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PARAMETERS AFFECTING COAGULATION / FLOCCULATION OF DRINKING WATER UNDER COLD TEMPERATURES

by

Omar Alshikh

A Thesis
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of the Requirements for the Degree of
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ABSTRACT

Raw water temperatures in Ontario drop below 5.0 °C for several months during the year. Bench scale experiments were conducted using jar test apparatus to examine the effect of raw water temperatures on the treatment efficiency of the coagulation/flocculation (CF) process, using alum as the primary coagulant, and a cationic polymer Maganafloc LT-22 as a coagulant aid, over a temperature range of 1.0 – 22.0 °C. Temperature adversely affected alum coagulation, with residual turbidity increasing with reducing temperatures. The adverse effect on residual turbidity was partly compensated by increasing alum and Magnafloc LT-22 dosages.

Test results at about 3.5 °C suggest that polyaluminum chloride (PACl) blend (Sumaclear -750) may be a better primary coagulant than alum for the CF process at low temperatures. Residual turbidity levels similar to or lower than that observed with alum were obtained with the PACl blend at about one-fourth of the dosage level with alum.

DEDICATION

To my wife Fatma and daughters Lubna & Lamess

ACKNOWLEDGEMENTS

The author is indebted to his advisors Professor Nihar Biswas and Dr. Rajesh Seth for their guidance and support throughout this research and thesis writing. Without their timely suggestions and advice this work would be incomplete.

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LIST OF ABBREVIATIONS AND SYMBOLS

Abbreviations:

APHA	American Public Health Association
ASCE	American Society for Civil Engineers
AWWA	American Water Works Association
CF	Coagulation/ Flocculation
DOC	Dissolved Organic Carbon
MAC	Maximum Acceptable Concentration
NOM	Natural Organic Matter
NTU	Nephelometric Turbidity Unit
PACl	Polyaluminum Chloride
r.p.m	Revolution per minute
SD	Standard Deviation
THM's	Trihalomethanes
TOC	Total Organic Carbon
TOX	Total Organic Halides
WWTP	Weeks Water Treatment Plant

Symbols:

A	Pre-exponential or frequency factor
B	Boltzman constant
°C	Degree Celsius
d	Colloidal particle diameter

D	Dielectric constant
E	Activation energy
g	Gram
G	Mean velocity gradient
J_P	Perikinetic particles rate change
J_O	Orthokinetic particles rate change
$K_{(T)}$	Reaction rate constant
L	Litre
ml	Millilitre
mg	Milligram
N	Total particle concentration
P	Power
Q	Volumetric flow rate
R	Ideal gas constant
sec	Second
S	Speed of mixing in r.p.m
t	time
T	Absolute temperature
V	Volume of the basin
ZP	Zeta potential
μL	Microlitre
μm	Micrometer
μeq	Microequivalent

μ	Dynamic viscosity
ψ	Electrophoretic velocity
α	Particle – particle collision efficiency factor
τ	Residence time

1 INTRODUCTION

This chapter discusses the availability and importance of fresh water, which is the source for most drinking water treatment facilities. The role of the coagulation / flocculation process in producing drinkable water, and typical raw water temperature's seasonal variations in Windsor, Ontario are reviewed.

1.1 Background

Fresh water is one of the most important and valuable substances on Earth, and as the population grows day after day it is only natural that the demand for fresh water will be increased accordingly. Out of the 1,385,984,000 cubic kilometer of water available on Earth, only 2.5% is considered as fresh water and that includes lakes, rivers, ice, snow and underground aquifers (Environment Canada, 2006). It is interesting to note that river's share is only 0.0002% and lakes account for 0.007 %. World wide, almost 1.0 billion people do not have access to safe drinking water. With the United Nations (UN) Millennium Development Goals, UN member states pledged to reduce by half the proportion of people without sustainable access to safe drinking water, by 2015 (Environment Canada, 2006).

Fortunately, almost 9%, or 891163 square kilometers of Canada's total area is covered by fresh water. However, since water bodies can get contaminated easily through indiscriminate dumping of wastes, drinking water treatment facilities everywhere are facing big challenges. For example, a single drop of oil in a freshwater body can render up to 25 liters of water that is unsafe to drink (Environment Canada, 2006). Because of this, the treatment process in producing drinking water is receiving increasing attention. General contaminants for raw water include, but are not limited to, various organic and inorganic chemicals, suspended solids, and microorganisms.

Canada Drinking Water Guidelines list maximum allowable concentrations for different substances/ compounds and classified them as A) Microbiological parameters such as E-coli, total Coliform and viruses, B) Chemical and Physical parameters, specifically78 substances/compounds ranging from pure substances such as arsenic to chlorinated compounds such as trihalomethanes, C) Radiological parameters, specifcally78 radio emitting substances and isotopes (Health Canada, 2006). All mentioned parameters are regulated and those regulations are revised periodically, tending towards more stringent maximum acceptable concentrations (MAC) in produced drinking water. Any parameter that exceeds its MAC may cause a threat to human health (Health Canada, 2006).

The coagulation/ flocculation (CF) process is one of the most common unit processes in any drinking water treatment facility, and is aimed at removing colloidal organic/ inorganic particles that are suspended in raw source water. These colloidal particles, which are usually <10 μm in size and are negatively charged, form a stable suspension in water due to the repulsive forces. By increasing the size of these particles through the process of charge destabilization and inter-particle bridging, the CF facilitates their removal in the subsequent settling unit. Low temperature is one of the factors that can significantly impact the CF process negatively; however, the impact could be partly minimized by selecting the most appropriate coagulant (Davis, 1983). The CF process using alum, which is one of the most commonly used coagulants for drinking water treatment, has been shown to be particularly susceptible to cold temperatures (Morris and Knocke, 1984).

1.2 Raw water temperatures in Ontario

Water has a high heat capacity compared to other substances such as air; thereby, it can retain cold temperatures for longer periods of time, especially in winter when the ambient air temperature often drops below zero. In Ontario, raw water temperature drops below 5.0 °C for several months during the year, usually between November and March.

In Ontario, the water temperature in a lake or reservoir can easily drop to 1.0 °C and, of course, the surface water temperature in a river must drop to 0 °C before ice covers it (Hanson and Cleasby, 1990). Hutchinson and Foley (1974) reported that Lake Huron water is < 3.3 °C for three months of the year. It is surprising to see the length of time each year when temperate zone surface water is very cold.

According to data (Year 2005) provided by A.H Weeks Water Treatment Plant in Windsor, Ontario, raw water temperatures at the treatment plant intake in the Detroit River were 3.5 °C or below for the period between December and March (Figure 1-1); also, the variation of raw water temperature is small compared to other months (Figure 1-2). Further information about raw water temperatures at different locations in Ontario can be found in Drinking Water Surveillance program (MOE, 2007).

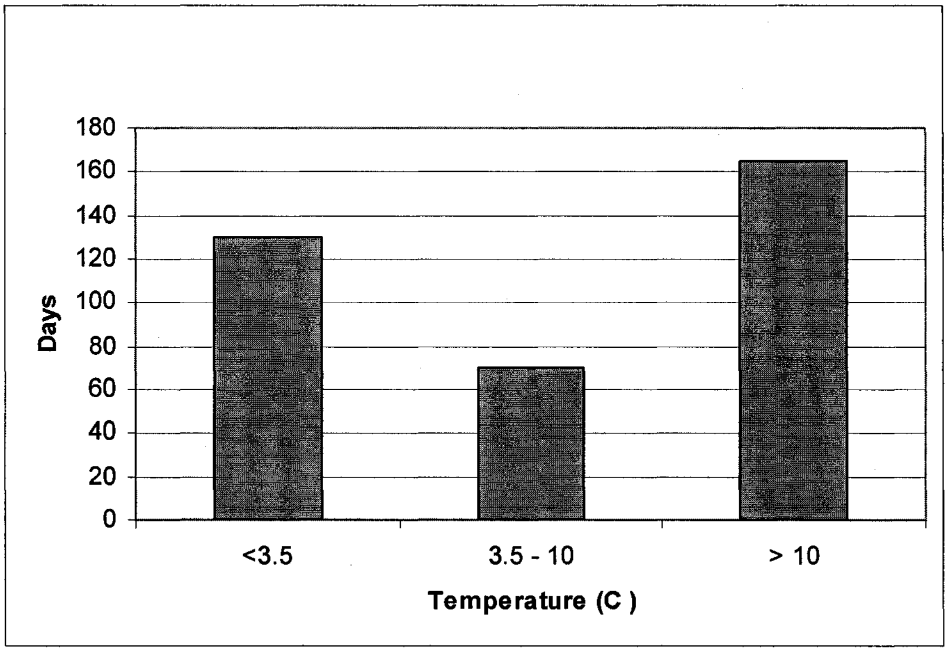

Figure 1-1: Raw water temperature distribution for A.H. Weeks Treatment Plant -2005

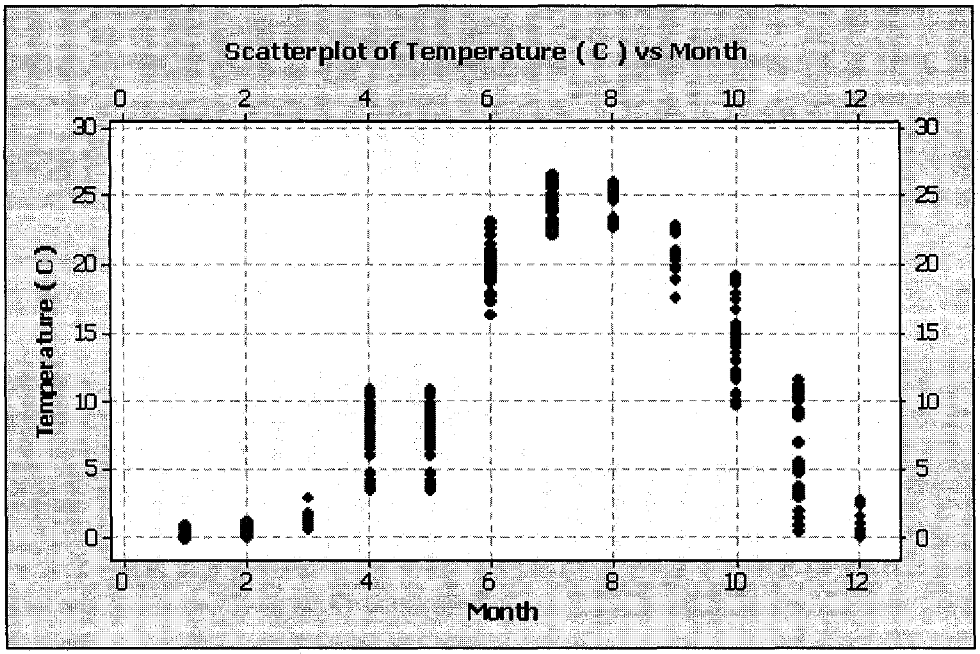

Figure 1-2: Detroit river raw water temperature variation during the year 2005

Given the fact that Windsor is located at the south west part of Ontario (N 42:16, W 82:57) and it has mild weather compared to the northern parts of the province, it is expected that most of the raw waters sources for the drinking water treatment plants would have a similar range of temperatures or may be lower than Windsor for several months in a given year.

Cold raw water temperature has a direct impact on the performance of any treatment plant because a number of physical and chemical characteristics change, and consequently operating parameters that are used in the summer time are no longer valid (Davis, 1983). The effect of raw water temperature had been investigated by several researchers, yet the relationship between the level of impact and the level of temperature has not been clearly established (Davis, 1983; Viraraghavan and Mathavan, 1988; Ammary and Cleasby, 1995; Binnie et.al., 2002).

1.3 Research objectives

The main objective of this study was to evaluate the coagulation /flocculation process efficiency under cold temperatures at the A.W. Weeks Treatment Plant in Windsor (WWTP), Ontario using the Detroit River water as the raw water source. The main operating parameters that have been varied during the course of this work were temperature, coagulant dose, and coagulant aid dose. The specific objectives of the study were:

- ☐ To examine the effect of temperature ranging between 1 and 22 °C on residual turbidity with alum coagulation. Alum and polymer (Magnafloc LT-22) dosages were fixed at 30 and 0.05 mg/L, respectively.
- ☐ To evaluate the effect of varying alum and polymer dosages on residual turbidity at selected low temperatures.
- ☐ To compare the performance of alum and alternate coagulant (polyaluminum blend Sumaclear-750) on residual turbidity and dissolved organic carbon (DOC) at selected low temperatures.

1.4 Organization of thesis

This thesis is organized to include five chapters. Chapter one is used for introduction where the need for the study has been established. Here, the role of the coagulation and flocculation process and the associated difficulties when raw water temperature drops has also been presented. Seasonal variations in raw water temperature in bodies of water, such as lakes and rivers are discussed and a specific example for the Detroit River is shown.

In chapter two a literature review and theoretical background for the CF process is discussed. The topics covered are: zeta potential theory and its applications in water treatment, the nature of colloidal particles and natural organic matter (NOM) and why the CF process is targeting them. The mechanisms whereby coagulant and coagulant aid initiate the CF process are reviewed. All the parameters, both controllable and uncontrollable, that can have an impact on the CF process are cited.

In chapter three, all materials that have been used in the study are reviewed, experimental set up and the equipment specifications and the required modification are mentioned. Various phases of the study and operating conditions for each phase are listed. Finally, type of measurements and the analytical methods followed are detailed.

In chapter four, all results have been presented. Analysis and discussion of those results are reported. Finally, chapter five provides a summary of research outcomes for the different phases, lessons learned during the course of the work, conclusions and recommendations for future work.

2 REVIEW OF LITERATURE

This chapter reviews the theoretical background of the Flocculation /Coagulation (CF) and details the factors that significantly impact the process.

2.1 Overview on coagulation / flocculation process

Drinking water treatment process usually consists of more than one stage; it typically includes CF, particle settling, filtration, and disinfection. Other processes involving chemical treatment are also not uncommon. Disinfection is the last stage before treated water is sent into the distribution network. Figure 2-1 shows a schematic diagram for the A.H Weeks Water Treatment Plant in Windsor (WWTP), Ontario.

High efficiency of the CF process is vital because it could decide the fate of suspended/colloidal/ dissolved organic particles that are embedded in raw water; these particles along with the microorganisms are the main targets in most drinking water treatment processes. Coagulation is the process by which a chemical is added to destabilize suspended particles and to react with dissolved organic materials. Flocculation allows particles to collide and aggregate, significantly increasing filtration performance. Additionally, coagulation/flocculation efficiency also controls disinfection by- product formation, which can impose a health risk to humans (Pernitsky, 2003).

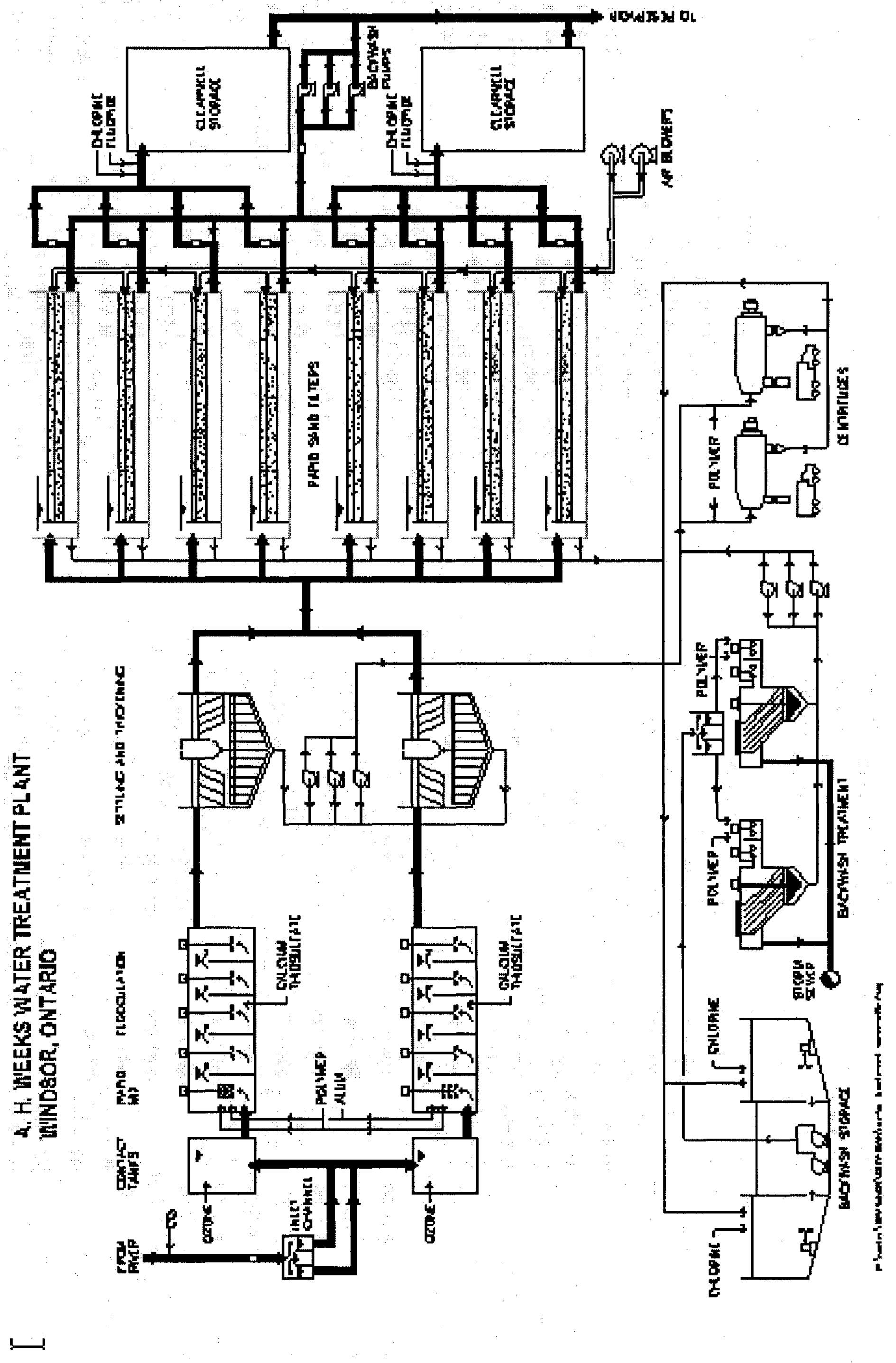

Figure 2-1: Schematic diagram for A.H. Weeks Water Treatment Plant

2.1.1 Colloidal particles and natural organic matter (NOM)

Natural water usually contains a variety of impurities, and a wide range of particles. Solids may refer to the inorganic materials in raw water and may have three forms:

A) Suspended solids, such as clay, silt, sand and vegetable matter (Binnie et al, 2002), and in some other definitions iron oxide, silicates, calcites, aluminum oxide and other minerals are included (Wiesner and Klute, 1997). Suspended particles may range from big particles that are removed by screens and strainers down to 10μm.

B) Colloids are very fine particles, typically ranging from 10 nm to 10μm. Colloids present a real challenge since their settling velocities are intolerably slow and they could easily escape filtration (Ravina, 1993).

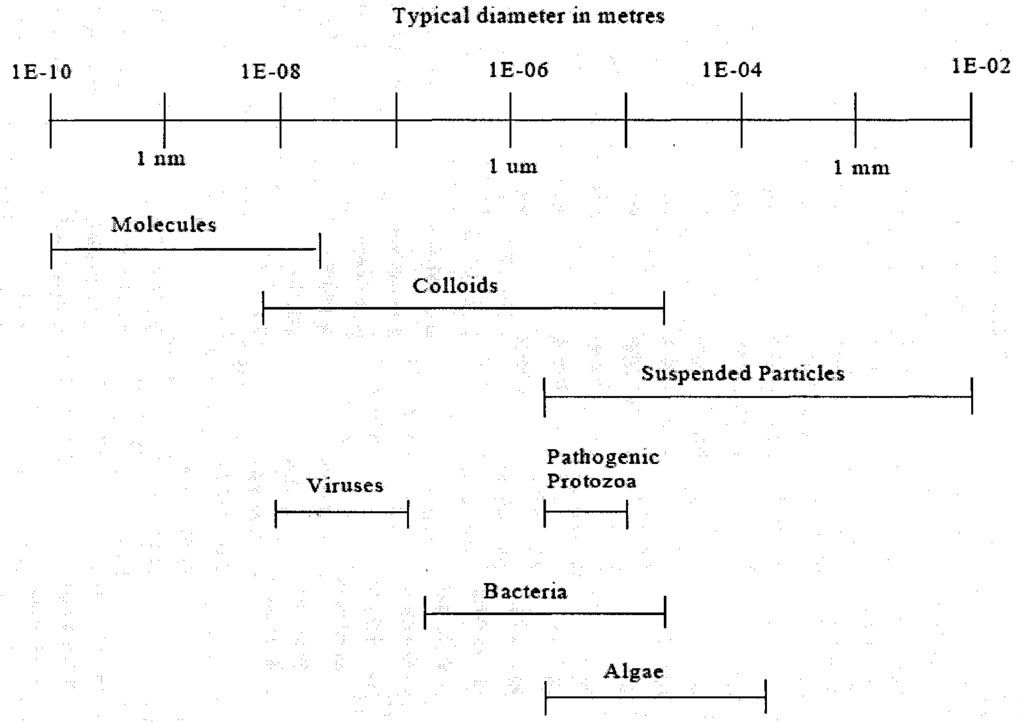

Figure 2-2: Particles size range (Binnie et. al, 2002)

C) Dissolved molecules are present as individual molecules or as ions. Figure 2-2 shows the size range for different particles. The type and size of particles in each watershed are usually different and may be unique; however, most raw waters show similar electrochemical behavior. Their surfaces are covered with hydroxyl (OH^-) groups and under the pH levels of most natural waters these particles have a negative surface charge typically in the range of 0.1 to 1.0 μeq/mg (Pernitsky, 2003).

Natural organic matter (NOM) can be found in almost every source of natural waters; the main sources are soil, higher plant life, algae, forest litter and other living organisms (Malley et al., 1988). The largest component of NOM is aquatic humic matter, and it comprises almost 60% of the dissolved organic matter in fresh waters (Thurman, 1985). The exact physical and chemical nature of NOM is highly variable and site specific; usually they are colored and polyelectrolytic in nature. Humic matters or substances can be divided into two divisions, those are humic and fulvic acids (Thurman, 1985).

NOM molecules are large and contain many functional groups as shown in Figure 2-3. Those groups can affect their chemical behavior. What makes the behavior even more complex is that the charge on those different groups can also change with pH (Croue et. al., 1999).

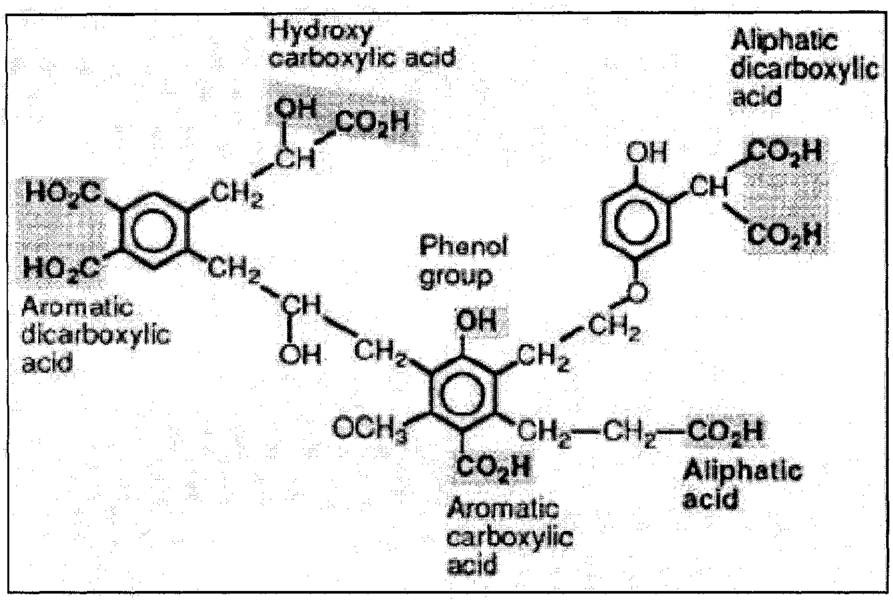

Figure 2-3: NOM molecule showing different functional groups (Prenitsky, 2003)

In many treatment plants, the coagulant doses are determined by the NOM concentrations rather than by turbidity alone. The charge density of NOM species is typically 10-100 times greater than the charge density of inorganic particles, which are mostly responsible in creating turbidity. Water with 10 mg/L of clay-based turbidity having a negative charge of 0.5 μeq/ mg should require 5.0μeq/L of positive charge, while 3.0 mg/L of DOC with a negative charge of 10 μeq/ mg requires a positive charge of 30 μeq/L for neutralization, which shows six times more charge demand than the needed for clay (Edzwald and Van Benschoten, 1990).

2.1.2 Interaction between NOM and inorganic matter

The presence of NOM in water can cause coloring of water, interfere with treatment processes and produce taste and odor when using chlorine for disinfection purposes. This also may cause adsorption and transport of toxic metals into the distribution system (Saar and Weber, 1982).

It is believed that NOM can react with inorganic clay colloids in a number of ways (Van Olphen, 1963). The main reaction is to act as a stabilizing agent for the clay suspension, thus hindering the destabilization process. Also, sometimes NOM might be absorbed on the negative surfaces of clay and result in destabilization and precipitation, or penetrating between clay layers and replacing the inter-water layer (Green, 1951).

The reaction that causes the formation of trihalomethanes (THMs) is considered to be very important because these products are believed to be carcinogens. The formation of chlorinated organics in water treatment occurs from the reaction of free chlorine with acidic carbons and carbon containing methylene groups of humic matter under basic conditions (Morris and Baum, 1978) as shown in the simple reaction below:

$$\text{NOM} + Cl_2 \rightarrow \text{Total Organic Halides (TOX)} \qquad 2\text{-}1$$

$$\text{TOX} = \text{THM's} + \text{other organic halides} \qquad 2\text{-}2$$

THMs can be chloroform ($CHCl_3$), bromodichloromethane ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$) and bromoform ($CHBr_3$) (APHA, 1998). The formation of those products will depend on several factors such as the concentration of organic matter and chlorine, the pH, temperature and reaction time. Due to the fact that NOM is a precursor in the formation of those toxic substances, it is best to remove NOM before reaching the chlorination step in the treatment plant (Malley et al., 1988). Health

Canada has set a 0.1 mg/L limit for the total of all THMs in drinking water (Health Canada, 2003).

2.1.3 Zeta potential

The previous section stated that colloids and most NOM particles hold a negative charge on their surfaces. Those particles have small diameters, and thereby have a high surface area to volume ratio. The effect of repulsion forces due to similar charge, distributed on the surface, keeps these small particles apart from each other; hence, they develop a stabilized status in the water column (Malley et.al, 1988).

The double layer model is often used to describe ionic atmosphere in the vicinity of charged colloids (Steel and Terence, 1981). Since the core of most the colloids encountered in raw waters is negatively charged, positive ions are attracted and attached to form a positive layer called a stern layer. A mixed layer of both positive and negative ions is formed due to repulsion forces between those counter ions and is called the diffused layer (Steel and Terence, 1981). As a result, an electrical potential is created and this has greater magnitude near the surface of the colloid and it gradually decreases with distance from the colloid surface towards the bulk water. Figure 2-4 illustrates the double layer model. The potential at the junction of the stern and diffuse layers is known as the Zeta Potential (ZP), in fresh waters. And since the double layer is extended, ZP is a good approximation for the surface potential (Ravina, 1993).

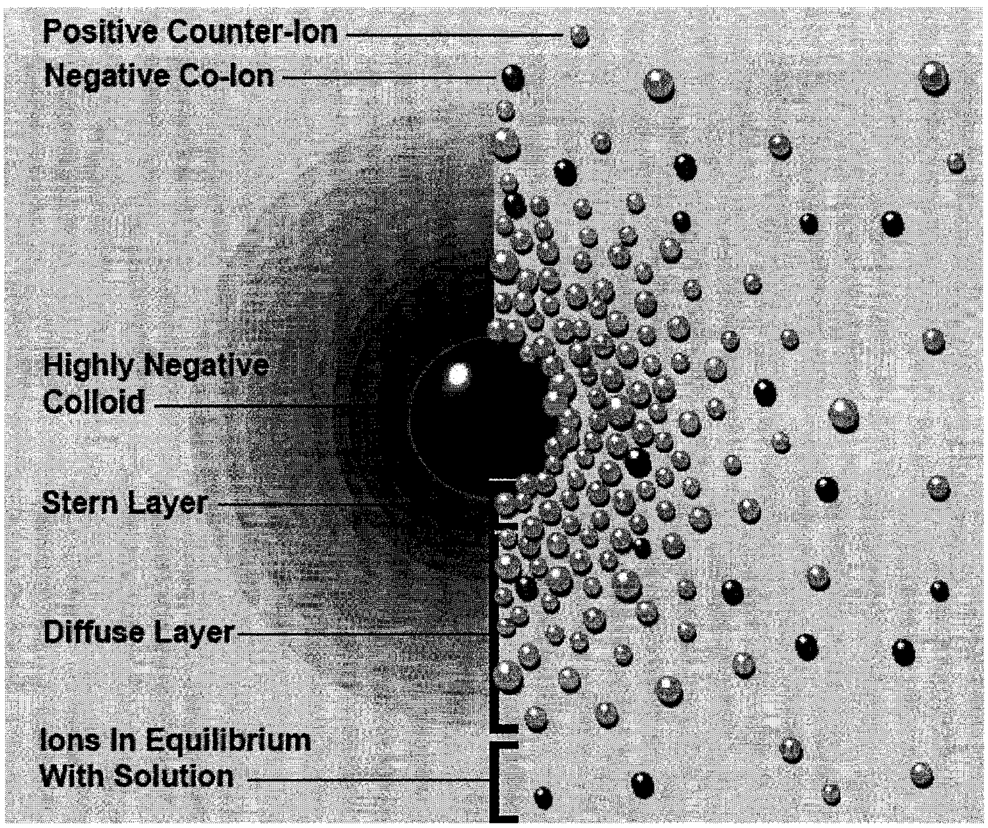

Figure 2-4: Double layer model (Courtesy of Zeta-meter Inc.)

Often ZP is used as a measure for colloid particles stability. When ZP is high, the stability of colloids is also high and vise versa. The mathematical expression for ZP is (Reynolds and Richards, 1996):

$$ZP = \frac{4\pi\psi\mu}{D} \tag{2-3}$$

ZP: Zeta potential (millivolt)
μ: Dynamic viscosity (N-s/ m^2)
ψ: Electrophoretic velocity (m /s)
D: Dielectric constant

Dynamic viscosity and dielectric constant for water are both temperature dependant, thereby seasonal variation of temperature will lead to greater ZP value in winter.

There are two opposing forces working on the particles; an electrostatic repulsion force and an attraction force known as Vander Waals (Ravina, 1993). Electrostatic repulsion, originating from different ion charges in the diffused layer, becomes significant when two particles approach each other and their electrical double layer begins to overlap. Energy is required to overcome this repulsion. On the other hand, the Vander Waals attraction force is the result of forces between molecules. This force effect is additive; a molecule in one colloid has a Vander Waals attraction force to each molecule in another colloid. This is exists in each molecule in the first colloid, and the resultant force is the sum of all of these. DLVO theory (developed by the scientists Derjaguin, Landau, Verwery, and Overbeek) is the explanation of how particles interact; basically, it looks at the balance between these two opposing forces. The net effect resulting from them creates a virtual energy barrier. In order to have an effective flocculation, colliding particles must have sufficient kinetic energy to overcome this barrier, then agglomeration will occur (Ravina, 1993).

2.1.4 Coagulation mechanisms

Coagulation refers to the destabilizing process of colloidal particles in raw water. This brings the ZP to a minimum value near zero. The electrical potential is reduced and the energy barrier is minimized. Essentially, the coagulation process is comprised of two steps, first is the addition of a certain amount of chemical (coagulant) at certain point, and the second step is to disperse this chemical quickly in the bulk water. This is done usually by using mechanical mixers (Sajjad, 1995).

Many studies have described this process and how different parameters can affect coagulation efficiency (Hanson and Cleasby, 1990; Sajjad, 1995). Mixing intensity (speed of mixer), mixing time, mixer geometry and chemical addition sequence are some examples of these parameters studied. Coagulation is often termed as rapid mixing and usually has a short detention time in the rapid mixing tank. Destabilization can have several mechanisms and each coagulant can perform by more than one mechanism. Four well known mechanisms are (O'Melia, 1972):

- Double layer compression
- Adsorption / Charge neutralization
- Enmeshment (Sweep floc)
- Interparticle bridging

Double layer compression can be achieved by increasing the ionic concentration. That is why in saline water the thickness of double layer is small compared to fresh waters (Ravina, 1993). This technique is mentioned as a coagulation mechanism; however, it is impractical to use it in drinking water treatment, because of the large amounts of salts and needed to achieve this goal. Application of such technique can be found in the wastewater treatment (Ravina, 1993). Figure 2-5 shows double layer compression.

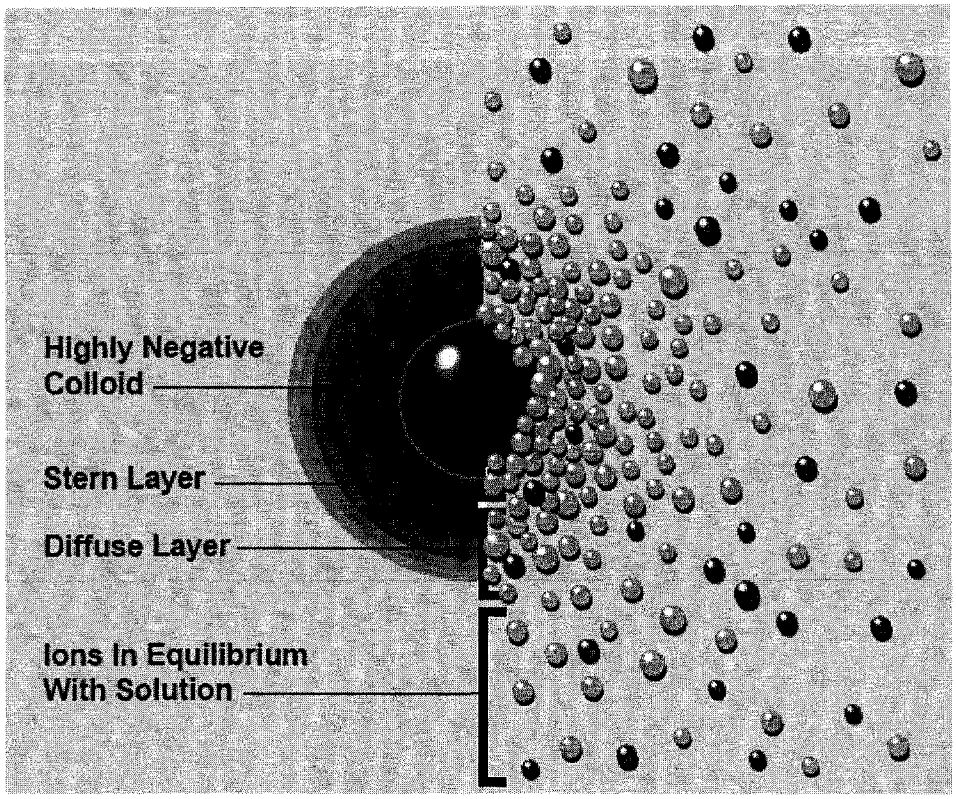

Figure 2-5: Double layer compression (Courtesy of Zeta-meter Inc.)

Charge neutralization occurs when coagulants added to raw water hydrolyze and dissociate and provide positive ions that are dispersed in the bulk water and adsorb onto colloid surfaces (Bagwell et.al, 2001). Due to this neutralization, charge density surrounding the colloids decreases followed by reduction in electrical potential, opening the chance for more collision between adjacent colloids to take place (Bagwell et.al, 2001). Figure 2-6 shows the charge neutralization effect. Aluminum and ferric salts are commonly used coagulants. Alum, which refers to the chemical $Al_2(SO_4)_3.XH_2O$, is an example of those salts which dissociate in water and form a variety of positive ions (Steel and Terence, 1981).

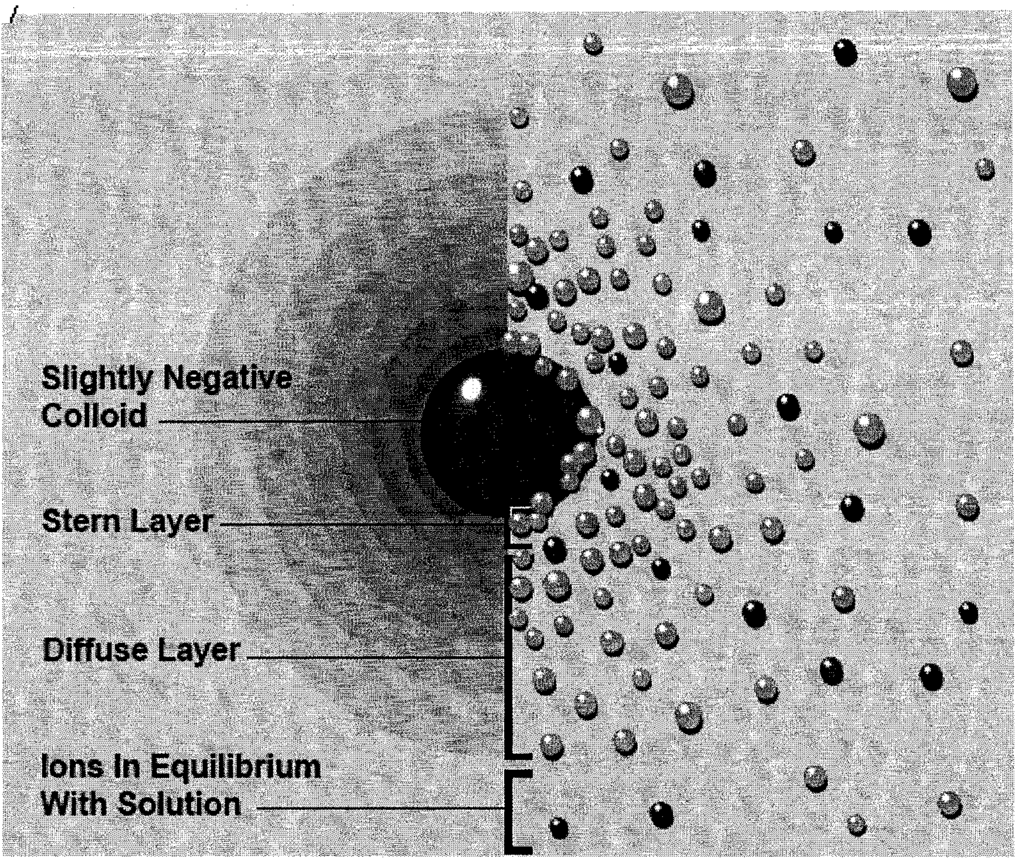

Figure 2-6: Charge neutralization effect (Courtesy of Zeta-meter Inc.)

Lowering charge density by utilizing the charge neutralization technique is one of the most important techniques used in drinking water treatment (Ravina, 1993). Charge neutralization can not only be achieved by using inorganic metal coagulants but also when using cationic polymers. These polymers usually have big molecules and high molecular mass, with positive sites along their surface attracting negatively charged particles which induces neutralization.

Enmeshment or colloids entrapment effectively occurs when chemical reactions produce insoluble compounds such as Al $(OH)_3$. In fact, these compounds are in equilibrium with dissolved positive ions depending on the pH of the water. This mechanism occurs at high concentrations of coagulant dose and high pH. The region for those conditions is called the "sweep floc" region (Hanson and Cleasby, 1990). The precipitated compounds collide and aggregate as they start settling, resulting in water clarification.

Interparticle bridging is mostly related to polymers used either as coagulant aids or as primary coagulants (Steel and Terence, 1981). The effect of colloidal attachment to the polymer molecule could be related to coulomb attraction if the charges are opposite, and to ion exchange, hydrogen bonding and Vander Waals forces in other cases (Bagwell et. al., 2001). Bridging can also be achieved by threads and fibers from large polymer molecules assisting in capturing small sized newly created micro flocs. The net effect is a macro size floc that resembles a chain. Figure 2-7 is a schematic representation for enmeshment and bridging.

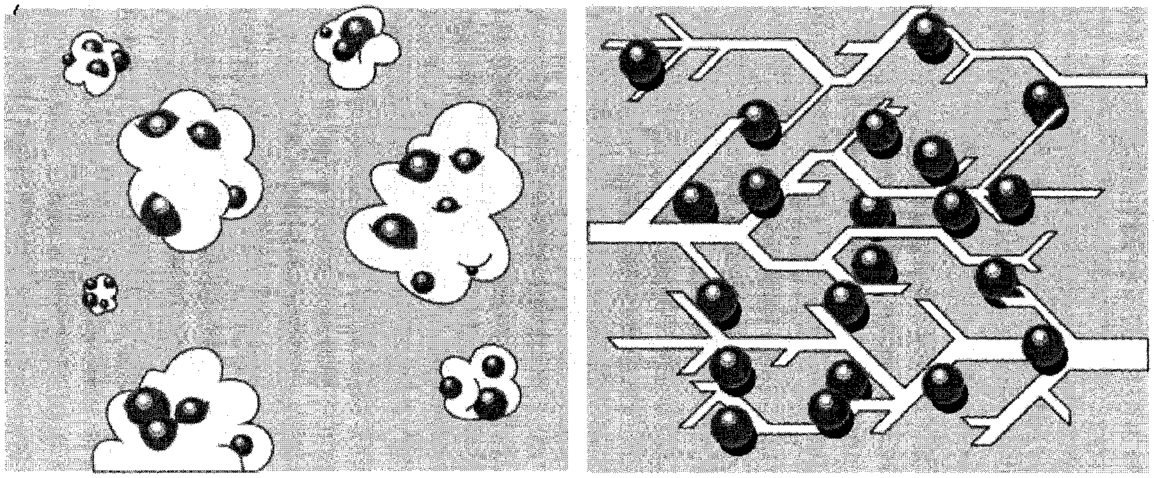

Figure 2-7: Enmeshment and Bridging coagulation mechanisms

2.1.5 Flocculation and particle transport in water

Flocculation refers to the successive collision between stabilized colloids and micro flocs. The result of this process promotes particle growth to the size of a macro floc. Flocs are easily removed either through settling or filtration. The size of macro flocs can be different from one plant to another depending on the operating conditions and incoming water characteristics (Prenitsky, 2001). One study showed agglomerated macro flocs ranging from 10 – 300 μm with the bulk being around 50 -100 μm (Geng, 2005). Particle transport during the flocculation process might have different mechanisms including (O'Melia, 1972):

- Thermal Brownian motion
- Bulk fluid movement induced by mixing
- Differential settling, where fast settling particles collide with slow ones

Collisions induced by thermal motion are often termed as perikinetic flocculation, while those which are induced by the bulk fluid movement are termed orthokinetic flocculation, which results in inter-particle contacts (Binnie et. al., 2002).It is important to understand these mechanisms which may identify the dominant mechanism in the process, which in turn may relate to the particle size as shown in the following equations:

$$J_p = \frac{dN}{dt} = \frac{-4}{3} * \frac{\alpha * B * T * N}{\mu} \qquad 2\text{-}4$$

$$J_o = \frac{dN}{dt} = \frac{-2}{3} * \alpha * G * d^3 * N \qquad 2\text{-}5$$

J_P , J_O are the rates of change of the total particle concentration N with time (t) due to perikinetic and orthokinetic flocculation respectively.

α : Particle – particle collision efficiency factor
B : Boltzman constant
T : Absolute temperature
d : Colloidal particle diameter
G : Mean velocity gradient
μ : Kinematics viscosity

The ratio of the two equations will show the importance of particle size.

$$\frac{J_o}{J_p} = \frac{\mu * G * d^3}{2B * T} \qquad 2\text{-}6$$

If we assume the following conditions: water temperature 25 °C, particle size 1.0µm and mean velocity gradient of 10 sec^{-1} (a typical value in flocculation), then the ratio of rates is equal to 1.0. Accordingly, particles with a diameter less than 1.0 µm exhibit predominantly perikinetic flocculation, thus temperature will influence flocculation of particles with this size or smaller. Particles with diameters more than one micron would exhibit predominantly orthokinetic flocculation (Han and Lawler, 1992).

2.2 Coagulants and their reactions

Understanding the aqueous chemistry after adding coagulants to raw water is considered a key factor in evaluating the performance of coagulants. Metal salts, such as aluminum sulfates and chlorides, ferric sulfates and chlorides are traditional coagulants. When adding these salts into the system, they are dissolute and are injected in a liquid form. A majority of treatment plants use aluminum sulfate due to its availability, low cost, and fair performance in terms of turbidity removal. Recently, polymeric aluminum is believed to have a better performance especially under cold temperatures (Matsui et.al., 1998; Wang et. al., 2002).

2.2.1 Aluminum sulfate (Alum)

Reactions of alum when added to water are too complex to describe fully; however, the main reactions taking place can be summarized as:

1) Dissolution

$$Al_2(SO_4)_3 \longrightarrow 2Al(H_2O)_6^{+3} + 3SO_4^{-2} \qquad 2\text{-}7$$

2) Hydrolysis

In this process, H_2O is replaced in the hydration shell with OH^- ions. Sometimes the H_2O molecule with the aluminum compound can be seen and sometimes it is hidden (Steel and Terence, 1981). Reactions may be written in the following manner (Steel and Terence, 1981):

$$Al(H_2O)_6^{+3} + H_2O \longrightarrow Al(H_2O)_5OH^{+2} + H^+ \qquad 2\text{-}8$$

$$2Al(H_2O)_5OH^{+2} + H_2O \longrightarrow Al(H_2O)_4(OH)_2^{+1} + H^+ \qquad 2\text{-}9$$

Other authors represented $Al(H_2O)_6^{+3}$ as Al^{+3} for simplification purposes and re-wrote hydrolysis reactions as follows (Cotton and Wilkinson, 1980; O'Melia and Dempsey, 1982):

$$Al^{+3} + H_2O \longrightarrow AlOH^{+2} + H^+ \qquad 2\text{-}10$$

$$Al^{+3} + 2H_2O \longrightarrow Al(OH)_2^+ + 2H^+ \qquad 2\text{-}11$$

$$Al^{+3} + 3H_2O \longrightarrow Al(OH)_3 + 3H^+ \qquad 2\text{-}12$$

$$Al^{+3} + 4H_2O \longrightarrow Al(OH)_4^- + 4H^+ \qquad 2\text{-}13$$

3) Polymerization

Products of the hydrolysis step combine to form a variety of polymerized species such as:

$$13Al^{+3} + 28H_2O \longrightarrow Al_{13}O_4(OH)_{24}^{+7} + 32H^+ \qquad 2\text{-}14$$

The compound $Al_{13}O_4(OH)_{24}^{+7}$ is abbreviated as Al_{13}^{+7} (Prenitsky, 2003). Alum chemistry is often described by the presence of Al_{13}^{+7}, $AlOH^{+2}$ and $Al(OH)_4^-$ species which are in equilibrium with amorphous $Al(OH)_3$ solid phase (Van Benschoten and Edzwald, 1990); however, there are many reactions producing different positively charged hydroxy-alumina complexes.

Existence of those alum compounds depends on two factors, concentration and pH value at the time of the dissociation. Alum can work in two different ways; at low turbidity raw waters, high concentrations might be added leading to the formation of $Al(OH)_3$. This compound precipitates, thus working in the sweep floc region and trapping colloids as it settles. In high turbidity raw waters, alum positive compounds would be adsorbed on the negatively charged colloids, and destabilization occurs through a charge neutralization mechanism. Overlap between those mechanisms depends on the characteristics of raw water and operating conditions. It is widely believed that alum does not deliver adequate results under cold temperature (Knock et.al, 1986) compared to other coagulants such as ferric chloride and ferric sulfate and poly aluminum chloride and poly aluminum sulfate. Alum could be the coagulant of choice during the summer (Davis, 1983); while in winter, other alternatives could be used.

2.2.2 Polymers (coagulant aids)

Polymers are increasingly being used due to their ability to enhance and improve water quality. Three categories of polymers are produced. Cationic polymer, which is positively charged, anionic polymer, which is negatively charged and non-ionic polymer and that type do not hold any charges. By using polymer as a coagulant aid, the residual turbidity in the final effluent is reduced. Use of polymers also reduces sludge production (Ammary and Cleasby, 1995). Polymers are characterized by three features: A) molecular weight, B) structure, and C) charge density. Molecular weights have a wide range and can vary from 50,000 – 1,000,000 g/mol (Ravina, 1993). Generally, the higher the molecular mass, the higher the efficiency in performing the bridging mechanism (Ravina, 1993).

Monomers are attached in different ways to form a certain polymer structure; thereby, two polymers with the same molecular weight could have a different structure and performance (Ravina, 1993). Also, some monomers are charged and others are not; a net charge density is created for a certain polymer (Ravina, 1993).

2.2.3 Poly aluminum chloride (PACl)

Polymers are being used extensively since they have been shown to perform well in cold temperatures (Matsui et.al, 1998; O'Melia, 1985). Many countries in Europe and Japan are switching to use PACl coagulation instead of the traditional alum. PACl is produced by adding a controlled amount of a base such as sodium hydroxide to aluminum solutions in the presence of chloride or nitrate ions. Usually an OH / Al ratio between 2.4 – 2.7 is used (O'Melia and Dempsey, 1982). This ratio can characterize the degree of neutralization (r) and determine the basicity of the PACl, (Pernitsky, 2003) where:

$$r = [OH^-] / [Al_T] \qquad 2\text{-}15$$

$$\text{Basicity} = (r / 3) \times 100\% \qquad 2\text{-}16$$

Here the hydroxyl ion [OH⁻] represents the quantity of the base added during the production. The value of (r) can range from 0 to 3 corresponding to basicity of 0 – 100%. Manufacturers produce commercial PACl with the basicity in the range 15-85%; the higher the basicity, the lower fraction of $Al_{13}O_4(OH)_{24}^{+7}$ is present. Basicity value determines alkalinity consumption as well as the amount of polymeric species present (Pernitsky, 2003). As in any chemical reaction, the end product or the final form of the PACl depends on the concentration of aluminum chloride that is used, type and concentration of the base added, solution pH, mixing intensity and finally the time (Pernitsky, 2003).

The predominant species in the commercially produced PACl are primarily $Al_{13}O_4(OH)_{24}^{+7}$ then $Al(H_2O)_6^{+3}$ and colloidal $Al(OH)_3$ (Buffle et. al, 1985, Van Beschoten and Edzwald, 1990). Depending on the species that are dominating the product, PACl can perform destabilization through one of the known mechanisms. For example, if $Al_{13}O_4(OH)_{24}^{+7}$ dominates, then destabilization is through charge neutralization, while if $Al(OH)_3$ dominates, then sweep floc complex precipitation will take place.

Bridging can also be performed if the molecular weight of the produced PACl is high. Manufacturers are producing many types of PACl compounds nowadays, some of them are blends containing PACl, polyamines and other compounds at the same time. These products can be used for different water characteristics; however, no clear molecular structure, charge density and molecular weight are provided by the manufacturers for those products.

2.3 Parameters affecting coagulation/ flocculation process

Coagulation and Flocculation can be affected by many factors including interacting constituents, surrounding environment, kinetics of aluminum hydrolysis and precipitation (Bagwell et.al, 2001). Matsui et.al (1998) reported a required destabilization time of 10^{-5} to 10^{-3} second for hydroxyl-aluminum complexes. This figure may give some indication of how fast hydrolysis reaction occurs, and accordingly how they might be influenced instantaneously by the operating conditions.

2.3.1 Controllable parameters

These parameters are under the control of the treatment facility operators and thus can be manipulated to overcome any changes in raw water characteristics.

A) Coagulant dose:

Regardless of the type of the main coagulant, dose can be increased or decreased according to the incoming turbidity type and level. The general trend is increasing dose with higher turbidities and low temperatures (Budd et.al, 1997). If an excess dose of alum is applied, then very slight or no improvement to turbidity removal may be observed (Morris and Knock, 1984). In addition, higher amount of coagulants produces the adverse effect by generating extra sludge that needs to be treated later (Ammary and Cleasby, 1995). Figure 2-8 is a scatter plot for incoming turbidity vs. alum dose for the WWTP.

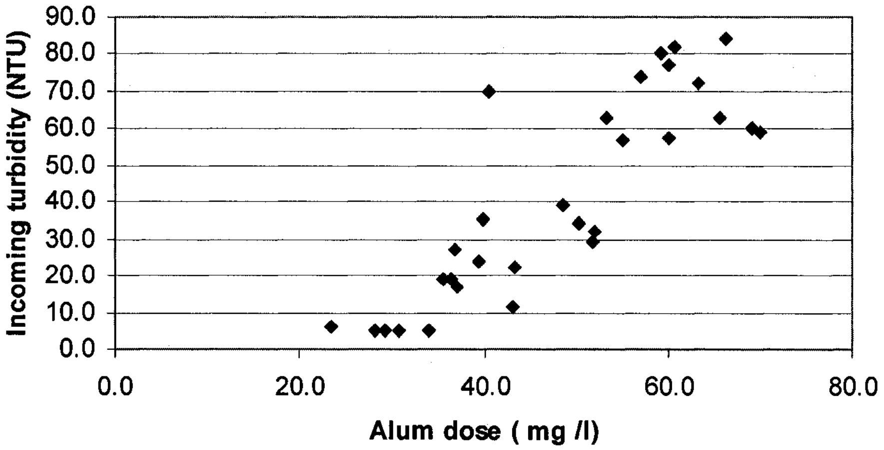

Figure 2-8: Addition of alum with increasing incoming turbidity level.
Source: WWTP. Data for November 2005

B) Coagulant aid dose

Coagulant aids are used to enhance and improve the CF process. Their main function is to establish the bridging mechanism, and therefore, it is more aiding flocculation rather than the coagulation stage. Coagulant aids are added in small concentration; however, their effect on the final turbidity levels is considerable. Additionally, they can lead to the reduction of concentration for the main coagulant. Coagulant aid role could be considered as complementary to the main coagulant (Ammary and Cleasby, 1995).

Several types of coagulant aids are used, such as activated silica. It consists of a preparation of colloidal sodium silicate which can act as coagulant by itself or as a coagulant aid when used with alum by establishing bridges (Steel and Terence, 1981). One drawback is that the material must be prepared continuously because of rapid aging of the coagulant aid solution leading to gel within a matter of hours. Usage of activated silica may expand the pH range for effective coagulation, produce larger and tougher flocs, and increase color removal (Steel and Terence, 1981).

Polyelectrolytes (polymers) now are widely used as coagulants aid because of their large molecule size. The bridging mechanism is effective, producing a floc size up to 100 times greater than those produced by using metallic coagulants alone (Steel and Terence, 1981). The optimum combinations and/or ratios for coagulant to coagulant aid are not always known. This varies according to the nature of the chemicals and raw water characteristics, as well as their interactions.

C) Coagulation (rapid) mixing intensity & G-value

The importance of the rapid mixing intensity and its effect on the coagulation / flocculation process is often overshadowed by chemical overdosing in treatment plants (Sajjad, 1995). This parameter can play a major role in the CF process due to the ability of the operators to change mixing speed and time, consequently the energy that is imparted to the water changes. Rapid mixing provides the required kinetic energy to particles to overcome the energy barrier and allow the collision between colloids.

Hudson (1981) suggested various mixing times during rapid mixing. The suggested values ranged from 0.5- 5.0 minutes. During rapid mixing, not only dispersion of the coagulant in the raw water is carried out, but also it brings about the initial stage of particle collisions and subsequent aggregation. These aggregates act as the nuclei for further growth. It should be pointed out that for every set of conditions there is an optimum rapid mixing intensity (Ammary and Cleasby, 1981). A relation is developed between the velocity gradient (G-value) and speed of mixing as shown:

$$G = a\,S^{b} \qquad 2\text{-}17$$

Where G is the velocity gradient sec $^{-1}$; S is the speed of mixing in (r.p.m); (a) and (b) are constants and they are temperature dependent, and for a specific impeller geometry. Above equation is for two blade turbine impeller at 23 °C (Sajjad, 1995).

It has been reported (Ghosh et.al, 1985) that G-values between 300 and 1000 sec $^{-1}$ proved to be optimum for cationic polymers, while Mc Bride et al. recommended 1000 sec $^{-1}$ to be used with a combination of alum and cationic polymer.

D) Flocculation (slow) mixing intensity and mixing regime

Flocculation often refers to the successive collisions of destabilized colloids and/or microflocs required to promote particle growth. During this stage, sweep floc and bridging mechanisms take place; therefore, the mixing speed is different from that for coagulation. G- values between 10 -60 sec $^{-1}$ for conventional flocculation are typically used in this stage (ASCE & AWWA, 1998).

Because of multiple basins in the flocculation stage, and subsequent different mixing patterns, tapered mixing speeds are implemented. This entails gradual decrease in the mixing speed, which allows the microflocs to develop into macro-flocs, development of bridging between the macro-flocs, and maintenance of the flocs at the biggest possible size. Choosing the appropriate mixing regime by the treatment facility may improve the CF process.

E) Mixer type

Mixing in the CF process can be varied by either changing mixer type or the mixing pattern in time and intensity. Researchers found that different impeller geometry can make the flocculation process more efficient with respect to power input, while others (Sajjad, 1995; Hanson and Cleasby, 1990) found that there is a significant impact on flocculation kinetics, which may be explained by the relationship between the impeller shape and G-value imparted to water.

F) Residence time

Residence or detention time is defined as:

$$\tau = \frac{V}{Q} \tag{2-18}$$

Where V is the volume of the basin, and Q is the volumetric flow rate going into that basin. When the treatment facility encounters problems, and since the physical geometry can not be changed for the existing basins, increasing residence time can only be made by decreasing hydraulic loadings for the plant. Production capacity will be affected, but sometimes it is necessary to take such a measure in order to meet required specifications for effluent water and comply with regulations.

2.3.2 Uncontrollable parameters

Parameters not under the control of the treatment plant operators may refer mainly to the characteristics of the incoming raw water (sometimes referred to as the nature of raw water); this characteristic is location specific and it can change widely from one place to another. The treatment techniques, chemicals used and concentrations may have different results when applied to various treatment facilities. The main features that are common to all types of raw water are:

1) Alkalinity and pH

Alkalinity by definition is the measurement of water buffering capacity to neutralize any acidic solution added to water. Alkalinity may refer to the presence of bicarbonate (HCO_3^{-1}), carbonate (CO_3^{-2}) and also hydroxide in natural waters and it is measured as $CaCO_3$. Alkalinity is essential to make the reaction with alum occur and let the coagulation mechanisms proceed. During the process alkalinity is consumed by added coagulants (Tseng et.al, 2000).

Since most coagulants and coagulant aids are acidic in nature, alkalinity is consumed and pH value decreases for two reasons, bicarbonate consumption and carbonic acid formation as shown in the reaction below (Ravina, 1993).

$$Al_2(SO_4)_3 + 3Ca(HCO_3)_2 + 6H_2O \longrightarrow 3CaSO_4 + 2Al(OH)_3 + 6H_2CO_3 \qquad 2\text{-}19$$

Natural waters have different alkalinities; thereby the effectiveness of the chemical reaction which takes place can vary accordingly. The pH of natural raw waters also changes from one place to another. Normally it varies from 6 – 8.5, and it is related to alkalinity as well. The pH plays a vital role in the reaction kinetics; most of the treatment facilities using alum are adjusting raw water pH by either adding acidic solutions or CO_2 gas. Lower pH values, between 5.5- 7.5 (ASCE &AWWA, 1998), can be used to keep positive hydroxy - alum hydrolyzed species in the coagulated bulk water.

Higher pH values would give a chance for $Al(OH)_3$ to form and precipitate. From the above discussion it can be seen that the pH values can dictate the coagulation mechanism. Generally, it is not permitted to have final pH value of the treated water well below 7.0 in order to avoid problems caused by acidity in the distribution network.

2) Turbidity

Turbidity is the measure of relative clarity of water caused by suspended and colloidal matter, such as clay, silt, and finely divided organic and inorganic matter. Also, it can include biological organisms such as algae, cyanobacteria, zooplankton, and filamentous or macro bacterial growths. Guidelines have been set by Health Canada to reduce turbidity in treatment facilities as low as possible, depending on the treatment type and technology used as follows (Health Canada, 2006):

- For chemically-assisted filtration, shall be less than or equal to 0.3 NTU in at least 95% of the measurements made, and shall not exceed 1.0 NTU at any time.
- For slow sand or diatomaceous earth filtration, shall be less than or equal to 1.0 NTU in at least 95% of the measurements, and shall not exceed 3.0 NTU at any time.
- For membrane filtration, shall be less than or equal to 0.1 NTU in at least 99% of the measurements made, and shall not exceed 0.3 NTU at any time (Health Canada, 2006).

Turbidity is not a direct measure of suspended particle concentration in water but it is rather the measure of the scattering effect that such particles have on light. Because several factors affect the intensity of light scattering, such as size, distribution, shape, refractive index and adsorptive capacity of the particle, it might not give a precise measurement every time.

Turbidity measurements are very widely used as a good indicator of water quality. Species causing turbidity might have different implications for raw water quality; inorganic particles such as silt, clay, and natural precipitants, e.g., $CaCO_3$, MnO_2, Fe_2O_3, might raise or lower pH and alkalinity, be sources of micronutrients and affect zeta potential (Health Canada, 2006). While organic particles such as decomposed plant and animal debris and humic substances, might be sources and supply energy for micro-organisms, impart taste and odor, serve as precursors for the formation of chlorinated or ozonated compounds, might form complexes with toxic elements, affect pH and finally might shield colloids (Health Canada, 2006). The presence of organic materials may result in high disinfectant demand, high coagulant dose and reduced filter run time. Finally, biological species such as algae and zooplankton may impart taste and odor, be a disease carrier, and corrode tanks and pipes. The presence of biological species may have some implications on the treatment process and can block filters.

3) Particle size distribution and charge density

Properties of particles, such as size, shape, density, porosity, charge density may influence their interactions with the added chemicals. Among those, size might be considered crucial in stabilizing colloids in waters (Geng, 2005).

Particle removal efficiency can be monitored by using several measurement techniques such as turbidity, conductivity and particle counting. Today, instruments can analyze particles in the nanometer range which gives a more thorough indication of the particle distribution and its nature. This can assist treatment facilities in selecting the appropriate coagulant(s).

4) Temperature

Raw water in rivers and lakes experiences drastic changes in temperature during the year. This can have a direct impact on several water properties. A classification of temperature ranges was made in the following manner (Womba et.al, 2001):

- Temperature < 4°C [Cold water]
- 4 °C > Temperature < 14 °C [Cool water]
- Temperature > 15°C [Warm water]

In the range between 0 and 22 °C, where most of the treatment facilities in Ontario work, water density varies between 0.999 and 0.0997 g/mL, which is a change of only 0.2%. Over this range, the dielectric constant changes from 88.026 to 79.463, and this reflects a change of 10%. The physical property which significantly changes with the change in temperature is water viscosity. In the above temperature range, dynamic viscosity will change from 1.7921 to 0.9608 cP (Chapra, 1997), which is a change of 46%. Figure 2-9 shows the effect of temperature on water physical properties. Changing viscosity by such a high percentage will have an impact on zeta potential, required energy for mixing the bulk of water, and particle settling velocity. The CF process efficiency will be impaired, resulting in an observed deficiency.

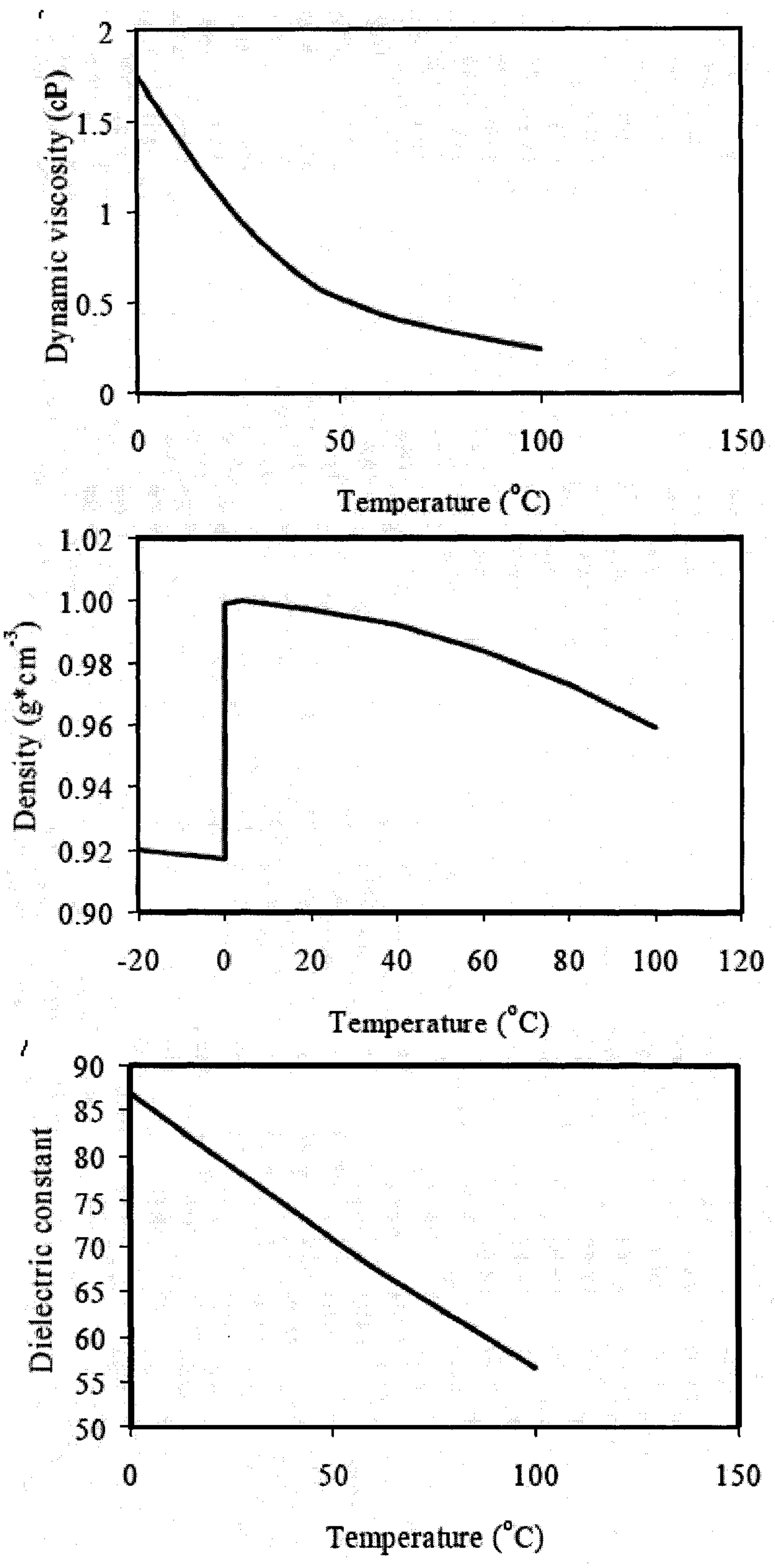

Figure 2-9: Water physical properties change with temperature (Heinanen, 1987)

2.4 Temperature effect on different parameters

The temperature effect has been studied by several researchers (Mohtadi and Rao, 1973; Morris and Knock, 1984; Hanson and Cleasby, 1990; Ammary and Cleasby, 1995; Kang and Cleasby, 1995; Sajjad, 1995; Wobma et.al, 2001; Pernitsky, 2003) and each of them added more understanding to the CF process phenomena under cold temperatures. Most of them used synthetic water and chose two temperatures, one high, and the other low to study the effect on kinetics, solubility, fluid dynamics, settling rate, mixing regime and filtration time.

2.4.1 Effect on solubility

Generally, solubility such as solid- liquid, liquid-liquid and gas-liquid are affected and they decrease with lowering of temperatures (Bagwell et.al, 2001). The CF process and the solubility of the coagulant follow this general rule. Coagulant solubility (dissociation) is the first step in a series of chemical reactions and reducing it may affect the whole process efficiency. At the time of adding the coagulant, pH for the bulk solution plays a vital role in solubility and can direct solubility products either to have the positive hydroxy – aluminum ions which neutralize charge, or aluminum hydroxide precipitates which are active in the sweep floc (enmeshment) mechanism. Solubility graphs often illustrate different aluminum species against pH (Hanson and Cleasby, 1990; O'Melia and Dempsey, 1982; Pernitsky, 2003).The following equations show how the relations between them and pH are developed based on Table 2-1 shown below.

Table 2-1: Aluminium ions solubility constant (Pernitsky and Edzwald, 2003)

Chemical reaction	Equilibrium expression	pK (20 °C)	pK (5 °C)
$Al^{+3}+H_2O= Al(OH)^{+2}+H^+$	$K_{11}=[Al(OH)^{+2}][H^+]/ [Al^{+3}]$	5.12	5.65
$Al^{+3}+2H_2O= Al(OH)_2^{+}+2H^+$	$K_{12}=[Al(OH)_2^{+}][H^+]^2/ [Al^{+3}]$	10.45	11.56
$Al^{+3}+4H_2O= Al(OH)_4^{-}+4H^-$	$K_{14}=[Al(OH)_4^{-}][H^+]^4/ [Al^{+3}]$	23.57	25.33
$Al(OH)_{3(S)}= Al^{+3}+ 3OH^-$	$Ksp = [Al^{+3}] [OH^-]^3$	31.67	32.4

$$Al(OH)_{3(S)} \longrightarrow Al^{+3} + 3OH^{-1} \qquad 2\text{-}20$$

$$K_{SP} = [Al^{+3}][OH^{-1}]^3 \qquad 2\text{-}21$$

$$\log K_{SP} = \log[Al^{+3}] + 3\log[OH^{-1}] \qquad 2\text{-}22$$

$$\log[Al^{+3}] + 3(pH - 14\ ) = -31.6 \qquad 2\text{-}23$$

$$\log[Al^{3}] = 10.33 - 3pH \qquad 2\text{-}24$$

$$Al^{+3} + 4H_2O \longrightarrow Al(OH)_4^{-1} + 4H^{+1} \qquad 2\text{-}25$$

$$K_{14} = [Al(OH)_4^{-1}][H^{+1}]^{+4} /[Al^{+3}] \qquad 2\text{-}26$$

$$\log K_{14} = \log[Al(OH)_4^{-1}] + 4\log[H^{+1}] - \log[Al^{+3}] = -23.57 \qquad 2\text{-}27$$

Substituting equation 2-24 into 2-27

$$\log[Al(OH)_4^{-1}] = pH - 13.91 \qquad 2\text{-}28$$

$$Al^{+3} + H_2O \longrightarrow Al(OH)^{+2} + H^{+1} \qquad 2\text{-}29$$

$$K_{11} = [Al(OH)^{+2}][H^{+1}]/[Al^{+3}] \qquad 2\text{-}30$$

In the same fashion equation 2-24 is substituted into equation 2-30

$$\log[Al(OH)^{+2}] = 5.21 - 2pH \qquad 2\text{-}31$$

Figure 2-10 shows the concentration as a function of pH, and trend lines are plotted based on the above equations. PACl is more soluble than alum, when basicity is increased the pH for minimum solubility increases for different types of PACl. Since PACl can work in a higher pH range, acidification of raw water could be avoided. Testing of alum and PACl at two different temperatures (20 and 5 °C) showed that solubility is reduced considerably for both compounds. Alum solubility drops from 16 to only 3µg/L, while for PACl at high basicity, the solubility drops from 52 to 5 µg/L (Pernitsky, 2003).

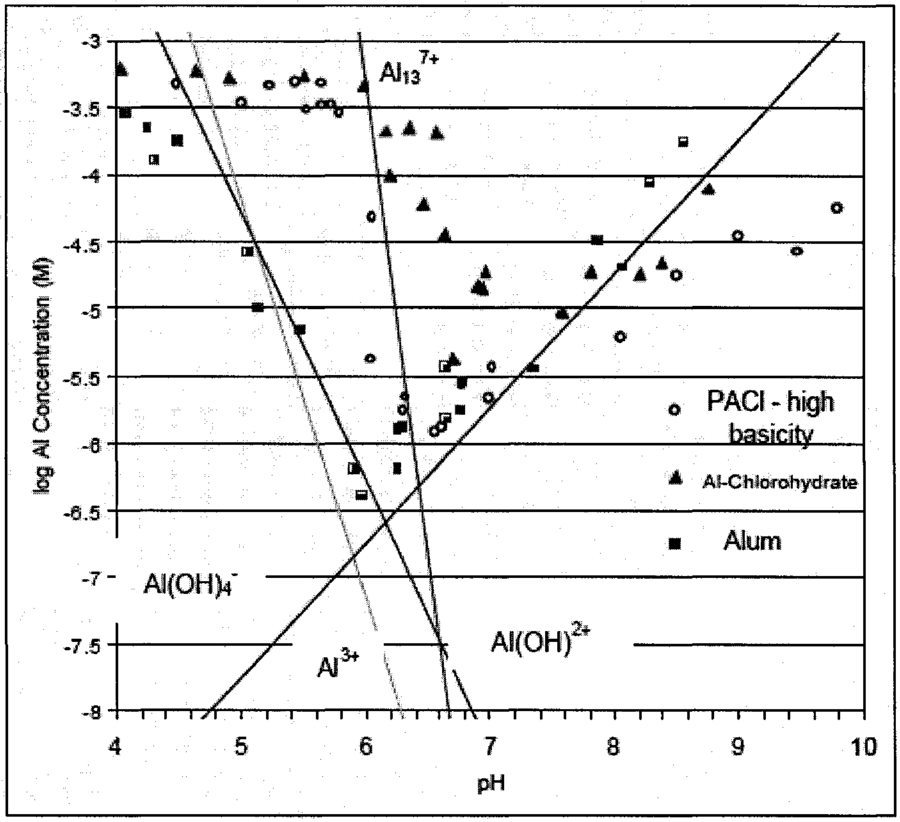

Figure 2-10: Solubility of various aluminium species (Pernitsky, 2003)

2.4.2 Effect on reaction rate

Chemical reactions are the key factor for efficient CF process and any retardation will have its direct impact on the process. By reducing the temperature by 10 °C, the reaction rate is reduced to half of its original value (Chapra, 1997). This is illustrated by the taking the ratio for *Arrhenius* equation at two different temperatures, as follows:

$$K_{(T)} = A * e^{\frac{-E}{RT}} \quad \text{or} \quad \ln K_{(T)} = \ln A - \frac{E}{R*T} \qquad \text{2-32}$$

$K_{(T)}$: Reaction rate constant
A : Pre-exponential or frequency factor (mole / sec)
E : Activation energy (J /mole)
R : Ideal gas constant (8.134 J/mole. K)
T : Absolute temperature (K)

$$\frac{K(T_2)}{K(T_1)} = e^{\frac{E(T_2-T_1)}{RT_2T_1}} \qquad \text{2-33}$$

$$\theta \equiv e^{\frac{E}{RT_2T_1}} \qquad \text{2-34}$$

$$\frac{K(T_2)}{K(T_1)} = \theta^{(T_2-T_1)} \qquad \text{2-35}$$

Values for θ can range between 1.024 and 1.08 depending on the type of chemical reaction taking place (Chapra, 1997). Researchers tend to believe that reaction rate is the dominating factor (Kang and Cleasby, 1995). Mixing patterns and intensities have been well studied; nevertheless they are not as important as reaction kinetics. When reactant molecules in a slow reaction are uniformly distributed throughout the system, the speed of reaction (reaction rate) would not change radically because the rate is controlled by the thermodynamic conditions (Sajjad, 1995).

The result of the CF reactions is the formation of flocs with different size and strength. Studies on floc strength showed that internal binding forces for macro flocs are affected by temperature. The floc strength was measured at two temperatures by comparing the particle size distributions for various floc samples after floc breakup with an impeller. Alum flocs at 5 °C were much weaker than those at 20°C; also floc size was smaller (Hanson and Cleasby, 1990; Morris and Knock, 1984). Slower rate of floc formation was observed at lower temperatures especially for low turbidity levels (Kang and Cleasby, 1995). At a temperature of 3.3 °C, slow formation was pronounced (Hutchison and Foley, 1974).

2.4.3 Effect on velocity gradient

Velocity gradient (G-value) is a very important parameter and plays a significant role in the coagulation of colloids. It affects the growth of microflocs in the flocculation stage. There is an optimum G-value for each process. In engineering application the product of G-value times the residence time (Gt) is used in a specified flocculation basin to describe the operating conditions. Typical values for G or Gt can be found in different references such as those published in the American Society of Civil Engineers and the American Water Works Association (1998). Practical values for a particular treatment plant depend on the operating conditions and characteristics of raw water. If G-value is more than required, that could lead to flocs breakup. If it is appropriate then colloids would jump over the energy barrier and aggregation will takes place.

$$G = \left(\frac{P}{\mu V}\right)^{\frac{1}{2}} \qquad \text{2-36}$$

P = power applied to a mixed tank in Watts
V = tank volume in m^3
μ = Dynamic viscosity of water N-s/m^2

Equation 2-36 shows the relationship between velocity gradient and power input and water viscosity. Power requirement is related to speed of mixing. A plot can be developed between G- value and speed of mixing in r.p.m as shown in Figure 2-11. For a given volume of water and velocity gradient, a 50% reduction in water temperature would increase the water horsepower approximately two times (Viraraghavan and Mathavan, 1988) as shown in the Table 2-2. Increasing mixing time sometimes could compensate for low temperature deficiency; however, production capacity will be reduced.

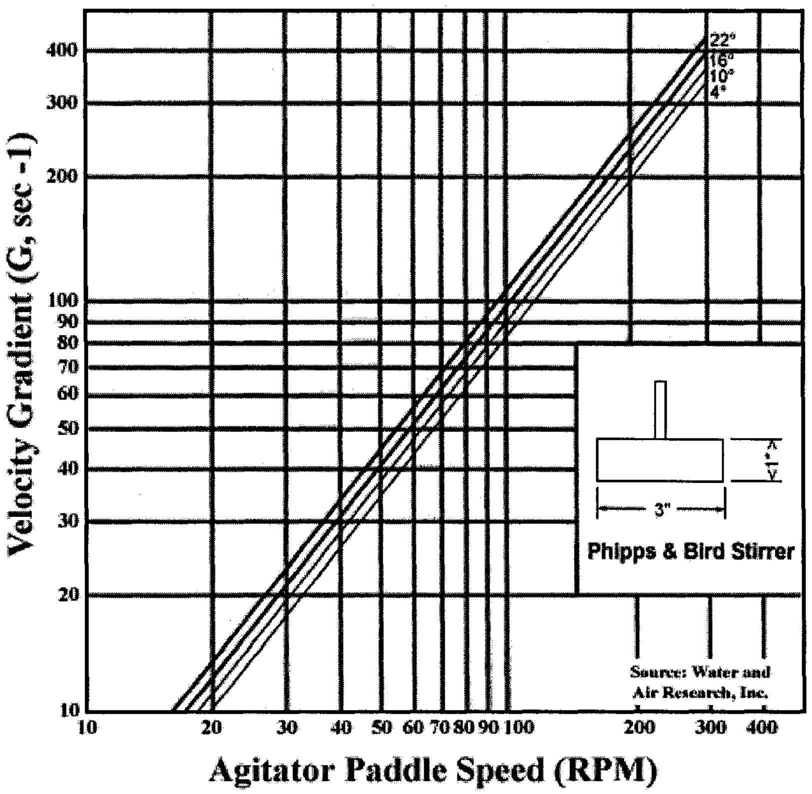

Figure 2-11: Relation between mixing speed and velocity gradient at different temperatures. (Courtesy of Phipps and Bird Inc.)

Table 2-2: Temperature and power relationship (Nomographs on velocity gradients, 1978)

Viscosity (lb-S/ft^2)	Temperature (°F)	Volume (ft^3)	Velocity gradient (1/ S)	Horse power (HP)
1.80E+05	80	300000	15	2.2
3.30E+05	40	300000	15	4.3
1.80E+05	80	20000	100	6.8
3.30E+05	40	20000	100	12.5

2.4.4 Effect on flocculation and filtration

Filtration is effected by low temperatures to the extent that head losses through the filters are proportional to viscosity (Viraraghavan and Mathavan, 1988). The relative increase in head loss in the filters is around 3.5% per degree centigrade temperature change. If the temperature decreases from 20 to 5 °C, the head loss might increase from 1.0 to 1.5 m. It is reported that the use of multimedia might be more efficient at low temperatures (Smith, 1986); also, the energy required for equal filtration rates doubles when the temperature changes from 25 to 0 °C. Filtration time was evaluated in a pilot testing program in Winnipeg (Womba, 2001); the results showed a steady decrease in filtration time as the temperature increased. Duration of 13.3 minutes was needed for cold temperatures < 4 °C while only 8.4 minutes was needed for temperature > 15 °C.

2.5 Summary

The theoretical background and the fundamentals of the coagulation /flocculation process for drinking water treatment have been discussed. The parameters that affect the CF process are classified into controllable, which is within the control of the treatment facility, and uncontrollable parameters. As temperature of raw water is one of the uncontrollable parameters, seasonal variations of temperature, especially in water viscosity, play a role in the reduction of treatment efficiency occurring during winter time. The deficiency is measured in terms of reduced turbidity and TOC removal, as well as in duration of flocculation and filtration run time. Coagulant performance for alum and PACl has been discussed. During winter time PACl out-performed alum in terms of turbidity removal, and sludge generation. Among many conditions that are affected by low temperature, solubility, reaction rate and power requirements have been reviewed.

3 MATERIALS AND METHODS

In this chapter a bench scale experimental set up is described. All the materials and equipment that had been used are specified. Raw water characteristics and chemical preparations are cited and operating conditions for each phase of the work are defined. Initial and final water quality was determined by using analytical instruments. Methods of their use for analysis are described.

3.1 Raw materials

Raw materials consisted of the natural raw water and the coagulants and coagulant aid that had been used during the work.

3.1.1 Raw water

During the course of this work three batches of raw water were collected from the main raw water pipe for WWTP; those batches and their characteristics are shown in Table 3.1. A total of 450 liters of water were collected by using six buckets of size 25 liters; the buckets had a wide circular opening to enable easy filling, transfer and mixing of water. Raw water in those buckets was stored in a cold room at 4.0 °C in the university; and before transferring raw water from the buckets to the jars, it was homogenized using a locally manufactured mixer tailored to fit the size and shape of the bucket.

Table 3-1: Collected raw water specification

Batch #	Date	Avg. turbidity (NTU)	pH	Raw water temperature (°C)
1	Nov.8, 2006	9	8.1	6.8
2	Dec.6, 2006	40	8.2	2.4
3	Jan.23,2007	36	7.95	0.3

3.1.2 Chemicals

Coagulants and coagulant aid were collected from the treatment plant. They were industrial grade, while sulfuric acid used to adjust raw water acidity was analytical grade. Aluminum Sulfate (alum) was collected in 500 ml plastic bottles from the main feeding tank in the treatment plant, and it was used in a liquid form. It has the chemical formula $Al_2 (SO_4)_3.14H_2O$ and manufactured by General Chemical Performance Products Ltd, Mississauga, Ontario. It is a colorless solution with a specific gravity of 1.33, pH of 2.5 and molecular weight of about 549 g/mol. It should have a very good solubility in water and generally it is a stable solution; however, shelf live should not exceed 2 months.

The Polymer used as a coagulant aid has a product name (Magnafloc LT-22). It belongs to the chemical family called (quaternary acrylate salts and acrylamide), manufactured by Ciba Specialty Chemicals Corporation, VA, U.S.A. It is originally delivered as a white granular powder and then dissolved in water and fed as a solution at the treatment plant and also in our experiments. Magnafloc LT-22 has a specific gravity of 0.8 -1.0, pH of 3.3 and its solubility is limited by viscosity. Shelf live should not exceed 2 months.

The PACl blend used has the commercial name (Sumaclear- 750) manufactured by Summit Research Labs. It is in a liquid form and collected using a 500 ml plastic bottle from the main feeding tank. Basically, the blend consists of poly aluminum chloride, polyamines, and poly diallyldimethyl ammonium chloride. It has a yellowish color with a specific gravity of 1.3 – 1.36 and pH < 4, and it has a very good solubility in water. Generally, the blend is stable but if thermal decomposition occurs, it might release hydrogen chloride gas or chlorine vapors.

3.2 Analytical methods

The parameters that had been monitored during the course of the work were temperature, turbidity, pH and TOC. Standard Methods for the Examination of Water and Wastewater, 20th edition, were followed for most of the analysis (APHA, AWWA, and WEF, 1998).

3.2.1 Turbidity

Standard Methods 2130 B - Nephelometric method was followed for the turbidity measurement. Reference turbidity solutions of 1.8 and 18 NTU were purchased and used for calibrating the turbidimeter. Instrument model Hatch Ratio/XR turbidimeter was used. The instrument has four different scales 0-2, 0-20, 0-200, and 0-2000 NTU. The accuracy for the device is within ±2% of full scale. The appropriate scale was selected when doing the measurements to give the most accurate reading. Sample measurements were taken three times and the average value was reported to the nearest 0.1 NTU. To avoid condensation on the outer surface of the sampling tube, it was carefully dried and cleaned before making the measurements.

3.2.2 pH

pH measurement followed Standard Methods 4500- H^+ B. Calibration was done with a buffer solution having a known pH value. Analysis was conducted with pH meter model 8100 manufactured by VWR Scientific Products with Symphony probe. Measurements of pH may take a few minutes, thereby a supporting piece was manufactured to hold the probe; at the same time thorough mixing for the water in the jar was established by using a magnetic stirrer. Figure 3-1 shows the setup.

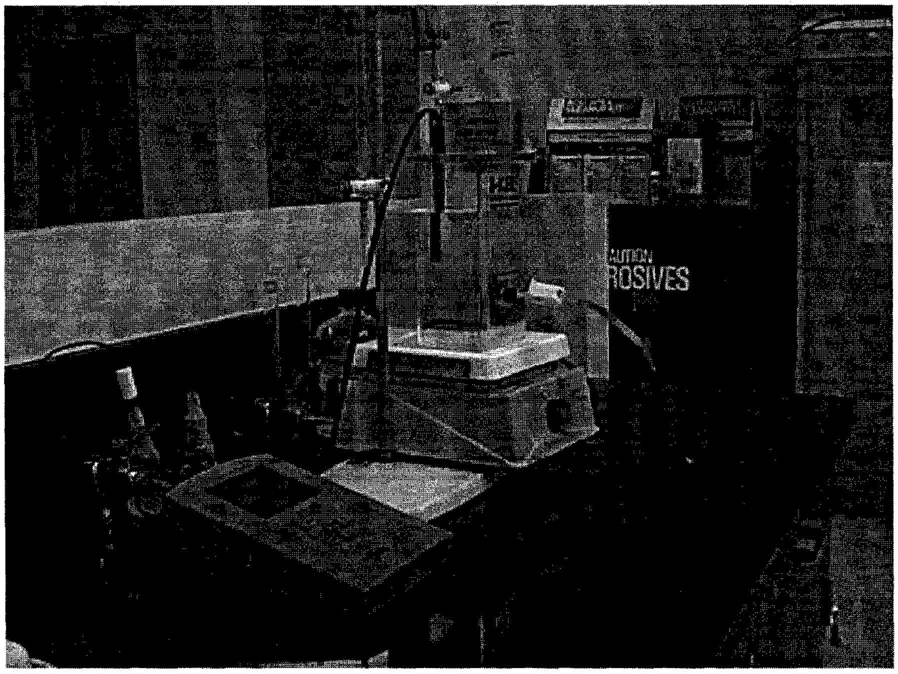

Figure 3-1: pH measurement setup

3.2.3 Temperature

Temperature measurements were conducted according to Standard Method 2550B. Readings were recorded utilizing three instruments, a regular thermometer, and a portable digital thermometer, which is designed in a way that its operating battery is not affected under cold temperatures; and finally, another digital thermometer, which is part of the incubator, and can be read from the outside front panel. Deviation between those instruments is ± 0.5 °C. Temperature measurements were taken twice for each jar and the average value was reported to the nearest 0.1°C.

3.2.4 Total Organic Carbon

Total Organic carbon (TOC) was measured according to Standard Method 5310 B High-temperature combustion method. A calibration curve was prepared using the multi point calibration method. 1000 mg C/L of total carbon stock was prepared. The calibration curve was checked with one secondary standard that was diluted from the stock solution. A TOC analyzer model TOC-VSH manufactured by Shimadzu Corporation was used. A 50μL sample is drawn from the aqueous raw or treated water and three measurements for the same sample were taken each time. A non-purgable organic carbon (NPOC) mode was used, where sample is acidified by phosphoric acid H_3PO_4, and then nitrogen purging for 3 minutes to take out inorganic carbon.

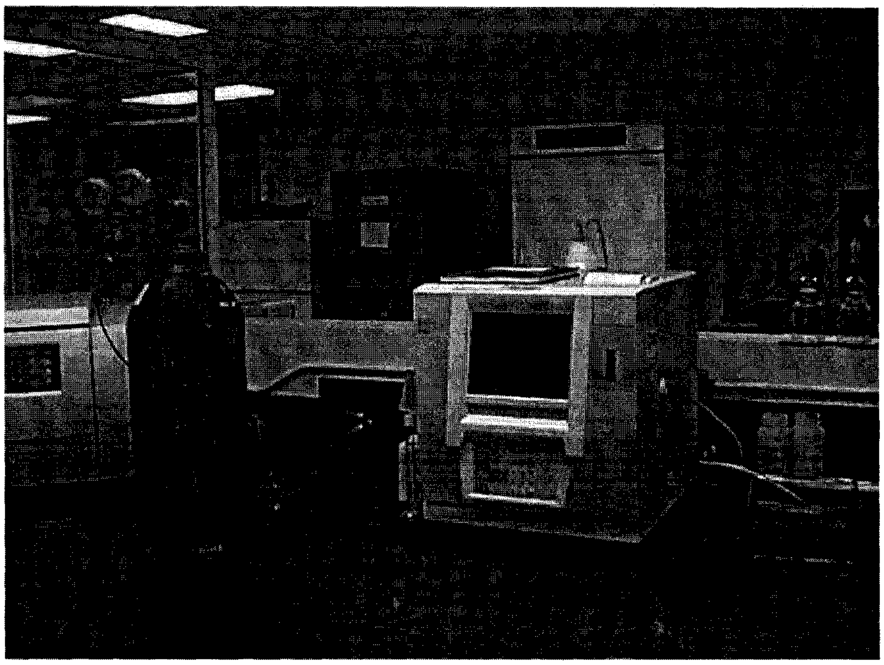

Figure 3-2: TOC analyzer

3.3 Experimental setup and chemical solutions preparation

This section describes the main equipment setup and the preparation for the chemicals used in the experiments.

3.3.1 Equipment setup

Two main pieces of equipment were used for the experiments; the incubator, which provides temperature control and the jar test apparatus to simulate the coagulation and flocculation process.

The incubator was used to stabilize the raw water to the required temperature before conducting the run, and to maintain the temperature unchanged inside during the run. It has a temperature control of ± 0.5°C and can be used efficiently down to 1.0°C. It is provided with an internal electrical outlet to enable operating a device while it is completely closed. The incubator was manufactured by Sheldon manufacturing Inc., Oregon, and model 2020.

The jar test apparatus was used to run the experiments with four jars. The supporting steel structure was modified in order to fit inside the incubator. Jar size and shape are shown in Figure 3-3. The apparatus was manufactured by Phipps and Bird Inc., and is a model 7790-100 HS-4, with two-liter acrylic type B-KER^{2}square jars. The sampling port located at 10 cm from the 2.0 liter mark at the top is available to easily draw off samples. The apparatus is provided with four stirrers, each with a two blade turbine type impeller. Also, the apparatus is provided with a speed controller from 0 – 315 r.p.m; it can establish a convenient way to adjust the speed of mixing for each of the coagulation and flocculation stages. The jar test set up is shown in Figure 3-4.

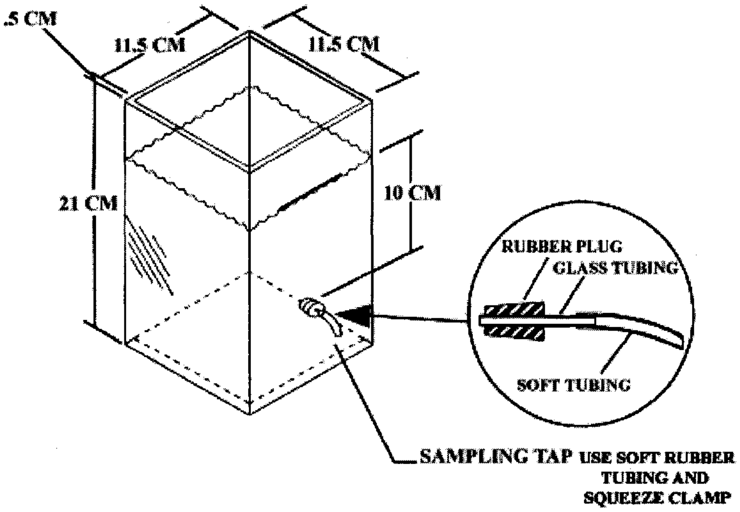

Figure 3-3: Dimensional drawing for B-KER^2 two litre jar.

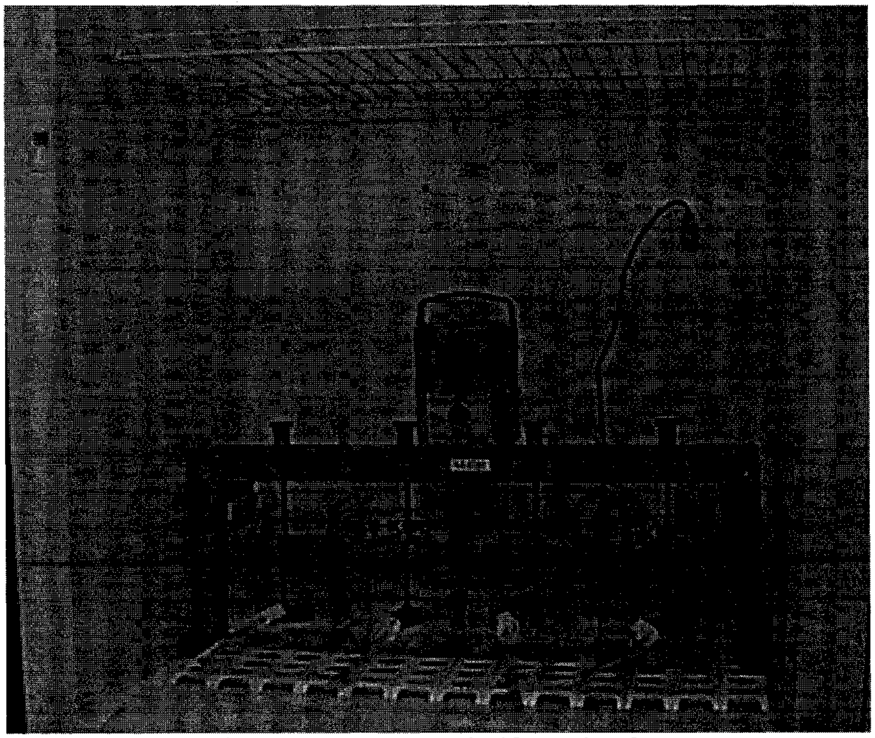

Figure 3-4: Jar test apparatus inside the incubator

3.3.2 Working solutions preparation

The preparation work included the following:

- Preparation of alum working solution (1000 mg/Liter)

By using a micro pipette, 0.8 ml of concentrated alum was added to 1.0 liter volumetric flask and filled up to 1000 ml mark with distilled water; the flask was well shaken to enable good mixing. Each 1.0 ml of working solution is equal to 1.0 mg/L of alum used in our test. The prepared solution was used within 1- 2 days.

- Preparation of polymer (Magnafloc LT-22) working solution (10 mg /liter)

The polymer was supplied as a powder; thereby 1.35 kg of powder was dissolved into 900 liters of water at the treatment plant to have a liquid with 0.15% concentration. Then, 6.7 ml of that solution was added to a 1.0 liter volumetric flask and filled up to the1000 ml mark with distilled water; the flask was well shaken to ensure good mixing. Every 10 ml of working solution is equivalent to 0.1 mg /L of polymer. The prepared solution was used within 1- 2 days for the intended experiment.

- Preparation of PACl blend (Sumaclear – 750) working solution

Since the specific gravity for Sumaclear -750 is almost the same as alum, the same procedure was adopted to prepare the working solution for our experiments, and each 1.0 ml of working solution was equal to 1.0 mg/L.

- Preparation of 0.1 Normal sulfuric acid

Standard methods for examination of water and wastewater were used. The concentrated sulfuric acid was 96- 98 % by weight H_2SO_4 and specific gravity of 1.83. A volume of

2.8 mL was added to a 1.0 liter volumetric flask and diluted with distilled water up to the1000 mL mark.

3.4 Selection of operating parameters

The selection was based on gathered information from the literature and the procedure used in the lab of the WWTP. Selected parameters included temperature, dosages for coagulant and coagulant aid, pH and mixing regime.

To show the effect of temperature, experiments were conducted over a temperature range from 1.0 – 22.0 C. During the progress of the work, a specified low temperature was selected to show the effect of increasing coagulant and coagulant aid dosages and also during the comparison between PACl and alum.

Chemical doses for alum, polymer and the addition sequence were based on reviewing the dosages that were used during the past two years from the data provided by WWTP. Relatively low dosages for alum and polymer were selected. It was anticipated that "stressed" conditions could assist to make the temperature effect clear.

Raw water pH for the different batches of the collected raw water were in the range of 7.9 – 8.2, and in order to simulate conditions at the treatment plant, pH was reduced to 7.6; this value was mentioned by Matsui (1998) and also by Amirtharaja (1982). It is believed that alum coagulation is more efficient between 5.5 and 7.5 pH (Ravina, 1993).

Finally, the mixing regime which includes speed of mixing and time for coagulation and flocculation stages was as follows:

- Rapid mixing: 10 -20 second at 312 r.p.m (Maximum available speed).
- Rapid mixing: 2 minutes at 100 r.p.m
- Flocculation: 3 minutes at 50 r.p.m
- Flocculation: 3 minutes at 40 r.p.m
- Flocculation: 3 minutes at 30 r.p.m

A tapered pattern was adopted for flocculation to enable the flocs to agglomerate. G-value was in the range from 16 - 45 sec^{-1} in the flocculation stage, which matched the recommended range set by American Water Works association (ASCE&AWWA, 1998).

3.5 Experimental phases

During the course of the work, three experimental phases were conducted to extract the data needed, and to achieve research objectives.

3.5.1 Phase I: Effect of temperature on residual turbidity

The objective of this phase was to find out a profile that reflects the effect of temperature on residual turbidity. Temperature set points were 1, 3, 5, 10, 16 and 22°C, and the actual experiment temperatures were within ± 0.5 °C of the above values. The first three points may reflect the effect of cold temperatures on process efficiency, while the other three were to show the trend at higher temperatures. To ensure accuracy, a triplicate measurement for each selected temperature was used, and the average temperature for the raw water inside the jars was recorded. Two sets of experiments were conducted, one on relatively low turbidity (9 NTU) raw water from batch #1, and the second on moderately high turbidity (40 NTU) from batch #2 . A summary of operating conditions used in Phase I is shown in Table 3-2.

Table 3-2: Operating conditions summary for Phase I - temperature effect

Parameter	Operating condition
Raw water pH	8.1- 8.2
Adjusted starting pH	7.5 - 7.6
Alum dose (mg/ L)	30
Polymer dose (mg/ L)	0.05
Coagulation regime	10- 20 second at 312 r.p.m followed by 2.0 minutes at 100 r.p.m
Flocculation regime	3 minutes for each 50, 40 and 30 r.p.m
Settling time	10 minutes

The experiment was conducted as per the following steps:

- Raw water in the bucket was homogenized by using a mechanical mixer manufactured and tailored to the bucket size and dimensions.
- Raw water was transferred from the bucket to the four jars by using a hand pump.
- Raw water samples from each jar were drawn off to measure initial turbidity.
- Burette was filled with 0.1 N sulfuric acid, and then slowly the acid was dripped into the jar while the pH meter was monitored until the required pH value is reached. The volume added varied between 2.2 – 2.5 ml depending on the initial raw water pH. This addition adjusted the raw water pH to 7.5 – 7.6.
- Stirrers of the jar apparatus were turned on at the maximum speed (312 r.p.m)
- An alum dose of 30 mg/L and polymer dose of 0.05 mg/L were drawn from the prepared working solution by syringes and injected simultaneously into the jars.
- The speed was lowered to100 r.p.m for 2 minutes, then further lowered to 50, 40, 30 r.p.m with 3 minutes for each speed.
- Stirrers were turned off and 10 minutes settling time was allowed.

- Samples of 125 mL were drawn from each jar; half of it was used in the turbidity measurements and the rest for TOC measurements.
- Residual turbidity, initial and final temperature, and pH are measured and recorded.

3.5.2 Phase II: Effect of different alum and polymer dose at low temperature

This set of experiments was aimed at determining the optimum operating conditions at low temperatures, and to study whether or not this optimum dose could compensate for any lack of process efficiency. Since the experiments were conducted inside the incubator, only 4 jars were used and that means 4 different concentrations at one time can be implemented.

The approach to find the optimum combination of alum and polymer was to vary alum concentration and to find out the best turbidity removal. Then, this alum concentration was used with four polymer concentrations to find out which combination was the optimum. Alum concentrations of 20, 30, 40, and 60 mg/ L and then polymer concentrations of 0.05, 0.1, 0.15 and 0.2 mg /L were used. Batch #2 raw water was used in this Phase (40±2.5 NTU), and the steps for conducting the experiment are the same as in the previous phase; however, the temperature selected to conduct the experiments was around the raw water temperature at the time of collection (2.4 °C). A summary of the operating conditions is shown in Table 3-3.

Table 3-3: Operating conditions summary for Phase II - dose effect

Parameter	Operating condition
Raw water pH	8.2
Adjusted starting pH	7.5 - 7.6
Initial temperature (°C)	2.0 ± 0.5
Alum dose (mg/ L)	20,30, 40 ,60
Polymer dose (mg /L)	0.05, 0.1, 0.15, 0.2
Coagulation regime	10- 20 second at 312 r.p.m followed by 2.0 minutes at 100 r.p.m
Flocculation regime	3 minutes for each 50, 40 and 30 r.p.m
Settling time	10 minutes

3.5.3 Phase III: Effect of using PACl and alum at low temperature

The purpose of running Phase III was to use an alternate coagulant that may have a better performance under a selected low temperature of 3.5 ± 0.5 °C. Since a new batch of raw water was used, both alum and PACl blend were tested to compare the results for that specific water.

Experiment steps were similar to the previous phases; however, selecting PACl dose was different. At the beginning, an arbitrary concentration range for the PACl of 10, 20, 30, 40 mg/L was chosen. After knowing the results, it was refined to a reasonable range of 5, 10, 15 and 20 mg /L. Alum concentrations were similar to the previous phase at 20, 30, 40 and 60 mg /l while the polymer (Magnafloc LT-22) was kept constant at 0.05 mg/L in the comparison runs. In the subsequent runs, MaganflocLT-22 was varied in the range of 0.05, 0.1, 0.15 and 0.2 mg/L to find the optimum combination for each of system 1 (alum plus polymer) and system 2 (PACl plus polymer). Batch #3 raw water was used in this phase (36± 4 NTU).

This phase also included Total Organic Carbon (TOC) measurements, which were measured with a TOC analyzer. Further measurements were conducted on the treated water to quantify the amount of colloidal particles remaining in the effluent. This was accomplished by vacuum filtration using a standard filtration flask and an acrylic membrane filter with100 μm pore size to separate particles less than that size. A filter paper size1.5 μm was used to further separate particles in the colloids range.

4 RESULTS AND DISCUSSION

4.1 Results

In the present study, the effect of cold temperature on the coagulation /flocculation (CF) process for drinking water was examined in several phases, as detailed in Chapter 3. Results obtained from the study are organized and presented in the same order in the following sections.

4.1.1 Results for phase I

The effect of temperature on the CF process using alum as the primary coagulant was examined during this phase. The alum dose was fixed at 30 (mg/L) and Magnafloc LT-22 was used as a coagulant aid and its dose was fixed at 0.05 (mg/L). Other details of the experiment are presented in Section 3.4.1 of Chapter 3. The effect was examined on two batches of water, one with low turbidity of about 9 NTU (batch #1), and the other with moderately high turbidity of about 40 NTU (batch #2).

Treatments were conducted in triplicate at each temperature. The residual turbidities observed after each treatment at varying temperatures with batch #1water are presented in Table 4.1. A summary of the residual turbidity results is presented in Figure 4-1, and that for percent turbidity removals is plotted in Figure 4-2.

Table 4-1: Residual turbidity at various temperatures for batch #1. Values shown for temperature and initial turbidity are average ±SD.

Temperature (°C)	Initial turbidity (NTU)	Residual turbidity (NTU)	Turbidity removal %
1.2 ± 0	9.0 ± 0	6.5	27.8
		6.8	24.4
		6.6	26.7
3.3 ± 0.1	9.0 ± 0	6.5	27.8
		7.2	20.0
		6.5	27.8
5.2 ± 0.3	8.0 ± 0.1	6.3	20.3
		6.3	22.2
		5.3	33.8
9.8 ± 0.2	8.0 ± 0.1	6.0	24.1
		6.5	19.8
		5.6	30.9
16.2 ± 0	8.0 ± 0.1	4.6	43.2
		5.0	37.5
		5.6	30.0
21.6 ± 0.1	8.0 ± 0.1	4.8	38.5
		4.0	51.2
		4.3	46.9

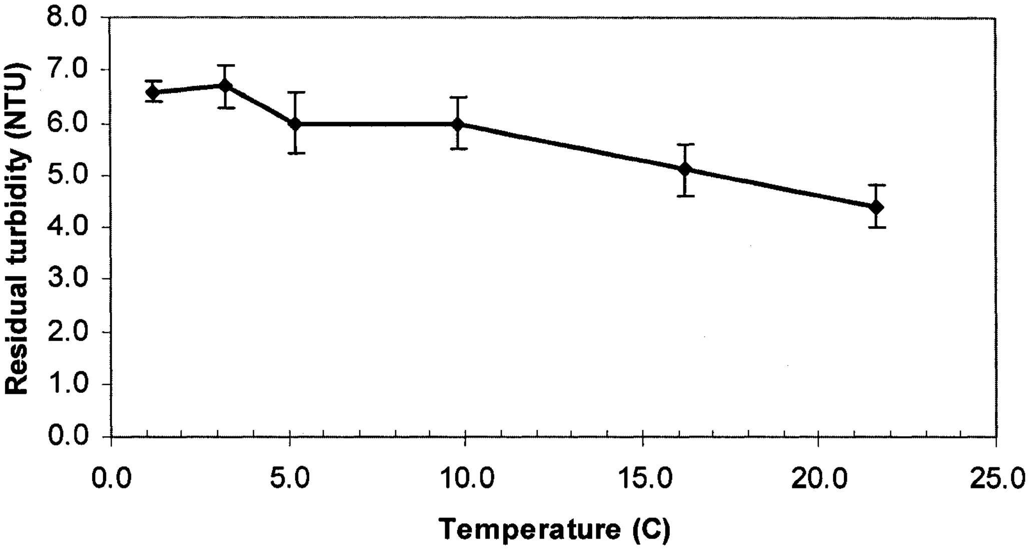

Figure 4-1: Effect of temperature on residual turbidity with alum coagulation. Raw water turbidity=9.0 ±1.1 NTU. Alum and polymer dosages=30 and 0.05 mg/L respectively. Values shown are average ±SD based on triplicate treatments (Table 4.1).

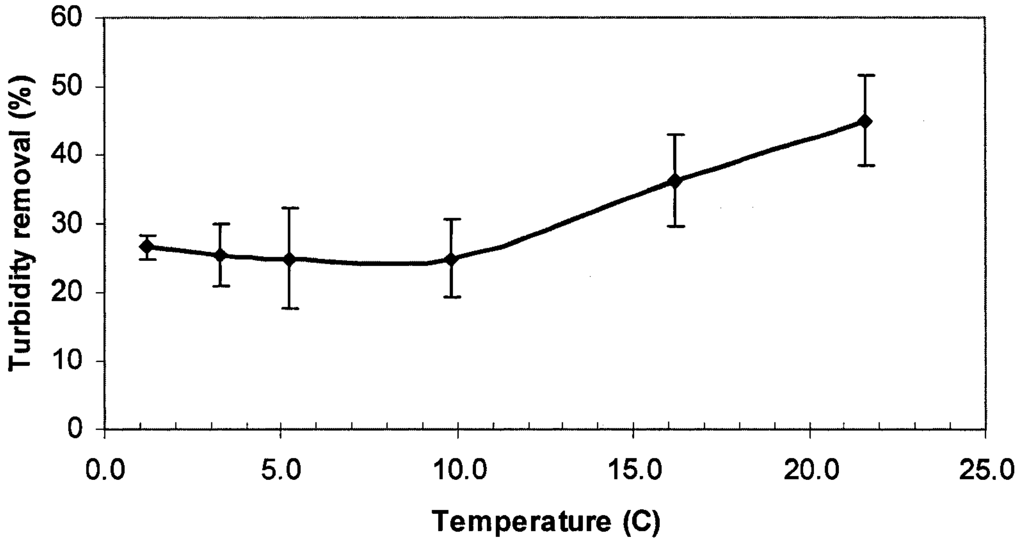

Figure 4-2: Percentage turbidity removals with temperature. Raw water turbidity=9.0 ± 1.1 NTU. Alum and polymer dosages=30 and 0.05 mg/L respectively. Values shown are average ±SD based on triplicate treatment for each temperature.

The results show that temperature had an impact on the residual turbidity and its removal efficiency. A steady and almost linear increase in residual turbidity was observed for reduction in temperature from 22 to 10 °C (Figure 4-1) with a corresponding reduction in the removal efficiency from about 45 to 25% (Figure 4-2). Further changes in residual turbidity were insignificant at temperatures lower than 10 °C, with turbidity removal efficiencies maintained in the range of 25%.

The results obtained with batch #2 water with moderately high turbidity (40 ± 2.5 NTU) are presented in Table 4-2 and a summary of the residual turbidity results is presented in Figure 4.3. Similar results were observed as with low turbidity (batch #1) water; these results also show that temperature had an impact on the residual turbidity and its removal efficiency. However, the observed trend was different for temperatures below 10 °C. A continuous increase in residual turbidity was observed with drop in temperature from 22 to 1 °C with batch #2 water (Figure 4-3). A significant increase in residual turbidity was observed at temperatures below 10°C, which was unlike the results observed with batch #1 water (Figure 4-1), where the change in residual turbidity was minimal in the same temperature range. Further, the significance of the effect of temperature also seems to increase with lower temperature (Figure 4-3). The rate of increase of turbidity at temperatures below 5.5 °C was observed to be higher than that between 5.5 and 10 °C, which in turn is higher than the observed rate between 10 and 22 °C.

Table 4-2: Residual turbidity at various temperatures for batch #2. Values shown for temperature and initial turbidity are average ±SD.

Temperature (°C)	Initial turbidity (NTU)	Residual turbidity (NTU)	Turbidity removal %
1.2 ± 0.2	40.4 ± 0.8	9.7	76
		12.1	71
		11.1	73
3.6 ± 0.2	41.5± 0.9	9.4	78
		10.3	75
		9.4	78
5.5 ± 0.1	41.3 ± 1.0	7.0	84
		6.8	84
		7.3	82
10.1 ± 0.1	41.0 ± 1.1	5.4	87
		5.0	87
		5.6	86
21.0 ± 0.8	39.2 ± 0.5	3.7	91
		4.1	89
		3.4	91

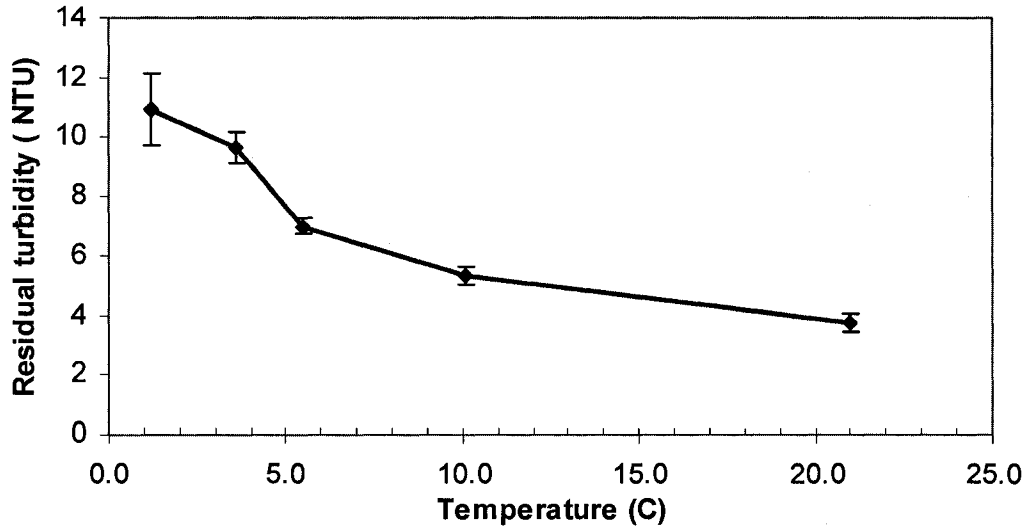

Figure 4-3: Effect of temperature on residual turbidity with alum coagulation. Raw water turbidity=40 ±2.5 NTU. Alum and polymer dosages=30 and 0.05 mg/L respectively. Values shown are average ±SD based on triplicate treatments (Table 4.2).

A comparison of residual turbidity data presented in Tables 4-1 and 4-2 show that although the initial turbidity of the two batches of water was different, the residual turbidity after treatment was similar for temperatures of 10 °C and higher.

This may explain the much higher turbidity removal efficiencies observed with batch #2 water as compared to those with batch #1 water (Figure 4-4). At temperatures below 10 °C however, the residual turbidity for batch #2 continued to rise and were higher than those observed with batch #1 water for which the values remained more or less constant.

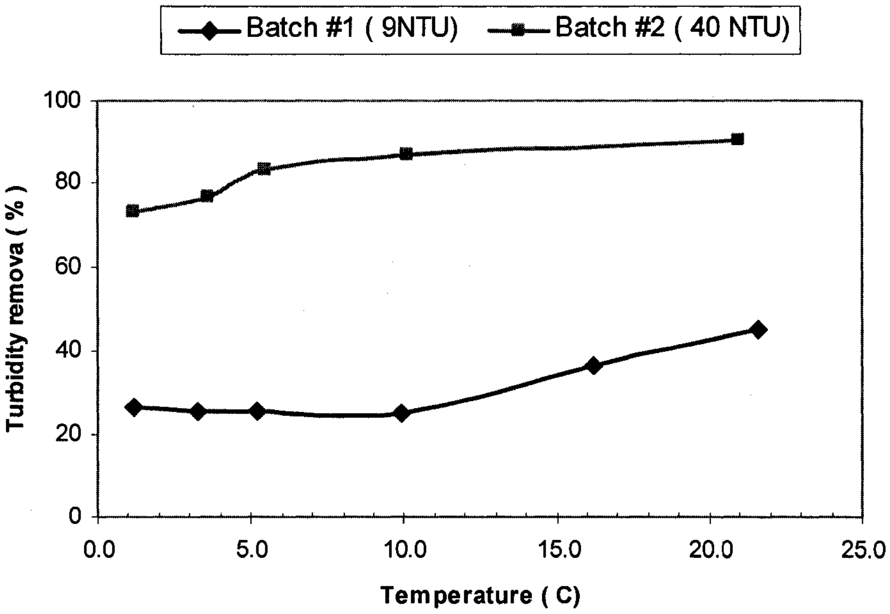

Figure 4-4: Comparison turbidity removals between batch #1 with low turbidity and batch #2 with moderately high turbidity. Values shown are average based on triplicate treatments.

4.1.2 Results for phase II

The effect of varying alum and polymer dosages on the CF process at a fixed low temperature < 5 °C was examined during this phase. In the first run, the alum dose was varied between 20 and 60 mg/L, and the polymer (Magnafloc LT-22) dose was fixed at 0.05 mg/L. Other details of the experiment are presented in Section 3.4.2 of Chapter 3. The effect was examined on water for batch #2 with moderately high turbidity of 40± 2.5 NTU, at a temperature of 2.0± 0.5 °C. Results are shown in Figures 4-5, 4-6, 4-7and 4-8, and a summary table can be found in Appendix A.

The results show that alum dose increase had an impact on the residual turbidity and its removal efficiency. A steady and almost linear decrease in residual turbidity was observed for dose increase from 20 to 40 mg/L (Figure 4-5) with a corresponding increase in the removal efficiency from about 48 to 86% (Figure 4-6). Further changes in residual turbidity were insignificant at dosages higher than 40 mg/L, and the slope of the curve remained almost constant with slight decrease in turbidity removal efficiency to 84% when the alum dose reached 60 mg/L.

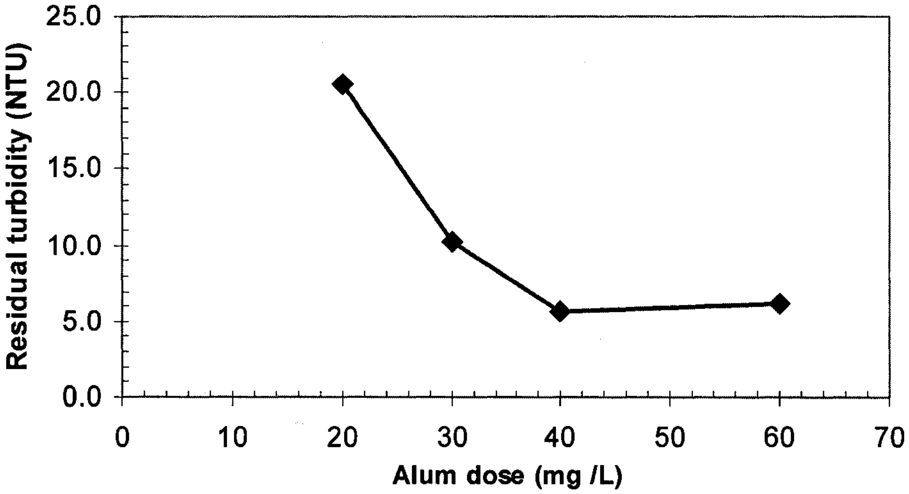

Figure 4-5: Effect of alum dose change on residual turbidity. Raw water=40 ± 2.5 NTU. Polymer dose fixed at 0.05 mg/L. Temperature =2 ± 0. 5 °C

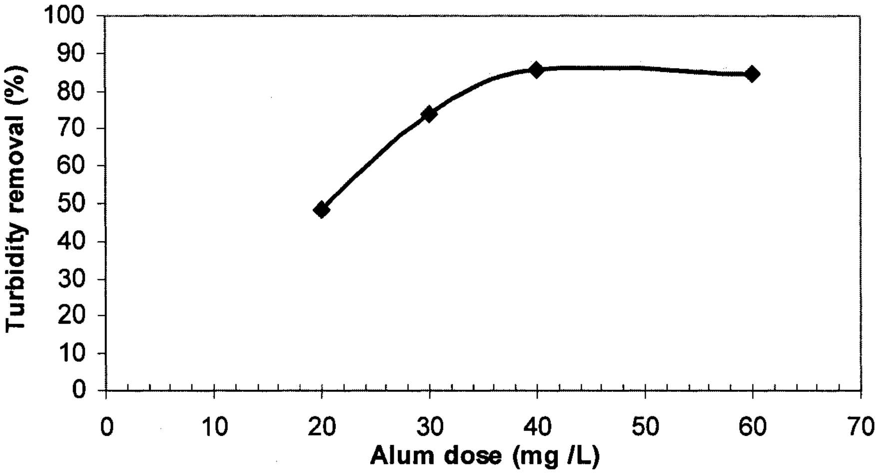

Figure 4-6: Percent turbidity change with different alum dosages. Raw water=40±2.5 NTU. Polymer dose fixed at 0.05 mg/L. Temperature=2± 0.5 °C

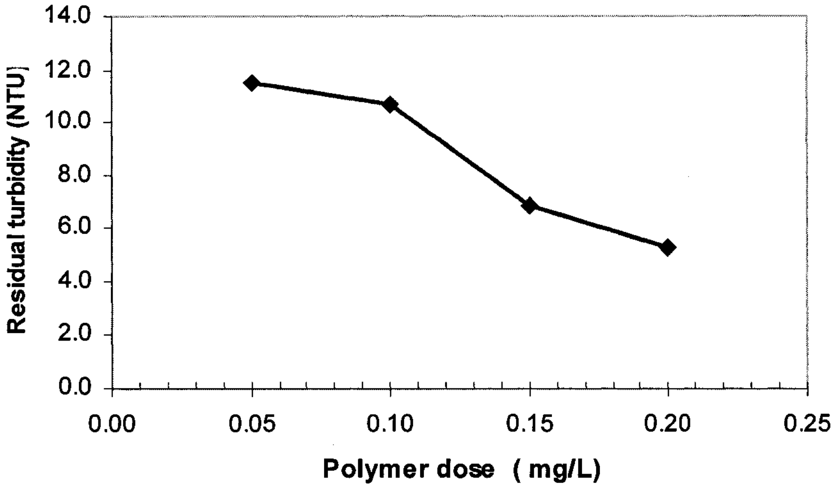

Figure 4-7: Effect of polymer dose change on residual turbidity. Raw water=40 ± 2.5 NTU. Alum dose fixed at 40 mg/L. Temperature =2 ± 0. 5 °C

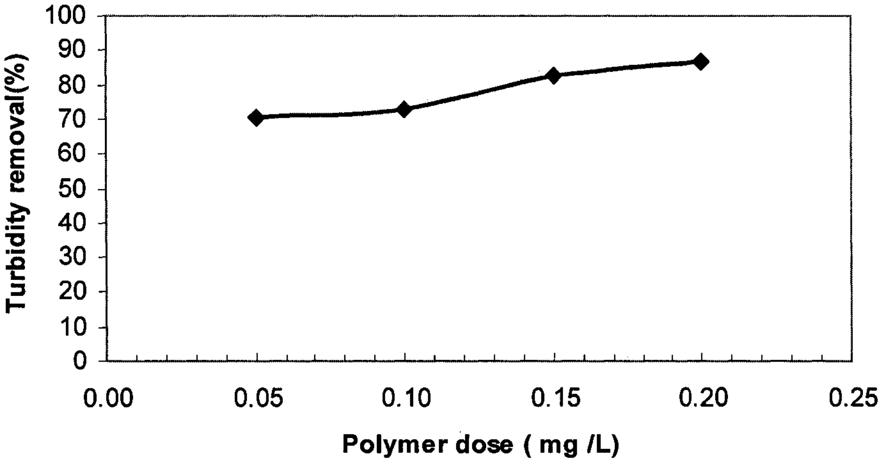

Figure 4-8: Percent turbidity change with different polymer dosages. Raw water =40 ±2.5 NTU. Alum dose fixed at 40 mg/L. Temperature=2±0.5 °C.

In the second run, the alum dose was fixed at close to the optimum value of 40 mg/L based on the results from the first run, and the polymer dose was varied between 0.05 and 0.2 mg/L. The gradual increase of polymer dose showed a steady but a small decrease in residual turbidity (Figure 4-7). For the entire range from 0.05 – 0.2 mg/L, the corresponding removal efficiency varied between 71- 87% (Figure 4-8). Since the main turbidity removal was achieved by using alum, the role of polymer was complementary.

4.1.3 Results for Phase III

The effect of using alternative coagulant polyaluminum blend (Sumaclear-750) was tested against traditional alum, under selected low temperature of 3.5 ± 0.5 °C. The objective was to compare the performance of both using the same specific raw water (batch #3) collected from the treatment plant.

In this set of experiments, alum plus polymer, and PACl plus polymer were examined at different concentrations. The set consisted of three runs as follows:

Run #1:

The objective for this run was to determine the appropriate working range for PACl. Two experiments were conducted in this run. First, the PACl dose was varied between10 and 40 mg/L while the polymer dose was fixed at 0.05 mg/L. Second, alum dose was varied between 20 and 60 mg/L and the polymer dose was kept constant at 0.05 mg/L. Other details of the experiment are presented in Section 3.5.3 of Chapter 3.

The results are shown in Figure 4-9, and a summary table can be found in Appendix A. The results for alum coagulation presented in Figure 4-9 are similar to these with batch #2 water during Phase II runs (Figure 4-5). Residual turbidity decreased with increasing alum dose from 20 to 40 mg/L. No significant decrease in residual turbidity was observed with further increase in alum dose to 60 mg/L.

The results for PACl coagulation presented in Figure 4-9 showed that the trend for residual turbidity with changing PACl dose was somewhat different from those for alum. Lower residual turbidity was observed for PACl dose of 10 and 20 mg/L. Residual turbidity increased with further increase in PACl dose to 30 mg/L, and the highest residual turbidity for PACl was at 40 mg/L, and that was the lowest for alum.

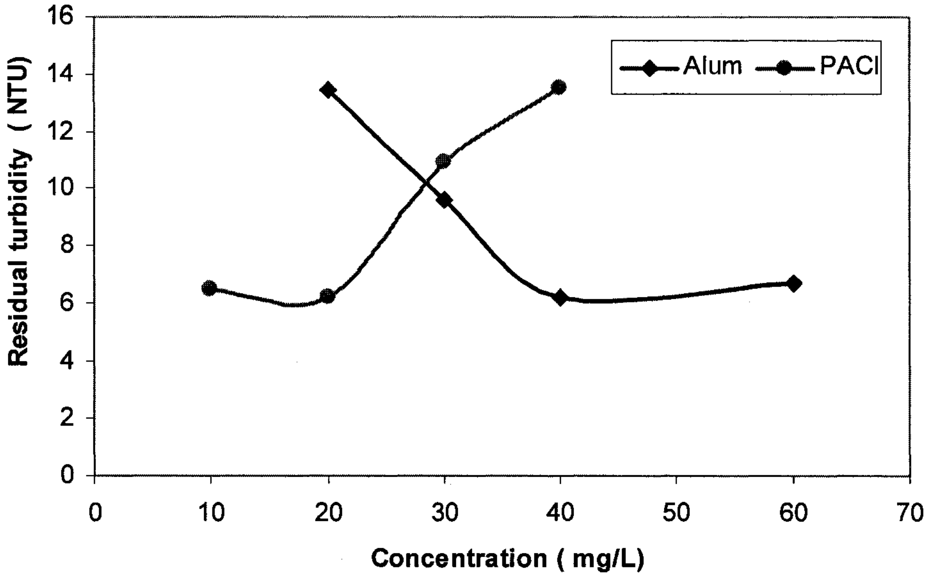

Figure 4-9: Dose change effect for PACl and alum on residual turbidity. Run #1. Raw water =36 ±4 NTU. Polymer dose=0.05mg/L. Temperature=3.5± 0.5

Run #2:

The objective of this run was to find out the optimum concentrations for PACl and alum, and to validate the results previously obtained. Two experiments were conducted, one for each coagulant. First, PACl dose was varied between 5 and 20 mg/L, and polymer dose was fixed at 0.05 mg/L. Second, the alum dose was varied between 20 and 60 mg/L, and the polymer dose was fixed at 0.05 mg/L.Other details of the experiment are presented in Section 3.5.3 of Chapter 3.

Figures 4-10 and 4-11 show the results and a summary table can be found in Appendix A.

The results for alum coagulation presented in Figures 4-10 and 4-11 showed that residual turbidity had somewhat similar trend as in run #1. A steady and almost linear decrease in residual turbidity was observed for an increase in alum dose from 20 to 40 mg/L with a corresponding increase in the removal efficiency from about 64 to 85% (Figure 4-11). Further increase in alum dose showed an increase in residual turbidity. The results for PACl coagulation presented in Figure 4-10 and 4-11 showed a decrease in residual turbidity between 5 and 15 mg/L with a corresponding increase in the removal efficiency from about 68 to 82%; then, a steady increase in residual turbidity between 15 -20 mg/L was observed.

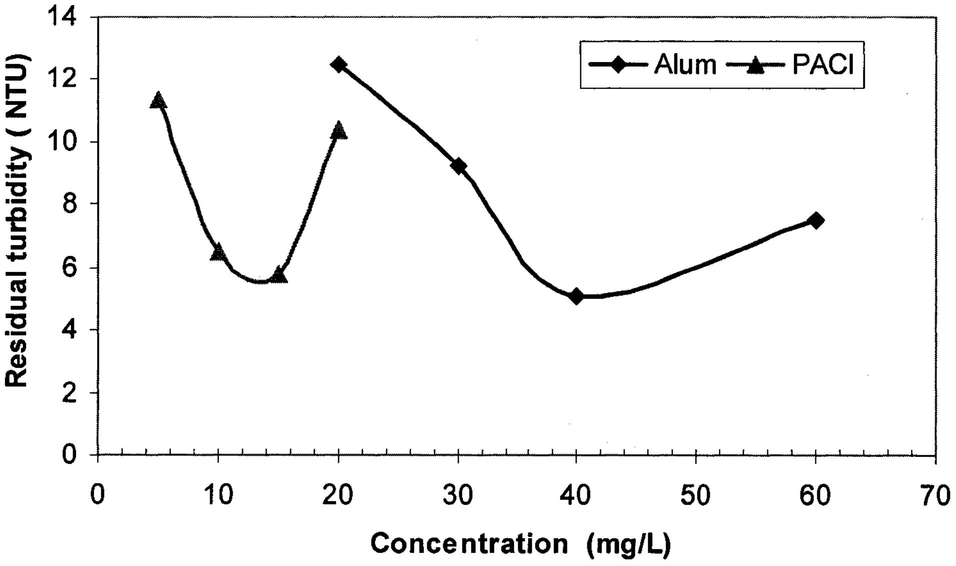

Figure 4-10: Dose change effect of refined PACl dose and alum dose on residual turbidity. Run#2. Raw water=36±4 NTU. Polymer dose=0.05mg/L. Temperature=3.5±0.5

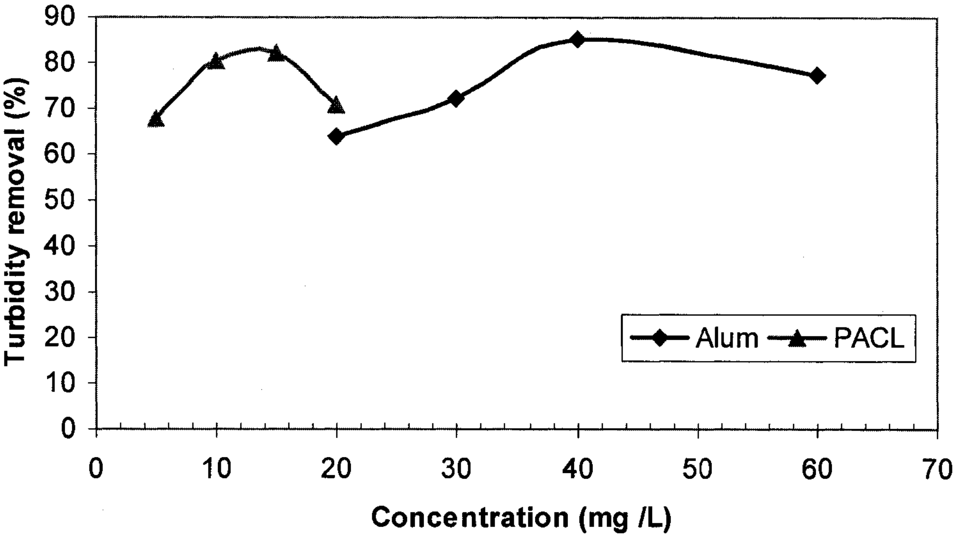

Figure 4-11: Percent turbidity removals for alum and PACl. Run #2. Raw water =36 ±4 NTU. Polymer dose=0.05mg/L. Temperature=3. 5± 0.5

Run #3:

The final run was aimed to find out close to optimum combination for PACl plus polymer, and alum plus polymer. Two experiments were conducted. First, PACl dose was fixed at 10 mg/L, based on the results of the previous run, and polymer dose was varied between 0.05 and 0.2 mg/L. Second, alum dose was fixed at 40 mg/L, based on the results from the previous run, and polymer dose was varied between 0.05 and 0.2 mg/L. Figure 4-12 shows the results, and a summary table can be found in Appendix A.

The results for alum coagulation presented in Figure 4-12 showed that alum was less sensitive to polymer dose increase. A constant residual turbidity was observed for polymer dose increase from 0.05 to 0.1 mg/L, and then followed by a marginal decrease between 0.1 to 0.15 mg/L, and remained after that almost unchanged.

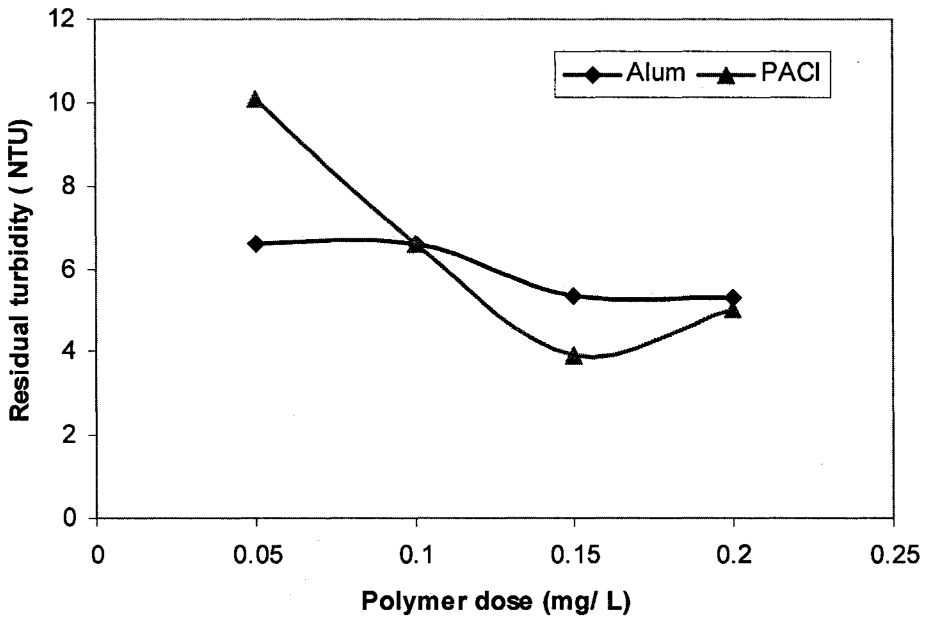

Figure 4-12: Effect of changing polymer dose for system 1 and 2. Run #3. Raw water =36 ±4 NTU. Alum dose=40mg/L and PACl dose=10 mg/L. Temperature=3.5±0.5

The results for PACl coagulation presented in Figure 4-12 showed that PACl was more sensitive to polymer dose than alum. A steady and almost linear decrease in residual turbidity was observed for polymer dose change from 0.05 to 0.15 mg/L, with a corresponding increase in the removal efficiency from about 69 to 89%. Further increase in polymer dose did not make any improvement, and a slight increase in residual turbidity was observed at 0.2 mg/L. Both, in alum and PACl coagulation the optimum addition of the polymer was at 0.15 mg/L.

Apart from jar test runs, Phase III included measurements to determine the efficiency for colloidal particles removal, and total organic carbon content in the raw and treated water. In order to separate the particles in the colloidal range, vacuum filtration with 1.5μm filter paper was used for treated water of run #3. Figure 4-13 shows the results and a summary table can be found in Appendix A.

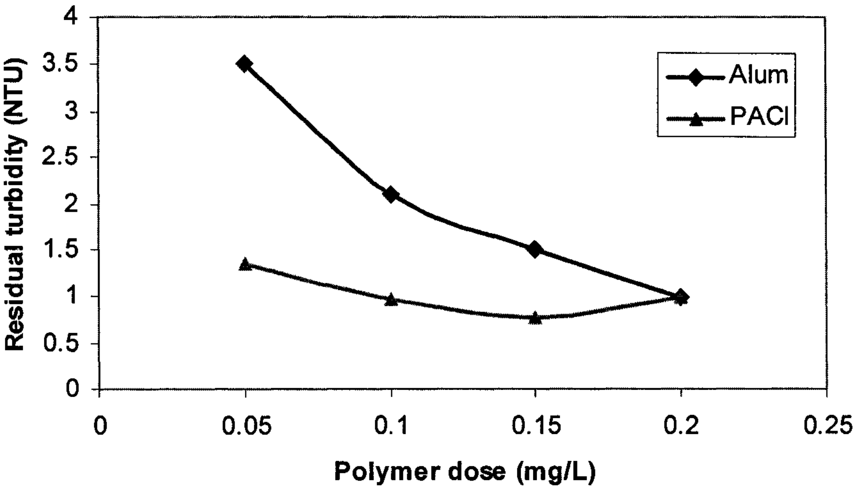

Figure 4-13: Colloids removal comparison for system 1 and 2. Run #3. Values shown are for treated water filtered to1.5μm. Alum dose=40mg/L and PACl dose=10 mg/L. Temperature=3.5±0.5

For alum, a steady and almost linear decrease in colloids removal was observed with increasing polymer dose, while for PACl the decrease occurred between 0.05 and 0.15 mg/L of polymer dose, and then followed by a slight increase at 0.2 mg/L. Although initial turbidity was the same for both alum and PACl, the final turbidity at the optimum operation conditions at 0.15 mg/L for polymer was different. Turbidity measurements for alum showed that the remaining colloids have 1.5 NTU, while it was 0.77 NTU for PACl.

In addition to the above, this phase included TOC measurements. The purpose of these measurements was to show the effect of the CF process on the removal efficiency of the TOC, and attempt to identify the particle size that TOC species were associated with.

Table 4-3: TOC in treated water using alum and polymer. Raw water=36 ±4 NTU. Initial temperature3.5 ±0.5

Alum (mg/L)	Polymer (mg/L)	Residual turbidity (NTU)	Initial TOC (mg/L)	TOC 100μm (mg/L)	TOC 1.5μm (mg/L)
40	0.05	6.6	3.07	2.95	2.26
40	0.10	6.6	3.07	2.67	2.11
40	0.15	5.4	3.07	2.50	2.50
40	0.20	5.3	3.07	2.65	2.58

Table 4-4: TOC in treated water using PACl and polymer. Raw water =36 ± 4 NTU. Initial temperature=3.5± 0.5

PACl (mg/L)	Polymer (mg/L)	Residual turbidity (NTU)	Initial TOC (mg/L)	TOC 100μm (mg/L)	TOC 1.5μm (mg/L)
10	0.05	10.1	3.07	2.85	2.77
10	0.10	6.6	3.07	2.54	2.03
10	0.15	3.9	3.07	2.22	1.96
10	0.20	5.0	3.07	2.23	2.21

Results for alum coagulation (Table 4-3) show that TOC value for particles with size less than 100 μm had insignificant change from the initial value. The values under 1.5μm suggest that the bulk of TOC concentration was in the colloidal particle size range. At the optimum addition for alum of 40 mg/L with polymer of 0.15 mg/L, removal efficiency for TOC did not exceed 18 %.

Similar to alum coagulation, PACl coagulation (Table 4-4) shows almost the same result. An insignificant change after treatment was observed, and the bulk of TOC species were under 1.5 μm, which falls under the colloidal particle size range. At the optimum addition for PACl of 10 mg/L and polymer of 0.15 mg/L, removal efficiency did not exceed 28 %.

4.2 Discussion

4.2.1 Effect of temperature on alum coagulation

Water viscosity is the physical property most affected by temperature changes. Reduction in temperature from 22 to 0 °C would cause an increase in viscosity from 0.9608 to 1.7921 cP, which corresponds to an increase of about 46%. Changing in viscosity has two main effects. First, increase in viscosity causes an increase in the zeta potential, thus colloids could be more stable. Second, viscosity change would affect the mixing intensity (represented by G-value). As shown in Table 4-5, under the same mixing intensity of 300 r.p.m, the corresponding G-value changes from 430 to 330 over a temperature range from 22 to 4 °C, which is a 23% reduction.

Table 4-5: G-values for different temperatures for Phipps and Bird jars

r.p.m	G (1/sec) at 4 °C	G (1/sec) at 10 °C	G (1/sec) at 16 °C	G (1/sec) at 22 °C
300	330	360	400	430
100	85	90	100	120
50	35	38	42	45
40	26	29	32	35
30	16	19	22	24

Over the temperature range from 1- 22 °C in which all the experiments were conducted, a temperature impact on residual turbidity was observed; however, the impact was different for raw waters having different initial turbidities. The effect on low turbidity water (batch #1) was unclear in the low temperature range (less than 10 °C). The effect was clearer at temperatures higher than 16 °C. The effect on moderately high turbidity water (batch #2) was also clearer; it showed an increasing impact on residual turbidity as the temperature of the runs was lowered gradually from 21 to 1.2 °C. The change in slope can clearly be observed (Figure 4-3), especially in the segment where temperature is below 5.5 °C. The effect of temperature is attributed to a decrease in reaction rate at low temperatures. Pernitsky and Edzwald (2003) reported a significant decrease in alum solubility and thus in reaction rate as indicated in section 2.4.1. Hutchison and Foley (1974) observed slow floc formation at 3.3 °C; Kang and Cleasby (1995) specified a slow rate of floc formation at low turbidity levels. All these observations confirm the slowing down of the reaction and collision rate at low temperatures, which was also observed in this study.

For raw water batches 1 and 2, low water turbidity batch #1 (9 NTU) showed a poor turbidity removal efficiency which ranged between 25 and 45%, while moderately high turbidity batch # 2 (40 NTU) showed much higher removal efficiency and ranged from 73 -90%. Differences in results might be attributed to the lower number of collisions of colloids that may have occurred because of the lower number of particles per unit volume. Ammary and Cleasby (1995) showed in one of their experiments that using low initial turbidity of 4.8 NTU resulted in a residual turbidity of 2.6 NTU; in contrast, using a higher initial turbidity of 24 NTU resulted in lower residual turbidity of 1.4 NTU.

4.2.2 Effect of alum and polymer dose at low temperature

The results shown in Figure 4-5 indicated an improvement for process efficiency by increasing alum dose. In the previous runs, 30 mg/L alum was used, and a residual turbidity of 9.6 NTU was achieved at 3.6 °C, while by increasing alum dose from 30 to 40 mg/L, a residual turbidity of 5.7 NTU was observed at a lower temperature of 2.0 °C. However, beyond 40 mg/L of alum dose, insignificant improvement on residual turbidity was observed.This trend for alum was almost repeated and confirmed in the results shown in Figures 4-9 and 4-10 for alum coagulation part. These results indicate a limitation for alum dose increase to compensate for the CF process deficiency under cold temperatures. Hanson and Cleasby (1990) attributed such behavior to the shift in pH when excess amounts of alum are used, which could shift alum coagulation out of the optimum sweep floc region. Morris and Knock (1984) indicated that increasing alum dose from 11. 55 to 110 mg/L at 1.0 °C reduced the size of the coagulated flocs leading to process inefficiency.

Results with increasing polymer dose were not encouraging (Figure 4-7 and Figure 4-8). By using alum with minimum polymer dose of 0.05 mg/L, a removal efficiency of 71% was observed. While by increasing polymer dose up to 0.2 mg/L, 87% removal efficiency was accomplished. This would be considered to be a small improvement when we consider that the polymer dosage was increased by four-fold. The effect was repeated in the results shown in Figure 4-12. This indicates that the main working mechanism under cold temperature was charge neutralization, established with alum and not the polymer. Hanson and Cleasby (1990) indicated that although polymers could form larger and stronger flocs, alum appears to be more efficient than cationic polymers for charge neutralization and in sweeping up the primary particles.

4.2.3 Effect of using PACl blend as an alternative at low temperature

Results for run #1 using PACl blend at a low temperature of 3±0.5 °C (Figure 4-9) shows that the required concentration to achieve minimum residual turbidity was well below the concentration used for alum. This is attributed to the large size of the molecule, and the highly charged polymeric aluminium species formed with the addition of PACl blend. Overdosing by increased PACl concentration (from 20 - 40 mg/L) resulted in deterioration in water quality with residual turbidity increasing from 6.2 to 13.5 NTU.

In run #3, residual turbidity decreased as the coagulant-aid dose was increased at a fixed PACl dose; on the other hand, residual turbidity at fixed alum dose did not show the same behaviour (Figure 4-12), which might be attributed to a possible differences in interaction between the coagulant and the coagulant-aid. Results for run #3 in Appendix A show that when using alum coagulation, pH value changed from 7.5 at the start of the run to 6.8-6.9 at the end. PACl coagulation had limited effect on the pH, and it changed from 7.5 to 7.4. Matsui et.al (1998) observed a similar marginal change in pH value before and after treatment with PACl. This marginal change by using PACl would allow a better control of pH during the water treatment process.

At the optimum operating conditions for run #3, and compared to alum, only 25 % by volume or mass (both alum and PACl have similar density) of PACl was needed to achieve similar or better residual turbidity results. Similar results have been reported by Wang et. al (2002) who found that even with a lower dosage and shorter coagulation /flocculation time, PACl performed as effectively as alum for the treatment of cold water at 5.5 °C. Reduction in the volume required for the PACl blend could have positive implications on the CF process: A) Cost wise Sumaclear-750 has a price of $825/metric ton, while alum costs $230/metric ton, thereby any volumetric flow for PACl less than 28% would mean savings. B) Less power would be required for pumping. C) Smaller quantities of sludge would be produced.

Also, at the optimum conditions, flocs shape and size were completely different. Alum settled floc was small and rounded, while PACl floc size and shape was significantly larger with sharp edges, several flocs were attached together forming a chain. That indicates that the bridging mechanism was more effective with PACl as compared to alum. Ammary and Cleasby (1995) indicated that polymers produce larger and stronger flocs that can tolerate higher shear forces encountered in mixing, and they function independent of some raw water characteristics such as alkalinity and pH. Geng (2005) had contradicting findings on the size of floc; he indicated that PACl flocs were smaller than those obtained from alum coagulation.

5 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In this study, the coagulation / flocculation process was investigated to show the impact of temperature on its performance in natural water. The laboratory experiments were conducted in three phases. The following conclusions may be drawn based on these work phases.

Phase I

- Temperature has a detrimental effect on coagulation / flocculation process. This effect was more pronounced as temperature decreased.
- Effect of temperature on turbidity was not conclusive for all temperature ranges tested. It somewhat depended on initial raw water turbidity. At low initial turbidity of about 9 NTU, the effect was ambiguous below 10 °C; while with moderately high initial turbidity of about 40 NTU, the effect was prominent at temperatures below 5.0 °C.

Phase II

- At a temperature of 2.0± 0.5 °C, increasing alum dose did partially compensate for process deficiency. However, that improvement had limitations, and excess alum dosages could lead to efficiency deterioration.
- Increasing polymer dose (MaganaflocLT-22) from 0.05 to 0.2 mg/L did not show a significant improvement in removal efficiency. A plausible conclusion from this could be that the main mechanism responsible for coagulation under cold temperatures was charge neutralization.

Phase III

- For same operating conditions, PACl blend (Sumaclear-750) achieved lower residual turbidity than with alum at cold temperature of 3±0.5 °C.
- Based on mass calculation, it was 75% less than the mass needed using alum.
- At the optimum operating dosage, combination of PACl and polymer was more efficient in removing colloidal particles as that achieved using alum with polymer.
- When added to the raw water, PACl blend had very limited effect in changing the pH value, and this could provide a better control for the CF process.

For the TOC measurements the following conclusions were drawn:

- Insignificant change in TOC concentration was observed after treatment under cold temperatures.
- Most of the organics were in the colloidal particle size range.

5.2 Recommendations

- Raw water temperature drops below 1.0 °C for many days during winter, encouragement of studies for this temperature.
- Alum performance at high temperatures was excellent, while PACl blend showed a better performance under cold temperatures, therefore it might be useful to consider switching the type of coagulant, based on the season.
- Developing a data base for raw water specification around the year for each treatment plant is essential, and could assist in selecting the type of treatment,

type of coagulants and coagulant aids that should be used. Chemical and physical analysis of raw water when there are abnormal characteristics that might be repeated is also important.

- Each of the controllable and uncontrollable parameters have a certain level of influence on the process efficiency, it is recommended that to investigate as much as possible of those parameters together, each at 2 – 3 levels. This is to find out the best operating conditions for the process, and to determine the interactions between those parameters.
- Many types of polyaluminum blends are produced today by a single manufacturer. Exact molecular weight, structure, constituents, OH /Al ratio and charge density are ambiguous, hence the reactions are likely to be different from one type to another, and consequently the results could be different. Jar tests in this regard could be beneficial for a preliminary assessment for the various types.
- Utilizing new coagulant and especially PACl blends should be accompanied with caution, usually those blends provide more aluminum species than traditional alum. If the remaining aluminum ions after treatment are beyond compliance with regulations, then using that particular coagulant type should be reconsidered.

APPENDIX A: Data for experiments

Table A.1: Phase II. Effect of alum dose change

Alum (mg/L)	Polymer (mg/L)	Initial turbidity (NTU)	Residual turbidity (NTU)	Initial temp. (°C)	Final temp. (°C)	Adjusted pH	Final pH	Percent removal (%)
20	0.05	39.7	20.6	2.00	3.70	7.60	7.20	48
30	0.05	39.0	10.2	2.20	3.60	7.60	7.20	74
40	0.05	40.0	5.7	2.10	3.70	7.60	7.30	86
60	0.05	39.2	6.1	2.20	3.50	7.60	7.30	84

Table A.2: Phase II. Effect of polymer dose change.

Alum (mg/L)	Polymer (mg/L)	Initial turbidity (NTU)	Residual turbidity (NTU)	Initial temp. (°C)	Final temp. (°C)	Adjusted pH	Final pH	Percent removal (%)
40	0.05	39.1	11.5	2.10	3.50	7.60	7.30	71
40	0.10	39.2	10.7	1.50	3.20	7.60	7.40	73
40	0.15	39.5	6.9	1.50	3.40	7.60	7.30	83
40	0.20	40.0	5.3	1.70	3.40	7.60	7.30	87

Table A.3 (a): Phase III. Run #1. Selection of a working range for alum

Alum (mg/L)	Polymer (mg/L)	Initial turbidity (NTU)	Residual turbidity (NTU)	Initial temp. (°C)	Final temp. (°C)	Adjusted pH	Final pH	Percent removal (%)
20	0.05	37.2	13.4	3.9	5.5	7.53	7.30	64
30	0.05	37.5	9.6	3.6	5.3	7.52	7.16	74
40	0.05	36.5	6.16	3.3	5.2	7.53	7.01	83
60	0.05	36.2	6.66	3.3	5.4	7.47	6.89	82

Table A.3 (b): Phase III. Run #1. Selection working range for PACl

PACl (mg/L)	Polymer (mg/L)	Initial turbidity (NTU)	Residual turbidity (NTU)	Initial temp. (°C)	Final temp. (°C)	Adjusted pH	Final pH	Percent removal (%)
10	0.05	35.5	6.5	3.5	5.5	7.52	7.4	82
20	0.05	35.0	6.2	3.6	5.4	7.51	7.38	82
30	0.05	36.0	10.9	4.0	5.2	7.51	7.35	70
40	0.05	35.5	13.5	4.0	5.5	7.52	7.36	62

TableA.4 (a): Phase III Run #2. Effect of alum dose change

Alum (mg/L)	Polymer (mg/L)	Initial turbidity (NTU)	Residual turbidity (NTU)	Initial temp. (°C)	Final temp. (°C)	Adjusted pH	Final pH	Percent removal (%)
20	0.05	34.5	12.5	3.9	5.0	7.45	7.16	64
30	0.05	33.5	9.3	3.8	4.7	7.52	7.15	72
40	0.05	34.5	5.1	3.8	4.8	7.52	7.0	85
60	0.05	33.3	7.5	3.9	5.0	7.5	6.9	77

TableA.4 (b): Phase III Run #2. Effect of PACl dose change

PACl (mg/L)	Polymer (mg/L)	Initial turbidity (NTU)	Residual turbidity (NTU)	Initial temp. (°C)	Final temp. (°C)	Adjusted pH	Final pH	Percent removal (%)
5	0.05	35.2	11.35	3.4	5.2	7.45	7.4	68
10	0.05	33.5	6.5	3.9	4.8	7.47	7.36	81
15	0.05	32.5	5.8	3.8	4.9	7.47	7.32	82
20	0.05	35.4	10.35	3.6	5.1	7.49	7.29	71

TableA.5 (a): Phase III Run #3. Effect of polymer dose change with fixed alum dose

Alum (mg/L)	Polymer (mg/L)	Initial turbidity (NTU)	Residual turbidity (NTU)	Initial temp. (°C)	Final temp. (°C)	Adjusted pH	Final pH	Percent removal (%)
40	0.05	32	6.6	2.8	4.3	7.51	6.84	79
40	0.1	32	6.6	2.9	4.1	7.5	6.89	79
40	0.15	34	5.35	2.8	4.2	7.51	6.9	84
40	0.2	32	5.3	3	4.5	7.52	6.93	83

TableA.5 (b): Phase III Run #3. Effect of polymer dose change with fixed PACl dose

PACl (mg/L)	Polymer (mg/L)	Initial turbidity (NTU)	Residual turbidity (NTU)	Initial temp. (°C)	Final temp. (°C)	Adjusted pH	Final pH	Percent removal (%)
10	0.05	33	10.1	3.1	4.0	7.52	7.37	69
10	0.10	32	6.6	2.8	3.9	7.51	7.39	79
10	0.15	34	3.9	2.9	3.9	7.52	7.40	89
10	0.20	32	5.0	3.2	4.1	7.5	7.37	84

Table A.6 (a): Phase III. Run #3. Treated water with alum coagulation filtered to 1.5 μm

Alum (mg/L)	Polymer (mg/L)	Initial turbidity (NTU)	Residual turbidity (NTU)	Filtered turbidity to1.5μm (NTU)
40	0.05	32	6.6	3.5
40	0.1	32	6.6	2.1
40	0.15	34	5.4	1.5
40	0.2	32	5.3	0.99

Table A.6 (b): Phase III. Run #3. Treated water with PACl coagulation filtered to 1.5 μm

PACl (mg/L)	Polymer (mg/L)	Initial turbidity (NTU)	Residual turbidity (NTU)	Filtered turbidity to1.5μm (NTU)
10	0.05	33	10.1	1.35
10	0.1	32	6.6	0.96
10	0.15	34	3.9	0.77
10	0.2	32	5.0	0.98

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