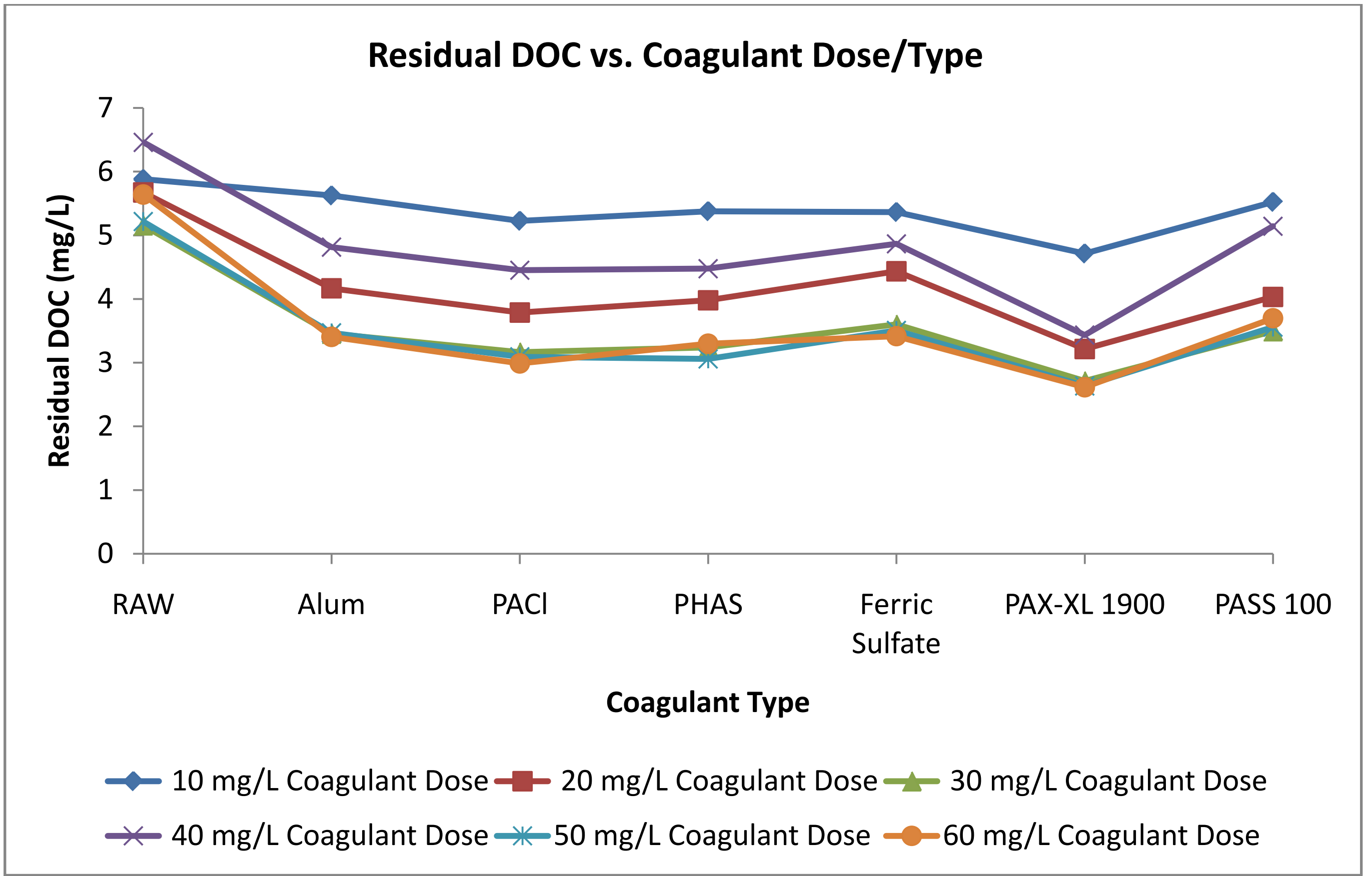
Summary plots for Phase I

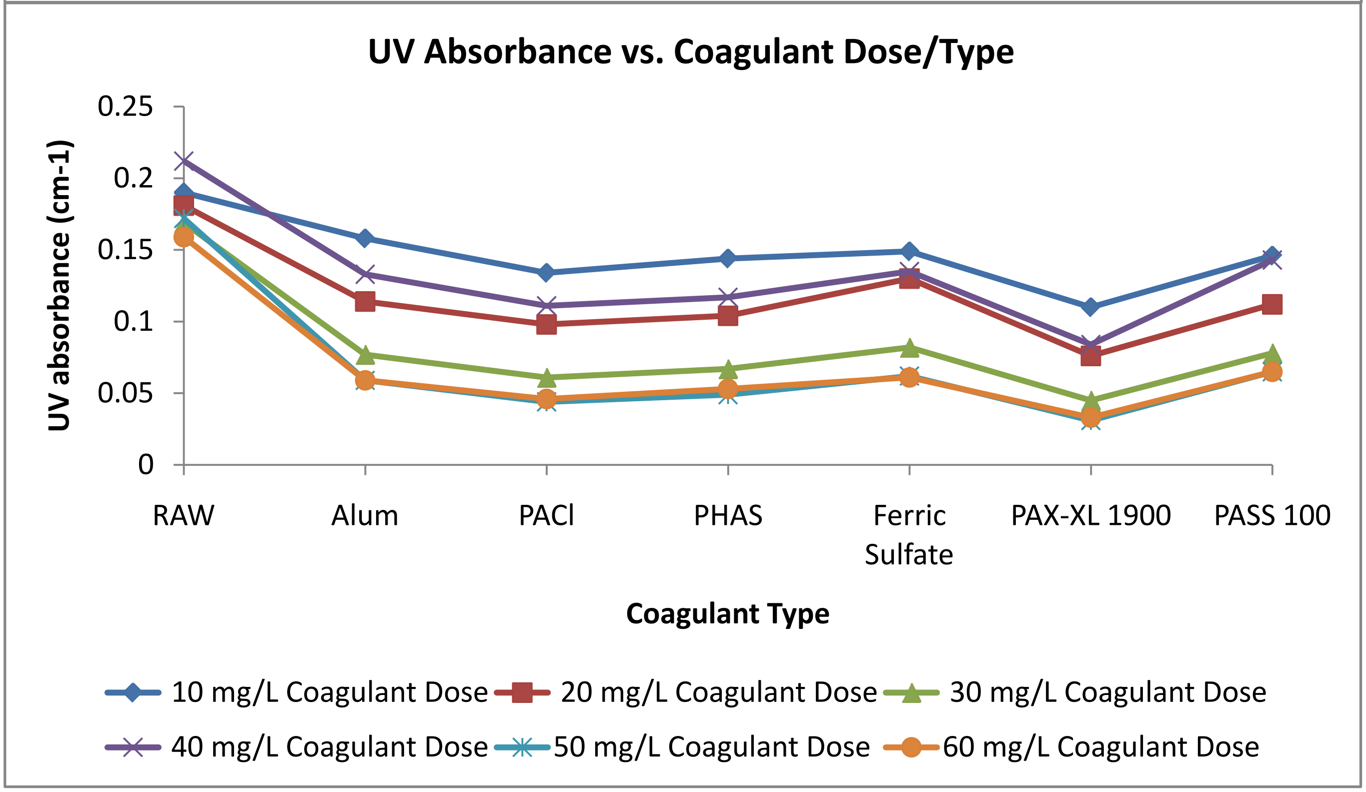
Figure B5 (I A)

Analysis on treated/finished water (Lines 6, 6A, 7 (finished))

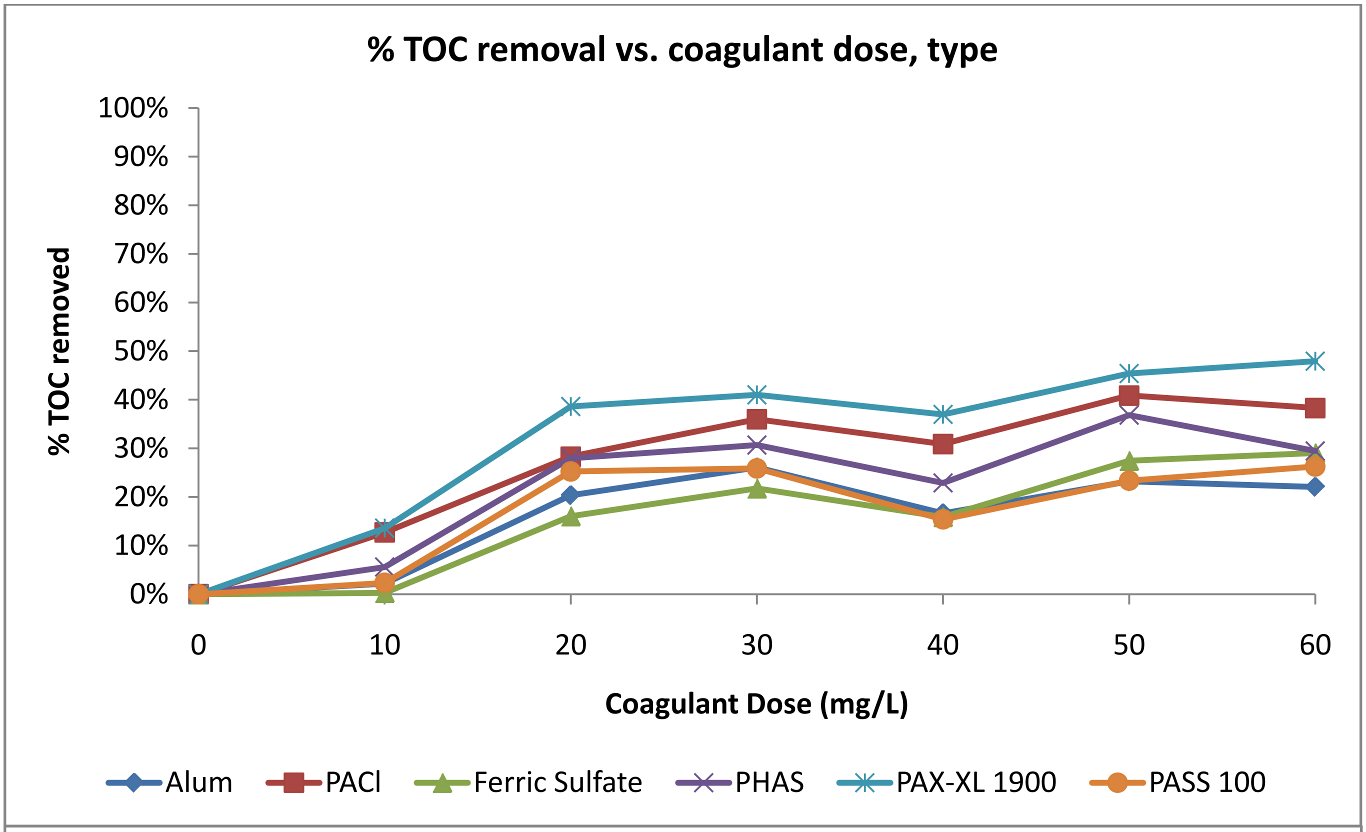
Date		Post filtration (Line 6)	Post reservoir (Line 6A)	Finished water (Line 7)	Date		Post filtration (Line 6)	Post reservoir (Line 6A)	Finished water (Line 7)
Aug 5th, 2008 @ 11:30 am	DO (mg/L)	7.65	9.34	8.64	Aug 6th, 2008 @ 12:00 pm	DO (mg/L)	7.79	8.39	8.3
	pH	7.23	7.19	7.12		pH	7.17	7.31	7.35
	Turbidity (NTU)	0.12	0.14	0.15		Turbidity (NTU)	0.15	0.14	0.14
	UV254 (cm^{-1})	0.095	0.096	0.095		UV254 (cm^{-1})	0.075	0.088	0.09
	Temperature	25	26	25		Temperature	25	25	24.5
	TOC (mg/L)	3.758	3.79	4.037		TOC (mg/L)	3.038	3.703	3.738
	DOC (mg/L)	4.01	4.059	4.068		DOC (mg/L)	3.352	3.87	3.89
	Chloride (mg/L)	97	100	110		Chloride (mg/L)	78	92	110
	Sulfate (mg/L)	68	73	69		Sulfate (mg/L)	39	64	64
	CSMR	1.43	1.37	1.59		CSMR	2.00	1.44	1.72

Figures B6, B7 (I A)





Figures B8, B9 (I A)



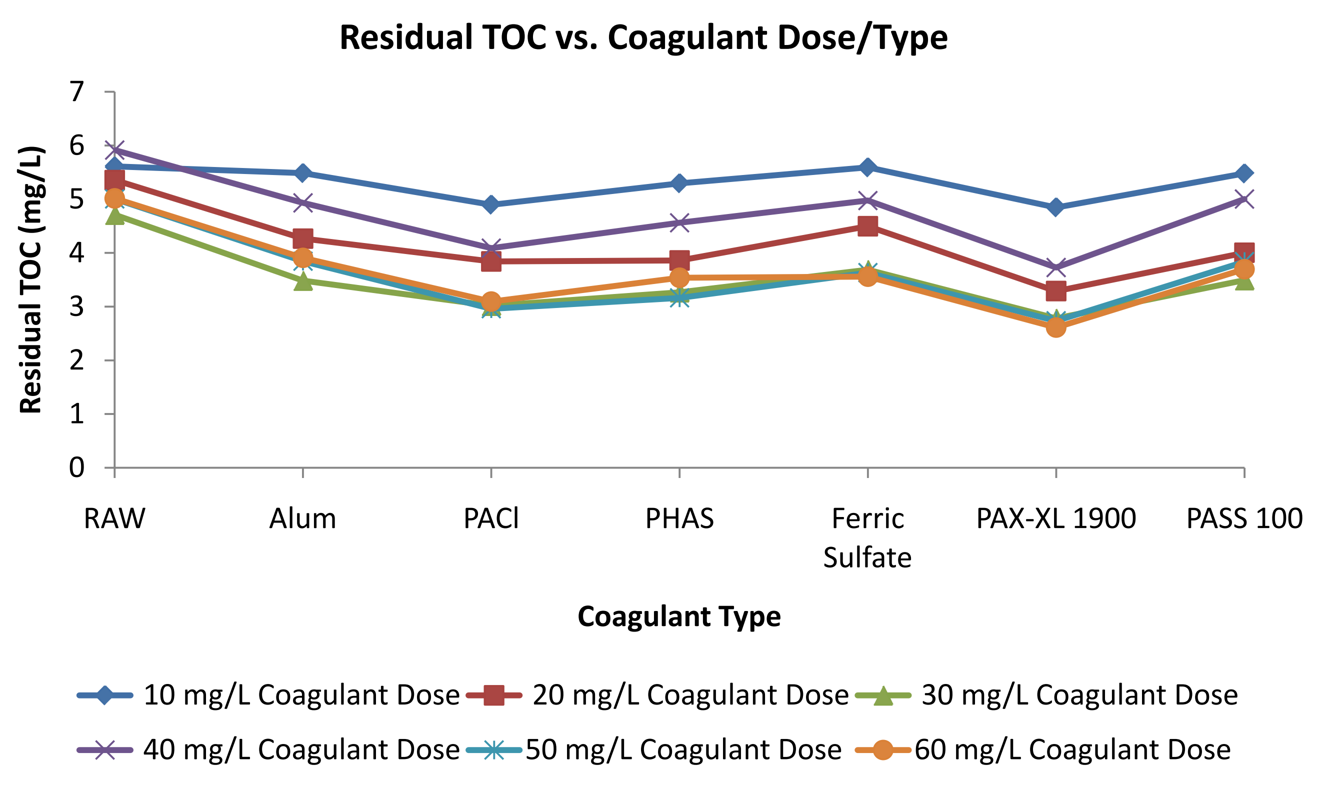
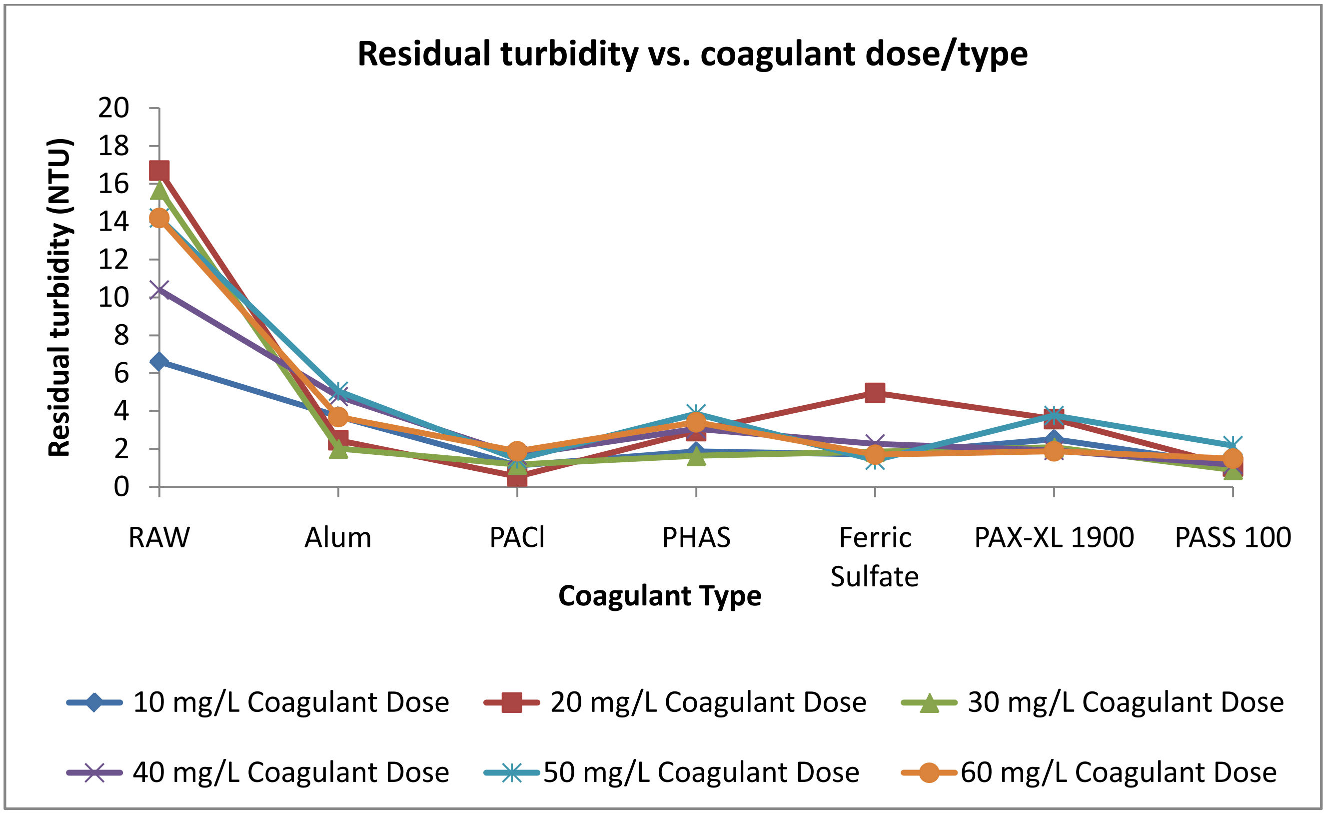
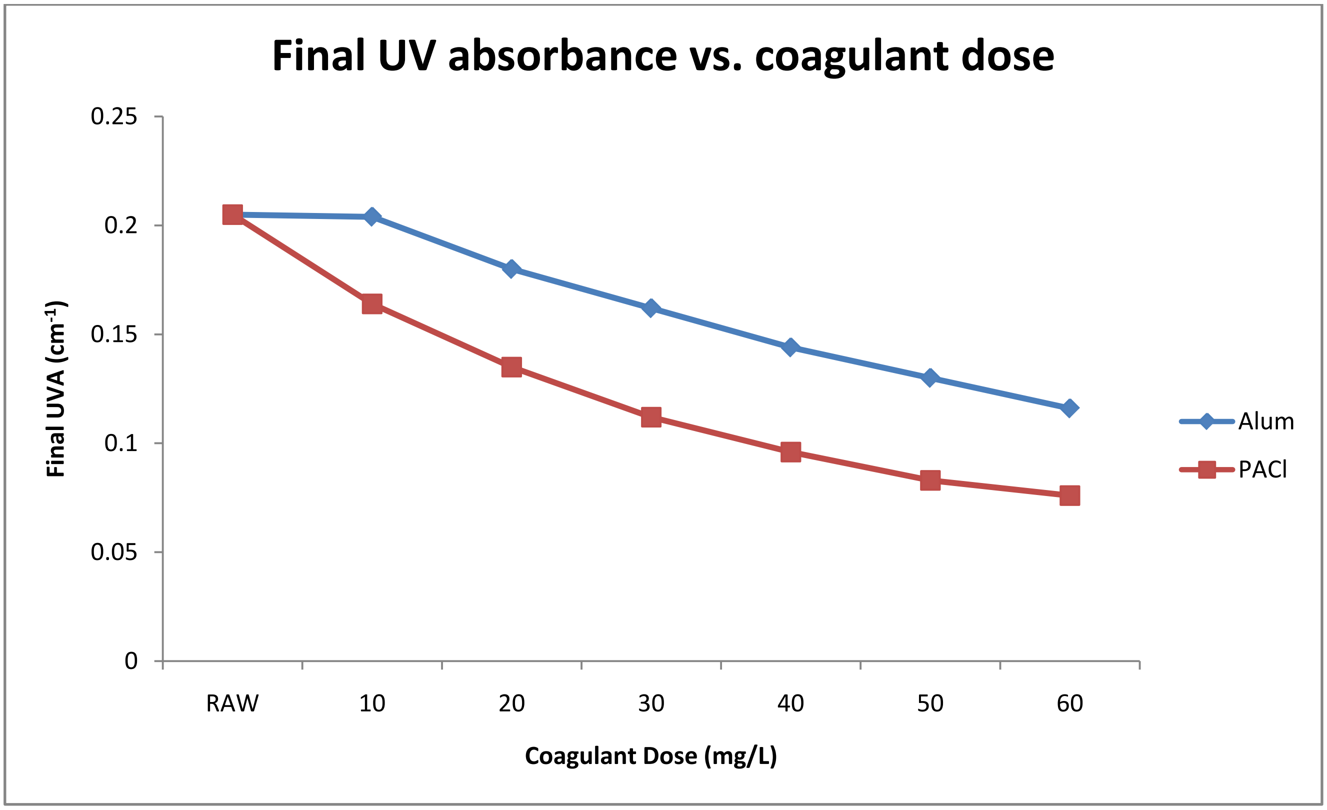
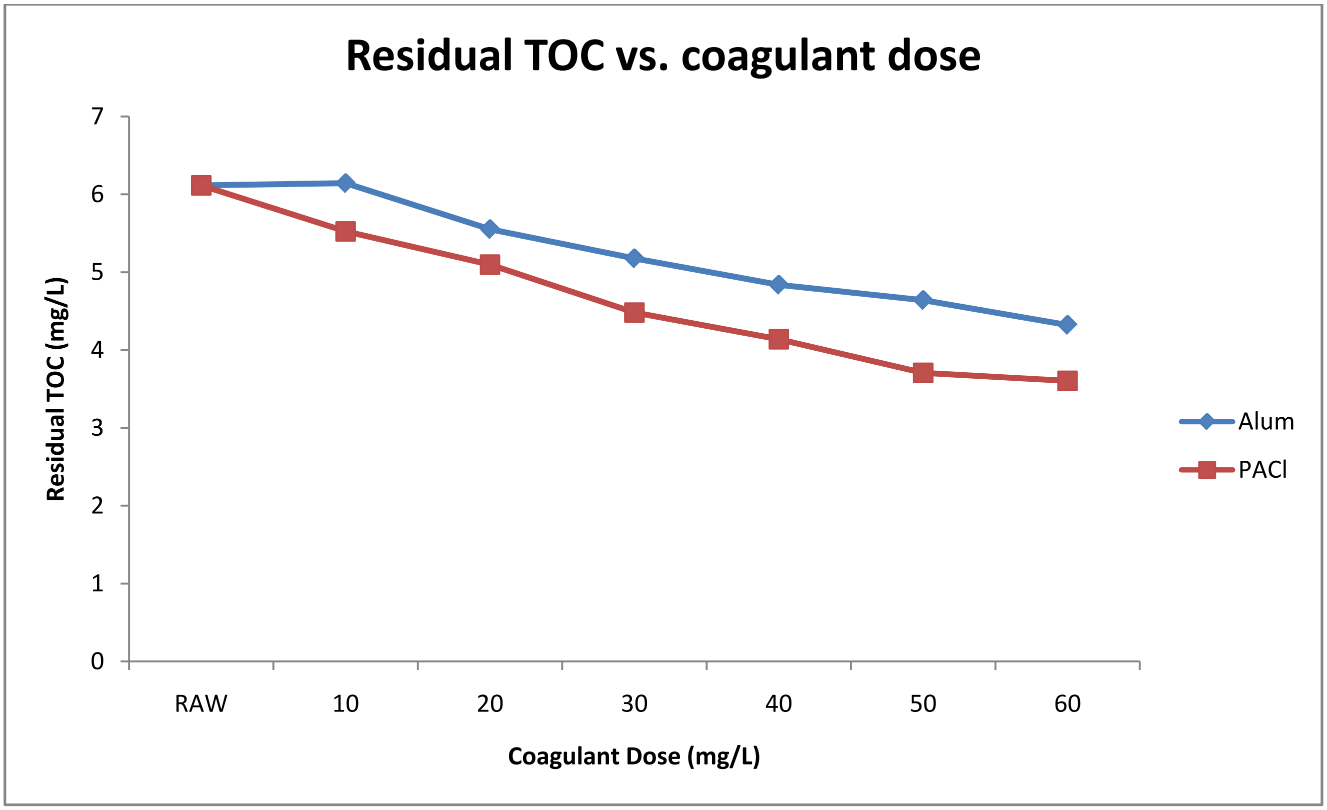


Figure B10 (I A)



Figures B11, B12 (I B)

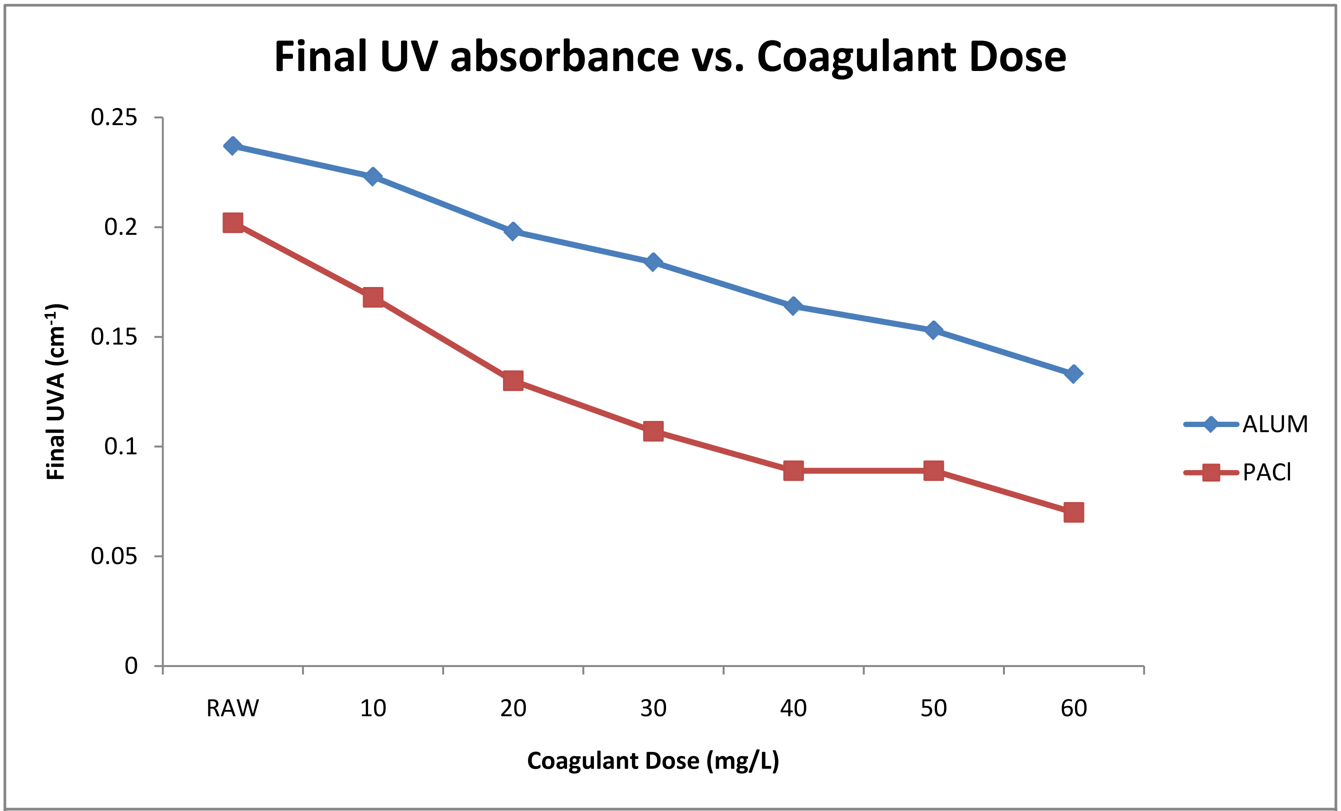


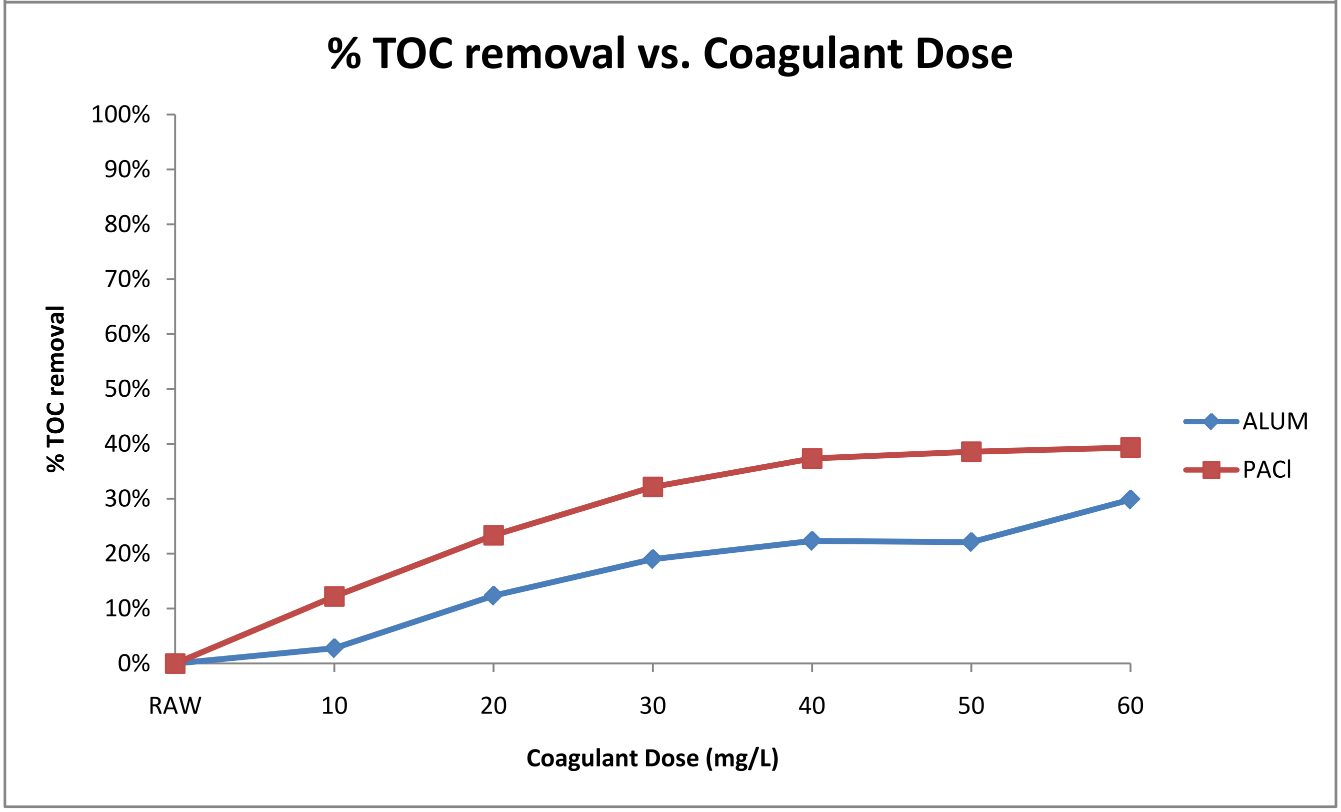


Figures B13 – B14

Summary plots for Phase II

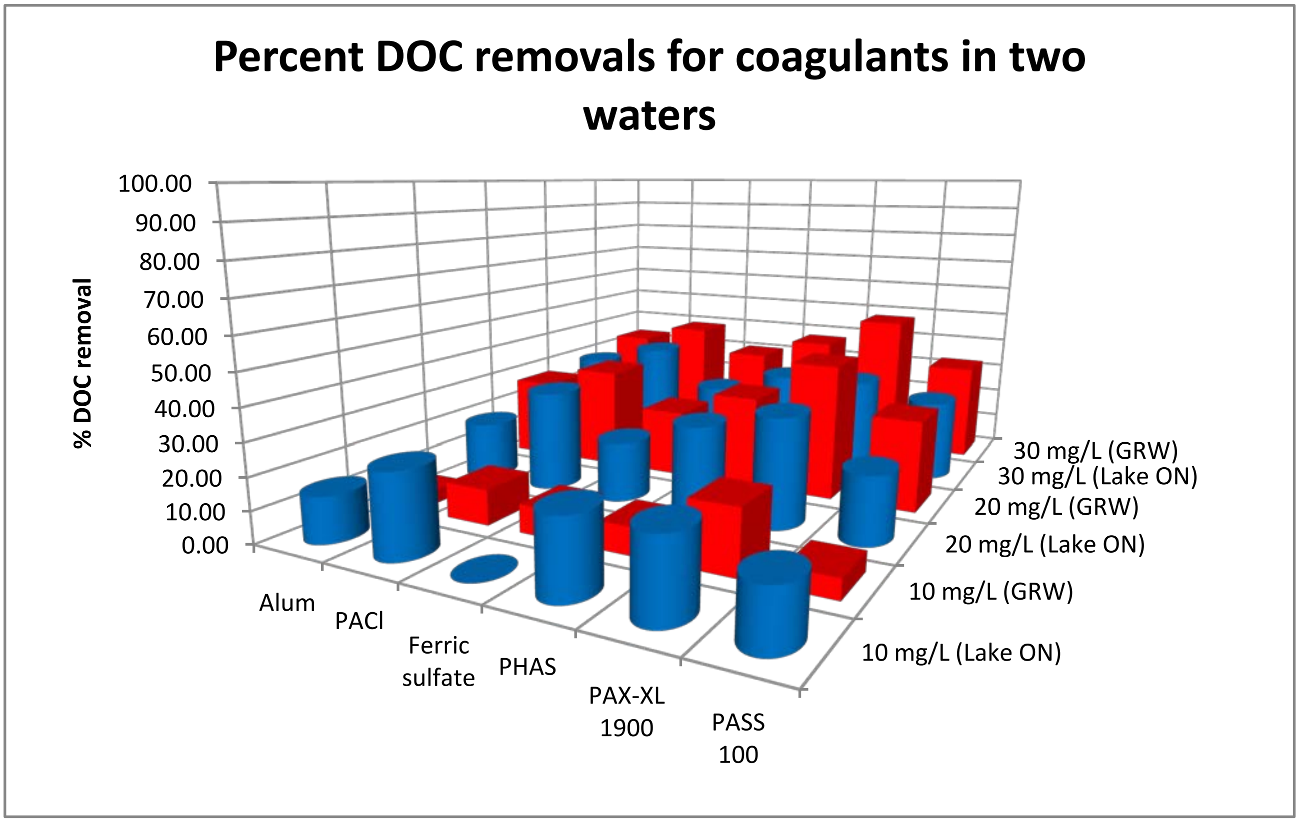
Figures B13, B14



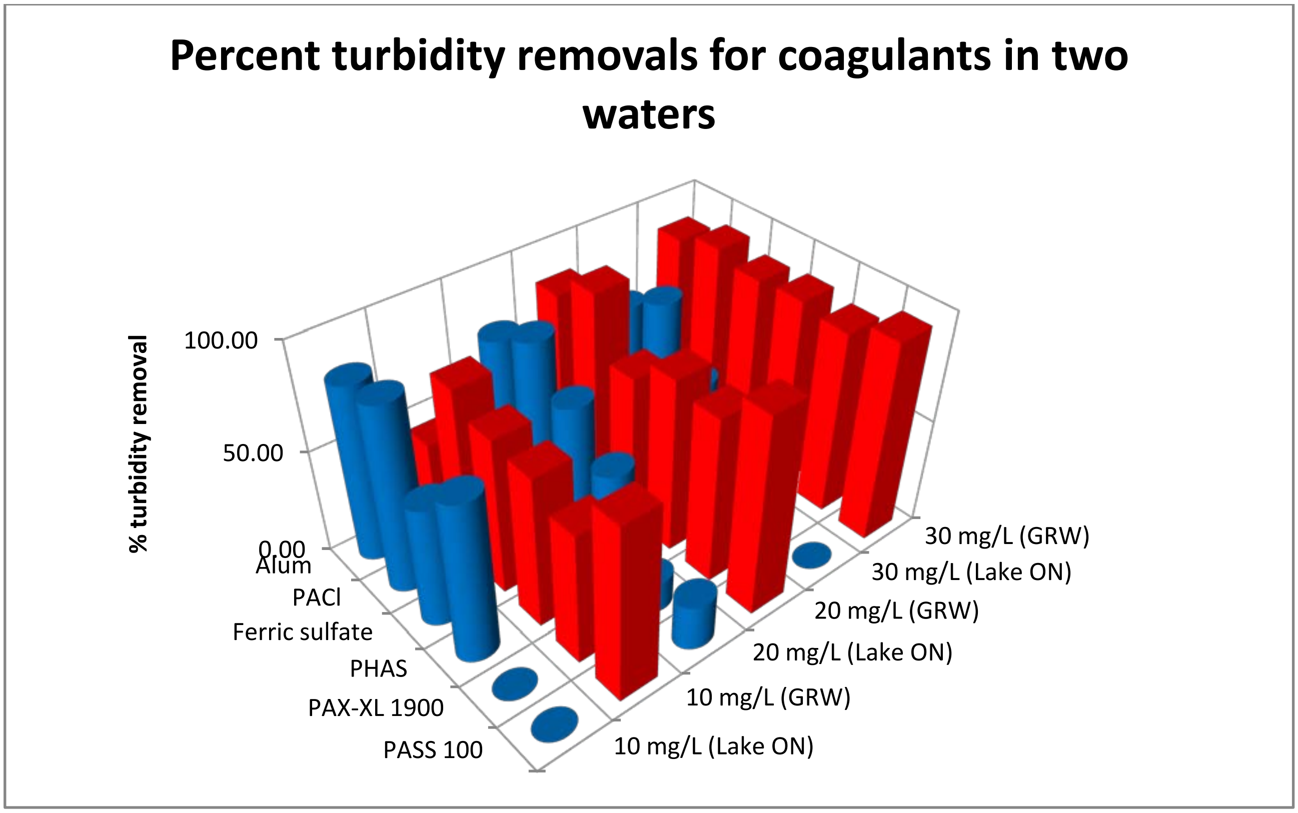


Appendix C: Comparing between two waters

Figures C1, C2



Percent DOC removals for coagulants in two waters



Percent turbidity removals for coagulants in two waters

Appendix D: Raw data

Part I

Stage I Raw data

Coagulant: **ALUM**

Walid El Henawy

Data Sheet - Hamilton water (Preliminary experiments)

Date: Thurs, November 8th, 2007	Time: 8:30 pm
	Concentration
Stock Solution (coagulant):	8 mg/mL
Add 3.4 mL Alum to 246.6 mL D.I. Water	
Chlorine:	-

Source Water / Raw Water				
pH	Turbidity (NTU)	Conductivity (µS/cm)	UV254 absorbance (cm^{-1})	Temperature (°C)
7.54	0.52		-0.01391	23.4

			Jar Number					
			1	2	3	4	5	6
Rapid Mix		G (s^{-1})	523	523	523	523	523	523
		rpm	200 (201)	200 (201)	200 (201)	200 (200)	200 (200)	200 (200)
		Duration (s)	30	30	30	30	30	30
Flocculation	Primary	G (s^{-1})	60	60	60	60	60	60
		rpm	60 (63)	60 (63)	60 (63)	60 (64)	60 (64)	60 (64)
		Duration (mins)	15	15	15	15	15	15
	Secondary	G (s^{-1})	40	40	40	40	40	40
		rpm	40 (41)	40 (41)	40 (41)	40 (41)	40 (41)	40 (41)
		Duration (mins)	15	15	15	15	15	15
Coagulant Dose (mg/L)			0	4	8	12	16	20
Volume of Coagulant Added (mL)			0	1	2	3	4	5
Depth of Sampling (cm)	Settling Time (min)		Turbidity (NTU)	Turbidity (NTU)	Turbidity (NTU)	Turbidity (NTU)	Turbidity (NTU)	Turbidity (NTU)
7.3	0		0.38	0.41	0.87	0.61	0.75	1.07
7.3	5		0.47	0.44	0.53	0.37	0.53	0.54
7.3	10		0.41	0.55	0.42	0.27	0.5	0.37
7.3	15		0.5	0.44	0.16	0.53	0.39	0.49
Volume of Flocs produced (mL)								
Floc characteristics								
Final pH	@ time: 45:30 mins		8.09	7.92	7.8	7.72	7.6	7.55
Final UV254 absorbance (cm^{-1})	@ time: 45:30 mins		0.022970	0.0043295	-0.0093803	-0.0069103	-0.0086908	-0.0104000
Final Temperature (°C)	@ time: 45:30 mins		22.8	22.8	22.8	22.8	22.8	22.8
Conductivity (µS/cm)	@ time: 45:30 mins							

Settled water will be preserved with phosphoric acid for TOC analysis

Raw water temperature at time of collection = 10 °C

Coagulant: **PACl (SternPAC)**

Walid El Henawy

Data Sheet - Hamilton water (Preliminary experiments)

Date: Thurs, November 8th, 2007	Time:
	Concentration
Stock Solution (coagulant):	8 mg/mL
Add 6mL PACl to 244 mL D.I. Water	
Chlorine:	-

Source Water / Raw Water				
pH	Turbidity (NTU)	Conductivity (µS/cm)	UV254 absorbance (cm^{-1})	Temperature (°C)
7.54	0.52		-0.01391	23.4

			Jar Number					
			1	2	3	4	5	6
Rapid Mix		G (s^{-1})	523	523	523	523	523	523
		rpm	200 (200)	200 (200)	200 (200)	200 (201)	200 (201)	200 (201)
		Duration (s)	30	30	30	30	30	30
Flocculation	Primary	G (s^{-1})	60	60	60	60	60	60
		rpm	60 (62)	60 (62)	60 (62)	60 (65)	60 (65)	60 (65)
		Duration (mins)	15	15	15	15	15	15
	Secondary	G (s^{-1})	40	40	40	40	40	40
		rpm	40 (41)	40 (41)	40 (41)	40 (42)	40 (42)	40 (42)
		Duration (mins)	15	15	15	15	15	15
Coagulant Dose (mg/L)			0	4	8	12	16	20
Volume of Coagulant Added (mL)			0	1	2	3	4	5

Depth of Sampling (cm)	Settling Time (min)	Turbidity (NTU)	Turbidity (NTU)	Turbidity (NTU)	Turbidity (NTU)	Turbidity (NTU)	Turbidity (NTU)
7.3	0	2.02	1.14	1.49	1.05	1.5	1.97
7.3	5	1.19	0.87	0.47	0.75	0.75	0.95
7.3	10	1.15	0.49	0.17	0.43	0.54	0.69
7.3	15	1.25	0.2	0.49	0.29	0.31	0.65
Volume of Flocs produced (mL)							
Floc characteristics							
Final pH	@ time: 45:30 mins	7.83	7.8	7.75	7.65	7.51	7.45
Final UV254 absorbance (cm^{-1})	@ time: 45:30 mins	-0.0043621	-0.0129740	-0.0186280	-0.0172380	-0.0159980	-0.0218510
Final Temperature (°C)	@ time: 45:30 mins	22.8	22.8	22.8	22.8	22.8	22.8
Conductivity (µS/cm)	@ time: 45:30 mins						

Settled water will be preserved with phosphoric acid for TOC analysis

Raw water temperature at time of collection = 10 °C

TOC results for preliminary experiment - Hamilton water (Nov 8, 2007)

Dose (mg/L)	Settled Water TOC (@15 mins) (Average) [mg/L]			% TOC removal		
	Alum	PACl	CAS	Alum	PACl	CAS
0	2.319	2.307	2.342	0	0	0
4	2.277	2.006	2.34	1.81%	13.05%	0.09%
8	2.199	1.818	2.269	5.17%	21.20%	3.12%
12	2.051	1.695	2.283	11.56%	26.53%	2.52%
16	1.896	1.625	2.187	18.24%	29.56%	6.62%
20	1.975	1.891	2.555	14.83%	18.03%	-9.09%
RAW Nov. 8		2.406				
RAW Nov. 17		2.585				

Part I

Stage II A Raw data

CAS Project - Experiments with Alum & PACl alone

Walid El Henawy

Data Sheet - **PACl**

Date: Tues, February 5th, 2008	Time: 12:45 am
	Concentration
Stock Solution (coagulant):	10 mg/mL
Chlorine:	Unchlorinated

Source Water / Raw Water				
DOC	pH	Turbidity (NTU)	UV254 absorbance (cm-1)	Temperature (°C)
	8.1	0.29	2.0687E-02	20.7
			B: -6.67572E-06	

			Jar Number					
			1	2	3	4	5	6
Rapid Mix		G (s-1)						
		rpm	200					
		Duration (s)	32					
Flocculation	Primary	G (s-1)						
		rpm	63					
		Duration (mins)	15					
	Secondary	G (s-1)						
		rpm	43					
		Duration (mins)	15					
Presumed Temperature (?C)			20	5	20	20	20	20
Coagulant Dose (mg/L)			3	5	5	10	15	20
Volume of coagulant stock solution added (mL)			0.6	1	1	2	3	4
Depth of Sampling (cm)	Settling Time (min)		Turbidity (NTU)	Turbidity (NTU)	Turbidity (NTU)	Turbidity (NTU)	Turbidity (NTU)	Turbidity (NTU)
7.3								
Volume of Flocs produced (mL)								
Floc characteristics								
Final pH	@ time: 45:30 mins		8.2	7.9	8.1	7.9	7.8	7.7
Final UV254 absorbance (cm-1)	@ time: 45:30 mins		1.4606E-02	3.0023E-02	1.2372E-02	1.0456E-02	9.0350E-03	8.1816E-03
Final Temperature (°C)	@ time: 45:30 mins		20.8	10.2	20.8	20.8	20.8	20.8
Final DOC	@ time: 45:30 mins							
Final Turbidity (NTU)	@ time: 45:30 mins		0.29	0.3	0.29	0.19	0.17	0.23
Final Chlorine (mg/L)	@ time: 45:30 mins		WATER IS NON-CHLORINATED					
Bottle/vial labels			P0320x040208	P0505x040208	P0520x040208	P1020x040208	P1520x040208	P2020x040208

*Chlorine concentration has to be monitored water is pre-chlorinated before coagulation

Notes:
UV absorbance was analysed approx. 2 hrs following the end of experiment
Cold water was poured into jars immediately before experiment (different containers)
UV absorbance of remaining raw water at end of experiments with alum & PACl: 1.8387E-2

Data Sheet - **Alum**

Date: Mon, February 4th, 2008	Time: 2:45 pm
	Concentration
Stock Solution (coagulant):	10 mg/mL
Chlorine:	Unchlorinated

Source Water / Raw Water

DOC	pH	Turbidity (NTU)	UV254 absorbance (cm-1)	Temperature (°C)
	8.1	0.29	2.0687E-02	20.7
			B: -6.67572E-06	

			Jar Number					
			1	2	3	4	5	6
Rapid Mix		G (s-1)						
		rpm	201					
		Duration (s)	31					
Flocculation	Primary	G (s-1)						
		rpm	62					
		Duration (mins)	15					
	Secondary	G (s-1)						
		rpm	41					
		Duration (mins)	15					
Presumed Temperature (?C)			20	5	20	20	20	20
Coagulant Dose (mg/L)			3	5	5	10	15	20
Volume of coagulant stock solution added (mL)			0.6	1	1	2	3	4
Depth of Sampling (cm)	Settling Time (min)		Turbidity (NTU)	Turbidity (NTU)	Turbidity (NTU)	Turbidity (NTU)	Turbidity (NTU)	Turbidity (NTU)
7.3								
Volume of Flocs produced (mL)								
Floc characteristics								
Final pH	@ time: 45:30 mins		7.9	8	8	7.7	7.7	7.7
Final UV254 absorbance (cm-1)	@ time: 45:30 mins		1.9516E-02	1.6917E-02	1.6376E-02	1.2888E-02	1.1540E-02	1.1730E-02
Final Temperature (°C)	@ time: 45:30 mins		21.6	20.2	21.6	21.6	21.6	21.6
Final DOC	@ time: 45:30 mins							
Final Turbidity (NTU)	@ time: 45:30 mins		0.32	0.20	0.19	0.21	0.23	0.22
Final Chlorine (mg/L)	@ time: 45:30 mins		WATER IS NON-CHLORINATED					
Bottle/vial labels			A0320x040208	A0505x040208	A0520x040208	A1020x040208	A1520x040208	A2020x040208

*Chlorine concentration has to be monitored water is pre-chlorinated before coagulation

Notes:
UV absorbance was analysed approx. 4 hrs following the end of experiment
Cold water was poured into jars immediately before experiment (different containers)
UV absorbance of remaining raw water at end of experiments with alum & PACl: 1.8387E-2

	Alum DOC @ 20°C			**PACl DOC @ 20°C**	**DOC**
	Coagulant dose (mg/L)			Coagulant dose (mg/L)	
	0	2.424		0	2.424
	3	2.246		3	2.029
	5	2.139		5	1.987
	10	1.973		10	1.74
	15	1.87		15	1.722
	20	1.77		20	1.817
Alum DOC @ 5°C	5	2.028	PACl DOC @ 5°C	5	2.174
			% DOC removal		
	Alum DOC removal @ 20°C			PACl DOC removal @ 20°C	DOC
	0	0.00%		0	0.00%
	3	7.34%		3	16.30%
	5	11.76%		5	18.03%
	10	18.61%		10	28.22%
	15	22.85%		15	28.96%
	20	26.98%		20	25.04%
Alum DOC removal @ 5°C	5	16.34%	**PACl DOC removal @ 5°C**	5	10.31%

Sample ID	Sample description	Chloride (mg/L)	Sulfate (mg/L)	CSMR (Cl:SO4 mass ratio)	Initial Chlorine (mg/L Cl2)	Final chlorine (mg/L Cl2)	Chlorine demand (5 d)
2008-02-03 A0320x 040208	Alum-3 mg/L	23.6	28.9	0.82	5.1	3.3	1.8
2008-02-03 A0505x040208	Alum-5 mg/L	23.5	30.1	0.78	5.1	3.8	1.3
2008-02-03 A0520x040208	Alum-5 mg/L	23.6	30.2	0.78	5.1	3.4	1.7
2008-02-03 A1020x040208	Alum-10 mg/L	23.7	33.1	0.72	5.1	3.9	1.2
2008-02-03 A1520x040208	Alum-15 mg/L	23.6	36.2	0.65	5.1	4.3	0.8
2008-02-03 A2020x040208	Alum-20 mg/L	23.6	39.2	0.60	5.1	4.2	0.9
Average Alum		**23.6**	**33.0**	**0.72**	**5.1**	**3.8**	**1.3**
2008-02-03 F280108	FSP filter effluent	26.5	27.9	0.95	8.5	7.5	
2008-02-03 P0320x040208	PACl-3 mg/L	24.8	27.9	0.89	5.1	4.3	0.8
2008-02-03 P0505x040208	PACl-5 mg/L	25.3	27.9	0.91	5.1	4.1	1.0
2008-02-03 P0520x040208	PACl-5 mg/L	25.6	28.1	0.91	5.1	4.0	1.1
2008-02-03 P1020x040208	PACl-10 mg/L	27.4	28.5	0.96	5.1	4.1	1.0
2008-02-03 P1520x040208	PACl-15 mg/L	29.4	29.1	1.01	5.1	4.1	1.0
2008-02-03 P2020x040208	PACl-20 mg/L	31.3	29.5	1.06	5.1	4.1	1.0
Average PACl		**27.3**	**28.5**	**0.96**	**5.1**	**4.1**	**1.0**
2008-02-03 RAWNC280108	Raw-non chlorinated	23.9	27.6	0.87	5.1	3.8	
2008-02-03 RAWPC080208	Raw-prechlorinated	32.5	28.3	1.15	5.1	4.6	
Average Raw		**29.3**	**29.0**	**1.01**	**5.1**	**4.1**	**1.0**
PACl average minus alum average =		**3.7**	**-4.45**	**0.23**	**0**	**0.3**	**-0.3**
Average percentage reduction in CSMR switching from PACl to alum (%)				24.2			

Pre-chlorine sample much higher in chloride

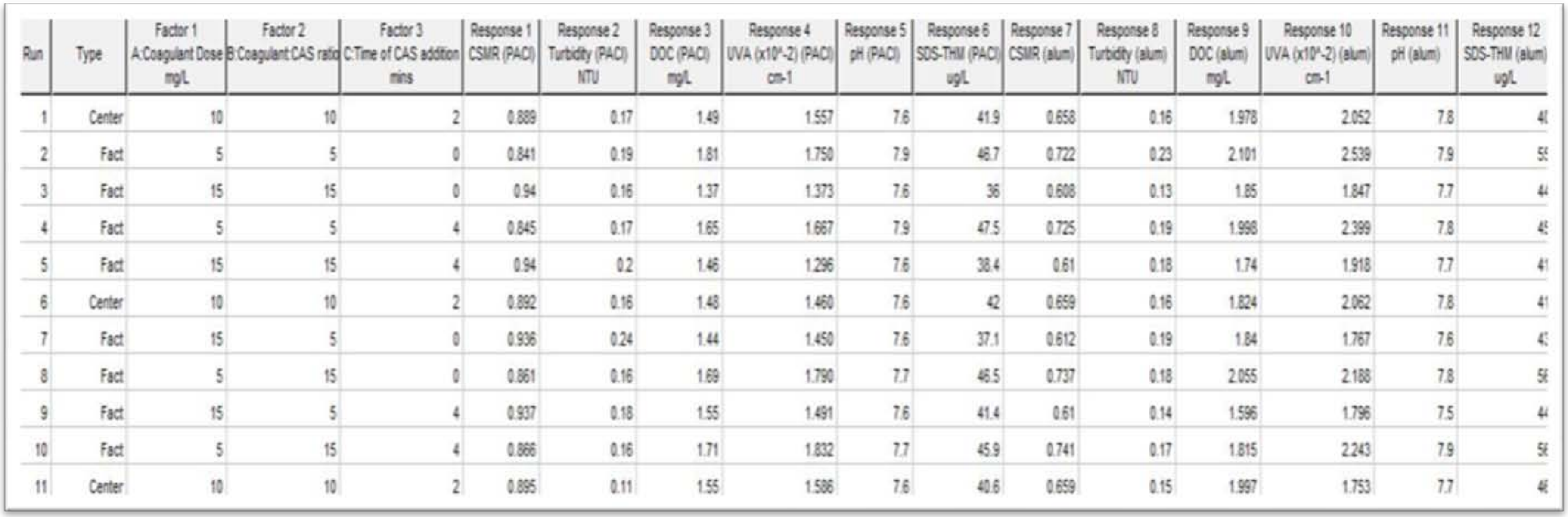
Increasing alum dose eventually gets CSMR ratio down to 0.6 (going from 3 to 20 mg/L)

SDS-THM data for Stage IIA

Coagulant Dose	Alum @ 20℃	PACl @ 20℃
0	80.3	80.3
3	57.9	59.2
5	53.6	48.3
10	47	42.7
15	45.1	38.2
20	38.5	37.3
	Alum @ 5℃	**PACl @ 5℃**
5	51.5	45.5

Part I

Stage II B Raw data



Run	Type	Factor 1 A:Coagulant Dose mg/L	Factor 2 B:Coagulant:CAS ratio	Factor 3 C:Time of CAS addition mins	Response 1 CSMR (PACl)	Response 2 Turbidity (PACl) NTU	Response 3 DOC (PACl) mg/L	Response 4 UVA (x10^-2) (PACl) cm-1	Response 5 pH (PACl)	Response 6 SDS-THM (PACl) ug/L	Response 7 CSMR (alum)	Response 8 Turbidity (alum) NTU	Response 9 DOC (alum) mg/L	Response 10 UVA (x10^-2) (alum) cm-1	Response 11 pH (alum)	Response 12 SDS-THM (alum) ug/L
1	Center	10	10	2	0.889	0.17	1.49	1.557	7.6	41.9	0.658	0.16	1.978	2.052	7.8	4
2	Fact	5	5	0	0.841	0.19	1.81	1.750	7.9	46.7	0.722	0.23	2.101	2.539	7.9	5
3	Fact	15	15	0	0.94	0.16	1.37	1.373	7.6	36	0.608	0.13	1.85	1.847	7.7	4
4	Fact	5	5	4	0.845	0.17	1.65	1.667	7.9	47.5	0.725	0.19	1.998	2.399	7.8	4
5	Fact	15	15	4	0.94	0.2	1.46	1.296	7.6	38.4	0.61	0.18	1.74	1.918	7.7	4
6	Center	10	10	2	0.892	0.16	1.48	1.460	7.6	42	0.659	0.16	1.824	2.062	7.8	4
7	Fact	15	5	0	0.936	0.24	1.44	1.450	7.6	37.1	0.612	0.19	1.84	1.767	7.6	4
8	Fact	5	15	0	0.861	0.16	1.69	1.790	7.7	46.5	0.737	0.18	2.055	2.188	7.8	5
9	Fact	15	5	4	0.937	0.18	1.55	1.491	7.6	41.4	0.61	0.14	1.596	1.796	7.5	4
10	Fact	5	15	4	0.866	0.16	1.71	1.832	7.7	45.9	0.741	0.17	1.815	2.243	7.9	5
11	Center	10	10	2	0.895	0.11	1.55	1.586	7.6	40.6	0.659	0.15	1.997	1.753	7.7	4

Part I

Stage III Raw data

	Final pH						Final Turbidity (NTU)					
Coagulant Dose (mg/L)	Alum	PACl	Ferric sulfate	PHAS	PAX-XL 1900	PASS 100	Alum	PACl	Ferric sulfate	PHAS	PAX-XL 1900	PASS 100
0	7.9	7.9	8.1	8.1	8.1	7.9	1.27	1.27	1.02	1.02	0.70	0.38
5	7.7	7.8	7.8	7.6	8.0	7.7	0.34	0.16	0.45	0.25	0.44	0.23
10	7.6	7.7	7.6	7.6	7.9	7.6	0.20	0.14	0.44	0.25	0.70	0.62
15	7.5	7.6	7.5	7.5	7.9	7.6	0.24	0.17	0.48	0.33	0.59	0.62
20	7.5	7.6	7.5	7.4	7.8	7.5	0.31	0.17	0.31	0.49	0.60	0.30
25	7.4	7.5	7.4	7.3	7.7	7.4	0.42	0.19	0.33	0.48	0.44	0.42
30	7.4	7.4	7.4	7.2	7.6	7.4	0.45	0.29	0.51	0.87	0.30	0.51
RAW 1	8.1						0.70					
RAW 2	8.1						1.02					
RAW 3	7.9						1.27					
RAW 4	7.9						0.38					
Average	**8**						**0.84**					

	Final UV absorbance (cm-1)						DOC (mg/L)					
Coagulant Dose (mg/L)	Alum	PACl	Ferric sulfate	PHAS	PAX-XL 1900	PASS 100	Alum	PACl	Ferric sulfate	PHAS	PAX-XL 1900	PASS 100
0	2.0375E-02	2.0375E-02	1.7118E-02	1.7118E-02	2.5908E-02	2.2316E-02	2.1595	2.1595	2.1595	2.1595	2.1595	2.1595
5	2.0112E-02	1.7269E-02	3.7167E-02	1.8620E-02	1.8661E-02	2.1098E-02	1.966	1.735	2.153	2.016	1.705	2.138
10	1.7952E-02	1.2922E-02	3.3430E-02	1.6392E-02	1.9203E-02	2.0770E-02	1.849	1.598	2.21	1.654	1.642	1.784
15	1.5394E-02	1.1258E-02	2.6445E-02	1.5711E-02	1.7960E-02	2.0583E-02	1.703	1.893	1.783	1.685	1.387	1.764
20	1.3577E-02	1.1418E-02	2.3835E-02	1.5598E-02	1.5405E-02	1.4661E-02	1.765	1.464	1.747	1.558	1.421	1.701
25	1.4311E-02	1.0423E-02	2.3203E-02	1.3938E-02	1.6161E-02	1.6250E-02	1.554	1.505	1.936	1.647	1.439	1.565
30	1.5322E-02	9.3107E-03	2.1915E-02	1.4311E-02	1.6373E-02	1.5482E-02	1.54	1.399	1.669	1.512	1.499	1.595
RAW 1	0.0259						1.19972					
RAW 2	0.0171						0.79268					
RAW 3	0.0204						0.94351					
RAW 4	0.0223						1.03339					
Average	**0.0214**						0.99232					

Dose (mg/L)	Alum			PACl			Ferric Sulfate		
	chloride	sulfate	CSMR	chloride	sulfate	CSMR	chloride	sulfate	CSMR
0	29.8	28.9	1.031142	29.8	28.9	1.031142	29.8	28.9	1.031142
5	29.3	31.6	0.927215	30.6	29.2	1.047945	29.7	31.9	0.931034
10	29.2	34.5	0.846377	31.9	29.5	1.081356	29.6	35.1	0.843305
15	29.2	37.4	0.780749	33.4	30	1.113333	29.6	38.1	0.776903
20	29.2	40.2	0.726368	34.8	30.3	1.148515	29.6	41.2	0.718447
25	29.2	43	0.67907	36.2	30.6	1.183007	29.7	44.2	0.671946
30	29.1	45.7	0.636761	37.5	30.9	1.213592	29.7	47.3	0.627907
RAW	29.8	28.9	1.031142						

Dose (mg/L)	PHAS			PAX-XL 1900			PASS 100		
	chloride	sulfate	CSMR	chloride	sulfate	CSMR	chloride	sulfate	CSMR
0	29.8	28.9	1.031142	29.8	28.9	1.031142	29.8	28.9	1.031142
5	29.6	32.1	0.922118	30.6	28.8	1.0625	30	30.6	0.980392
10	29.5	35.3	0.835694	31.7	28.7	1.10453	30	35	0.857143
15	29.5	38.6	0.764249	32.7	28.5	1.147368	29.9	35	0.854286
20	29.5	41.8	0.705742	33.6	28.3	1.187279	30	39.3	0.763359
25	29.5	44.8	0.658482	34.6	27.9	1.240143	29.9	42.6	0.701878
30	29.5	47.9	0.615866	35.6	27.7	1.285199	30	44.9	0.668151

Part II

Phase I A Raw data

10 mg/L Coagulant Dose

	Final Turbidity (NTU)	Final DO (mg/L)	Final UV254 (cm^{-1})	Final pH	Final Temperature	Final TOC (mg/L)	Final DOC (mg/L)	Final Chloride (mg/L)	Final Sulfate (mg/L)	CSMR
RAW #3	6.61	6.43	0.19	7.91	23.5	5.61	5.882	86	63	1.37
Alum	3.73	7.36	0.158	7.66	24.7	5.486	5.625	86	69	1.25
SternPAC	1.13	7.4	0.134	7.71	24.7	4.897	5.227	90	65	1.38
PHAS	1.87	7.36	0.144	7.73	24.7	5.296	5.378	87	70	1.24
Ferric Sulfate	1.71	7.45	0.149	7.78	24.7	5.593	5.365	87	70	1.24
PAX-XL 1900	2.52	7.5	0.11	7.95	24.7	4.847	4.714	89	64	1.39
PASS 100	1.14	7.36	0.146	7.89	24.7	5.479	5.524	87	69	1.26

20 mg/L Coagulant Dose

	Final Turbidity (NTU)	Final DO (mg/L)	Final UV254 (cm^{-1})	Final pH	Final Temperature	Final TOC (mg/L)	Final DOC (mg/L)	Final Chloride (mg/L)	Final Sulfate (mg/L)	CSMR
RAW #4	16.7	6.95	0.181	7.58	23	5.357	5.675	63	33	1.91
Alum	2.46	7.44	0.114	7.25	25	4.267	4.169	63	43	1.47
SternPAC	0.55	7.48	0.098	7.44	25	3.841	3.789	68	34	2.00
PHAS	2.94	7.53	0.104	7.4	25	3.86	3.981	62	44	1.41
Ferric Sulfate	4.96	7.47	0.13	7.36	25	4.497	4.437	63	43	1.47
PAX-XL 1900	3.58	7.42	0.076	7.62	25	3.289	3.216	66	32	2.06
PASS 100	1.07	7.47	0.112	7.57	25	4.004	4.034	62	43	1.44

30 mg/L Coagulant Dose

	Final Turbidity (NTU)	Final DO (mg/L)	Final UV254 (cm^{-1})	Final pH	Final Temperature	Final TOC (mg/L)	Final DOC (mg/L)	Final Chloride (mg/L)	Final Sulfate (mg/L)	CSMR
RAW #4A	15.7	7.06	0.169	7.65	22.8	4.713	5.157	57	33	1.73
Alum	2.02	7.53	0.077	7.24	23.5	3.484	3.456	58	48	1.21
SternPAC	1.18	7.58	0.061	7.37	23.5	3.017	3.166	66	36	1.83
PHAS	1.64	7.55	0.067	7.28	23.5	3.267	3.241	55	51	1.08
Ferric Sulfate	1.85	7.6	0.082	7.18	23.5	3.687	3.601	59	51	1.16
PAX-XL 1900	2.09	7.63	0.045	7.49	23.5	2.78	2.713	65	34	1.91
PASS 100	0.89	7.61	0.078	7.41	23.5	3.493	3.495	59	49	1.20

40 mg/L Coagulant Dose

	Final Turbidity (NTU)	Final DO (mg/L)	Final UV254 (cm^{-1})	Final pH	Final Temperature	Final TOC (mg/L)	Final DOC (mg/L)	Final Chloride (mg/L)	Final Sulfate (mg/L)	CSMR
RAW #1/1A	10.4	6.68	0.212	7.88	23.5	5.915	6.461	84	50	1.68
Alum	4.77	7.46	0.133	7.4	25	4.931	4.815	84	68	1.24
SternPAC	1.67	7.33	0.111	7.41	25	4.088	4.453	96	51	1.88
PHAS	3.06	7.44	0.117	7.33	25	4.561	4.477	84	72	1.17
Ferric Sulfate	2.27	7.44	0.135	7.32	25	4.975	4.867	84	72	1.17
PAX-XL 1900	1.92	7.46	0.084	7.53	25	3.728	3.434	92	47	1.96
PASS 100	1.17	7.6	0.143	7.53	25	5.004	5.143	85	65	1.31

50 mg/L Coagulant Dose

	Final Turbidity (NTU)	Final DO (mg/L)	Final UV254 (cm^{-1})	Final pH	Final Temperature	Final TOC (mg/L)	Final DOC (mg/L)	Final Chloride (mg/L)	Final Sulfate (mg/L)	CSMR
RAW #2	14.2	6.17	0.172	7.74	23.2	5.008	5.216	65	50	1.30
Alum	5.05	6.88	0.059	6.95	23.5	3.846	3.468	66	75	0.88
SternPAC	1.46	6.89	0.044	7.07	23.5	2.961	3.093	80	53	1.51
PHAS	3.86	6.96	0.049	7.08	23.5	3.163	3.059	66	80	0.83
Ferric Sulfate	1.41	7.03	0.062	6.97	23.5	3.633	3.506	66	80	0.83
PAX-XL 1900	3.77	7.05	0.031	7.34	23.5	2.735	2.635	75	48	1.56
PASS 100	2.18	7.02	0.065	7.32	23.5	3.838	3.558	66	72	0.92

60 mg/L Coagulant Dose

	Final Turbidity (NTU)	Final DO (mg/L)	Final UV254 (cm^{-1})	Final pH	Final Temperature	Final TOC (mg/L)	Final DOC (mg/L)	Final Chloride (mg/L)	Final Sulfate (mg/L)	CSMR
RAW #2A	14.2	6.56	0.159	7.76	23	5.016	5.641	67	50	1.34
Alum	3.69	7.47	0.059	7.07	23.5	3.909	3.407	67	82	0.82
SternPAC	1.88	7.4	0.046	7.27	23.5	3.095	2.991	84	54	1.56
PHAS	3.41	7.43	0.053	7.16	23.5	3.538	3.299	67	86	0.78
Ferric Sulfate	1.7	7.45	0.061	7.12	23.5	3.559	3.418	68	86	0.79
PAX-XL 1900	1.88	7.46	0.033	7.48	23.5	2.612	2.616	78	48	1.63
PASS 100	1.49	7.54	0.065	7.4	23.5	3.698	3.699	67	81	0.83

Part II

Phase I B Raw data

Coagulant Dose (mg/L)	Activated Silica Dose (mg/L)	Alum									
		Final Turbidity (NTU)	Final DO (mg/L)	Final UV254 (cm^{-1})	Final pH	Final Temperature	Final TOC (mg/L)	Final DOC (mg/L)	Final Chloride (mg/L)	Final Sulfate (mg/L)	CSMR
10	4.37	0.66	8.1	0.204	7.62	23	6.144	6.574	64	46	1.39
20	8.74	0.53	8.11	0.18	7.5	23	5.553	5.975	63	52	1.21
30	13.15	0.52	8.09	0.162	7.43	23	5.178	5.506	64	58	1.10
40	17.52	0.53	8.07	0.144	7.31	23	4.839	5.109	74	65	1.14
50	17.52	0.61	8.07	0.13	7.19	23	4.642	4.865	64	69	0.93
60	17.52	0.79	8.13	0.116	7.12	23	4.323	4.603	63	75	0.84

Coagulant Dose (mg/L)	**Activated Silica Dose (mg/L)**	**PACl**									
		Final Turbidity (NTU)	Final DO (mg/L)	Final UV254 (cm^{-1})	Final pH	Final Temperature	Final TOC (mg/L)	Final DOC (mg/L)	Final Chloride (mg/L)	Final Sulfate (mg/L)	CSMR
10	4.37	0.83	8.19	0.164	7.67	23.5	5.524	5.749	70	42	1.67
20	8.74	0.48	8.05	0.135	7.6	23.5	5.097	5.181	73	43	1.70
30	13.15	0.37	8.04	0.112	7.53	23.5	4.482	4.643	76	45	1.69
40	17.52	0.26	8.02	0.096	7.44	23.5	4.14	4.389	79	47	1.68
50	17.52	0.27	8.03	0.083	7.29	23.5	3.708	3.944	82	48	1.71
60	17.52	0.31	7.96	0.076	7.21	23.5	3.605	3.834	81	49	1.65

RAW Water Quality

RW Code	Turbidity (NTU)	DO (mg/L)	UV254 (cm^{-1})	pH	Temperature	Time Analysed	TOC (mg/L)	DOC (mg/L)	Chloride (mg/L)	Sulfate (mg/L)	CSMR
RAW # 5	11.8	7.58	0.205	7.83	22.1	10:00 AM	6.115	6.32	63	40	1.58

Part II

Phase II Raw data

Coagulant Dose (mg/L)	Activated Silica Dose (mg/L)	Sand Dose (g/L)	Polymer Dose (mg/L)	**Alum**									
				Final Turbidity (NTU)	Final DO (mg/L)	Final UV254 (cm^{-1})	Final pH	Final Temperature	Final TOC (mg/L)	Final DOC (mg/L)	Final Chloride (mg/L)	Final Sulfate (mg/L)	CSMR
10	4.37	5	0.1	1.83	7.81	0.223	7.7	23	7.067	7.185	48	37	1.30
20	8.74	5	0.1	1.89	7.87	0.198	7.61	23	6.371	6.475	48	45	1.07
30	13.15	5	0.1	1.73	7.84	0.184	7.53	23	5.887	6.19	48	52	0.92
40	17.52	5	0.1	1.61	7.86	0.164	7.42	23	5.646	5.733	49	63	0.78
50	17.52	5	0.1	1.6	7.84	0.153	7.39	23	5.662	5.464	48	62	0.77
60	17.52	5	0.1	1.9	7.81	0.133	7.28	23	5.099	5.176	48	72	0.67

Coagulant Dose (mg/L)	Activated Silica Dose (mg/L)	Sand Dose (g/L)	Polymer Dose (mg/L)	**PACl**									
				Final Turbidity (NTU)	Final DO (mg/L)	Final UV254 (cm^{-1})	Final pH	Final Temperature	Final TOC (mg/L)	Final DOC (mg/L)	Final Chloride (mg/L)	Final Sulfate (mg/L)	CSMR
10	4.37	5	0.1	2.3	6.91	0.168	7.64	23	5.46	5.731	59	34	1.74
20	8.74	5	0.1	1.34	6.89	0.13	7.6	23	4.767	4.846	62	38	1.63
30	13.15	5	0.1	1.11	6.94	0.107	7.53	23	4.219	4.442	64	41	1.56
40	17.52	5	0.1	1.06	6.91	0.089	7.4	23	3.897	3.983	68	45	1.51
50	17.52	5	0.1	0.87	6.94	0.089	7.43	23	3.821	3.947	68	44	1.55
60	17.52	5	0.1	0.96	6.86	0.07	7.32	23	3.773	4.005	73	46	1.59

RAW Water Quality

RW Code	Turbidity (NTU)	DO (mg/L)	UV254 (cm^{-1})	pH	Temperature	Time Analysed	TOC (mg/L)	DOC (mg/L)	Chloride (mg/L)	Sulfate (mg/L)	CSMR
RAW #6	13.5	8.11	0.202	7.73	21	1:00 PM	6.22	6.216	54	31	1.74
RAW #7	14.1	8.41	0.237	7.94	19.9	10:00 AM	7.27	7.582	47	30	1.57

*** A - Afternoon**

**** RAW Water line flushed**