University of Alberta

STUDIES ON FLOCCULATION OF KAOLIN SUSPENSIONS AND MATURE FINE TAILINGS

by

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*This thesis is dedicated to my parents, **Mr. Ubadire M. Ezeagwula and Mrs. Chinonyerem Ezeagwula**, and my sisters – **Akudo, Ngozi, Ijeoma and Chinenye**. I would not have accomplished this feat without your love, prayers and support. I am forever grateful to God for making me a part of you. I love you with all of my heart!*

Abstract

Promoting accelerated fine solids settling in tailings ponds is key to managing/treating oil sands tailings. This thesis presents results of studies conducted on flocculation of kaolin suspensions (as model tailings) and mature fine tailings (MFT). Two synthetic polymers (Magnafloc 1011 and Al–PAM) were tested as flocculants and the effects of addition of a surfactant (dodecylamine hydrochloride), lime, gypsum, and/or coarse sands during flocculation were studied. The effect of "staged polymer addition and stirring" during flocculation was also studied.

Magnafloc 1011 was found to be effective for flocculation of mature fine tailings while Al–PAM was not. Test results also showed that "staged polymer addition and stirring" was beneficial to the flocculation process. The current study shows potential of flocculation as a viable means to treat MFT of the oil sands industry.

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List of Symbols

a	Particle radius (μm)
A	Hamaker constant (J)
D	Distance between particles (μm)
ε	Solvent permeability (cm/s)
κ	Inverse Debye length (μm)
Ω	Electric resistance (ohm)
ψ_s	Surface potential (mV)
ζ	Zeta potential (mV)
V_T	Total potential energy of interaction (J)
V_A	Potential energy due to London van der Waals attractive force (J)
V_R	Potential energy due to electrical double layer repulsive force (J)

List of Abbreviations

AERI	Alberta Energy Research Institute
AEUB	Alberta Energy and Utilities Board
CMC	Critical Micelle Concentration
CSS	Cyclic Steam Stimulation
CT	Composite/Consolidated Tailings
DAHCl	Dodecylamine Hydrochloride
DLVO	Derjaguin, Landau, Verway and Overbeek
FTFC	Fine Tailings Fundamentals Consortium
GCOS	Great Canadian Oil Sands
IEP	Isoelectric Point
MFT	Mature Fine Tailings
NEB	National Energy Board
NTU	Nephelometric Turbidity Units
OFC	Optimal Flocculation Concentration
PSD	Particle Size Distribution
SAGD	Steam Assisted Gravity Drainage
SDS	Sodium Dodecyl Sulphate
SFR	Sand to Fines Ratio

Chapter 1

INTRODUCTION

1.1 The Oil Sands – An Overview

The robust global demand for crude oil to meet the world's energy needs together with the rising geopolitical tensions in the Middle East and other petroleum exporting countries have led to a spike in the price of oil in recent years (now at about 120 dollars a barrel). This spike in oil prices coupled with growth in the world's demand for crude oil strengthen the notion that oil-producing countries, which manage their resource effectively, will continue to experience enormous boosts to their economy.

Canada is an example of a country that has experienced a boom in her economy due to the skyrocketing oil prices. Across Canada, crude oil is found in seven provinces, the biggest of which is the oil sands deposits rich province of Alberta. Oil sands are found in three locations in the province of Alberta: The Athabasca, Peace River and Cold Lake regions. The largest deposit in the world is in the Athabasca area located in Northeastern Alberta [Camp, 1976]. According to the Alberta Energy and Utilities Board (AEUB), the initial volume of crude bitumen in place in Alberta is estimated to be approximately 260 billion cubic meters (1.6 trillion barrels), with 11 percent or 28 billion cubic meters (175 billion barrels) recoverable under current technologies and economic conditions. This places Canada in the enviable position of holding the second largest oil reserves in the world after Saudi Arabia's total proven oil reserve of 42 billion cubic meters [National Energy Board (NEB), 2004].

The oil sands deposits are composed primarily of 8 to 14 percent bitumen, a heavy and viscous tar-like oil, contained in a mixture of sand, clay and water [NEB, 2004]. Bitumen is recovered from the oil sands by either surface mining or in-situ recovery methods. Surface mining operations are limited to areas where the overburden, situated above the bitumen deposit, has a thickness of 75 – 100 meters or less. In-situ recovery techniques, such as Steam Assisted Gravity

Drainage (SAGD) and Cyclic Steam Stimulation (CSS), are necessary for oil sands that are more deeply buried.

There has been commercial bitumen production from the Alberta oil sands since the Great Canadian Oil Sands (GCOS), now Suncor Energy Inc., began its surface mining operations near Fort McMurray in 1967. A second mine in the same area, operated by Syncrude Canada Ltd., began operation in 1978 and is the largest mine of any type in the world. A third mine, operated by the Albian Sands consortium of Shell Canada, Chevron Corporation and Marathon Oil Corporation, began operation in 2003. Petro-Canada is currently developing her $33 billion Fort Hills Project, in partnership with UTS Energy Corporation and Teck Cominco. There are also several dozen companies planning nearly 100 oil sand mines and in-situ projects in Canada worth billions of dollars in capital investment. Currently, there is a greater emphasis on surface mining operations. Section 1.2 gives an overview of water-based bitumen extraction from oil sands as practiced by surface mining operations.

1.2 Bitumen Extraction Process Description

The fundamental process used in commercial bitumen production from surface mining operations is founded on the water-based extraction technology developed by Dr. Karl Clark in the 1920s, [Petroleum Communication Foundation, 2000]. However, mining and extraction methodologies have evolved over time as technological advances have occurred.

There are three basic operations involved in bitumen production. They include: Mining, Extraction, and Upgrading [Masliyah et al., 2004].

Current mining operations utilize very large shovel excavators and mining haul trucks to excavate tones of oil sands ore for delivery to extraction operations. This is usually referred to as "truck and shovel" mining.

The mined oil sands are mixed with hot water and caustic soda to produce a slurry which is screened, with the oversized materials rejected for further crushing and reprocessing. The resulting slurry is then transported to a primary separation vessel via a hydrotransport pipeline. During the hydrotransport, the slurry is further conditioned, leading to bitumen liberation from the sand grains. Air is introduced which then attaches to bitumen. The aerated bitumen floats to the top of the slurry in the primary separation vessel, thereby forming a bitumen-rich froth product which is subsequently recovered while the coarse sands settle to the bottom and is removed as tailings.

The recovered bitumen-rich froth undergoes further processing where it is deaerated and mixed with diluents (naphtha or paraffin). Addition of diluents results in ample density difference between water and diluted bitumen and also reduces the bitumen viscosity. The reduced density and viscosity of the bitumen froth leads to the removal of entrained solids and water by use of inclined plate settlers, centrifuges and/or cyclones. This process removes essentially all of the remaining water and clay fines, leaving a relatively clean bitumen as feedstock for the upgrader where it is converted into a light synthetic crude oil.

The material remaining after the bitumen is extracted from the oil sands consists of water, sand, fine clay particles and some residual hydrocarbons. This material is sent to a tailings settling basin where the solids settle to the bottom and the clarified water is recycled for re-use in the extraction process. Figure 1.1 shows a generalized flow diagram for processing oil sands.

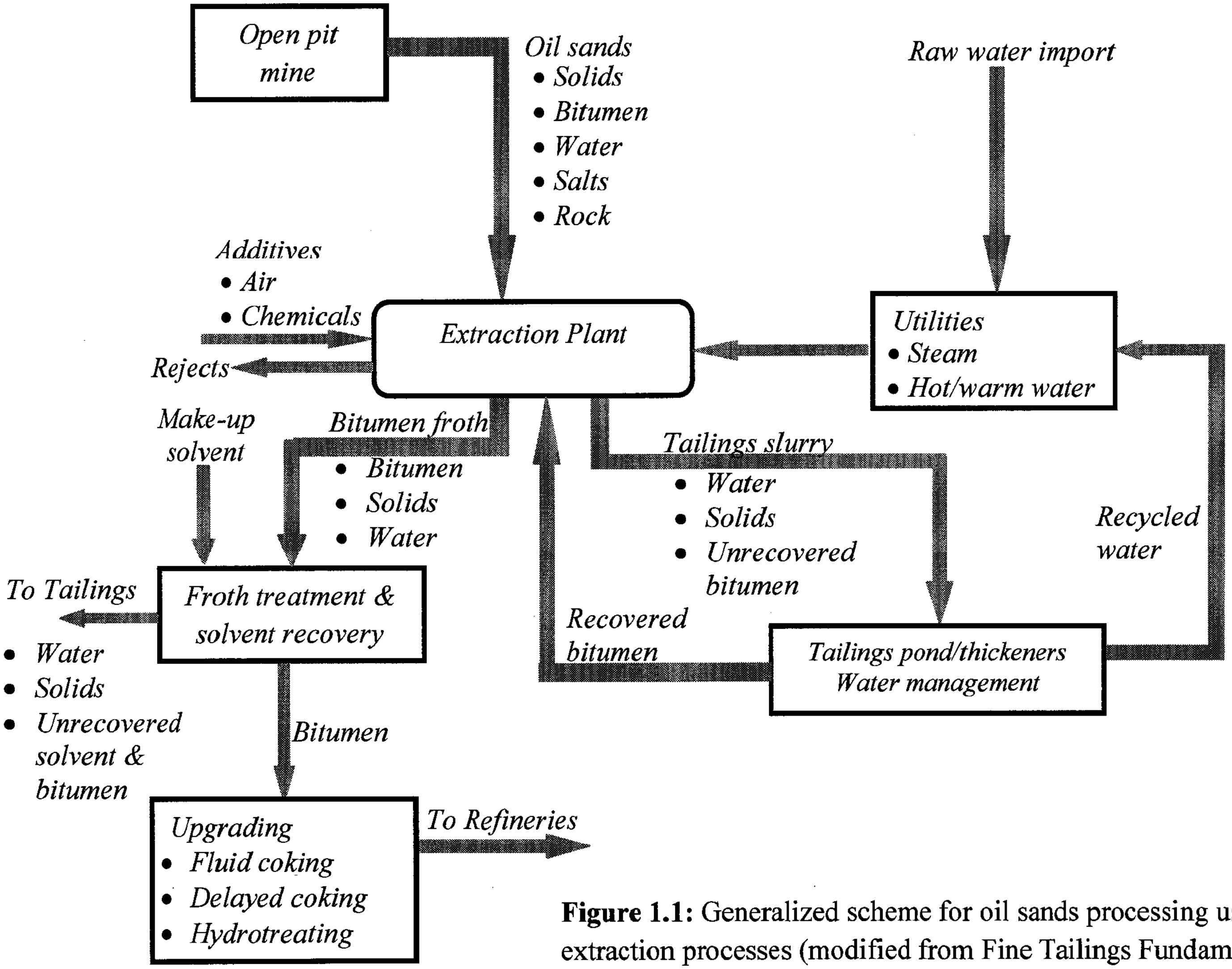

Figure 1.1: Generalized scheme for oil sands processing using water-based extraction processes (modified from Fine Tailings Fundamentals Consortium (FTFC), 1995).

1.3 Problem Definition

Despite all the economic advantages associated with oil sands development, commercial bitumen production from oil sands operations using the water-based extraction technology poses tremendous challenges. Amongst the various challenges, tailings operations present the most significant of all to the oil sands extraction process. This thesis focuses on effective tailings management as an essential ingredient for the continued success and development of the vast oil sands resources present in Alberta.

The rest of this introductory Chapter provides an overview on tailings operations, mature fine tailings and current tailings management practices in the industry. It concludes by demonstrating the relevance of continuous improvement on tailings management and outlines the thesis objectives.

1.4 Tailings Management

Oil sands tailings, which are composed of water, sands, silt, clay and residual bitumen, are produced as a by-product of the bitumen extraction process. The tailings have poor consolidation and water release characteristics. Neither the tailings solids nor the released water can be discharged into the environment (due to the containment of the entire water system within the extraction operating process) as part of the operating license agreements between the Alberta Provincial Government and any oil sands operator [FTFC, 1995]. Hence, all tailings from both the primary and secondary separation vessels and the froth treatment plant are discharged into a large settling basin usually referred to as a tailings pond, where the coarse solids settle out to form dykes and beaches while much of the fines and residual bitumen are carried into the pond as a thin slurry stream which generally has a solids content in the region of 8% by weight [FTFC, 1995]. These fine-grained clastic materials (silts and clays) and the residual bitumen sink in the pond to form a layer which consolidates very slowly, or not at all. The resulting deposit of fine-grained sediment, water, and bitumen are known as "fine tailings" or "fine tails".

Once the fine tails have been deposited into the pond, they begin to consolidate under gravity. The fine tails settle quickly to 20 wt% solids content and over a few years to 30 wt% solids (86% by volume water) with a stable slurry structure, which is called mature fine tails (MFT). This MFT will remain in a fluid state for decades because of its very slow consolidation rate [Kasperski, 1992; McKinnon, 1989]. The traditional tailings disposal procedure in a tailings settling pond is shown schematically in Figure 1.2.

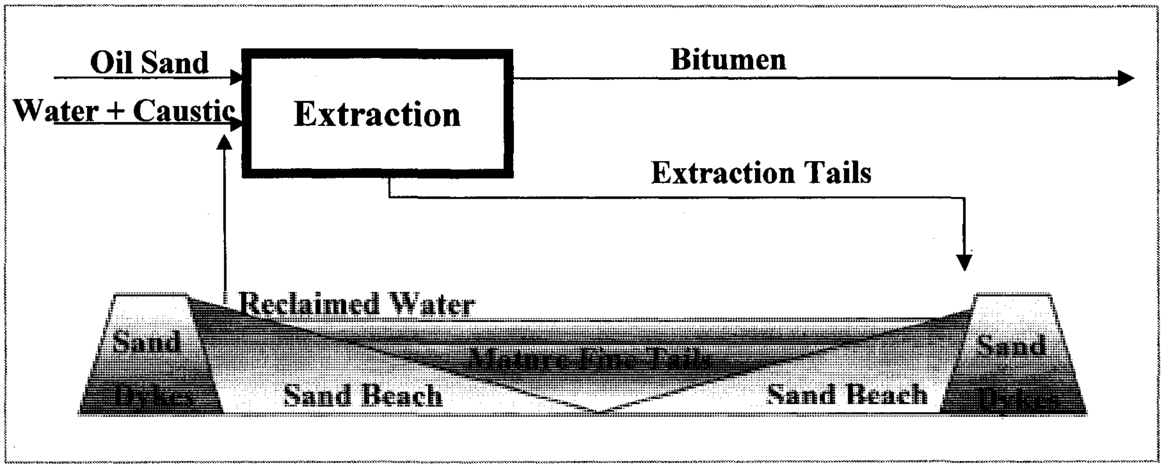

Figure 1.2: Traditional tailings disposal in a tailings settling basin (Cymerman et al., 1999).

1.4.1 Issues Related to Tailings Management

There are several key issues related to disposal of fine tailings that pose challenges to the oil sands industry:

- ***Accumulation of large volume of fine tailings***

The production and accumulation of large volumes of MFT poses a major environmental concern. Because of the no-discharge policy of tailings into the environment, the main loss of water in the fine tailings is to the voids in the tailings sand as the beaches are formed. Losses to evaporation are small, and thus only relatively minor quantities of water are lost. Fresh water required for make-up is small in comparison with the water which is recycled through the process. Without the benefit of addition of large quantities of clean dilution water, recycle of water between the process and the tailings ponds in this closed loop has resulted in accumulation of fine clays and dissolved inorganic ions in the tailings pond water system. Consequently, a large inventory of MFT has accumulated in the tailings facilities of the oil sands operators.

It is estimated that about 0.25 m^3 of MFT is produced per barrel of bitumen produced [Nelson, 2006]. With oil sands leases being granted to new oil sands operators such as Canadian Natural Resources Ltd. (CNRL), Total E&P Canada, Imperial Oil, etc; there will be an increasing presence of tailings facilities covering large areas of land and hence a further accumulation of fine tailings at an ever-increasing rate.

- ***MFT effects on the environment***

Mature fine tailings contain naphthenic acids and residues of hydrocarbonates that are toxic for the environment. Hydrological and geochemical studies that have been performed in the area of Athabasca Oil Sands have indicated large quantities of tailings with much of sulphide oxidation and high concentrations and mixtures of heavy metals. This has adverse acute and chronic effects on aquatic organisms and wild life in areas surrounding the MFT storage site. Research results indicate that the tailings that exist in the water and soils of the storage area continue to release elevated concentrations of metals and other elements to surface and groundwater for many years after they have been released [FTFC, 1995].

- ***Fresh water concerns***

The use of water in the oil sands has become an issue because of the large quantities of water required to extract and process bitumen from the oil sands. On average 3 barrels of fresh water is consumed to produce a barrel of bitumen [Nelson, 2006].

MFT traps water in the pores of the fine solids. This, coupled with the very slow settling of the fine solids in the tailings ponds and zero water discharge back into the environment, leads to the accumulation of a large water and solids inventory. With the expansion of the oil sands industry, there is also a growing demand for external water use. It is therefore necessary to develop processes to ensure efficient use of water with minimal water inventory and also reduce the use of fresh water.

1.5 Tailings Management – Current Industry Practices

In response to the challenge of fine tailings management, considerable efforts have been made by the oil sands operators, government and research institutions to identify suitable technologies aimed at reducing both the total MFT inventory and the MFT produced per barrel of bitumen produced.

The following discussion is limited to current tailings management techniques as used in the oil sands industry today.

1.5.1 Consolidated/Composite Tailings (CT) Process

The CT process is a non-segregating* disposal method to deal with MFT. It involves the addition of a chemical coagulant, calcium sulfate (gypsum), to a slurry comprising of coarse sand tailings and mature fine tails. This results in a slurry mix which becomes non-segregating during transport, discharge and deposition. The produced CT mixture, which is pumped to a pond where it consolidates into a stable deposit, will release water relatively quickly on deposition. The water released from the CT deposit is recycled and used for extraction. An outline of the CT process is shown in Figure 1.3.

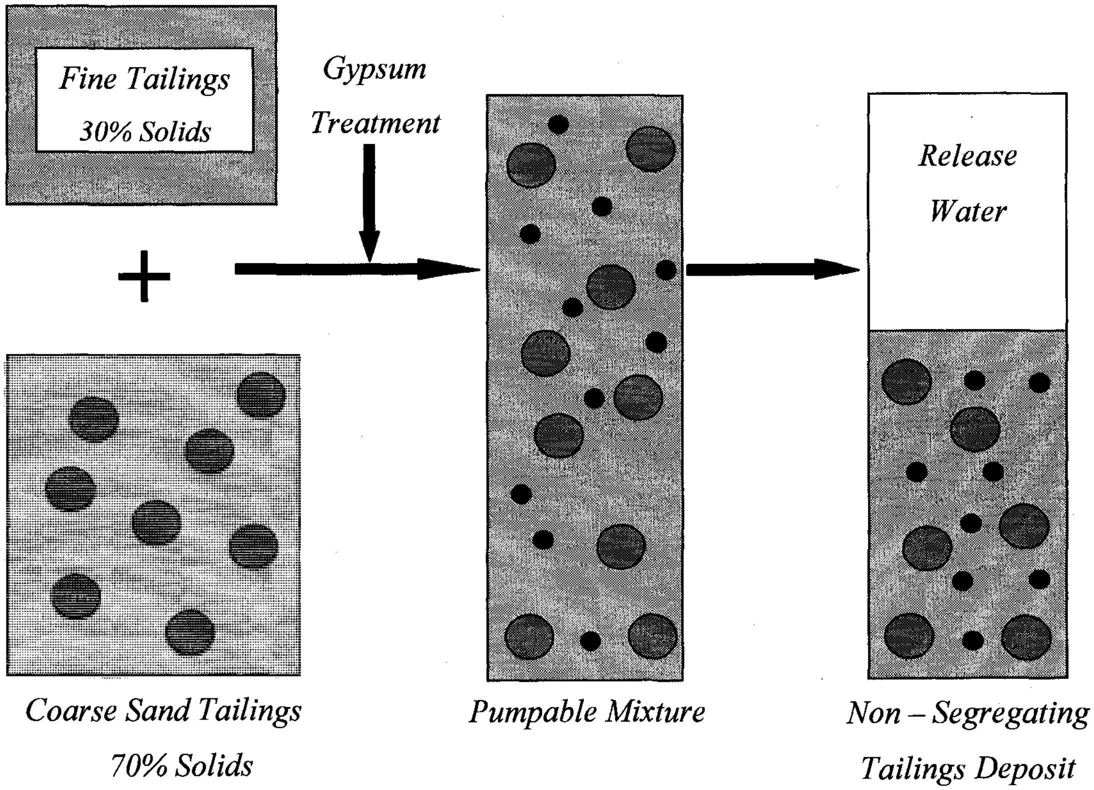

Figure 1.3: A Simplified Outline of the Composite Tailings Process.

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* Non – segregating tailings are a tailings mixture in which fines and coarse sand particles settle simultaneously to form a uniform deposit

The successful implementation of the CT process has led to reduced MFT inventory. This is already evident in the reduced volume of MFT of Leases 17/22 of Syncrude Canada Ltd [Mathews et al., 2002]. CT implementation also helps to alleviate stakeholder concerns regarding the long-term management of fluid fine tailings. However, the CT process has its drawbacks.

The addition of gypsum results in significant changes in the ionic content of CT and CT release water. Chemical analysis of the CT mix and its released water has revealed that this material contains high concentrations of ions including Na^+, Cl^-, and SO_4^{2-} [MacKinnon et al., 2001]. These high ionic concentrations in CT are considered a significant constraint to plant growth. Furthermore, the recycle water from the CT process contains Ca^{2+} which is said to have a negative impact on bitumen extraction [Kasongo et al., 2000]. This negative impact has been a challenge for sustainable implementation of the CT technology.

1.5.2 Thickened Tailings/Paste Technology

As shown in Figure 1.2, the traditional tailings disposal method involved hydrotransporting the tailings stream from the bitumen extraction plant to the tailings settling pond. Here, the coarse sand fraction of the tailings is used to build containment dykes. Figure 1.2 also shows that water is recycled back to the extraction plant after MFT is formed (which occurs after several years of settling).

This traditional tailings disposal method had drawbacks, some of which included high costs of construction and maintenance of the containment structures and loss of heat from the recycled warm process water as it is exposed to the cold climate in Northern Alberta. The continuous search for innovative technologies for maximizing energy efficiency and water re-use led to the development of "Thickened Tailings" (or "Beach and Paste Tailings" Disposal Concept).

In the thickened tailings process, extraction fine tails and beach run-off streams are combined and introduced into a process vessel (thickener) where chemicals are added to help "flocculate" the fine solids, leading to rapid settling of the fine solids. High molecular weight, medium charge anionic polymers such as Percol 727† (now known as Magnafloc 1011) or Percol LT27A were discovered to be most effective for flocculation of the fine tailings at a pH of about 8.5 [Cymerman et al., 1999].

Generally, the thickened tailings technology eliminates the production and storage of fluid MFT. It produces water which is suitable for re-use in the extraction process, with little loss in temperature. This results in lower energy costs and reduced greenhouse gas emissions. In addition, the faster settling rate of the fines produces a concentrated stream of fines solids which can be deposited with less land disturbance. This offers potential for speeding up land reclamation. The thickened tailings disposal concept is illustrated in Figure 1.4.

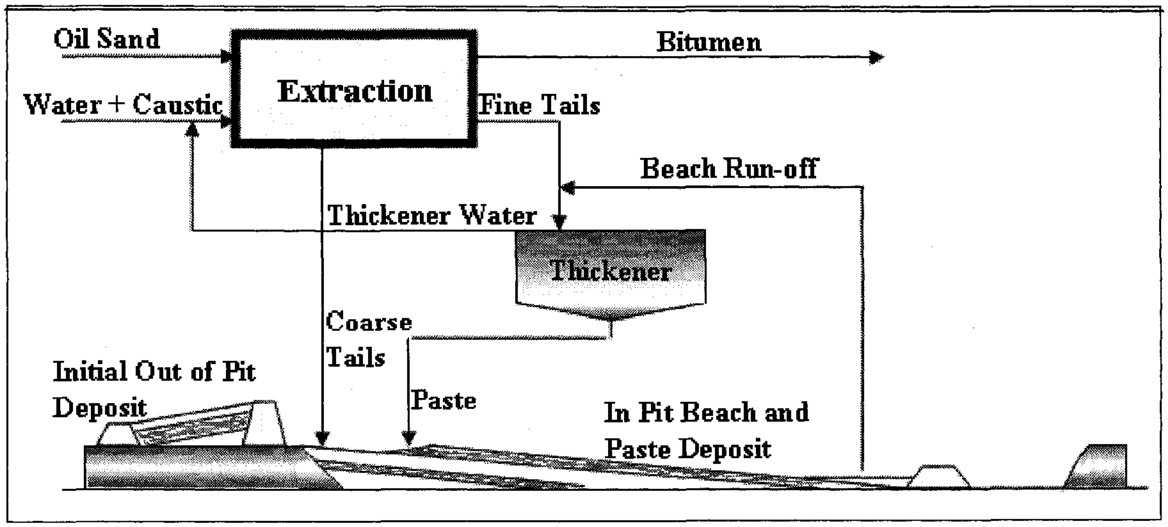

Figure 1.4: Thickened Tailings Disposal Concept (Cymerman et al., 1999).

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† Percol 727, now known as Magnafloc 1011, is a high molecular weight, medium charge anionic polymer produced by Ciba Specialty Chemicals. For the purpose of this thesis, Magnafloc 1011 replaces all references to Percol 727

1.6 **Summary**

As far as production of crude oil and its price remain profitable, surface mining of the Alberta oil sands will go on. A lot of resources will continuously be put into tailings management and disposal to ensure sustainability of the oil sands extraction process.

Research and collaborative efforts by oil sands industry operators, consultants, academics and regulatory agencies have led to the development of a variety of tailings handling technologies over the years to deal with MFT accumulation and to alleviate storage problems associated with the fluid fine tailings stream. Commercial implementation of the CT process provides improvement in tailings management efficiency and reduces the volume of fluid fines to be managed in the long term. With the recent implementation of thickeners (via thickened tailings), the clays and fines can be thickened to generate MFT-like paste in minutes and hours instead of months to years in tailings ponds, enabling recycling of warm water.

The success gained with implementation of the thickened tailings technology using the principle of polymer flocculation in thickeners presents opportunities for further development of the thickened tailings concept with an ultimate objective of creating a stable deposit that has a surface amenable to dry landscape reclamation as quickly as possible.

This thesis focuses on studies aimed at tailings management with the principle of flocculation by polymers.

1.7 Thesis Objective

This work investigates the effect of polymer addition on flocculation of MFT. It also explores the possibility of using additives (surfactants, lime and gypsum) and polymer flocculants to improve treatment of MFT.

Kaolin and illite are the main clay minerals found in the fines of oil sands. Typically, the clay minerals in fine tailings are composed of 40 – 70% kaolin, 30 – 50% illite and 1 – 15% montmorillonite [FTFC, 1995]. For the purpose of this study, flocculation and settling tests are conducted on both kaolin suspensions (as model tailings) and mature fine tails.

For a better understanding of the polymer flocculation process, chapter 2 presents a review on the flocculation of fine particle suspensions with main focus on flocculation by polymers and the factors that affect it. It also discusses previous work done by other researchers on flocculation of fine tailings and presents a summary of their findings.

Chapter 3 presents studies on surfactant/polymer interaction on flocculation of kaolin suspensions. Chapter 4 focuses on polymer flocculation of kaolin suspensions. The work is extended to mature fine tailings in chapter 5. A new approach of polymer addition for flocculation of kaolin suspension and mature fine tails is also introduced and the results are presented. Final conclusions from this study are presented in chapter 6.

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Chapter 2

LITERATURE REVIEW

2.1 Flocculation of Fine Particle Suspensions

As described in Chapter 1, oil sands extraction tailings segregate to form sandy beaches and fine tails runoff. MFT, a stable suspension of fine mineral particles in water, forms after many years of settling. Long-term storage of large volumes of MFT is both costly and an environmental liability. In a new process to eliminate MFT generation, referred to as the thickened tailings technique, fine tailings are "flocculated" and thickened into a paste and disposed of in "solid" form.

Flocculation is the process of forming large agglomerates (flocs) of particles in a suspension through high molecular weight polymeric chemicals. It is an efficient means of achieving solid-liquid separation. The key to effective flocculation is an understanding of how the individual fine particles in suspension interact with each other. The following discussion is intended to provide an overview of particle surface phenomena, the nature of the flocculation process, and how it can be controlled to achieve optimum performance.

2.2 Stability of Fine Particle Suspensions

The behavior of fine particles in a suspension is strongly influenced by the electrical charge on the particle surface. Each fine particle normally carries a similar charge, which in nature is usually negative [Hunter et al., 1979]. This similar charge causes adjacent particles to repel each other and leads to stabilization of the suspension. All particles exert mutual attraction forces, known as London – van der Waals forces, which are effective only at short distances of separation. However, the electrostatic repulsion of the surface charges opposes the particles from coming close enough for these attraction forces to take effect. Besides electrical repulsion, a suspension may become stable when water is adsorbed from the surrounding onto the surface of the particles, forming solvation layers, which repel one another [Tridib et al., 2006].

2.3 The Electrical Double Layer

To explain how the electrical repulsive forces occur, a double layer model is used to visualize the ionic environment in the vicinity of a charged particle. Masliyah et al. (2006) give details of both the Gouy-Chapman and Stern double layer models.

Figure 2.1 shows the structure of an electric double layer for a negatively charged surface according to the Stern model. In this model, ions of opposite charge, often called counter-ions, are attracted towards the surface and ions of like charge (co-ions) are repelled away from the surface. This, together with the mixing tendency of thermal motion, leads to the formation of an electric double layer made up of the charged surface and a neutralizing excess of counter-ions over co-ions distributed in a diffuse manner in the polar medium [Shaw, 1992].

The negatively charged surface and its positively charged atmosphere produce an electrical potential across the diffuse layer. As shown in Figure 2.1, this potential is highest at the surface and decreases linearly to the end of the Stern layer (away from the particle surface), after which there is an exponential decrease of the electric potential, approaching zero at the outside of the diffuse layer. A point of interest in the exponential decay curve is the potential at the shear plane between the Stern layer and the diffuse layer which is known as the zeta potential (ζ). The zeta potential is an important feature as it can be measured while the surface potential cannot. Knowledge of the zeta potential can be used to predict and control the stability of the fine particle suspension as changes in the zeta potential indicate changes in the repulsive force between the particles.

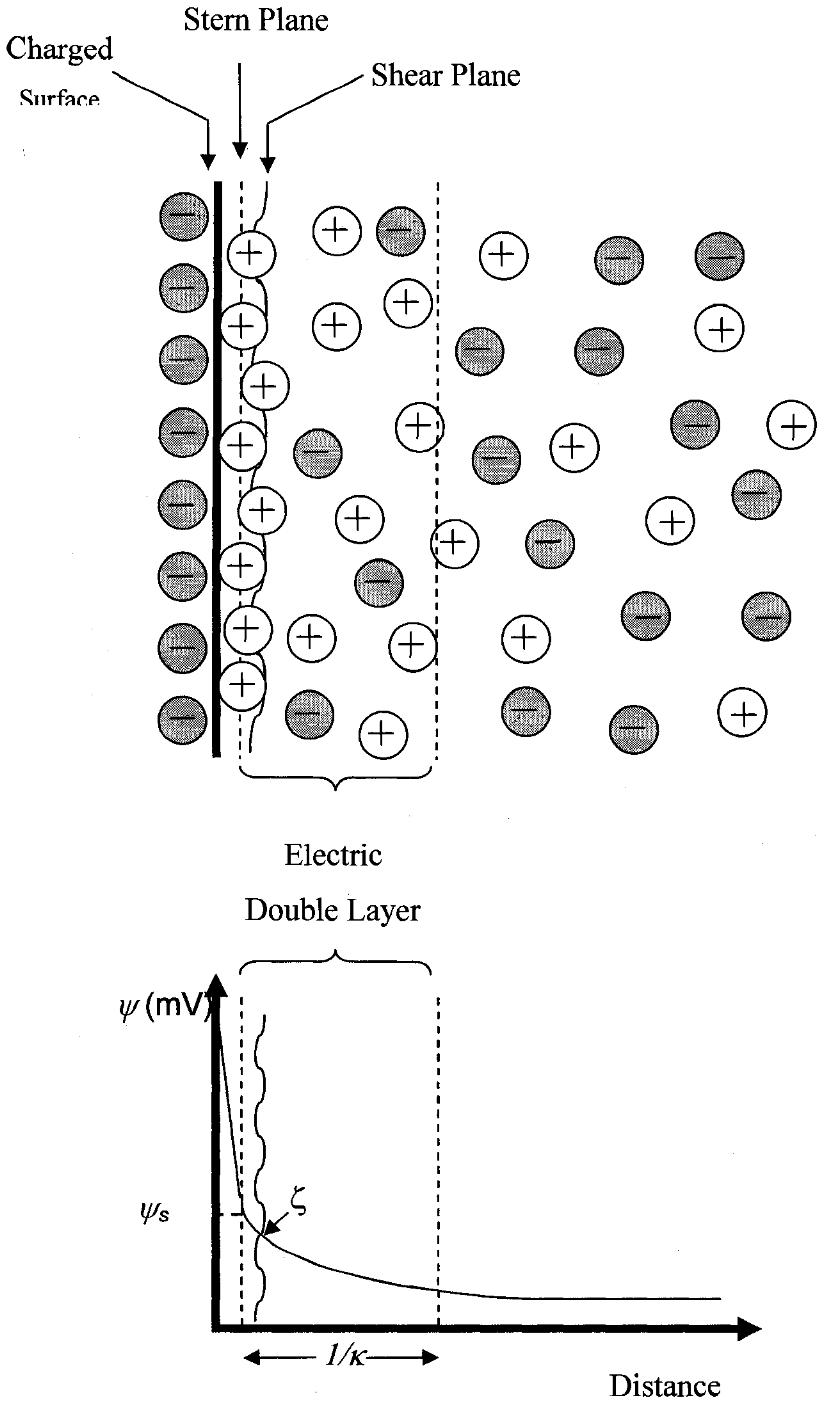


Figure 2.1: Schematic illustration of an electric double layer across a negatively charged surface and profile of electric potential distribution away from the surface according to the Stern model (Shaw, 1992).

2.4 DLVO Theory

Derjaguin and Landau [Derjaguin et al., 1941] and Verway and Overbeek [Verway et al., 1948] were able to use the double layer theory to predict the stability of colloidal particles. This has become what is known as the DLVO Theory.

The DLVO Theory uses the balance between two opposing forces – electrostatic repulsion and van der Waals attraction – to explain the tendency of spherical particles to either remain stable or to coagulate. It suggests that the stability of the spherical particles in a solution is dependent upon the total interaction energy, V_T, which is given by:

$$V_T = V_A + V_R \qquad (2.1)$$

where V_A is the van der Waals attractive force and V_R is the electrical double layer repulsive force [Rao, 2004].

For two spherical particles of the same size, the van der Waals attractive force is given by:

$$V_A = \frac{-Aa}{12D} \qquad (2.2)$$

where A is the Hamaker constant, a is the particle radius and D is the distance between the spherical particles, [Shaw, 1992].

The electrical double layer repulsive force is given by:

$$V_R = 2\pi\, \varepsilon\, a\, \zeta^2 \exp(-\kappa D) \qquad (2.3)$$

where *a* is the particle radius, ε is the solvent permeability, κ is the Debye-Huckel Parameter (a function of the ionic composition) and ζ is the zeta potential.

The theory proposes that there is an energy barrier which results from the repulsive force between two particles, thereby preventing the particles from approaching one another and agglomerating. In order to cause the particles of a stable suspension to coagulate, it is necessary to provide sufficient kinetic energy to the particles to overcome the energy barrier. Once the energy barrier is jumped, the net interaction energy is all attractive and the particles will coagulate. However, if the particles still have sufficiently high repulsion, the suspension will resist coagulation and the colloidal system will remain stable. Figure 2.2 shows a schematic diagram of the variation of free energy with particle separation according to the DLVO Theory.

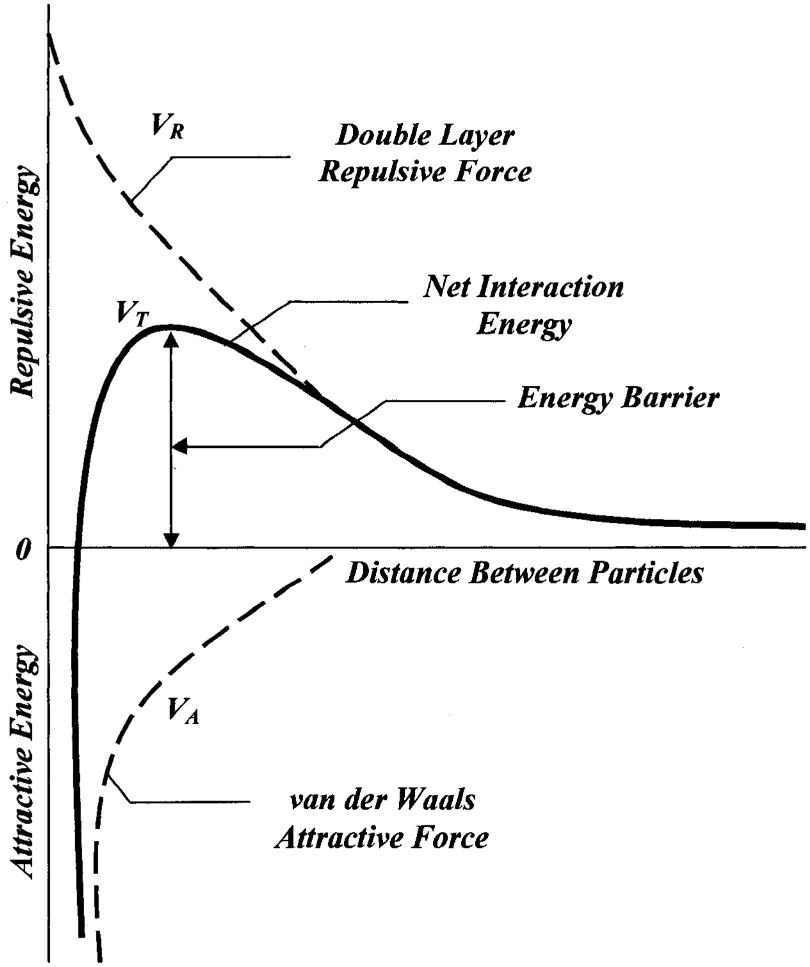


Figure 2.2: Schematic diagram of the variation of free energy with particle separation according to the DLVO Theory.

2.5 General Mechanisms of Flocculation

As discussed in the previous section, for an effective agglomeration of particles in a stable suspension to occur, it is necessary to provide sufficient kinetic energy to the particles so that they can overcome the energy barrier. Alternatively, the energy barrier could be lowered or completely removed so that the net interaction energy is attractive. This can be achieved by the following mechanisms:

2.5.1 Double Layer Compression

Double layer compression involves adding salts such as NaCl to the suspension (i.e. increasing ionic strength of solution). As enough of the ions that are opposite in sign to the net charge on the surface of the particles enter the diffuse layer surrounding the particles, the double layer is compressed until there is no longer an energy barrier. Hence, the particles are able to agglomerate because they can fall into the range where the van der Waals attractive forces dominate. Multivalent ions are especially effective for this purpose and reagents such as lime, alum, etc., are widely used in practice [Hogg, 2000].

2.5.2 Surface Charge Neutralization

Charge neutralization involves reduction of the net surface charge (and consequently, the zeta potential) of the particles in the suspension. As the net surface charge diminishes, the diffuse layer thickness surrounding the particles is reduced and the energy required to move the particles into contact is minimized.

Charge neutralization can be accomplished by addition of coagulants with charged ions opposite in sign to the net surface charge of the particles. Coagulants used to achieve this usually have a strong tendency to adsorb onto the particle surface. The tendency of the coagulants to adsorb is usually attributed to both poor coagulant–solvent interaction and a chemical affinity of the coagulant, or chemical groups on the coagulant, for the particle surface [Amirtharajah et al., 1999]. Highly charged cations such as Cu^{2+}, Al^{3+} and Fe^{3+} are usually effective for this type of agglomeration mechanism.

It should be noted that the agglomerates produced by both double layer compression and charge neutralization are generally small, compact and loosely bound. Hence they are highly susceptible to breakage in the presence of turbulence or shear. Agglomeration may be further improved by addition of a "bridging" flocculant.

2.5.3 Bridging Mechanism

Flocculation by bridging is the most important mechanism of agglomeration [Sworska et al., 2000]. When long chain polymers are added in small dosages to a suspension of colloidal particles, the polymers adsorb onto the particles in such a way that an individual chain can become attached to two or more particles thereby "bridging" them together. Polymer bridging requires that there is available particle surface for attachment of the polymer segments from chains attached to other particles. The polymer molecule must also be capable of spanning the gap between the particles to minimize double layer repulsion when the particles approach each other. As a consequence, low polymer dosage is insufficient to form adequate bridging links between the particles and excess polymer dosage may lead to restabilization of the suspension (also referred to as steric stabilization) as there is no longer sufficient particle surface available for attachment of the polymer segments [Tridib et al., 2006]. This suggests that bridging flocculation will always have an optimum flocculant dosage corresponding to a particle coverage that is considerably less than complete. An illustration of bridging flocculation and steric stabilization is shown in Figures 2.3a and 2.3b respectively.

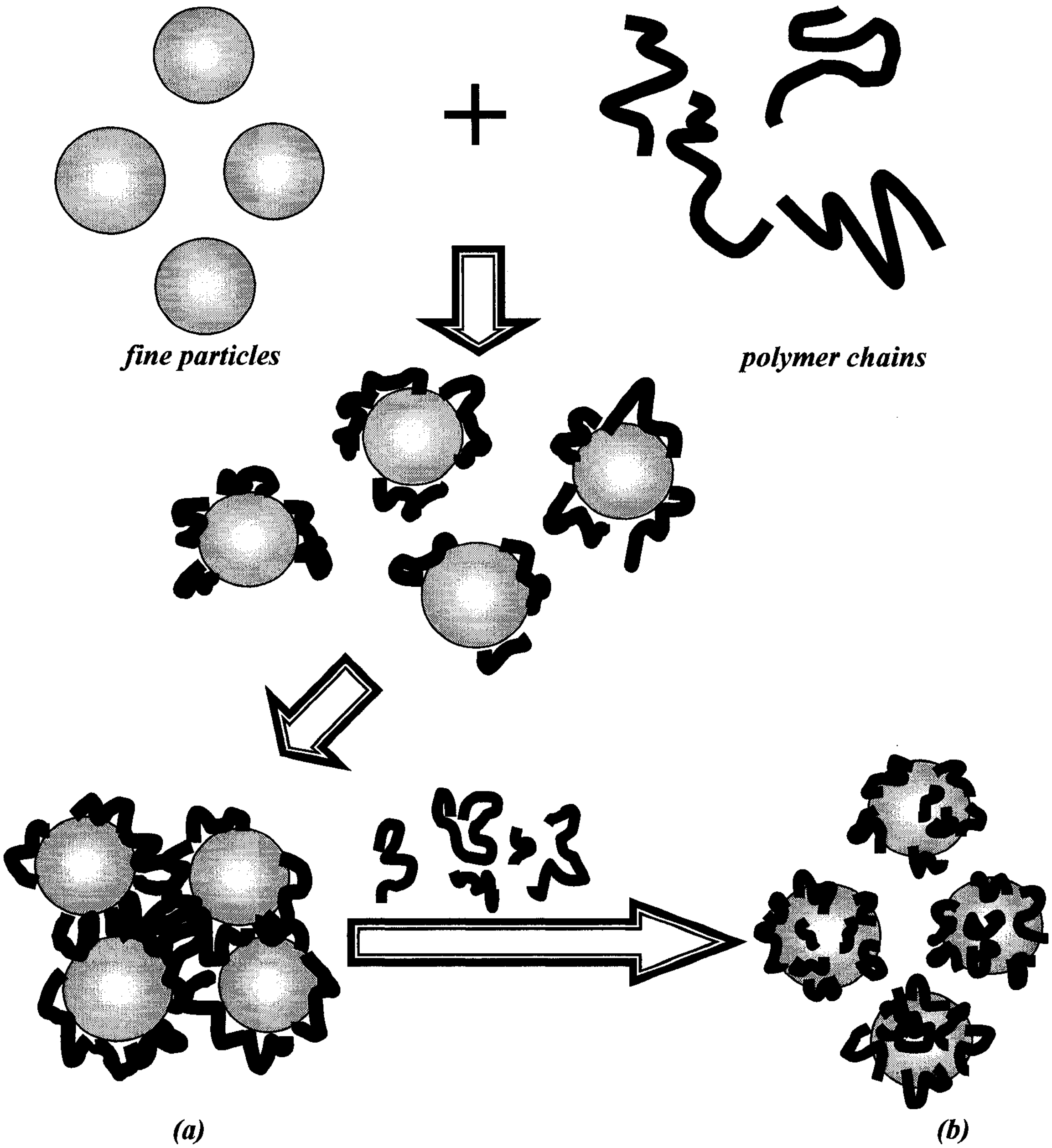


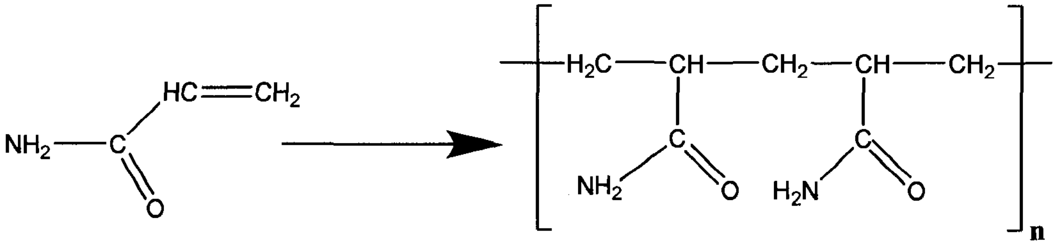
Figure 2.3: Schematic illustration of (a) bridging flocculation (b) restabilization by adsorbed polymer (steric stabilization) (Modified from Tridib et al., 2006).

2.6 Flocculating Materials

Flocculants are broadly classified into two groups; inorganic and polymeric. Polymeric flocculants offer various advantages over inorganic flocculants. The flocs formed by polymeric flocculants are larger and stronger and more rapidly formed. The dosage requirement is quite low (typically 1% on a dry weight basis) where as that of inorganic flocculants may be as high as 20% [Tridib et al., 2006]. Nevertheless, inorganic flocculants are cheap and are often used for economic reasons.

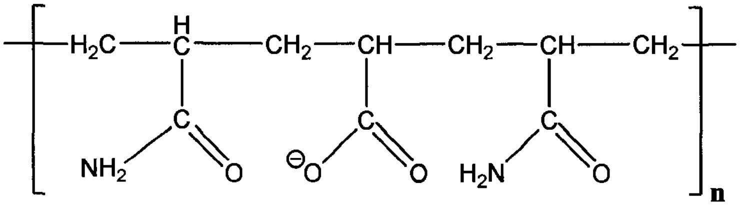
Polymeric flocculants which function as bridging flocculants are further classified into natural and synthetic polymers. Natural polymers such as starch, gums, glues, etc. have much lower molecular weight than synthetic polymers and are capable of a lesser degree of flocculation. Synthetic polymers, in contrast, are highly efficient flocculants and can be tailored in terms of functional groups, structure, and molecular weight to suit a particular application. However, they are very expensive and may be toxic [Bratby, 1980; Gregory, 1983].

The most commonly used synthetic flocculants are based on polyacrylamide and its derivatives [Moody, 1992]. Polyacrylamide itself is basically non-ionic and the ionic character is varied by copolymerization with other monomers. Anionic polyacrylamides may be prepared by copolymerization of acrylic acid with acrylamide or by partial hydrolysis of polyacrylamide. Cationic polyacrylamides are made by copolymerization of acrylamide with quaternary ammonium derivatives of acrylamide, the type of cationic material being variable, depending on the application. Figure 2.4 shows synthetic flocculants based on polyacrylamide and its derivatives.

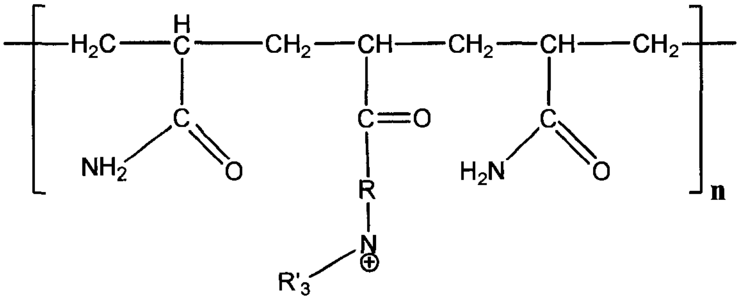


Acrylamide

Polyacrylamide



Anionic Polyacrylamide



Cationic Polyacrylamide

Figure 2.4: Synthetic flocculants based on Polyacrylamide and its derivatives (Moss and Dymond, 1978).

2.7 Factors Affecting Flocculation (Using Synthetic Polymers)

2.7.1 Effect of Polymer Dosage

The degree of flocculation achieved is markedly affected by polymer dosage [Gregory and Gubai, 1991]. Addition of polymer beyond a certain optimum polymer dosage usually results in decreased efficiency of the flocculation process. The optimum dosage is the maximum amount of polymer that the solid can utilize for flocculation and it has been suggested that this optimum flocculation occurs when half the area of the solid is covered with the polymer [Hogg, 1992; Gregory, 1988]. At higher polymer concentrations, the particle may be completely covered by the adsorbed polymer layer which could result in a stable suspension that is very difficult to separate.

2.7.2 Effect of Mixing Conditions

Excessive agitation of a flocculating suspension causes floc breakage. This has an adverse effect on flocculation efficiency as the smaller flocs formed have a lower settling rate. Even though floc breakage leads to exposure of fresh particle surfaces to polymer adsorption, thereby resulting in increased adsorption capacity of the flocculant, the flocs do not reform efficiently as the excess adsorbed polymer causes repulsion. This suggests that optimum dosage for a polymer only holds at a particular degree of agitation.

2.7.3 Effect of Polymer Molecular Weight

With synthetic bridging polymers, the higher the molecular weight, the better the flocculant. At higher molecular weight, as the polymer gets adsorbed, it can extend further away from the particle surface and is slower to reach equilibrium.

This, in turn, increases particle radius and collision number and hence flocculation rate [Tridib et al., 2006].

Moss and Dymond, (1978) reported that polymer molecular weight is not the only criterion for effective flocculation. They observed that two polymers A and B with the same apparent molecular weight gave considerably different flocculation performance. The difference in performance was attributed to their molecular weight distributions as Polymer A had a wide molecular weight spread, containing amounts of both high and low fractions, while polymer B had a narrower spread with more of the intermediate fractions than polymer A. They suggested that the actual difference in performance by polymers with similar molecular weight in a given situation may depend on the nature of the slurry being treated as well as the properties of the polymer.

2.7.4 Effect of Particle Size

Generally, on fine silica particles, the optimum polymer/solid ratio is directly proportional to the surface area of the solid. This suggests that a decreased particle size means an increase in flocculant demand [Moss and Dymond, 1978].

2.7.5 Effect of pH

The optimum polymer dosage needed for effective flocculation varies with the pH of the suspension as colloid surface charge is affected by pH changes. The pH also controls the degree of ionization of the polymer. This varies the amount of charge on the polymer chain, thereby determining the degree of extension of the polymer molecule. Consequently, bridging flocculants can only function over a certain pH range, depending on the type.

2.8 Previous Studies on Flocculation of Oil Sands Fine Tailings

The slow consolidation rate of MFT was identified in Section 1.3 as a major problem for commercial oil sand operations. For better oil sands tailings management, the settling characteristics of the fine tailings must be improved in an economic and environmentally acceptable manner.

For many years, research has been ongoing by several parties to identify methods of increasing the settling and consolidation rates of the oil sand fine tailings. Flocculation, amongst many other techniques, has been reported in literature as an effective method of increasing the efficiency of the fine tails consolidation process.

Some interesting early work on flocculation of the oil sand fine tailings include that of Baillie and Malmberg (1969) who tested many inorganic electrolytes and organic polymers as potential coagulation and flocculation reagents for the fine tailings. Their tests indicated that flocculation at the normal pH of the tailings slurry (~ 8.5) was slim and that good flocculation could only be attained by adjusting the pH to either below 7.5 or above 9.5. It was alleged, however, that pH adjustment of the tailings slurry would cause build up of undesirable ions in the recycle water. Rao (1980) tested many polymeric flocculants including Percol 140 (cationic), Percol 351 (non–ionic), Separan MG 200 (anionic) and Superfloc A130. He also made use of calcium and magnesium salts such as $CaCl_2$, $MgSO_4$, $CaSO_4$ and CaO as coagulants, and found that effective flocculation of the tailings could be achieved at a flocculant dosage of 125 g/m^3 tailings slurry. Even though this finding was encouraging, it was believed that flocculation by the stated polymers at the said dosages would be expensive due to the large volume of the tailings slurries.

More recently, studies conducted by Cymerman et al. (1999) showed that high molecular weight, medium charge anionic copolymers of acrylamide and acrylates, such as Magnafloc 1011, caused some flocculation of the fine tailings at the normal pH of the tailings slurry (i.e. pH ~ 8.5) at relatively low dosages. Their results showed that Magnafloc 1011 produced fast settling flocs and a turbid supernatant water layer containing about 1.5 % solids by weight. Subsequent pilot plant studies by Cymerman et al. (1999) led to the proposal of the "Beach and Paste" tailings disposal concept (as described in Section 1.5.2) in which anionic polymers are added into a tailings thickener where the fines are flocculated and thickened into a paste.

Sworska et al. (2000) studied the effect of Magnafloc 1011 flocculant, pH and divalent cations' concentration on settling rate and turbidity of Syncrude fine tailings. They found that the flocculation response (initial settling rate, solids content in the supernatant) of the fine tailings to Magnafloc 1011 depends on the pH of the slurry. According to their results, the optimum flocculation performance was located at a pH range from 4 – 6 and at a Magnafloc 1011 concentration of 80 ppm while the optimum shifted to the pH range 5 – 9 at a Magnafloc 1011 concentration of 40 ppm in the presence of Mg^{2+} ions. Since clays form stable suspensions in alkaline media, it is noted that the divalent cations' were added prior to addition of the flocculant in the above pH range (i.e. pH 5 – 9) to destabilize the suspensions. In general, Magnafloc 1011 was found to be more efficient in the presence of divalent cations (Mg^{2+}, Ca^{2+}) as the clarity of the supernatant was dramatically improved in an alkaline pH. Further studies conducted by Sworska et al. (2000) on Syncrude fine tailings showed that flocculation performance (solids content in sediment and initial settling rate) is also affected by mixing conditions. Their results revealed that adequate mixing and hydrodynamic conditions improve distribution of the polymer in the flocculating suspension and results in a lower polymer dosage required to obtain good flocculation. For instance, at a mixing speed of 200 rpm[‡], good flocculation was possible merely at 10 ppm[§] flocculant dosage.

[‡] rpm = revolutions per minute

[§] ppm = parts per million

The foregoing studies suggest that flocculation efficiency of fine tailings by polymer is measured by initial settling rate, turbidity or clarity of supernatant and solids content in the sediment. Fine oil sand tailings can be effectively flocculated in an alkali medium by high molecular weight, medium charge anionic polyacrylamide-based polymer such as Magnafloc 1011. Good flocculation response is influenced by many factors including optimization of polymer dosage, water chemistry (e.g. pH of tailings), and mixing conditions.

2.9 Summary

A review on the flocculation process has been presented in this Chapter. Factors that affect the interaction and aggregation of fine particles in suspension were outlined and different flocculation mechanisms have been discussed. Polymer dosage, mixing conditions, polymer molecular weight, particle size and pH were identified as some factors that affect bridging flocculation using synthetic polymers. Previous studies on flocculation of fine oil sands tailings have also been outlined and their results presented.

Following the background information presented in chapters 1 and 2, the following chapters therefore describe the research project that was carried out to meet the thesis objectives outlined in Section 1.7.

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Chapter 3

STUDIES ON FLOCCULATION OF KAOLIN SUSPENSIONS WITH POLYACRYLAMIDE IN THE PRESENCE OF A SURFACTANT

3.1 Introduction

In Chapter 2, high molecular weight, long chain synthetic polymers were identified as extensively being used for flocculating fine particle suspensions in many industrial applications. The polymers in solution generally act by adsorbing onto the solid surfaces and aggregating them together, leading to faster settling of the formed flocs and an enhanced separation of the solids from liquid. Besides polymers, surface-active agents such as surfactants are also used to modify the electrochemical nature of particle surfaces in suspension. Surfactant molecules change the properties of the solid–liquid interface by adsorbing onto particle surfaces and affecting the behavior of the suspensions. Section 3.2 presents a brief overview on surfactants and their dewatering ability on fine particle suspensions.

3.2 Surfactants and their Dewatering Ability

3.2.1 Surfactants

Surfactants are organic compounds that are amphiphilic, meaning they contain both hydrophilic (polar) “head” groups and hydrophobic (non-polar) hydrocarbon “tails”. Surfactants reduce the surface tension of water by adsorbing at the liquid–gas interface. They also reduce the interfacial tension between oil and water by adsorbing at the liquid–liquid interface. Many surfactants can assemble in the bulk solution into aggregates usually called micelles. The concentration of surfactants above which micelles are spontaneously formed is known as the “critical micelle concentration” (CMC). CMC is an important characteristic of a surfactant as it can be used to dictate surface tension changes. Before reaching the CMC, the surface tension changes significantly with the concentration of the surfactant. After reaching the CMC, the surface tension reaches a minimum and remains constant.

3.2.1.1 Classification of Surfactants

Surfactants can be classified into four categories depending on the type of charge on the hydrophilic "head":

- ***Anionic surfactants***

  In solution, the head carries a residual negative charge. Sodium dodecyl sulphate [$CH_3CH_2(CH_2)_9CH_2OSO_3Na$ or SDS] is an example of an anionic surfactant.

- ***Cationic surfactants***

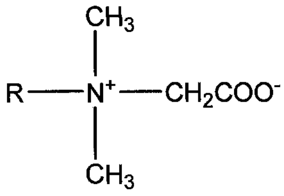
  The head carries a residual positive charge in solution. An example of a cationic surfactant is dodecylamine hydrochloride [$CH_3(CH_2)_{11}NH_2.HCl$ or DAHCl].

- ***Non – ionic surfactants***

  These surfactants do not carry any charge. The hydrophilic part is oriented towards water and renders the surfactant water soluble. The most commonly used non-ionic surfactants are ethers of fatty alcohols e.g. dodecyl alcohol ethoxylate, [$CH_3\,(CH_2)_{10}\,CH_2\,(OCH_2CH_2)_n\,OH$].

- ***Amphoteric surfactants***

  These surfactants may contain two charged groups of different sign. An example of an amphoteric surfactant is alkyl dimethyl betaine.



$$R - \underset{CH_3}{\overset{CH_3}{N^+}} - CH_2COO^-$$

where R is a hydrocarbon group of $C_{12/14}$

3.2.2 Surfactants as Dewatering Aids

In some applications where the end objective is to obtain dry solid from a suspension, high molecular weight long chain polymers are first used to flocculate the suspension resulting in rapid separation of solids from liquids. In addition to flocculation, these polymers have also been used as filtration and dewatering aids with the aim of increasing the filtration rate as well as reducing residual filter cake content. However, it has been observed that the high molecular weight polymers tend to entrap excess water with them in the flocs leading to high moisture content in the filter cake which is undesirable [Xiaomin et al., 1996].

Extensive work has been conducted and reported in literature showing that the addition of surfactants to a suspension leads to improvement in dewatering characteristics and a substantial decrease in the filter cake moisture content [Ayub et al., 1987; Cooper et al., 1988; Besra et al., 1998a]. The complex mechanism by which surfactants bring about dewatering is not understood properly [Besra et al., 1998b]. However, most of the work reported in literature have attributed the efficiency of surfactants as dewatering aids to their ability to reduce liquid surface tension and/or increase the solid–liquid contact angle (hydrophobicity) [e.g. Nicol, 1976; Puttock and Wainwright, 1984].

The effect of surfactant addition on filtration and cake moisture has gained considerable importance in recent years. This has prompted an investigation into understanding the interaction between flocculants, surfactants and the particle surface in order to control the properties of suspensions.

3.3 Flocculation in Polymer – Surfactant Systems

Flocculation by polymers in the presence of surfactants tends to be complex. This is because the polymers interact with the particle surface and may also interact with the surfactants. There are a good number of published works in the field of polymer – surfactant interaction. However, only a few studies have reported on flocculation by polymers in the presence of surfactants.

Studies on flocculation by polymers in the presence of surfactants reported in literature include that of Kurenkov et al. (1991). They found that adding an anionic surfactant to kaolin suspensions caused an increase in the flocculating ability of an anionic copolyacrylamide. This was attributed to the formation of surfactant-polymer complexes, by hydrophobic interactions, on the surfaces of the kaolin. Magdassi and Rodel (1996) conducted studies on flocculation of negatively charged montmorillonite particles by a polycation (polydiallyldimethylammonium chloride) followed by addition of an anionic surfactant (sodium dodecyl sulphate (SDS)). Their results showed that the particle size of the flocculated aggregates were larger in systems that contain polymer – surfactant, compared with those of just polymer only. Fan et al. (1998) found that the sequence of addition of polymers and surfactants during flocculation has a significant effect on the stability of the suspension. Baltar and Oliveira (1998) also observed that pre-conditioning of a colloidal silica suspension with dodecylamine hydrochloride (DAHCl) prior to addition of a non-ionic high molecular weight polyacrylamide induced formation of agglomerates which resulted in a sediment that was more compact than that obtained without pre-conditioning with DAHCl.

Magnafloc 1011, an anionic polyacrylamide, was earlier identified in Chapter 2 as being effective for flocculating oil sands fine tailings. The rest of this Chapter presents results on studies conducted on flocculation of kaolin clay particles with Magnafloc 1011 in the presence of DAHCl, a cationic surfactant. The aim of this particular study was to investigate the possibility of a synergistic effect of Magnafloc 1011 and DAHCl during flocculation as a potential method for treating oil sand tailings. A positive flocculation result here would mean that the presence of the surfactant during flocculation with Magnafloc 1011 would yield a higher settling rate as well as an improved supernatant clarity when compared to test results observed by flocculation with Magnafloc 1011 alone.

3.4 EXPERIMENTAL

3.4.1 Materials

3.4.1.1 *Kaolin*

Kaolin clay is an alumina silicate that comprises of a tetrahedral silica sheet bonded to an octahedral alumina sheet through the sharing of oxygen atoms between silicon and aluminum atoms in adjacent sheets. The general chemical composition of kaolin is $Al_2O_3.2SiO_2.2H_2O$.

The surface charge of kaolin in aqueous suspensions is usually negative. The negative charge could occur when Al^{3+} replaces Si^{4+} in the tetrahedral sheet of the clay surface. Charging mechanism of this form is known as isomorphous substitution of ions.

Kaolin can give a zero electrical potential depending on pH, ion concentration and valence of cations, among other things [Kaya et al., 2003]. The pH value giving a zero zeta potential value is called the isoelectric point (IEP). Figure 3.1a gives a plot showing the variation of the zeta potential of kaolinite with pH for different potassium KCl concentrations.

The kaolin clay used in this study was purchased from Fisher Chemicals (Napean, Ontario). The particle size analysis using a Mastersizer PSA Model 2000

(Malvern Instruments, Canada) showed an average diameter (d_{50}) of 6.9 μm. The Particle Size Distribution (PSD) result of the kaolin clay is shown in Figure 3.1b.

3.4.1.2 *Flocculant*

Magnafloc 1011, the polymer used in this study, is a partially hydrolyzed Polyacrylamide (HPAM) produced by Ciba Specialty Chemicals. It is a copolymer of sodium acrylate ($CH_2CHCOONa$) and acrylamide ($CH_2CHCONH_2$) with an average molecular weight of 17.5×10^6 and ~ 22% anionicity [Sworska et al., 2000].

3.4.1.3 *Surfactant*

Dodecylamine hydrochloride (DAHCl), a cationic surfactant, was purchased from Fisher Chemicals and used in this study. The molecular formula of DAHCl is $CH_3(CH_2)_{11}NH_2.HCl$ and it has a molecular weight of 221.81.

3.4.1.4 *pH modifiers*

The pH of the aqueous solutions was adjusted using either 0.1 M HCl or 0.1 M NaOH. Only analytical grade reagents from Fisher Chemicals were used. An Oakton pH meter (pH 11 series model) was used for pH measurements.

3.4.1.5 *Deionized water*

Deionized water with a resistivity of 18.2 MΩ.cm, prepared with an Elix 5 followed by a Millipore – UV Plus water purification system (Millipore Inc., Canada) was used where applicable throughout this study.

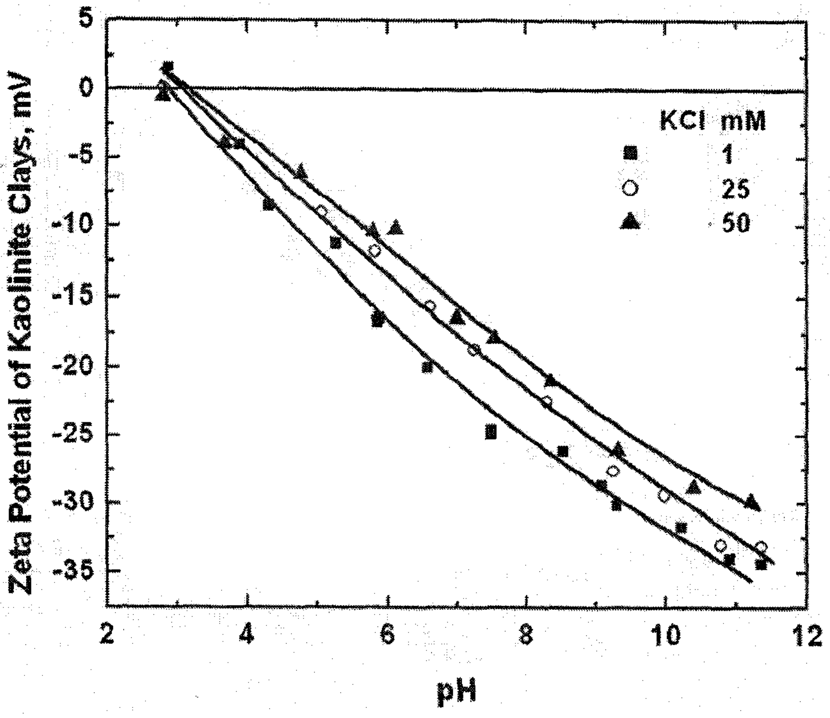


Figure 3.1a: Variation of the zeta potential of kaolinite with pH for different KCl concentrations (Masliyah, 2006).

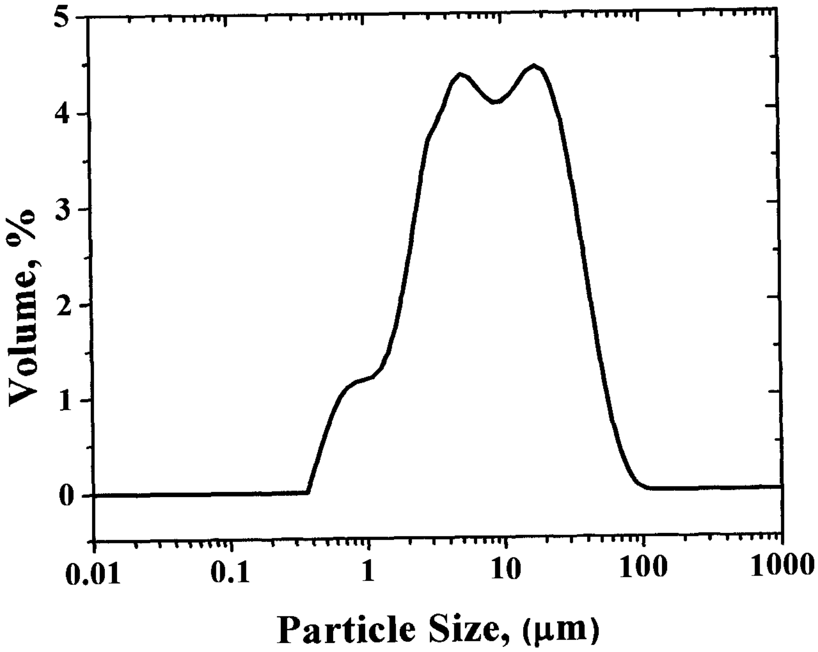


Figure 3.1b: Particle Size Distribution of the Kaolin.

3.4.2 Methodology

3.4.2.1 *Flocculation by Magnafloc 1011*

A stock polymer solution of 0.5 g / L was first prepared by dissolving 0.05 g of dry polymer in 100 mL[**] of deionized water. 5 wt % kaolin suspensions were then prepared by dispersing 5 g of kaolin clay into 95 mL of deionized water in a beaker fitted with baffles. The slurry was vigorously mixed with a mechanical stirrer at an impeller speed of 1000 rpm for 5 minutes to obtain a uniform suspension. The pH of the suspension was adjusted to 8.6 with the pH modifiers, while the stirring continued for another 5 minutes.

The flocculation tests were carried out by adding the required amount of polymer in the concentration range of 5 – 100 ppm[††] (mg of polymer / kg of kaolin) into the 5 wt% kaolin suspensions. The polymer was added continuously over a period of 1 minute while the suspension was stirred at a reduced impeller speed of 100 rpm. The entire suspension was then transferred to a 100 mL graduated cylinder and allowed to settle after inverting the cylinder five times. A clear liquid slurry interface could be seen descending. The height of this interface was noted at regular time intervals. Settling rates were estimated from the slope of the initial straight line portion of the plot of interface height versus settling time. After the first 5 minutes of settling, about 30 mL of the supernatant was removed from the top of the graduated cylinder with a syringe and used for turbidity measurement. The turbidity was measured with a HF – Micro 100 laboratory turbidimeter and expressed in Nephelometric Turbidity Units (NTU). Each experiment was conducted at room temperature (i.e. 23 ± 1 °C) and repeated three times. An average value for both the settling rate and turbidity was obtained and reported.

3.4.2.2 *Flocculation by DAHCl*

In this case, rather than using the polymer flocculant, various concentrations of DAHCl ranging from 1 mM – 10 mM were used for flocculation of the kaolin

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[**] mL = milliliter

[††] All polymer dosages in **ppm** givenn in Chapter 3 represent mg of polymer / kg of kaolin

suspensions following the same procedure described in Section 3.4.2.1. The turbidity was also measured after the first 5 minutes of settling.

3.4.2.3 *Flocculation by Magnafloc 1011 and DAHCl*

The effect of the presence of surfactant in the system on flocculation was studied by varying the sequence of addition of DAHCl and Magnafloc 1011. Two modes of surfactant addition were studied.

In Mode 1, referred to as the ***"DAHCl/Magnafloc 1011"*** mode, flocculation experiments were carried out by first pre-treating the kaolin suspension with varying concentrations of DAHCl for 1 minute at a stirring speed of 100 rpm before addition of a fixed Magnafloc 1011 concentration at its optimal flocculation concentration (OFC). The OFC of Magnafloc 1011 on 5 wt% kaolin suspension was determined by the experimental procedure described in Section 3.4.2.1. This is detailed further in Section 3.4.3.

In Mode 2, referred to as the ***"Magnafloc 1011/DAHCl"*** mode, Magnafloc 1011 at its OFC was added first to the kaolin suspension and allowed to stir for 1 minute at 100 rpm after which DAHCl of varying concentrations were added. The suspension was then allowed to stir for another minute at 100 rpm before it was transferred to a graduated cylinder for the settling tests.

3.4.3 Results and Discussion

3.4.3.1 *Effect of flocculation by Magnafloc 1011*

The ability of Magnafloc 1011 to cause flocculation of 5 wt% kaolin suspensions without the addition of the surfactant was first studied. The effectiveness of the flocculation process was measured in terms of settling rate and turbidity of the suspension.

As shown in Figures 3.2a – c, the unflocculated kaolin (i.e. 0 ppm polymer dosage) has a slow initial settling rate of 1.3 m/h. The settling rate increases rapidly with increasing dosage of Magnafloc 1011 and reaches a value of about 18.8 m/h at an optimum dosage of 20 ppm (point **A** in Figure 3.2b). Increasing the dosage of Magnafloc 1011 beyond this value does not improve settling rate any further. The same can be said for the turbidity of the suspension taken after the first 5 minutes of settling. Figure 3.2c shows a decrease in turbidity with increasing dosage of Magnafloc 1011 up to 20 ppm (point **B** in Figure 3.2c). In this case, at Magnafloc 1011 dosages above the optimum flocculation concentration (OFC) of 20 ppm, the supernatant quality deteriorates as is reflected in an increase in the turbidity values.

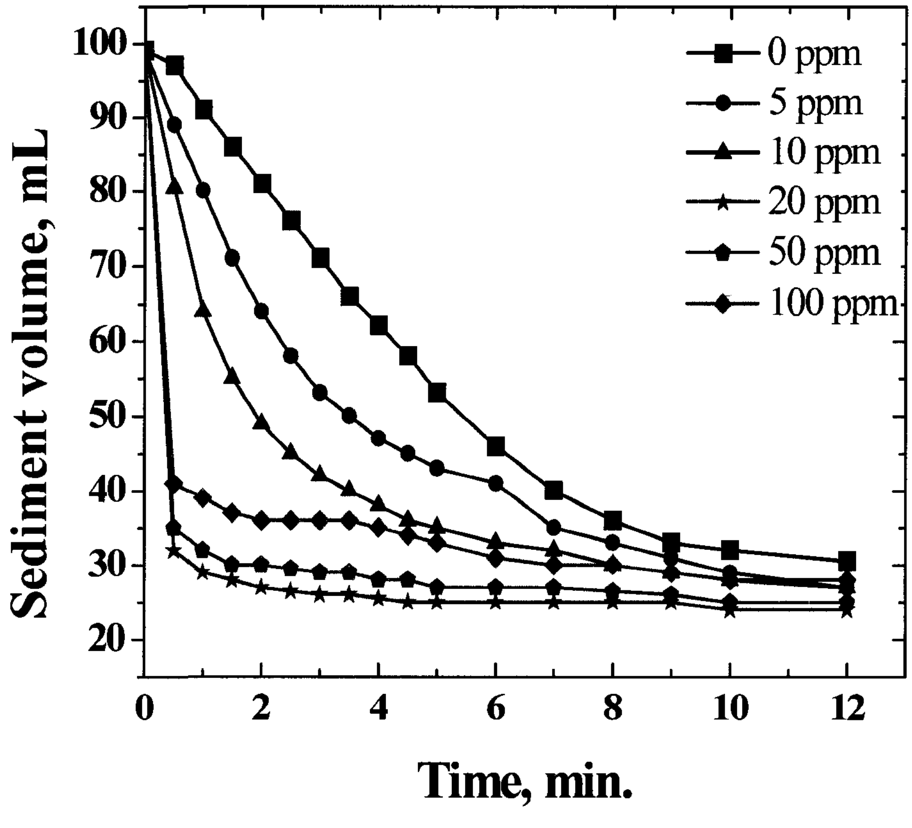

Figure 3.2a: Settling curve of 5 wt% kaolin suspension as function of Magnafloc 1011 dosage (pH: 8.6; stirring speed: 100 rpm; stirring time: 1 min).

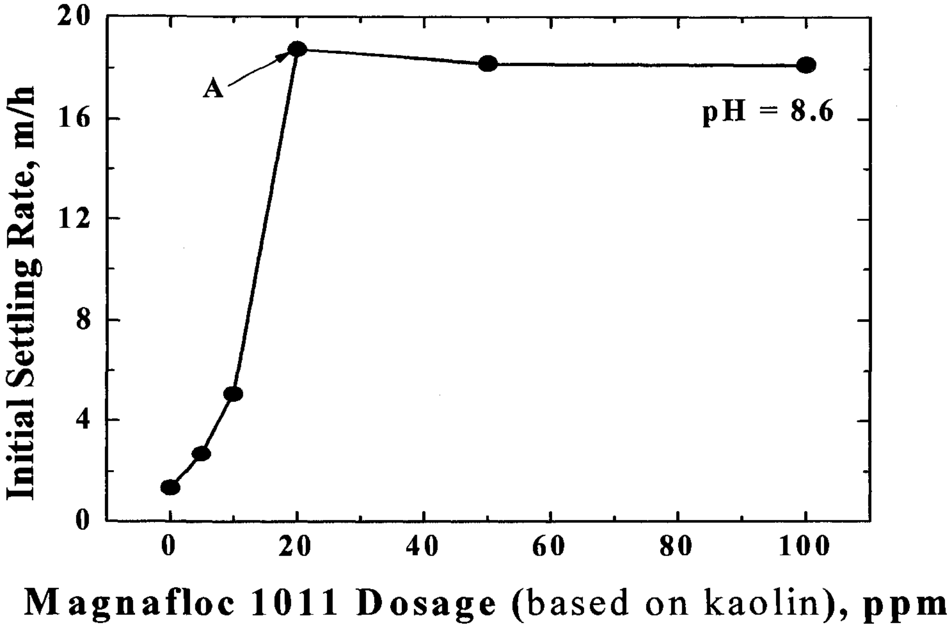

Figure 3.2b: Effect of Magnafloc 1011 dosage on initial settling rate of 5 wt% kaolin suspensions (pH: 8.6; stirring speed: 100 rpm; stirring time: 1 minute; no surfactant is added).

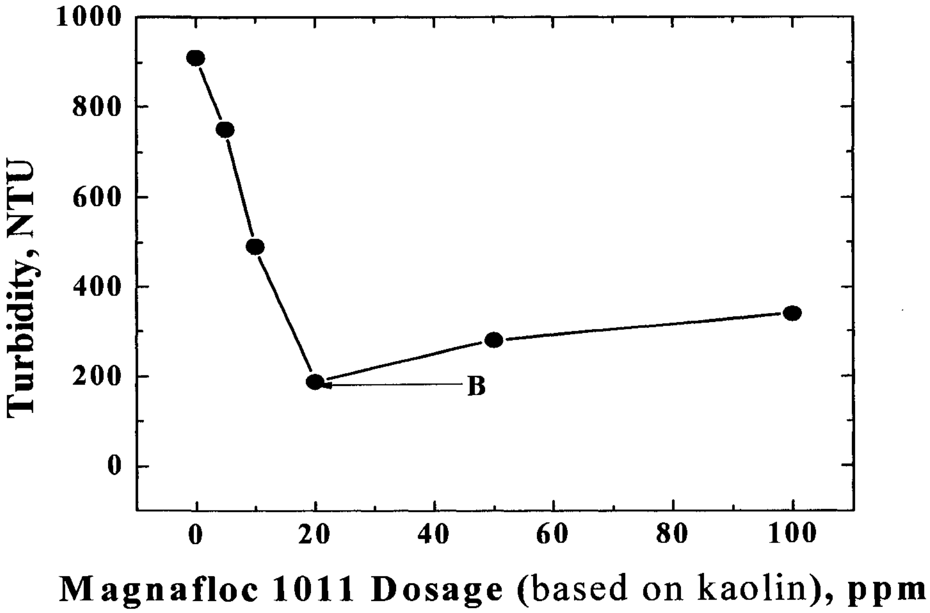

Figure 3.2c: Turbidity of 5 wt% kaolin suspension as a function of Magnafloc 1011 dosage. Turbidity measured after first 5 minutes of settling; no surfactant is added.

3.4.3.2 *Effect of flocculation by DAHCl*

The effect of DAHCl on the flocculation of 5 wt% kaolin suspension is presented in Figures 3.3a and 3.3b. It can be clearly seen that the initial settling rate (Figure 3.3a) of the kaolin particles is quite low compared to the settling rate observed for Magnafloc 1011 (Figure 3.2b). Figure 3.3a shows that the initial settling rate does not improve as DAHCl concentration is increased beyond 1 mM. However, there is a marked decrease in the turbidity of the suspension on addition of DAHCl as is evident in the lower turbidity values seen in Figure 3.3b. The flocculation of the kaolin particles by DAHCl can be attributed to reduced particle charge and improved hydrophobicity of the kaolin particles induced by the adsorbed surfactant. This mechanism of flocculation by surfactants has been reported by Besra et al. (1998) and Song et al. (2000).

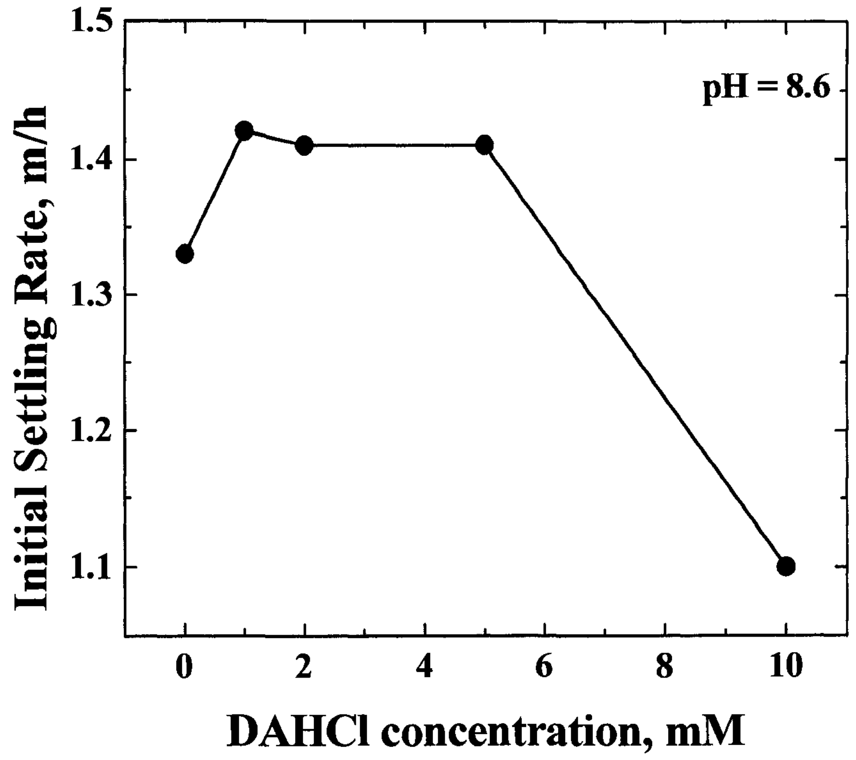

Figure 3.3a: Effect of DAHCl concentration on initial settling rate of 5 wt% kaolin suspensions (pH: 8.6; stirring speed: 100 rpm; stirring time: 1 minute; no polymer is added).

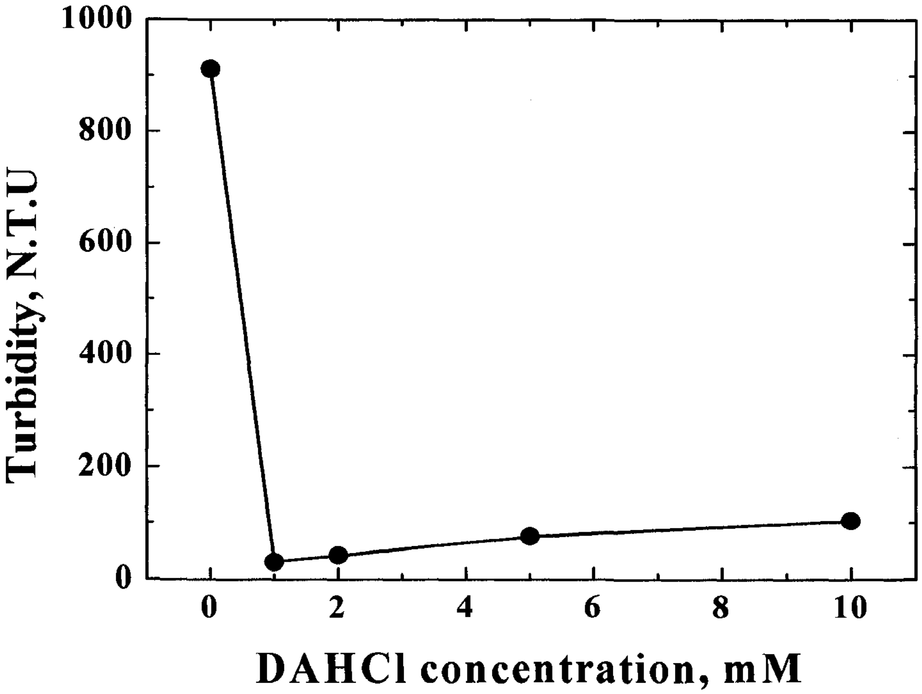

Figure 3.3b: Turbidity of 5 wt% kaolin suspension as a function of DAHCl concentration. Turbidity measured after first 5 minutes of settling; no polymer is added.

3.4.3.3 *Effect of flocculation by Magnafloc 1011 and DAHCl*

Two modes of addition of DAHCl and Magnafloc 1011 for flocculation of the kaolin suspensions were studied and each of them had peculiar characteristics.

- ***Addition mode 1: DAHCl/Magnafloc 1011***

After establishing that 20 ppm was the OFC of Magnafloc 1011 on the kaolin suspension (Figure 3.2b), two-step flocculation experiments were conducted in which the first step was addition of DAHCl at various concentration to the kaolin suspension, followed by addition of Magnafloc 1011 at its OFC (i.e. 20 ppm).

Figure 3.4a shows that pretreating the kaolin suspension with DAHCl led to a substantial decrease in the flocculation ability of Magnafloc 1011 as is evident in the lower settling rates observed over the range of DAHCl concentration tested. For example, the initial settling rate for a 1 mM DAHCl/20 ppm Magnafloc 1011 addition mode is about 3.7 m/h. This is much lower than 18.8 m/h obtained for Magnafloc 1011 alone at its OFC (point **A** of Figure 3.2b).

On the other hand, there was an improvement in the supernatant quality of the kaolin suspension pretreated with the surfactant prior to polymer addition. This is evident in the turbidity of the suspensions for the DAHCl/Magnafloc 1011 addition mode (Figure 3.4b). As can be seen in Figure 3.4b, the turbidity values are much lower than that obtained at the optimal flocculation concentration of Magnafloc 1011 alone (point B of Figure 3.2c).

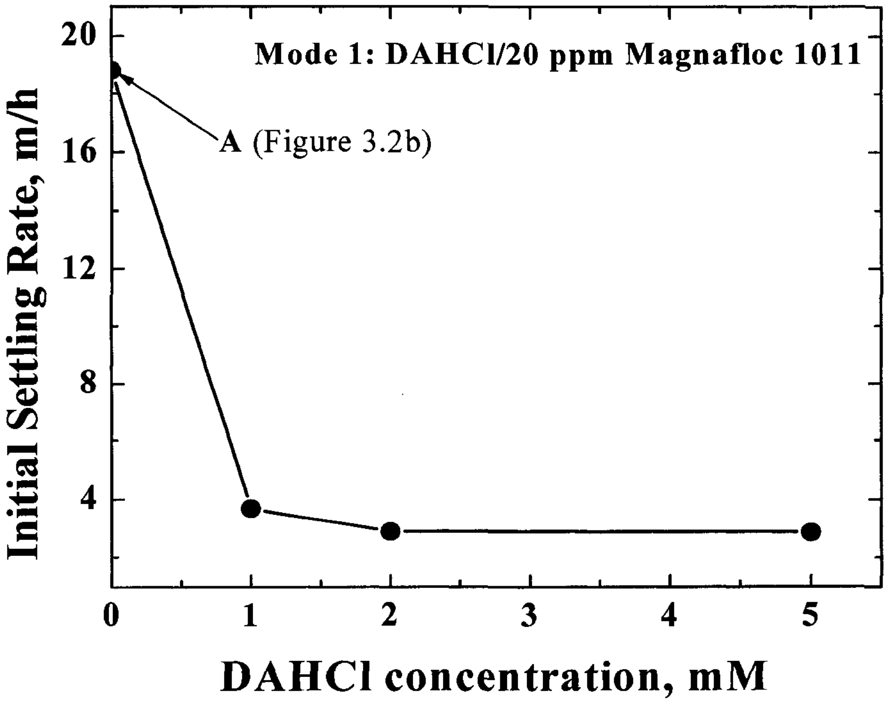

Figure 3.4a: Initial settling rate of 5 wt% kaolin suspension for DAHCl/Magnafloc 1011 addition mode (pH: 8.6; [Magnafloc 1011] = 20 ppm).

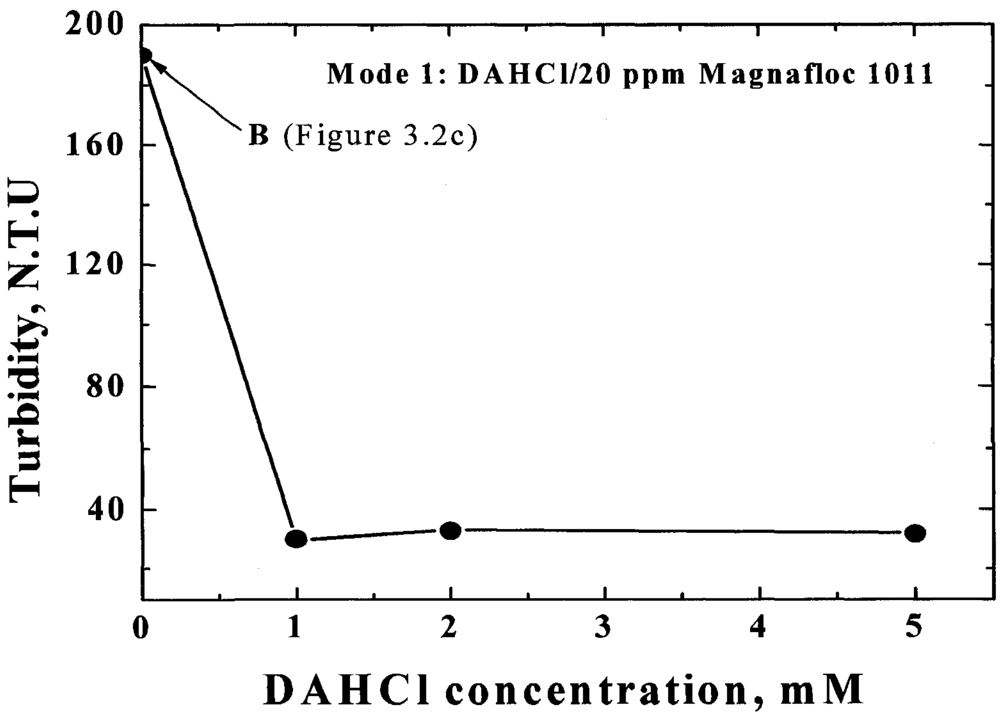

Figure 3.4b: Turbidity of 5 wt% kaolin suspension for DAHCl/Magnafloc 1011 addition mode (pH: 8.6; [Magnafloc 1011] = 20 ppm).

The flocculation results here suggest that addition of DAHCl before Magnafloc 1011 prevented adequate adsorption of Magnafloc 1011, which then resulted in its reduced flocculation efficiency (i.e. lower initial settling rate).

- ***Addition mode 2: Magnafloc 1011/DAHCl***

Adding Magnafloc 1011 first to the kaolin suspension prior to DAHCl addition resulted in a decrease in the initial settling rate and turbidity of the suspension in comparison to that obtained for Magnafloc 1011 alone (Figures 3.5a and 3.5b). It is important to note here that the initial settling rates obtained for the Magnafloc 1011/DAHCl addition mode, though lower than that of Magnafloc 1011 at its OFC, are much higher than the initial settling rates obtained for the DAHCl/Magnafloc 1011 addition mode (i.e. Mode 1). For instance, the highest settling rate obtained for addition mode 2 was 7 m/h (Figure 3.5a) while the highest settling rate obtained for addition mode 1 was 3.7 m/h (Figure 3.4a).

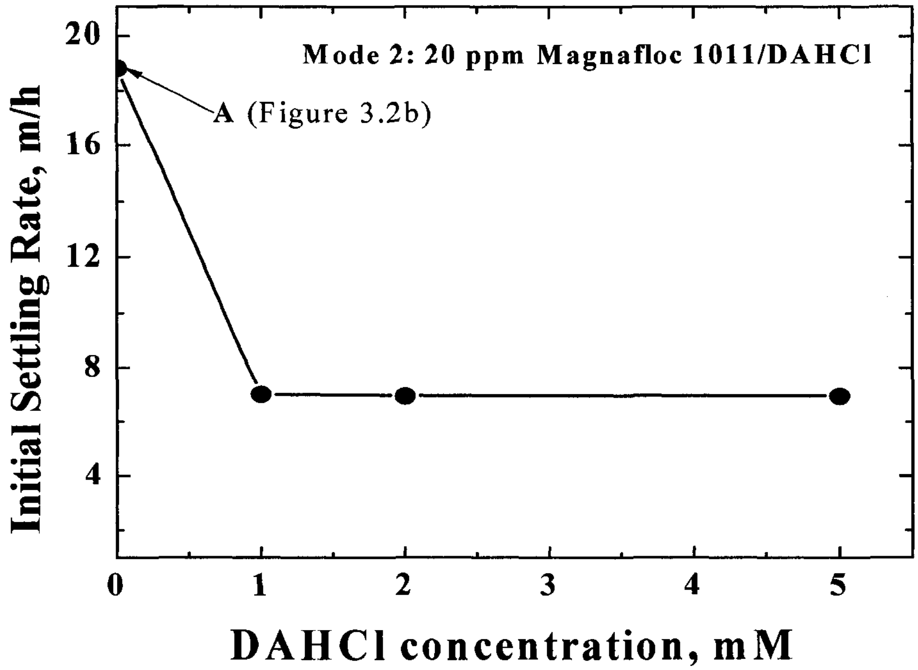

Figure 3.5a: Initial settling rate of 5 wt% kaolin suspension for Magnafloc 1011/DAHCl addition mode (pH: 8.6; [Magnafloc 1011] = 20 ppm).

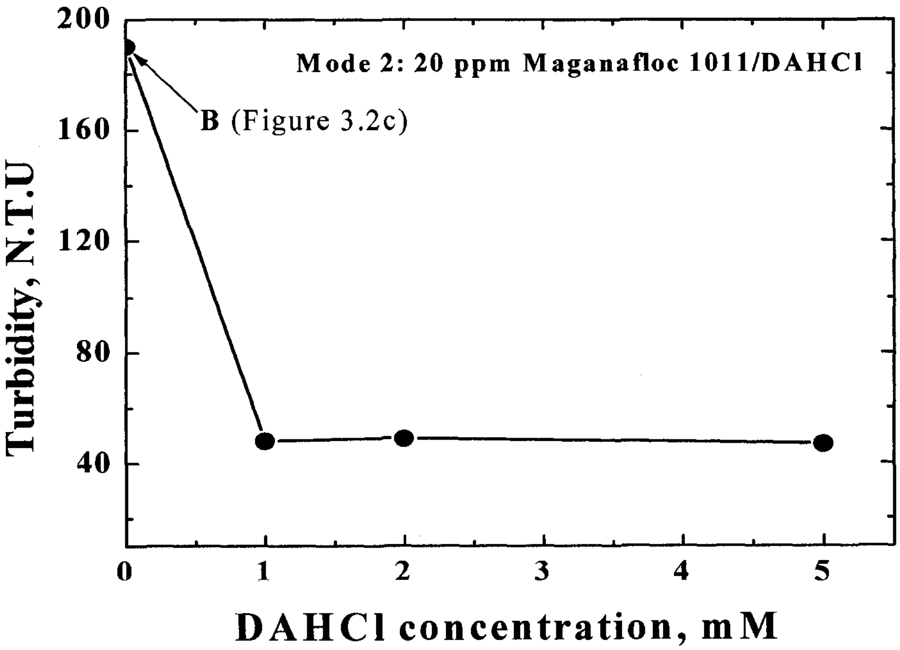

Figure 3.5b: Turbidity of 5 wt% kaolin suspension for Magnafloc 1011/DAHCl addition mode (pH: 8.6; [Magnafloc 1011] = 20 ppm).

Figure 3.6 shows a comparison of the settling curves corresponding to DAHCl/Magnafloc 1011, Magnafloc 1011/DAHCl, 'DAHCl only', and 'Magnafloc 1011 only' flocculation processes. It can be seen that the addition mode 2 (i.e. Magnafloc 1011/DAHCl) settling curve lies between those for addition mode 1 (i.e. DAHCl/Magnafloc 1011) and 'Magnafloc 1011 only'. This suggests that the chemical (either polymer or surfactant) added first always controls the flocculation process. Because the surfactant (optimal settling rate: 1.42 m/h) has a low flocculation efficiency on the kaolin suspension when compared to the polymer (optimal settling rate: 18.8 m/h) as is evident in their respective optimal settling rates, during flocculation of the kaolin suspensions by addition mode 1, the surfactant tends to deteriorate the flocculation efficiency of the polymer. In contrast, when the polymer is added first as in addition mode 2, the polymer plays a dominating role but its efficiency is hindered by the surfactant. This is why flocculation by addition mode 2 gives a better initial settling rate than that provided by addition mode 1.

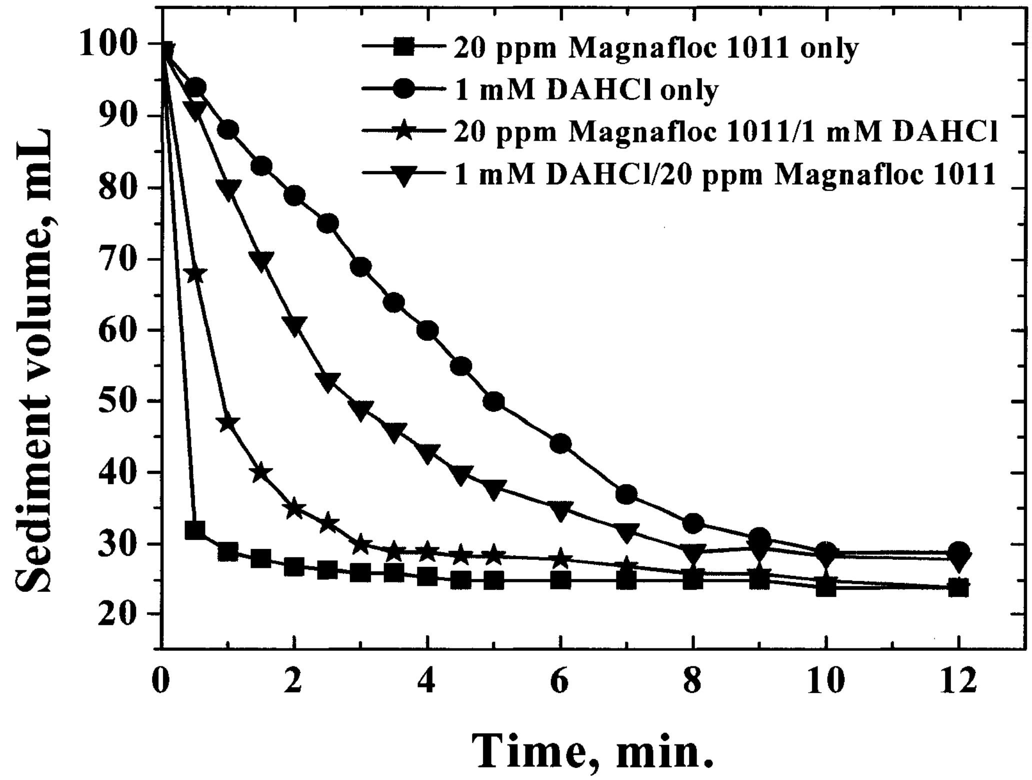

Figure 3.6: Settling curve of 5 wt% kaolin suspension comparing flocculation by DAHCl and Magnafloc 1011 in varying flocculant addition modes.

3.4.4 Summary

The effect of a polymer and surfactant on the flocculation of kaolin suspensions has been investigated. The following conclusions can be drawn from this study:

- Magnafloc 1011, an anionic polyacrylamide, exhibits an excellent flocculating ability for the kaolin suspension under the alkaline condition studied (i.e. at pH = 8.6). The settling rate of the kaolin suspension was improved by more than 10–fold (from 1.3 m/h to 18.8 m/h) at the optimum flocculation concentration of 20 ppm Magnafloc 1011.

- DAHCl, a cationic surfactant, was able to flocculate the kaolin suspension due to decreased particle charge and improved hydrophobicity impacted on the kaolin particles by the adsorbed surfactant.

- The experiments showed that the effect of a polymer and surfactant on the flocculation of kaolin suspension can be striking, depending particularly on the addition sequence of both the polymer and surfactant. It was discovered that the chemical (either polymer or surfactant) added first played a dominating role in the flocculation process. This finding suggests that the first chemical added adsorbs on most of the kaolin particle surface available for flocculation, thereby preventing the effective adsorption of the second chemical when it is added.

- Addition of DAHCl to the kaolin suspension prior to addition of Magnafloc 1011 (i.e. DAHCl/Magnafloc 1011 mode) during flocculation led to a substantial decrease in the settling rate of the kaolin in comparison to the settling rate when Magnafloc 1011 is used alone. However, there was an improvement in the supernatant clarity of the suspension as lower turbidity values were observed.

- The settling rate of the kaolin suspension also decreases when Magnafloc 1011 is added to the suspension before DAHCl (i.e. Magnafloc 1011/DAHCl mode).

In general, it can be concluded that the presence of DAHCl inhibits the flocculation efficiency of Magnafloc 1011 on kaolin suspensions. It was mentioned in Section 3.3 that success in this research project will be measured by an improvement in the settling rate of the kaolin particles as well as an enhanced supernatant clarity when the polymer and surfactant are used for flocculation. The results here show that there is only an improvement in the supernatant clarity. There is also deterioration in the settling rate of the kaolin particles. Based on these findings, this particular direction was not pursued further.

3.5 References

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Chapter 4

STUDIES ON FLOCCULATION OF KAOLIN SUSPENSIONS – STAGED FLOCCULATION

4.1 Introduction

In Chapter 1, management of MFT (a stable fine particle suspension containing 30 wt% fine solids) was identified as a major challenge in commercial oil sands operations. Because of the very slow settling of the MFT, there is a large accumulation of the fine tailings inventory. Chalaturnyk et al. (2002) estimated that the volume of MFT will increase over one billion cubic meters by the year 2020. This long term storage of large volumes of MFT is expensive and creates huge environmental challenges.

Over the last two decades, several efforts have been made by oil sands stakeholders and the research community to find ways to reduce both the total MFT inventory and MFT per barrel of bitumen produced. These efforts have led to the development of several processes for tailings treatment, including CT Process and Paste Technology which were discussed in Section 1.5. Despite the successes gained with both the CT process and paste technology, there are still some problems associated with the use of each of these tailings management practices in the oil sands industry. Hence, research work is ongoing by many parties to find other alternative methods to deal with MFT.

In this study, the effect of polymer addition on flocculation of MFT has been investigated. The possibility of using additives (lime and gypsum) and polymer flocculants to improve treatment of MFT has also been explored. This work was carried out in two parts: Studies on Kaolin Suspensions (as model tailings) and Studies on Mature Fine Tailings.

- ***Studies on Kaolin Suspensions***

Physical factors such as mixing and method of polymer addition have been shown to influence the performance of a flocculant [Xu and Cymerman, (1999); Sworska et al. (2000)]. Different mixing/polymer addition conditions could result in very different floc sizes and settling rates [Sworska et al. (2000)].

In Chapter 3, Magnafloc 1011 was shown to be very effective in flocculating 5 wt% kaolin suspensions. This chapter focuses on flocculation of 10 wt% kaolin suspensions with Magnafloc 1011 using a new approach to polymer addition. It is termed "staged polymer addition and stirring" and the procedure is described in a later section. The objective of this study was to investigate the effect of polymer dosage and staged polymer addition and stirring on the performance of the flocculant. Performance was measured in terms of settling rate, supernatant turbidity, and solids content in the sediment.

4.2 EXPERIMENTAL

4.2.1 Materials

The materials used in this study include kaolin clay, Magnafloc 1011 flocculant, pH modifiers (i.e. reagent grade NaOH and HCl), and deionized water. The characteristics of these materials are the same as described in Section 3.4.1.

4.2.2 Methodology

- ***Settling Tests***

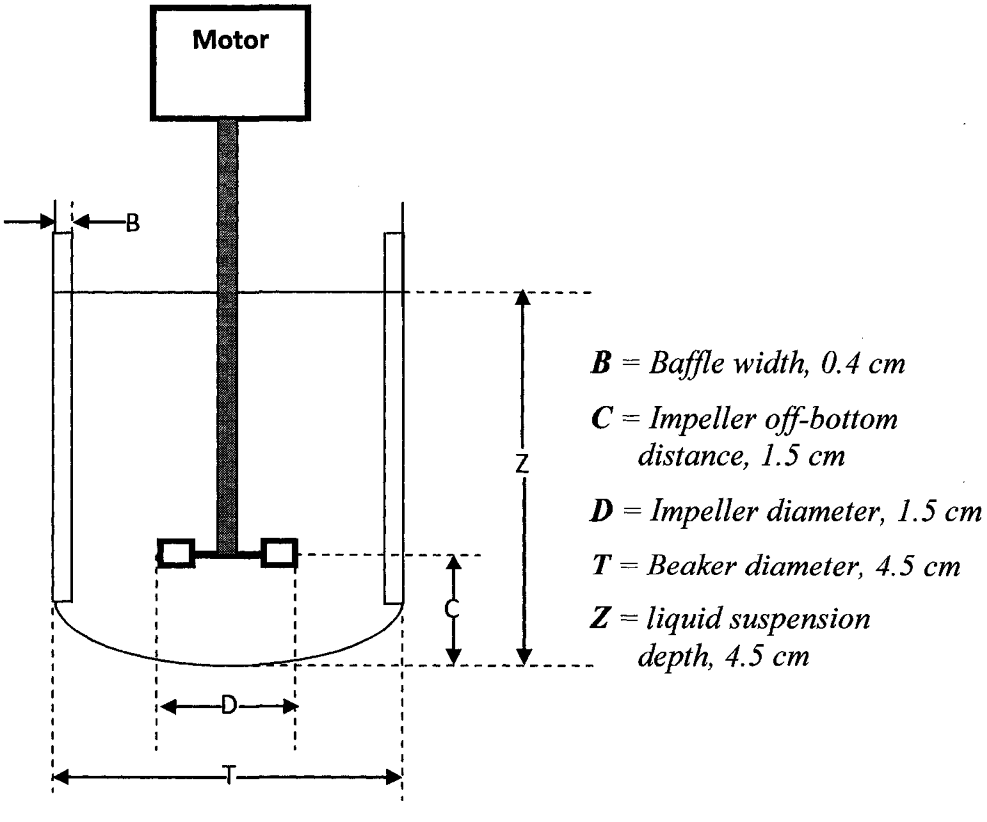
Clay suspensions of 10 wt% solids were prepared by dispersing 10g of kaolin into 90 mL of deionized water in a beaker fitted with four baffles. The slurry was mixed with a flat blade impeller at 1000 rpm for 5 minutes to ensure complete dispersion before flocculant addition. The pH of the suspension was adjusted to 8.6 using the pH modifiers while stirring. Magnafloc 1011 was then added at dosages of 0, 20, 50, 100, 200, and 300 ppm[‡‡], respectively, into the 10 wt%

[‡‡] All polymer dosages in **ppm** given in Chapter 4 represent mg of polymer / kg of kaolin

kaolin suspensions. The dosage in ppm refers to the dosage of the polymer in kaolin. The flocculant solutions were added continuously to the suspension for a mixing period of 40 seconds at an impeller speed of 150 rpm. The kaolin suspensions were then transferred to a 100 mL graduated cylinder for settling. The descent of the supernatant – sediment interface (mud line) was recorded as a function of time. Plot of the supernatant layer height versus time was used to determine the initial settling rate which is the slope of the initial linear portion of the plot.

For each test, a supernatant sample was withdrawn from the top of the graduated cylinder with a syringe after 10 minutes of settling for measurement of supernatant turbidity.

Figures 4.1a, 4.1b and 4.1c describe the mixing system used for the flocculation and settling tests. The beaker and impeller dimensions used are based on standard tank and impeller dimensions described in Oldshue (1983).



B *= Baffle width, 0.4 cm*

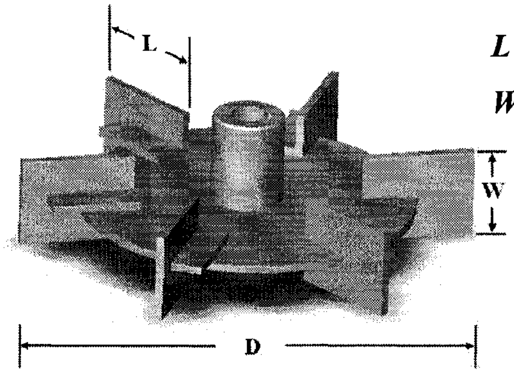
C *= Impeller off-bottom distance, 1.5 cm*

D *= Impeller diameter, 1.5 cm*

T *= Beaker diameter, 4.5 cm*

Z *= liquid suspension depth, 4.5 cm*

Figure 4.1a: Nomenclature used to describe the mixing system.



L = Impeller blade length, 0.4 cm

W = Impeller blade width, 0.3 cm

Figure 4.1b: Flat blade impeller.

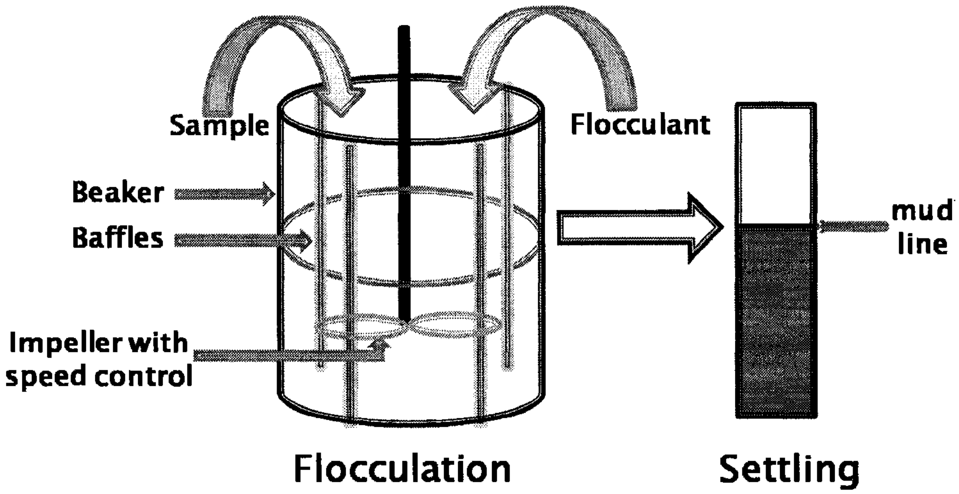


Figure 4.1c: Apparatus for Flocculation and Settling Tests.

4.2.3 Results and Discussion

4.2.3.1 *Effect of Polymer Dosage*

The initial settling rate of the kaolin suspension was calculated from the results of the settling tests in Figure 4.2. Figure 4.3 shows the results of the initial settling rate as a function of increasing dosage of Magnafloc 1011.

Figure 4.3 indicates that the settling rate increases with increasing polymer dosage up to an optimum (between 50 – 100 ppm), beyond which further addition of the polymer results in decreased efficiency. This is evident as the polymer dosage level goes above 200 ppm. Similar behavior was observed during flocculation of 5 wt% kaolin suspensions with Magnafloc 1011 as discussed in chapter 3.

Figure 4.4 shows a plot of supernatant turbidity as a function of polymer dosage. The plot indicates that supernatant clarity increases with increasing polymer dosage up to 50 ppm. This is due to increased capture of kaolin clay particles when more polymer molecules are available. However, beyond 50 ppm, the supernatant clarity starts to deteriorate, resulting in higher turbidity values. Based on the settling rate and turbidity results, the optimum flocculation concentration of Magnafloc 1011 used on the kaolin suspension is 50 ppm. The turbidity results suggest that at the optimal polymer dosage of 50 ppm, the surface of the kaolin particles are partially covered by the adsorbed polymer, which allows formation of a "bridge" between the kaolin particles. Above this dosage level, the surface of the kaolin particles become more covered by the adsorbed polymer, resulting in steric barrier which prevents the kaolin particles from approaching each other. This leads to more kaolin particles remaining in the suspension as it becomes more stabilized.

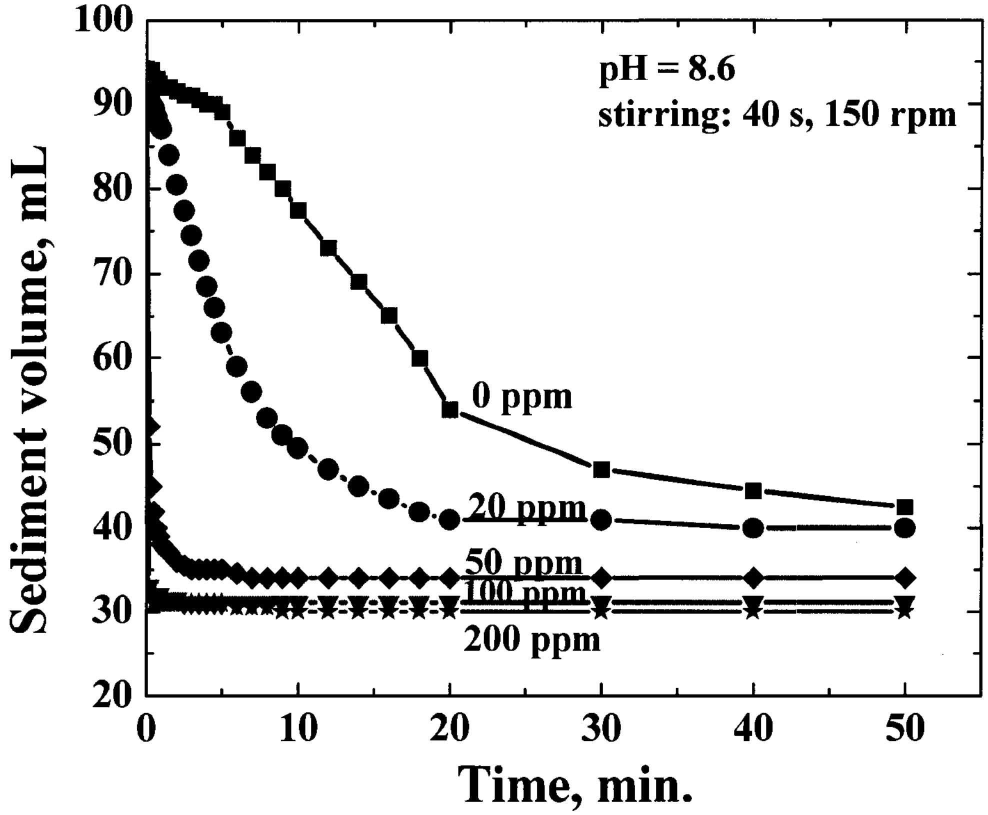


Figure 4.2: Settling curve of 10 wt% kaolin suspension as a function of Magnafloc 1011 dosage (polymer dosage in ppm is based on kaolin).

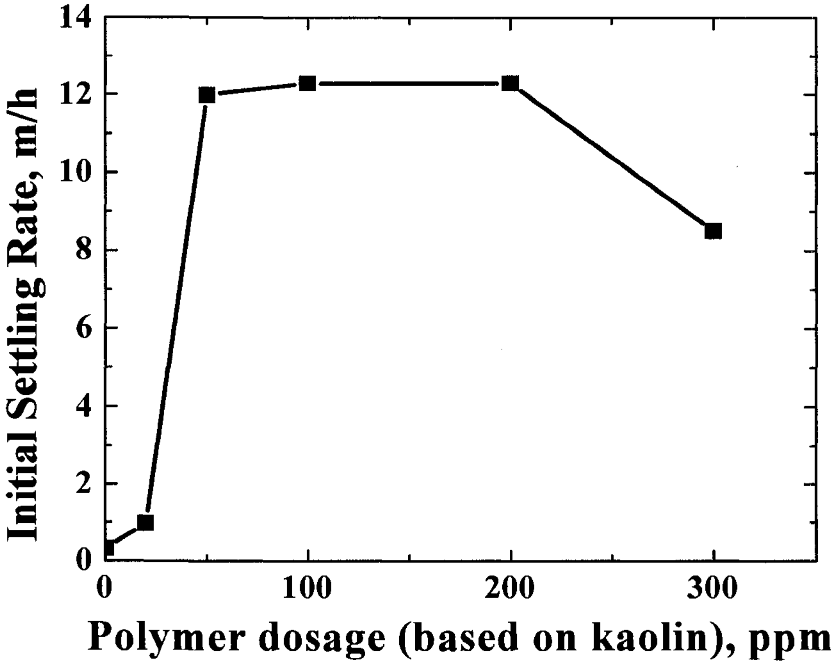


Figure 4.3: Initial settling rate as a function of Magnafloc 1011 dosage.

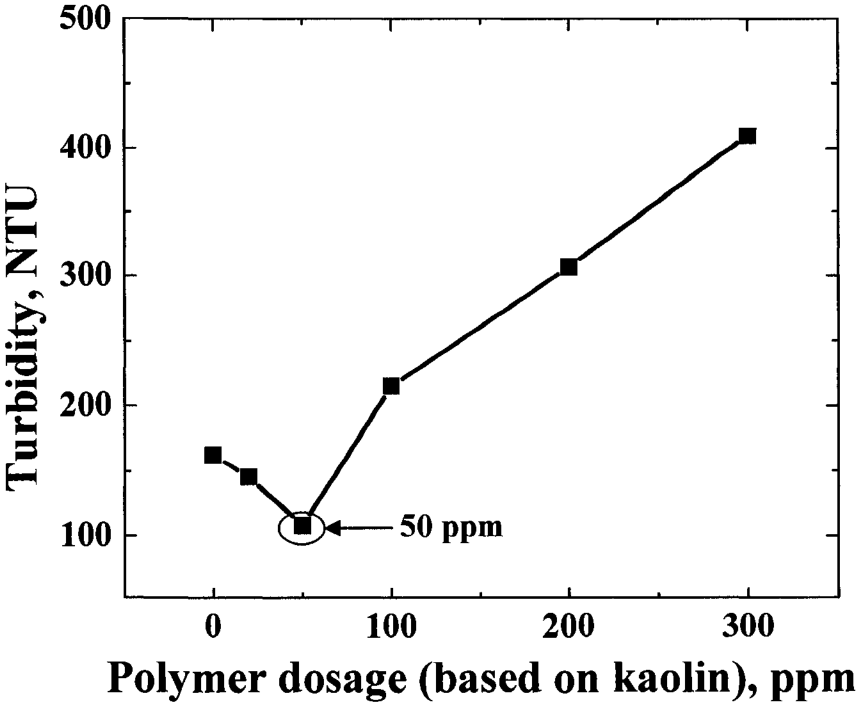


Figure 4.4: Turbidity as a function of Magnafloc 1011 dosage; Optimum polymer dosage used: 50ppm.

4.2.3.2 *Staged Polymer Addition and Stirring*

After establishing that 50 ppm was the OFC of Magnafloc 1011 for 10 wt% kaolin suspension (Figure 4.4), a new approach to polymer addition was tested. This involved a three-staged polymer addition and stirring process as depicted in Figure 4.5.

In Stage 1, 50 ppm Magnafloc 1011 was used to flocculate the kaolin suspension at a stirring speed of 150 rpm for 40 seconds. The stirring level here was used to ensure even distribution of the flocculant throughout the suspension. At the end of the 40 second stirring time, the suspension was allowed to settle for 10 minutes in a 100 mL graduated cylinder. After settling, the supernatant was removed from the graduated cylinder with a syringe, leaving only a volume of sediment referred to as Sediment 1.

In Stage 2, a predetermined concentration of Magnafloc 1011 was introduced into Sediment 1. The solution was stirred for 30 seconds at a reduced stirring speed of 75 rpm (which is half the stirring level used in Stage 1). The stirring speed was reduced to control breakage of flocs formed in Stage 1. At the end of stirring, the solution was allowed to settle for another 10 minutes. This led to further release of water from Sediment 1. The supernatant was removed from the graduated cylinder, leaving a new volume of sediment referred to as Sediment 2. For Stage 3, the procedure used in Stage 2 was repeated on Sediment 2. This resulted in additional release of water and a final sediment volume referred to as Sediment 3.

After completing the three-staged polymer addition and stirring process, the final sediment volume (i.e. Sediment 3) was taken out of the graduated cylinder for measurement of solids content. The total volume percent of water released from the kaolin suspension at the end of the three-stage polymer addition and stirring process was also measured by determining the ratio between the total volume of supernatant released from the suspension at the end of the staged polymer addition and stirring process (i.e. V_{end}) to the initial volume of water in the kaolin suspension (i.e. $V_{start} = 90$ mL).

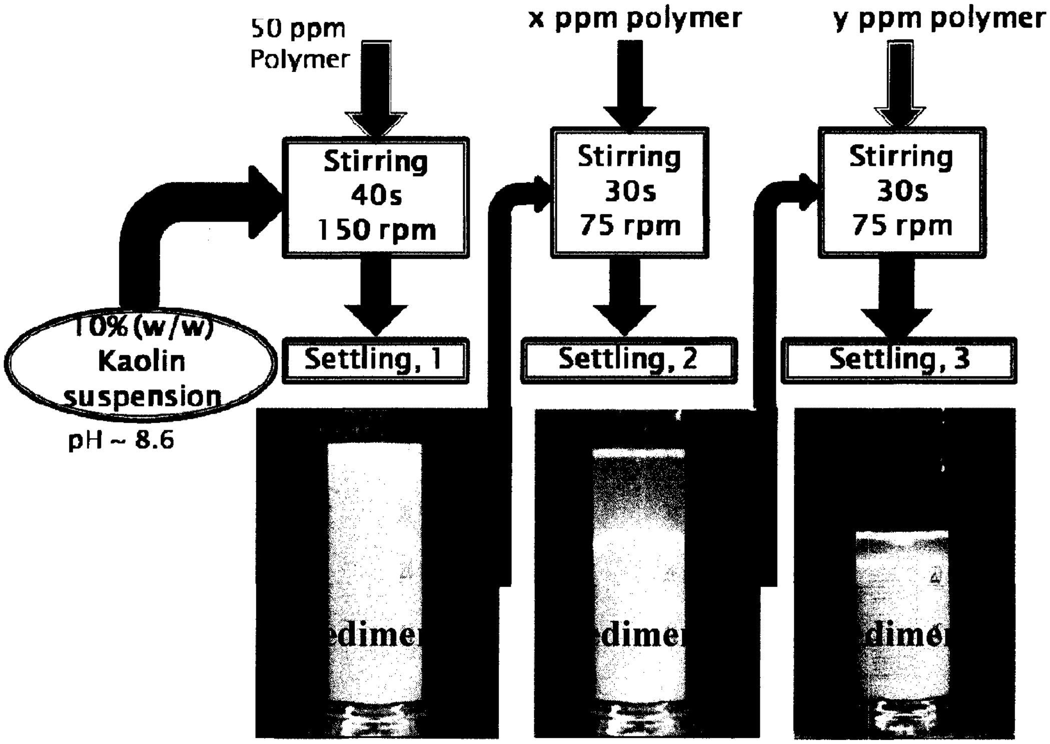


Figure 4.5: Schematic illustration of Staged Polymer Addition (50 + x + y) ppm and Stirring.

Figures 4.6a and 4.6b show comparisons of settling curves achieved with single polymer addition and three-staged polymer addition and stirring of 10 wt% kaolin suspensions. When 50 ppm Magnafloc 1011 was added, the solids content in the sediment at the end of the experiment was 21.1%. However, with 50 ppm polymer addition in Stage 1 and only stirring without polymer addition in Stages 2 and 3 (i.e. [50 + 0 + 0] ppm), there was a direct effect on the final sediment volume as seen in Figure 4.6a. The solids content increased from 21.1% (50 ppm) to 27.3% ([50 + 0 + 0] ppm). For the staged polymer addition and stirring process of (50 + 5 + 5) ppm, the final solids content in the sediment increased further to 31.1%.

The total volume percent of water released from the suspension (i.e. V_{end}/V_{start}) was measured and the results showed a steady increase in the volume of water released from the suspension as the three-stage polymer addition and stirring was employed. For example, the volume percent of water released after Settling 1 (i.e. when single stage polymer addition and stirring was employed) was measured as 59.5%. However, the volume of water released at the end of the (50 + 0 + 0) ppm and (50 + 5 + 5) ppm polymer addition and stirring process was measured as 68.5% and 77.7% respectively.

The test results in Table 4.1 show an increase in the final solids content in the sediment as well as an increase in the total volume of water released from the suspension, indicating that staged polymer addition and stirring has a positive effect on the flocculation performance of Magnafloc 1011 on the kaolin suspension.

Table 4.1: Effect of three-stage polymer addition and stirring on solids in sediment and total water release from kaolin suspension. Initial solid content in suspension = 10%; initial volume percent of water in suspension = 90%.

Polymer Dosage (ppm)	*Final Solids in Sediment (wt %)*	*Total Water Release (%)*
50	21.1	59.5
50 + 0 + 0	27.3	68.5
50 + 5 + 5	31.1	77.7

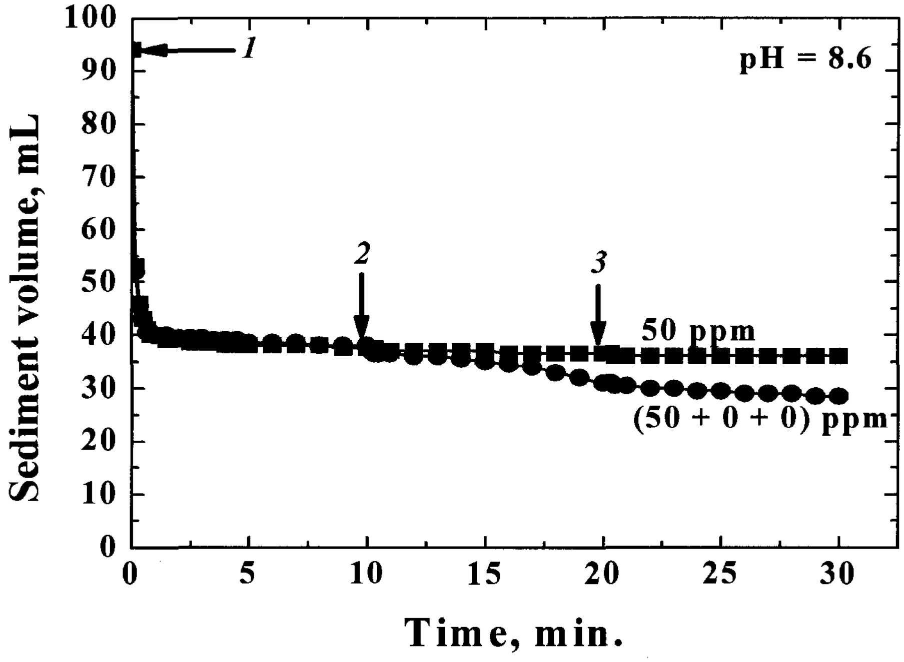


Figure 4.6a: Effect of Staged Polymer Addition and stirring on solids content in sediment. ■ 50 ppm; solids content in sediment = 21.1%; ● (50 + 0 + 0) ppm; solids content in sediment = 27.3%.

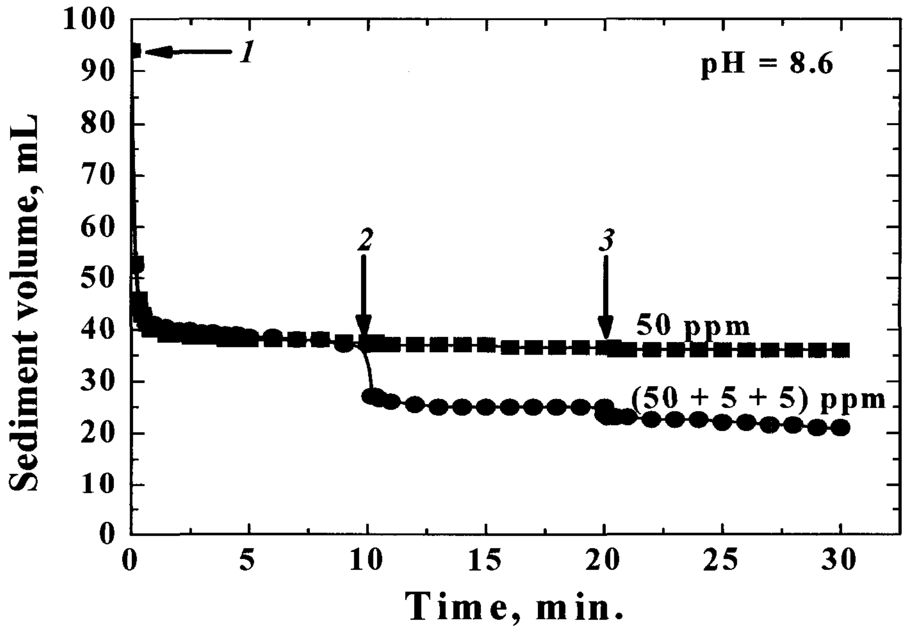


Figure 4.6b: Effect of Staged Polymer Addition and stirring on solids content in sediment. ● (50 + 5 + 5) ppm; solids content in sediment = 31.1%.

4.2.4 Summary of Studies on Kaolin Suspensions

Based on the results of studies carried out on kaolin suspensions, the following conclusions can be drawn:

- Magnafloc 1011 is effective for flocculation of kaolin suspensions.
- Staged polymer addition and stirring are beneficial to flocculant performance.

4.3 References

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Chapter 5

STUDIES ON FLOCCULATION OF MATURE FINE TAILINGS

5.0 EXPERIMENTAL

Yang et al. (2004) described the flocculation of kaolin suspensions using Al–PAM, a new type of hybrid flocculant prepared by polymerization of acrylamide in $Al(OH)_3$ colloidal solution. Their results showed that Al–PAM produced much denser and larger kaolin flocs resulting in higher settling rates in comparison to settling rates obtained with commercial polyacrylamides. This was attributed to electrostatic interaction between the positive $Al(OH)_3$ core and the negative particle of kaolin as well as the adsorption – bridging effect of polyacrylamide chains in Al–PAM.

In this study, the role of Al–PAM and Magnafloc 1011 as flocculants in the flocculation of MFT was investigated. The objective was to study the effect of polymer flocculant dosage, mixing conditions, staged polymer addition and stirring on settling rate, supernatant clarity, and solids content in the sediment. Chemicals such as gypsum and lime as well as coarse sands were added with the flocculants to explore their effect on MFT treatment.

5.1 Materials

- ***Mature Fine Tailings (MFT)***

Samples of MFT containing clays, sand and small amounts of bitumen were obtained from Suncor Energy Canada and utilized in the flocculation tests. The samples contained 32 wt% solids.

The particle size distribution of the MFT was determined with the use of the Malvern Mastersizer 2000 Particle Size Analyzer. The PSD result shown in Figure 5.1 revealed that 85% of the solids were finer than 44 μm while the d_{50} was 9.8 μm.

- ***Polymers***

The polymers used in this work were Magnafloc 1011 and Al – PAM. Magnafloc 1011 (supplied by Ciba Specialty Chemicals) was described in Section 1.5.2 as a high molecular weight polyacrylamide with a degree of anionicity of approximately 22%. Al–PAM was synthesized[§§] following the procedure described by Yang et al. (2004).

Concentrated polymer solutions of 2.5 g/L were prepared by dissolving 0.25 g of dry polymer in 100 mL of deionized water. The solutions were each stirred for 2 hours to ensure that all polymer particles were completely dissolved. The homogeneous stock polymer solutions were then diluted to a working solution of 0.5 g/L by adding 1 part polymer solution (by volume) to 4 parts deionized water (by volume) and stirring for 20 minutes. Any diluted polymer solution not used within 24 hours was discarded.

- ***Solutions***

Slurry pH was adjusted using either 1 M HCl or 1 M NaOH solutions prepared from analytical grade reagents. The pH was measured with an Oakton pH-meter (pH 11 series).

- ***Coarse Sand***

Coarse sand (with trade name Sil-7030) used in this study was purchased from Sil Industrial Minerals, Canada. The particle size analysis showed the average diameter (d_{50}) of the sands to be 198 μm. Figure 5.2 shows the particle size distribution of Sil-7030.

[§§] Al–PAM was synthesized by Dr. Xianhua Feng (xianhua@ualberta.ca)

- ***Chemical Additives***

Lime (CaO) and gypsum ($CaSO_4.2H_2O$) used in this study were of analytical grade (purchased from Fisher Chemicals).

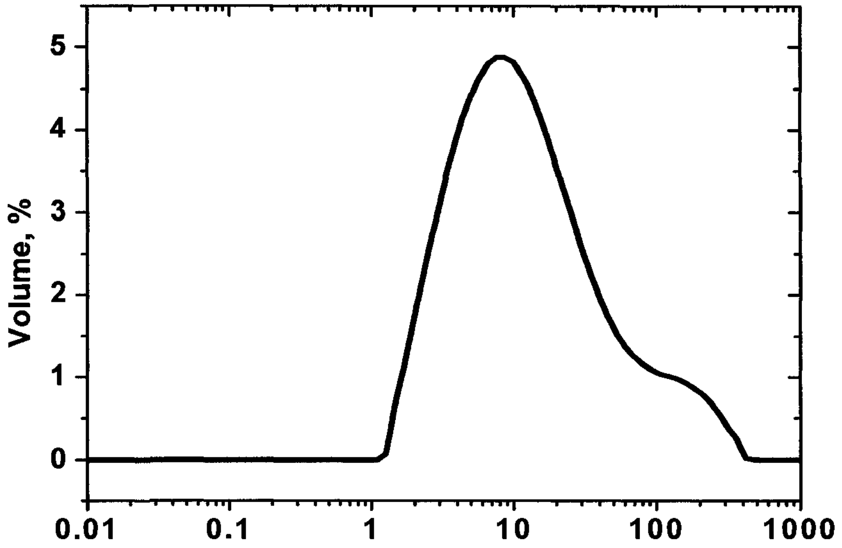

Figure 5.1: Particle Size Distribution of Mature Fine Tailings.

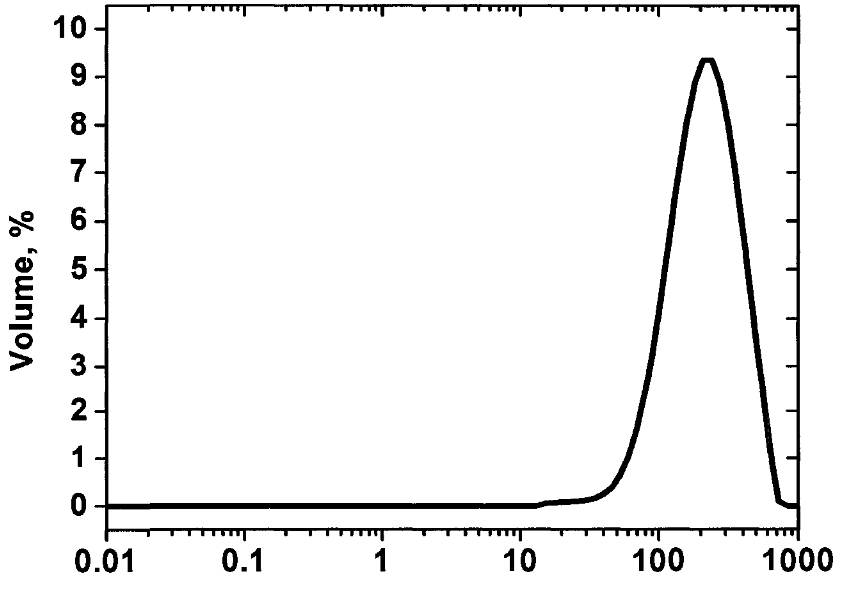

Figure 5.2: Particle Size Distribution of Silica Sand (Sil-7030).

5.2 Methodology

- ***Settling Tests***

The flocculation and settling tests were carried out using the experimental set up shown in Figure 4.1. For each test, 50 mL of MFT was used. The flat blade impeller was used to mix the MFT slurry in a beaker fitted with baffles for 5 minutes at a mixing speed of 1000 rpm to ensure complete dispersion. The impeller speed was then adjusted to 150 rpm while polymer of varying dosages ranging from 0 – 180 **ppm**[***] was added continuously using a syringe for a 3 minutes mixing period. It should be noted that the polymer dosage added refers to the concentration of the polymer in the solids present in MFT. After the mixing, the slurry was carefully transferred into a 50 mL graduated cylinder and inverted 5 times. The cylinder was then allowed to stand still for the settling tests. During settling, digital photographs were taken and the supernatant – sediment interface (mud line) was recorded as a function of time.

- ***Settling Rate***

The plot of the supernatant layer height versus time was used to determine the initial settling rate from the slope of the initial linear portion of the plot.

- ***Solids Content in the Supernatant and Sediment***

The solids content in the supernatant and sediment was determined by siphoning off the supernatant from the graduated cylinder and placing both the supernatant sample and sediment in separate glass beakers. The weights of the supernatant (W_1) and sediment (W_2) in the respective beakers were measured. The beakers containing both samples were then placed in an oven to dry at 110°C. After drying, the weight of the dry solids in the supernatant (W_3) and sediment (W_4)

[***] All polymer dosages in **ppm** given in Chapter 5 represent mg of polymer / kg of solids in MFT

were determined. The solids content in the supernatant and sediment were then calculated by weight fractions, i.e. W_3/W_1 as the solids content in the supernatant and W_4/W_2 as the solids content in the sediment.

- ***Water Release***

The volume percent of water released from MFT after the flocculation process was also measured. This was determined by comparing the volume of supernatant released from MFT after polymer addition (referred to as V_{end}) to the volume of water in the 50 mL MFT slurry prior to polymer addition (referred to as V_{start}). The volume of water in the 50 mL MFT slurry was calculated as approximately 42 mL. Hence the volume fraction of water released from MFT was determined as V_{end}/V_{start} (i.e. $V_{end}/42\ mL$).

5.3 Results and Discussion

5.3.1 *Effect of Polymer Dosage: Magnafloc 1011*

Figure 5.3 shows a photograph of the MFT suspensions with varying additions of Magnafloc 1011 at pH 8.6 after 2 hours of settling. The initial settling rates of MFT with varying Magnafloc 1011 dosages were obtained and are shown in Figure 5.4. The plot shows that initial settling rate increased with increasing Magnafloc 1011 dosage up to a maximum of 80 ppm. A further increase in Magnafloc 1011 dosage resulted in a decrease in the initial settling rate. This behavior follows the same trend observed during flocculation of the kaolin suspensions with Magnafloc 1011 as discussed in earlier sections of this thesis.

The variation of the initial settling rate of MFT with increasing Magnafloc 1011 dosage is consistent with the measured solids content in both the supernatant and sediment at pH of 8.6 as shown in Table 5.1. From Table 5.1, it can be observed that an increase in the solids content in the sediment correlates well with an increase of initial settling rate as shown in Figure 5.4. At 80 ppm polymer dosage, the solids content in the sediment is about 41.3 wt%, an increase from 32 wt% solids in the original MFT sample. Beyond 80 ppm, the solids content in the sediment begins to reduce. The same trend is observed in the volume percent of water released (i.e. V_{end}/V_{start}) from MFT as polymer dosage is increased (see Table 5.1). Table 5.1 also shows that the solids content in the supernatant decreases with increasing polymer dosage, reaching minimum at 80 ppm, beyond which it starts to increase. These results indicate that the optimum flocculation concentration of Magnafloc 1011 used on the MFT sample is 80 ppm. Hence in subsequent flocculation tests involving use of Magnafloc 1011, the polymer dosage was fixed at 80 ppm.

Table 5.1: Flocculation Test Results for MFT with Magnafloc 1011. Initial solids content in slurry = 32 wt%.

Dosage (ppm)	*Solids in Supernatant (wt %)*	*Solids in Sediment (wt %)*	*Volume of Water Released (%)*
16	-	-	-
40	10.3	38.4	9
64	7.6	40.7	24
80	**7.2**	**41.3**	**36**
120	8.4	38.8	28
160	9.1	38.1	24

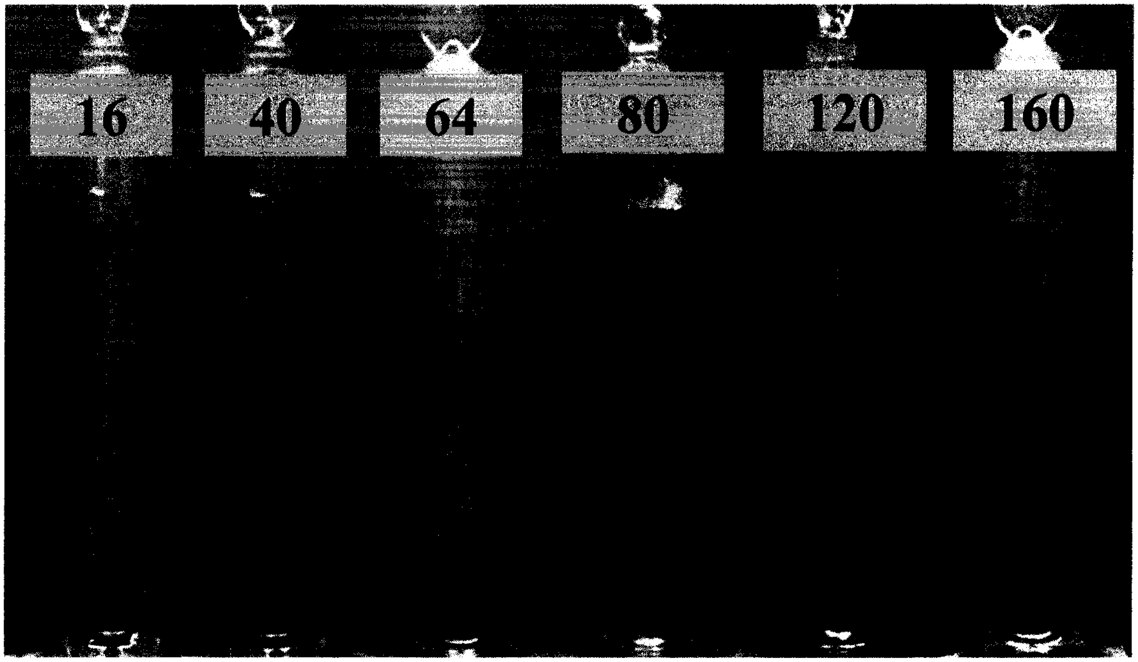

Figure 5.3: Photograph of MFT with varying dosages (in ppm) of Magnafloc 1011 at pH of 8.6 after 2 hours of settling. Impeller speed: 150 rpm; stirring time: 3 min.

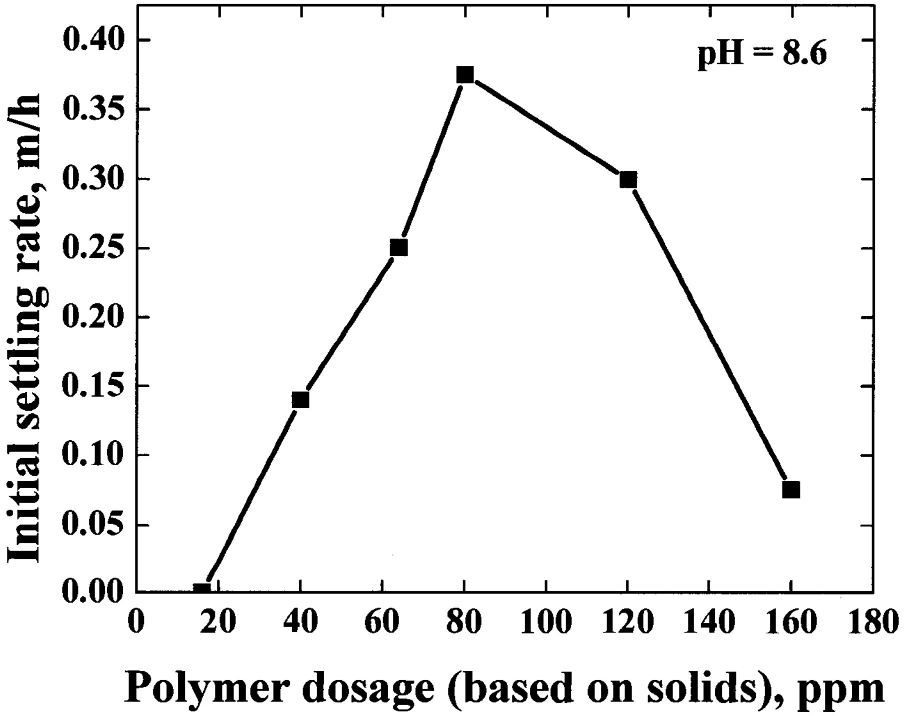

Figure 5.4: Effect of Magnafloc 1011 dosage on the initial settling rate.

5.3.2 *Effect of Polymer Dosage: Al–PAM*

Based on the better flocculation ability of Al–PAM over commercial polyacrylamide for kaolin suspensions as reported by Yang et al., 2004, the polymer was tested on MFT to investigate its flocculation performance.

Figure 5.5 shows the effect of Al–PAM on the flocculation of MFT. The photograph shows that Al–PAM addition up to 50 ppm had no visible effect on the settling rate of the mature fine tailings. Increasing Al–PAM dosage even up to 200 ppm (photograph not shown) did not cause any settling of the mature fine tailings as the suspension remained stable. The inability of Al–PAM to cause settling of MFT, even though it is effective for flocculating kaolin suspensions, could be due to the other components present in MFT. Earlier, it was mentioned that MFT contains not just clays, but also bitumen, sand, naphtha, etc. It is possible that the presence of these substances in MFT inhibit the flocculating ability of Al–PAM.

Following the poor performance of Al–PAM on flocculating MFT, further studies conducted on mature fine tails did not include the use of this polymer.

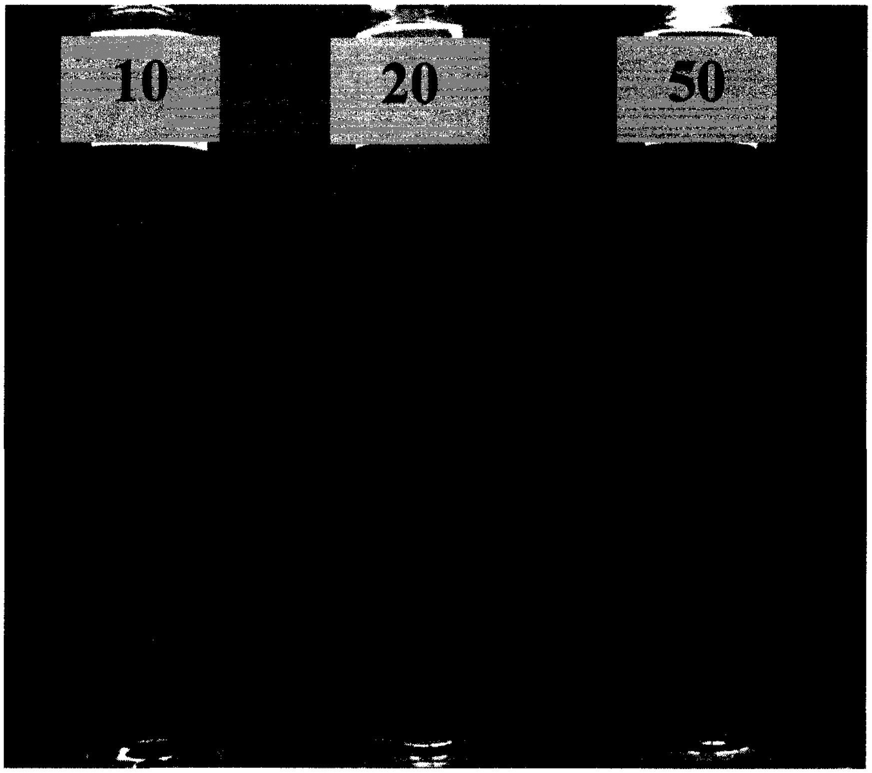

Figure 5.5: Photograph of MFT with varying dosages (in ppm) of Al–PAM at pH of 8.6 after 2 hours of settling. Impeller speed: 150 rpm; stirring time: 3 min.

5.3.3 *Effect of Impeller Speed*

The speed of mixing was varied from 100 – 400 rpm to investigate its effect on the flocculation efficiency of Magnafloc 1011. The polymer was added continuously to the slurry (at pH = 8.6) over a mixing period of 3 minutes and all tests were carried out using the optimum polymer dosage of 80 ppm as identified in Figure 5.4. The initial settling rate for each test was calculated and plotted against the impeller speed as shown in Figure 5.6. The solids content in the sediment corresponding to each impeller speed was also computed and the results are presented in Table 5.2. The photograph in Figure 5.7 shows the effect of impeller speed on MFT flocculation.

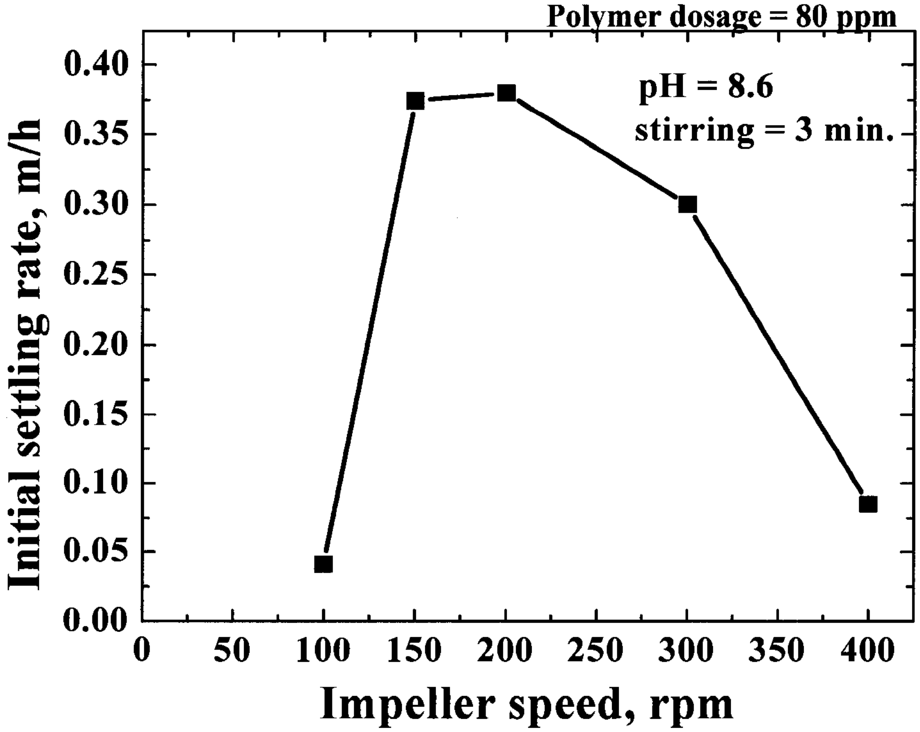

Figure 5.6: Effect of impeller speed on initial settling rate.

Table 5.2: Effect of impeller speed on solids content in sediment. Solids content determined after 2 hours of settling. Polymer dosage used: 80 ppm.

Impeller Speed (rpm)	*Solids content in Sediment (wt %)*
100	34.6
150	41.3
200	**44.0**
300	42.4
400	38.6

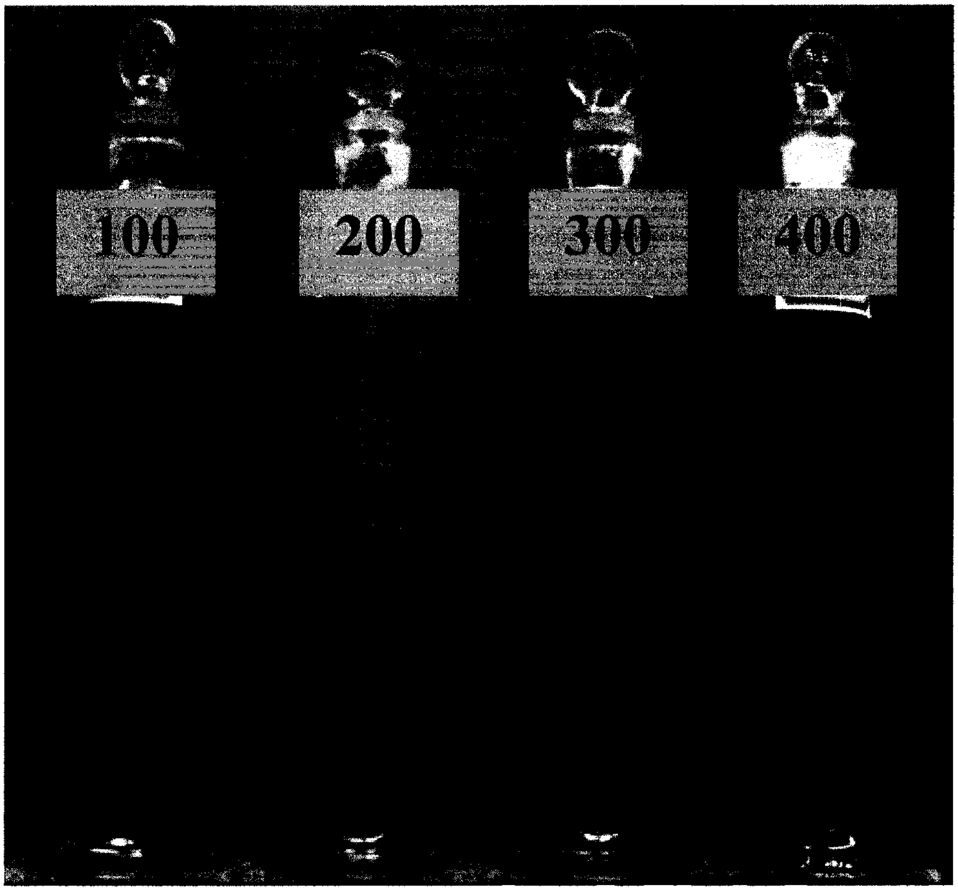

Figure 5.7: Photograph showing the effect of impeller speed (rpm) on flocculation of MFT with Magnafloc 1011 (80 ppm) at pH = 8.6 after 2 hours of settling.

It can be observed from the results that increasing the impeller speed resulted in higher settling rate and solids content in the sediment, up to an optimum value, above which the flocculation performance was poorer. An impeller speed of 200 rpm offered the best process efficiency as it gave the highest initial settling rate (0.38 m/h) and solids content in the sediment (44 wt%).

The results discussed above suggest that sufficient mixing (i.e. at optimum speed) avoids local excess flocculant and provides an even distribution of the flocculant throughout the MFT suspension. This leads to improved flocculation efficiency. However, excessive agitation (i.e. beyond the optimum mixing speed) leads to breakdown of the flocs formed, which eventually deteriorates the flocculation performance.

5.3.4 *Effect of Two–Staged Polymer Addition and Stirring*

In Section 4.2.3.2, staged polymer addition and stirring was shown to be beneficial for flocculation of kaolin suspensions. This paved the way for testing a two–staged polymer addition and stirring process for flocculation of MFT with Magnafloc 1011. The experimental procedure used was similar to the one illustrated in Figure 4.5.

For Stage 1, the tests were carried out at optimum polymer dosage of 80 ppm (Figure 5.4) and optimum impeller speed of 200 rpm (Figure 5.6) at slurry pH of 8.6. For Stage 2, polymer dosages ranging from 0 – 20 ppm were added at a reduced impeller speed of 100 rpm and a mixing period of 1 minute. At the end of the test, the final solids content in the sediment was determined as well as the total water release of the flocculation process.

A plot of the sediment volume versus settling time is shown in Figure 5.8. The plot shows that there was steady reduction in the final sediment volume when two-staged polymer addition and stirring was employed. This is also reflected in the measured solids content in the sediment at the end of Stage 2 as shown in Table 5.3. It is evident that the two-stage polymer addition and stirring process at (80 + 20) ppm yielded a higher final solids content in the sediment of 50.3 wt% in comparison to 44.0 wt% obtained with a single stage polymer addition process at 80 ppm. The photograph shown in Figure 5.9 depicts that there is also higher water release from the mature fine tailings with the two-stage polymer addition and stirring process. The results here are similar to the trend observed during the three-stage polymer addition and stirring process employed for flocculation of 10 wt% kaolin suspensions (discussed in Section 4.2.3.2).

Table 5.3: Effect of two – stage polymer addition and stirring on solids in sediment and total water release from MFT.

Polymer Dosage (ppm)	*Final Solids in Sediment (wt %)*	*Total Water Release (%)*
80	44.0	36
80 + 0	47.1	43
80 + 20	50.3	47

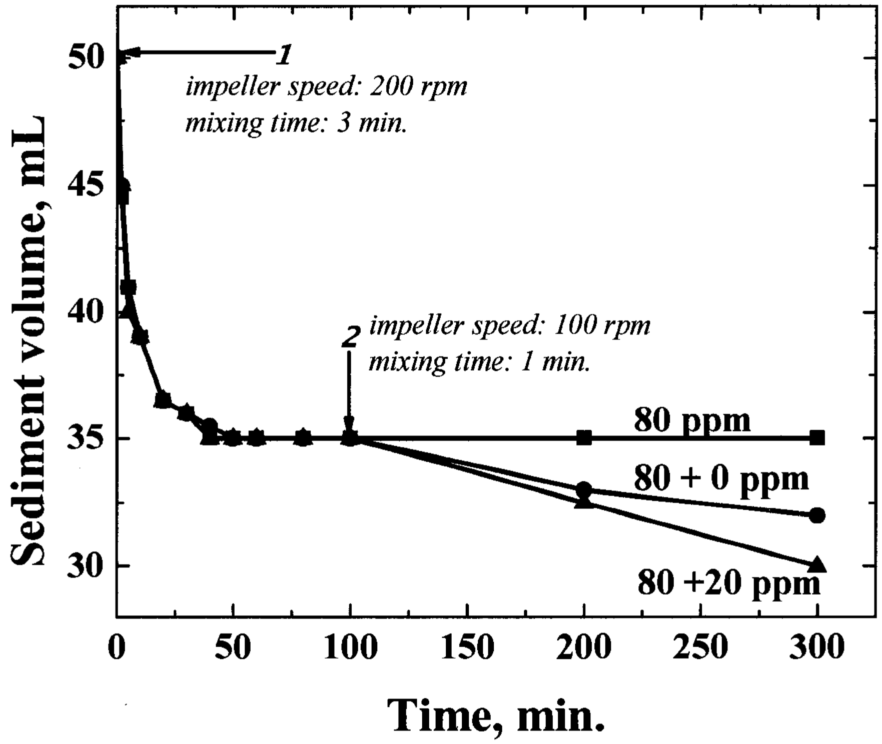

Figure 5.8: Effect of two-stage polymer addition and stirring on the settling curve of MFT.

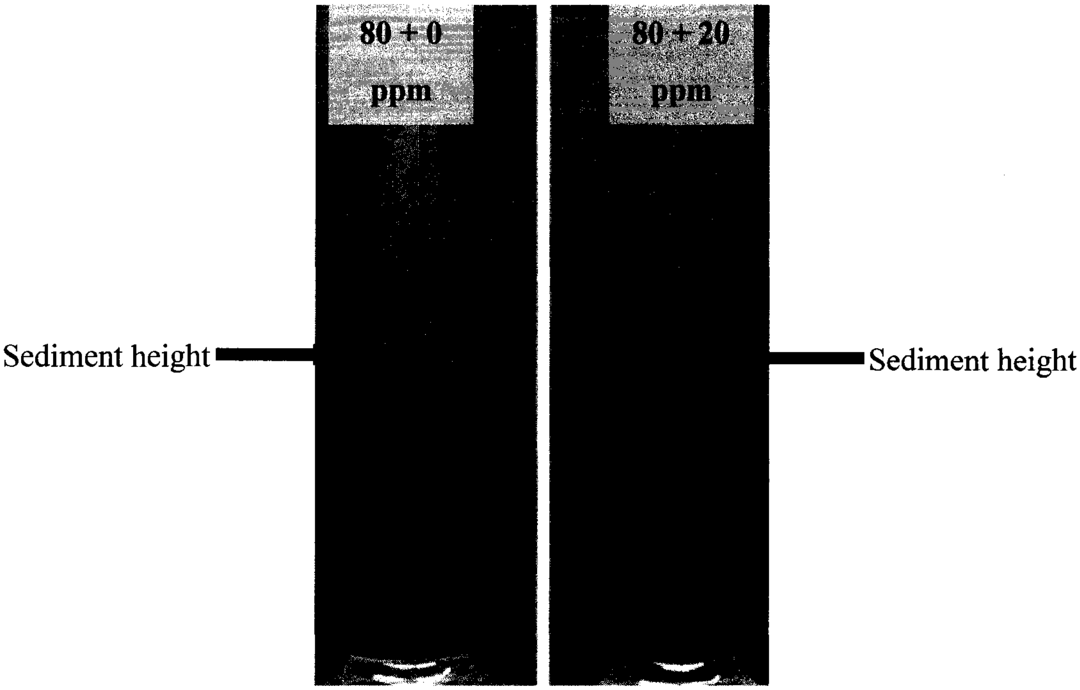

Figure 5.9: Photographs showing effect of two-stage polymer addition and stirring on MFT.

5.3.5 *Effect of Treatment of MFT with Chemical Additives and Magnafloc 1011*

In a flocculation process, the polymer may be applied either after destabilizing the suspension via coagulation, or without prior destabilization [Sworska et al. (2000)]. However, previous studies have shown that prior destabilization by coagulation before addition of polymer provides better flocculation results [O'Gorman and Kitchener, (1974); Wright and Kitchener, (1976)].

Chemical additives such as lime and gypsum are known to be effective coagulating and flocculating agents and are used in several industrial processes. In oil sands operations, gypsum ($CaSO_4$) is used as a source of Ca^{2+} to produce composite tails (non-segregating tails) by blending MFT and fresh sand tailings in the CT Process (described in Section 1.5.1). Hamza et al. (1996) also showed that treatment of oil sand whole tailings with slaked lime {$Ca(OH)_2$} followed by flocculation with polymer produces a stackable tailings product.

In the present study, the effect of addition of lime or gypsum to MFT prior to the addition of Magnafloc 1011 was investigated.

5.3.5.1 *Effect of Lime Addition*

Control tests were first conducted, which involved the addition of only lime or gypsum ranging from 1 mM – 5 mM to 50 mL MFT without polymer addition. These tests did not yield any settling and/or flocculation of MFT as the 50 mL MFT slurry remained stable. Subsequent flocculation tests were then carried out to determine the effect of lime addition to MFT prior to addition of Magnafloc 1011.

The flocculation experiments were carried out by first pre-treating the MFT with varying concentrations of lime (CaO) ranging from 0 – 8 mM. The slurry was stirred at an impeller speed of 150 rpm for 2 minutes after which 80 ppm Magnafloc 1011 was added. On addition of Magnafloc 1011, the slurry was stirred at an impeller speed of 200 rpm for another 3 minutes. After stirring, the MFT slurry was transferred to a 50 mL graduated cylinder for the settling tests.

As can be seen in Figures 5.10a and 5.10b, the addition of lime had no considerable effect on the final sediment volume. Also, the solids content in the sediment (see Table 5.4) remained at about the same level compared to the experiment without lime addition. For example, when 5 mM lime was added prior to polymer addition, the solids content in sediment was about 44.8 wt%. When only the polymer was added, the solids content in the sediment was 44.0 wt%. However, Figure 5.11 shows that the initial settling rate of MFT improved considerably, up to an optimum, on lime addition. The supernatant clarity also improved as there was a decline in the solids content in the supernatant from 6.9

wt% (no lime addition) to 3.8 wt% (5 mM lime addition). The PSD[†††] of the fine solids in the supernatant was also measured and it was observed that there was a steady decrease in the fines sizes as lime was added. The results are shown in Table 5.4.

Table 5.4: Effect of lime addition on solids content in supernatant and sediment and fines content in supernatant.

Sample (MFT + Lime + 80 ppm Polymer)	*Solids in Supernatant (wt %)*	*PSD of Solids in Supernatant (D_{50}; D_{90})*	*Solids in Sediment (wt %)*
0 mM Lime	6.9	0.30 µm; 19.13µm	44.0
2 mM Lime	4.7	0.28 µm; 8.97 µm	43.7
5 mM Lime	3.8	0.26 µm; 6.48 µm	44.8
8 mM Lime	4.6	0.35 µm; 17.01µm	43.5

[†††] The PSD of the fine solids in the supernatant after addition of 2 mM, 5 mM, and 8 mM lime are given in Appendix C

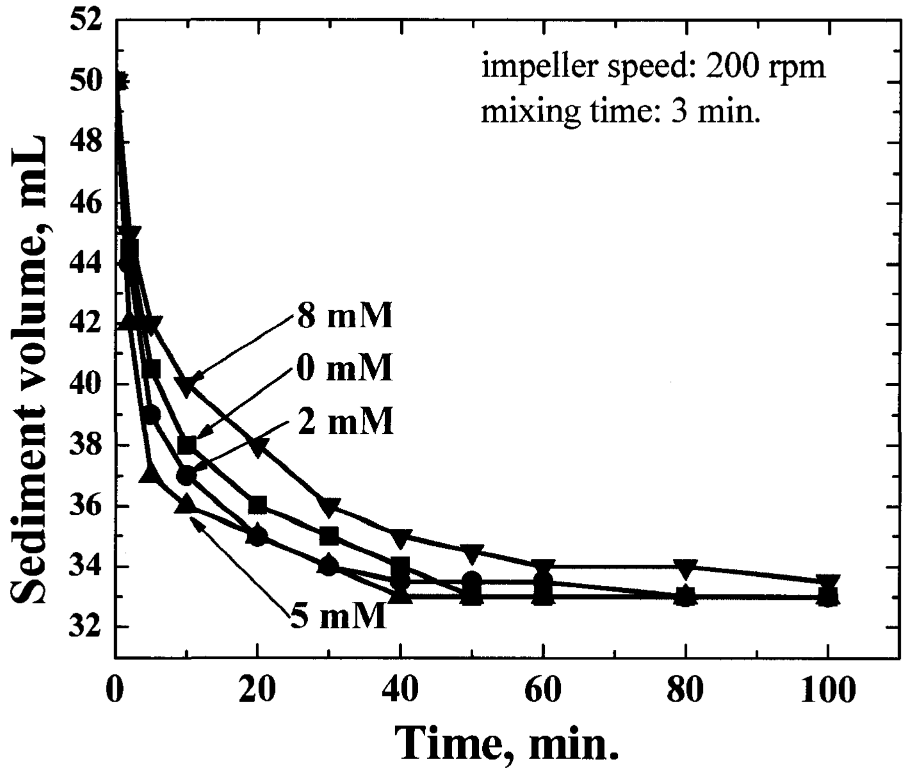

Figure 5.10a: Settling curve of lime and Magnafloc 1011 addition on flocculation of MFT. Magnafloc 1011 dosage: 80 ppm.

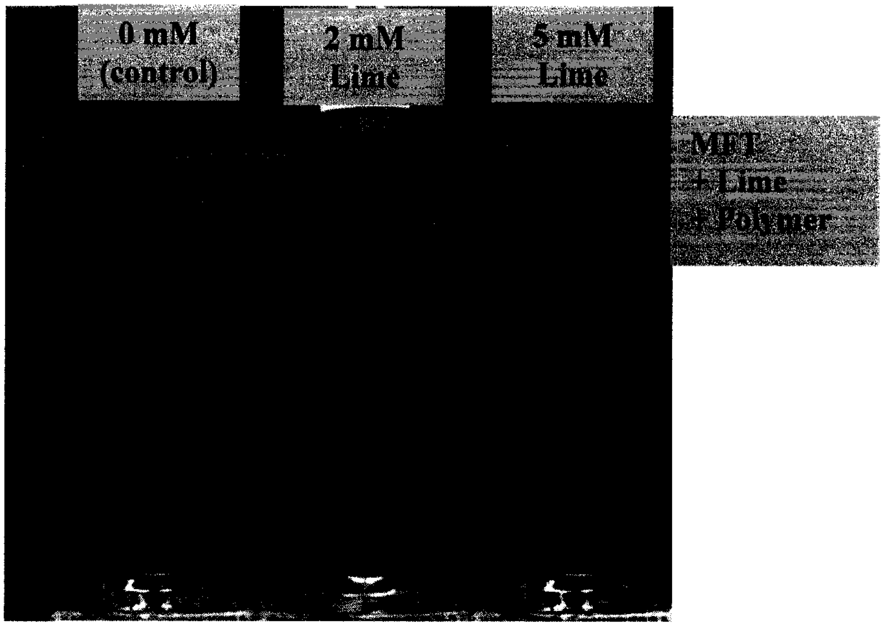

Figure 5.10b: Photograph showing effect of lime addition on final sediment volume. Polymer dosage: 80 ppm.

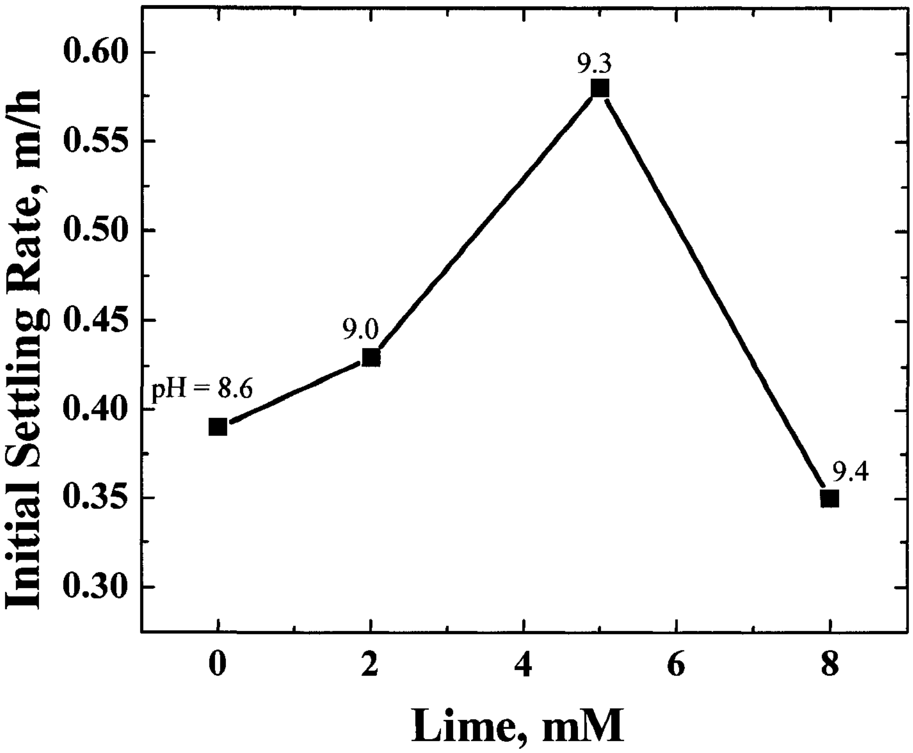

Figure 5.11: Effect of lime addition on initial settling rate of MFT. The optimum lime dosage used: 5 mM.

5.3.5.2 *Effect of Gypsum Addition*

The experimental procedure used in this set of flocculation tests was similar to the procedure used to study the effect of lime addition as described in Section 5.3.5.1.

Figure 5.12 shows the effect of gypsum addition prior to Magnafloc 1011 addition during flocculation of MFT. It can be seen that gypsum addition did not improve the flocculation of MFT. The presence of gypsum caused the gelation of the mature fine tailings, hence preventing any release of water.

To understand the difference in action observed between lime addition and gypsum addition before Magnafloc 1011 addition during flocculation of MFT, the pH of the slurry was measured before and after addition of each of the chemical additives. It was observed that on lime addition, the pH of the slurry changed from 8.6 to about 9.4. However, on gypsum addition, the pH of the slurry stayed relatively the same (i.e. 8.6). This observation suggests that the change in pH could account for the difference in the flocculation performance between lime and gypsum additions.

Figure 5.12: Photograph showing effect of gypsum addition on sediment volume. Polymer dosage: 80 ppm.

5.3.6 *Effect of Coarse Sands Addition*

Coarse sands (Sil – 7030) were added to MFT during flocculation tests with Magnafloc 1011 to investigate its effect on settling rate. Previous flocculation tests described in earlier sections involved MFT with approximately 32 wt%

solids (SFR[‡‡‡] = 1:5.6). For this particular study, the total solids content in the slurry was increased prior to the flocculation tests.

By mixing appropriate amounts of coarse sands with MFT, slurries with 40 wt% (SFR = 1:1.5), 50 wt% (SFR = 1.5:1) and 65 wt% (SFR = 3.6:1) total solids were prepared. The respective slurries with pH adjusted to 8.6 were then used to conduct flocculation tests with Magnafloc 1011(80 ppm dosage). The polymer was added continuously over a period of 3 minutes while the slurries were stirred at an impeller speed of 200 rpm.

Figures 5.13 and 5.14 show the settling curves and initial settling rates for flocculation of MFT with and without sand addition. The results indicate that adding sands produces a marked increase in the settling rate up to an optimum, beyond which further sands addition results in a negative flocculation performance. For example, with 50 wt% total solids in the slurry, the initial settling rate was 0.51 m/h. This was greater than the settling rate obtained with 32 wt% total solids in the slurry (i.e. 0.39 m/h). However, with 65 wt% total solids in the slurry, the initial settling rate reduced drastically to 0.15 m/h. Figure 5.15 shows a photograph of the effect of coarse sands addition.

[‡‡‡] SFR = sand to fines ratio

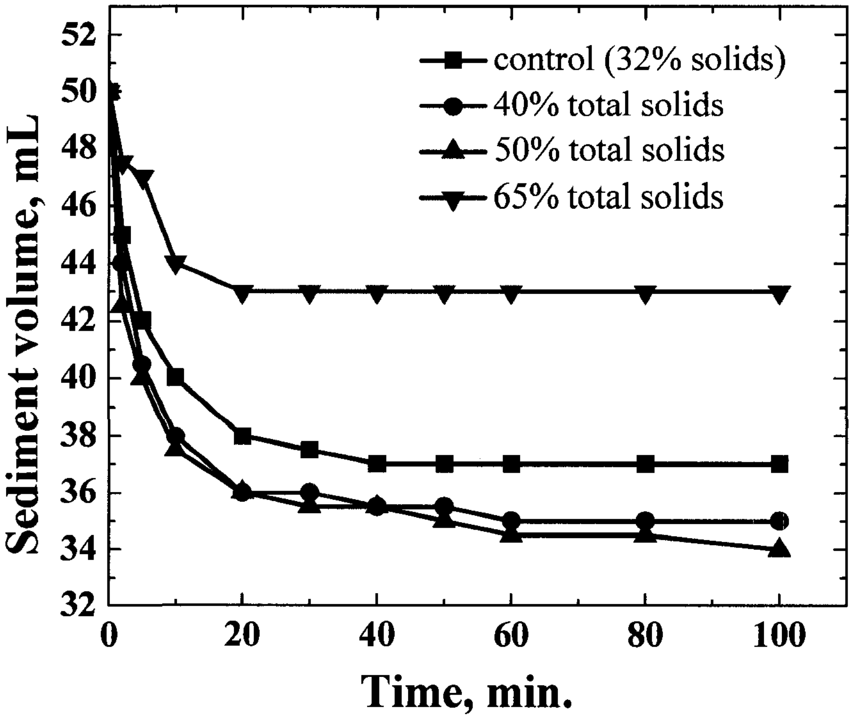

Figure 5.13: Settling curves for flocculation of MFT with and without sand addition. Polymer dosage: 80 ppm; pH = 8.6; mixing speed = 200 rpm.

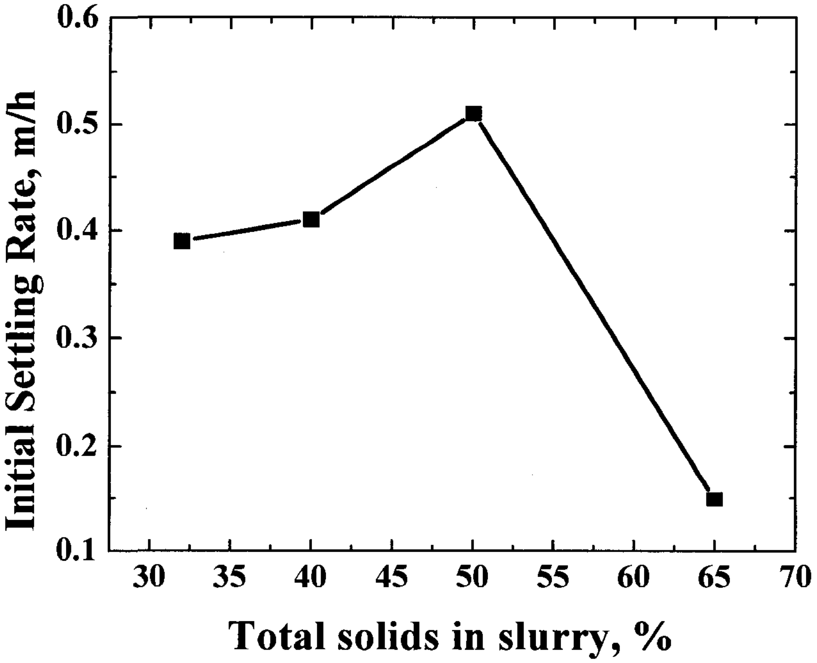

Figure 5.14: Effect of coarse sands addition on initial settling rate on flocculated MFT. Polymer dosage: 80 ppm, pH = 8.6, mixing speed = 200 rpm.

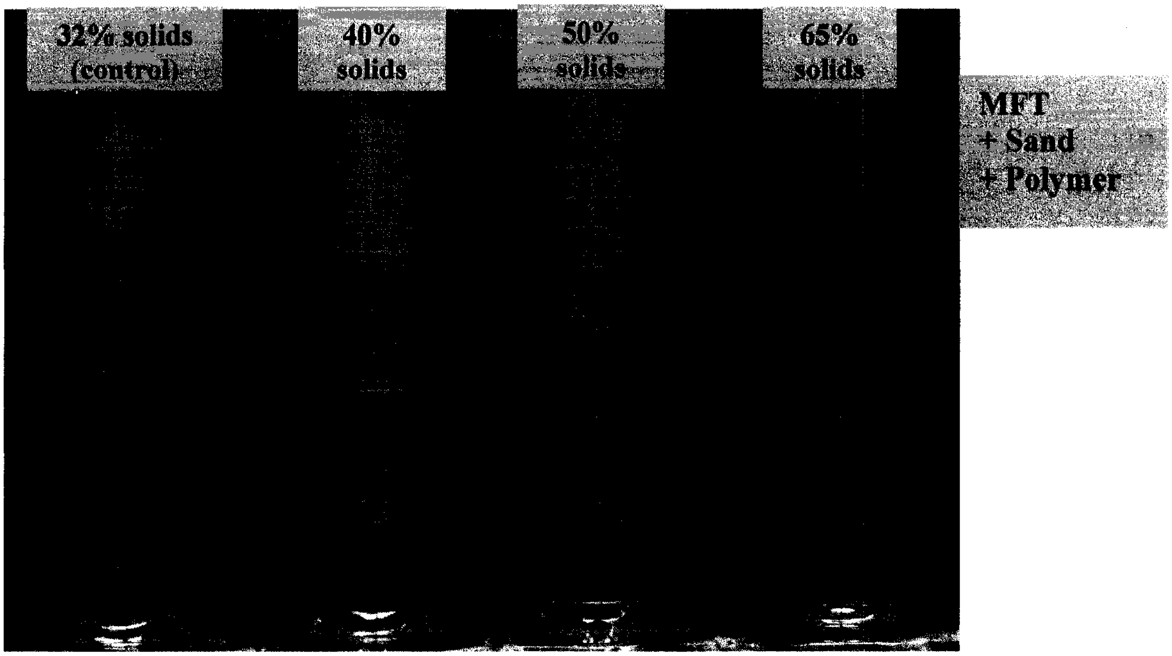

Figure 5.15: Photograph showing flocculated MFT with and without sand addition.

Table 5.5 shows the effect of coarse sands addition on the PSD[§§§] of the fine solids in the supernatant. The results show that D_{90} progressively reduced from 19.1 μm to 8.8 μm when the total solids in the slurry was increased from 32 wt% to 50 wt%. Table 5.5 also shows that there was a corresponding increase in the volume of water released as the total solids in the slurry was increased. However, it should be noted that despite an increase in the initial settling rate on coarse sands addition, the increase in volume of water released was not very significant (i.e. increased water release from 36% to 41%). This could be due to the ability of coarse solids to trap water, thereby underestimating the total volume of water released from the system.

The results presented here suggest that the additional weight provided by the coarse sands increases the total density of the flocs formed thereby resulting in higher initial settling rate and finer solids in the supernatant.

[§§§] The PSD of the fine solids in the supernatant after addition of coarse sands are given in Appendix C

Table 5.5: Effect of coarse sands addition on fines content in supernatant and volume of water released from MFT.

Sample (MFT + Coarse Sands + 80 ppm Polymer)	*Solids in Supernatant (wt %)*	*PSD of Solids in Supernatant (D_{50}; D_{90})*	*Volume of Water Released (%)*
Control: 32% total solids	6.9	0.30 µm; 19.13µm	36
40% total solids	5.9	0.32 µm; 11.29µm	38
50% total solids	6.1	0.30 µm; 8.82 µm	41
65% total solids	6.3	0.33 µm; 14.75µm	16

5.4 Summary of Studies on Mature Fine Tailings

The effects of Magnafloc 1011 dosage, impeller speed, two-stage polymer addition and stirring, lime addition, gypsum addition, and coarse sands addition on flocculation of mature fine tailings were investigated. Based on the test results presented, the following conclusions can be drawn:

- Flocculation of mature fine tailings was induced by Magnafloc 1011 as it improved the settling rate of MFT. The flocculation performance was affected significantly by mixing conditions. This was evident in the measured initial settling rate and solids content in the sediment as the mixing speed was varied.

- The flocculation performance was enhanced by the two-stage polymer addition and stirring process. This resulted in an increased solids content in the sediment and higher water release from MFT.

- Addition of lime prior to Magnafloc 1011 addition during flocculation of MFT resulted in an increase in the initial settling rate of MFT, decrease of fine solids in the supernatant, and an improved supernatant clarity. However, there was no significant improvement in the solids content in the sediment.

- Gypsum addition did not improve flocculation of MFT with Magnafloc 1011. The MFT became gelled with no water released after gypsum was added.

- The difference in action between lime addition and gypsum addition before Magnafloc 1011 during flocculation of MFT could be attributed to the change in pH of the slurry when lime is added in comparison to the negligible effect on pH of slurry when gypsum is added.

- Addition of coarse sands during flocculation of MFT with Magnafloc 1011 produced a marked increase in the initial settling rate of MFT up to an optimum, beyond which further sands addition led to a decline in the settling rate. However, the effective water released from MFT on coarse sands addition was not significant when compared to the water released from MFT without coarse sands addition.

5.5 **References**

Hamza, H. A., Stanonik, D. J., Kessick, Michael A., (1996). “Flocculation of Lime – Treated Oil Sands Tailings”, Fuel, 75 (3), 280 – 284.

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Chapter 6

CONCLUSIONS

6.1 Problem Review

Canada's oil sands reserves, regarded as the second largest oil reserve in the world after Saudi Arabia, continues to be a pride of the nation. As far as the world's demand for oil continues coupled with escalating oil prices, commercial production of bitumen from the oil sands will remain highly profitable. However, for the Canadian oil sands industry to remain competitive there should always be a commitment to overcoming the challenges the industry faces, with an aim of meeting expectations for sustainable development.

One of the major challenges faced by the oil sands industry is the management of fluid fine tailings generated during bitumen production. These fine tailings which are stored in large settling ponds form a stable slurry structure known as mature fine tailings (MFT). MFT remains in a fluid state that, if left alone, would take centuries to consolidate into a solid material. The effects of MFT to the environment, which has been discussed in Chapter 1, cannot be overemphasized and it has raised public and regulatory concerns regarding long term management of the fluid fine tailings.

A variety of tailings handling technologies have been developed over the years to deal with the accumulated MFT and to mitigate storage problems associated with this fluid fine tailings stream. The use of an anionic flocculant in thickener vessels have been implemented in order to create a densified underflow that is similar to MFT. This is known as the Thickened Tailings Technology. Another industrial practice implemented for modifying fluid MFT is called Composite Tailings (CT) Technology. This involves mixing gypsum and coarse sand tailings with MFT. By filling the sand voids with fine tailings, water is released for reuse and the overall fine tailings volume is reduced.

Even with the successes gained with current industrial tailings management practices, the search for alternative methods of dealing with MFT continues. The overall aim is to speed up the transformation of MFT so that tailings can be turned into solid material capable of supporting vegetation and wildlife.

6.2 Summary of Thesis Work

Promoting accelerated fine solids settling in tailings ponds is key to managing/treating oil sands tailings. This thesis explored this concept by conducting flocculation studies on both kaolin suspensions (i.e. model tailings) and mature fine tailings. The flocculation performance of two polymers (Magnafloc 1011 and Al–PAM) on treating MFT was investigated. The effects of addition of a surfactant (DAHCl), lime, gypsum, and coarse sands during flocculation were determined. A new approach to polymer addition during the flocculation tests was also analyzed. The results of these tests have been presented and discussed in earlier Chapters of this thesis.

In general, the results from the experiments conducted revealed that the flocculating ability of Magnafloc 1011 (an anionic polyacrylamide) on kaolin suspensions is deteriorated when DAHCl (a cationic surfactant) is added. Two addition modes of DAHCl were tested. Firstly, the pretreatment of kaolin suspension with DAHCl before Magnafloc 1011 addition, referred to as DAHCl/Magnafloc 1011 addition mode. The second addition mode, referred to as the Magnafloc 1011/DAHCl addition mode, involved the addition of Magnafloc 1011 to the kaolin suspension before DAHCl. Both addition modes resulted in a reduced settling rate of the kaolin particles in comparison to the case when the kaolin suspension was treated with only Magnafloc 1011. This suggested that the presence of DAHCl had an inhibitory effect on the flocculation efficiency of Magnafloc 1011.

Studies on flocculation of MFT with the polymers showed that Al–PAM (up to 100 ppm dosage) was not effective as there was no sign of settling of the MFT even after a 3 hour period. The poor performance of Al–PAM on flocculating MFT was attributed to the presence of substances such as bitumen, sands, etc., which may possibly inhibit the flocculating action of Al–PAM on MFT. On the other hand, Magnafloc 1011 caused settling of MFT with increasing dosage up to an optimum, beyond which the settling rate of MFT started to decrease. Test results also showed that the flocculation performance of Magnafloc 1011 was affected by the stirring speed used to effect mixing of the polymer with the fine tailings. An optimum stirring speed was needed to cause a maximum initial settling rate of the MFT. There was a reduction in the settling rate of MFT when this critical stirring speed was exceeded, indicating that the flocs were ruptured into smaller pieces due to the strong shear resulting from high speed stirring of the slurry.

Higher solids content in the sediment coupled with higher water release obtained during the "Staged Polymer Addition and Stirring" process suggested that this approach to polymer addition during flocculation is beneficial. Also beneficial to the flocculation process was addition of lime prior to Magnafloc 1011 addition. The positive flocculation result observed was attributed to the change in pH of the slurry as lime was added. However, prior addition of gypsum before Magnafloc 1011 caused the MFT to gel. Mixing coarse sands with MFT to increase the total solids content in the slurry before flocculation with Magnafloc 1011 gave better flocculation test results in comparison with test results obtained with flocculation of MFT without coarse sands addition.

In general, the results from this work have shown that there is a great possibility of flocculating mature fine tailings despite its slow consolidation rate. Even though Magnafloc 1011 has shown some positive flocculation performance on MFT, it will be interesting to seek out other derivatives of polyacrylamides that could perform much better. More research is needed in this direction as success here could bring about accelerated tailings dewatering. This could in turn result in significant improvements such as elimination of new tailings ponds, more rapid recycle of process water, less fresh water draw and creation of a more readily reclaimable tailings deposit. These improvements are pivotal to oil sands tailings management and the sustainability of oil sands operations as a whole.

APPENDIX A

DATA FOR FIGURES IN CHAPTER 3

A1. Figure 3.2a

	Sediment Volume (mL)					
Time (min.)	**0 ppm**	**5 ppm**	**10 ppm**	**20 ppm**	**50 ppm**	**100 ppm**
0	99	99	99	99	99	99
0.5	97	89	80.5	32	35	41
1	91	80	64	29	32	39
1.5	86	71	55	28	30	37
2	81	64	49	27	30	36
2.5	76	58	45	26.5	29.5	36
3	71	53	42	26	29	36
3.5	66	50	40	26	29	36
4	62	47	38	25.5	28	35
4.5	58	45	36	25	28	34
5	53	43	35	25	27	33
6	46	41	33	25	27	31
7	40	35	32	25	27	30
8	36	33	30	25	26.5	30
9	33	31	29	25	26	29
10	32	29	28	24	25	28
12	30.5	27	27	24	25	28

A2. Figure 3.2b

Magnafloc 1011 Dosage (ppm)	*Settling Rate (m/h)*
0	1.33
5	2.71
10	5.08
20	18.75
50	18.19
100	18.15

A3. Figure 3.2c

Magnafloc 1011 Dosage (ppm)	*Turbidity (N.T.U)*
0	911
5	751
10	491
20	190
50	280
100	340

A4. Figure 3.3a

DAHCl Concentration (mM)	*Settling Rate (m/h)*
0	1.33
1	1.42
2	1.41
5	1.41
10	1.1

A5. Figure 3.3b

DAHCl Concentration (mM)	*Turbidity (N.T.U)*
0	911
1	30
2	41
5	75
10	103

A6. Figure 3.4a

Addition mode 1: DAHCl/20 ppm Magnafloc 1011

DAHCl Concentration (mM)	*Settling Rate (m/h)*
0	18.8
1	3.7
2	2.9
5	2.8

A7. Figure 3.4b

Addition mode 1: DAHCl/20 ppm Magnafloc 1011

DAHCl Concentration (mM)	*Turbidity (N.T.U)*
0	190
1	30
2	33
5	32

A8. Figure 3.5a

Addition mode 2: 20 ppm Magnafloc 1011/DAHCl

DAHCl Concentration (mM)	*Settling Rate (m/h)*
0	18.8
1	7.02
2	6.96
5	6.95

A9. Figure 3.5b

Addition mode 2: 20 ppm Magnafloc 1011/DAHCl

DAHCl Concentration (mM)	*Turbidity (N.T.U)*
0	190
1	48
2	49
5	47

A10. Figure 3.6

Time (min.)	*Sediment Volume (mL)*			
	20 ppm	**1 mM**	**20 ppm/1 mM**	**1 mM/20 ppm**
0	99	99	99	99
0.5	32	94	68	91
1	29	88	47	80
1.5	28	83	40	70
2	27	79	35	61
2.5	26.5	75	33	53
3	26	69	30	49
3.5	26	64	29	46
4	25.5	60	29	43
4.5	25	55	28.5	40
5	25	50	28.5	38
6	25	44	28	35
7	25	37	27	32
8	25	33	26	29
9	25	31	26	29.5
10	24	29	25	28.5
12	24	29	24	28

APPENDIX B

DATA FOR FIGURES IN CHAPTER 4

B1. Figure 4.2

	Sediment Volume (mL)				
Time (min.)	**0 ppm**	**20 ppm**	**50 ppm**	**100 ppm**	**200 ppm**
0	94	94	94	94	94
0.17	94	91	52	33	33
0.33	94	90	45	32	32
0.5	93	89.5	42	32	31
0.67	93	88.5	40	32	31
0.83	92.5	87.5	39	32	31
1	92	87	38	31.5	31
1.5	92	84	37	31.5	31
2	91.5	80.5	36	31.5	31
2.5	91	77.5	35.5	31	31
3	91	74.5	35	31	31
3.5	90.5	71.5	35	31	31
4	90	68.5	35	31	31
4.5	90	66	35	31	31
5	89	63	35	31	31
6	86	59	34.5	31	30.5
7	84	56	34	31	30.5
8	82	53	34	31	30.5
9	80	51	34	31	30
10	77.5	49.5	34	31	30
12	73	47	34	31	30
14	69	45	34	31	30
16	65	43.5	34	31	30
18	60	42	34	31	30
20	54	41	34	31	30
30	47	41	34	31	30
40	44.5	40	34	31	30
50	42.5	40	34	31	30

B2. Figure 4.3

Magnafloc 1011 Dosage (ppm)	*Settling Rate (m/h)*
0	0.32
20	0.97
50	12
100	12.3
200	12.3
300	8.5

B3. Figure 4.4

Magnafloc 1011 Dosage (ppm)	*Turbidity (N.T.U)*
0	163
20	146
50	108
100	215
200	307
300	410

B4. Figure 4.6a

Time (min.)	*Sediment Volume (mL)*	
	50 ppm	**(50 + 0 + 0) ppm**
0	94	94
0.17	53	52
0.33	46	45.5
0.5	43	43
0.67	41	40.5
0.83	40	40.5
1	40	40
1.5	39	40
2	39	39.5
2.5	38.5	39.5
3	38.5	39.5
3.5	38.5	39
4	38	39
4.5	38	39
5	38	38.5
6	38	38.5
7	38	38.5
8	38	38
9	37.5	38
10	37.5	38
10..017	37.5	37
10.17	37.5	37
10.33	37.5	36.5
10.5	37	36.5

Time (min.)	*Sediment Volume (mL)*	
	50 ppm	**(50 + 0 + 0) ppm**
11	37	36.5
12	37	36
13	37	36
14	37	35.5
15	37	35
16	36.5	34.5
17	36.5	34
18	36.5	33
19	36.5	32
20	36.5	31
20.017	36.5	31
20.17	36.5	31
20.33	36.5	31
20.5	36	30.5
21	36	30.5
22	36	30
23	36	30
24	36	29.5
25	36	29.5
26	36	29
27	36	29
28	36	29
29	36	28.5
30	36	28.5

B5. Figure 4.6b

	Sediment Volume (mL)	
Time (min.)	**50 ppm**	**(50 + 5 + 5) ppm**
0	94	94
0.17	53	52.5
0.33	46	45
0.5	43	43
0.67	41	41
0.83	40	41
1	40	41
1.5	39	40.5
2	39	40
2.5	38.5	40
3	38.5	39.5
3.5	38.5	39.5
4	38	39
4.5	38	39
5	38	38.5
6	38	38.5
7	38	38
8	38	38
9	37.5	37
10	37.5	37
10..017	37.5	27
10.17	37.5	27
10.33	37.5	27
10.5	37	26.5
11	37	26
12	37	25.5
13	37	25
14	37	25
15	37	25
16	36.5	25
17	36.5	25
18	36.5	25
19	36.5	25
20	36.5	25
20.017	36.5	23.5
20.17	36.5	23
20.33	36.5	23
20.5	36	23
21	36	23
22	36	22.5
23	36	22.5
24	36	22.5
25	36	22
26	36	22
27	36	21.5
28	36	21.5
29	36	21
30	36	21

APPENDIX C

DATA FOR FIGURES IN CHAPTER 5

C1. Figure 5.4

Magnafloc 1011 Dosage (ppm)	*Settling Rate (m/h)*
16	0
40	0.14
64	0.25
80	0.375
120	0.3
160	0.075

C2. Figure 5.6

Impeller Speed (rpm)	*Settling Rate (m/h)*
100	0.041
150	0.375
200	0.38
300	0.3
400	0.085

C3. Figure 5.8

Time (min.)	*Sediment Volume (mL)*		
	80 ppm	**(80 + 0) ppm**	**(80 + 20) ppm**
0	50	50	50
2	44.5	45	45
5	41	41	40
10	39	39	39
20	36.5	36.5	36.5
30	36	36	36
40	35	35.5	35
50	35	35	35
60	35	35	35
80	35	35	35
100	35	35	35
200	35	33	32.5
300	35	32	30

C4. Figure 5.10a

Time (min.)	*Sediment Volume (mL)*			
	0 mM	**2 mM**	**5 mM**	**8 mM**
0	50	50	50	50
2	44.5	44	42	45
5	40.5	39	37	42
10	38	37	36	40
20	36	35	35	38
30	35	34	34	36
40	34	33.5	33	35
50	33	33.5	33	34.5
60	33	33.5	33	34
80	33	33	33	34
100	33	33	33	33.5

C5. Figure 5.11

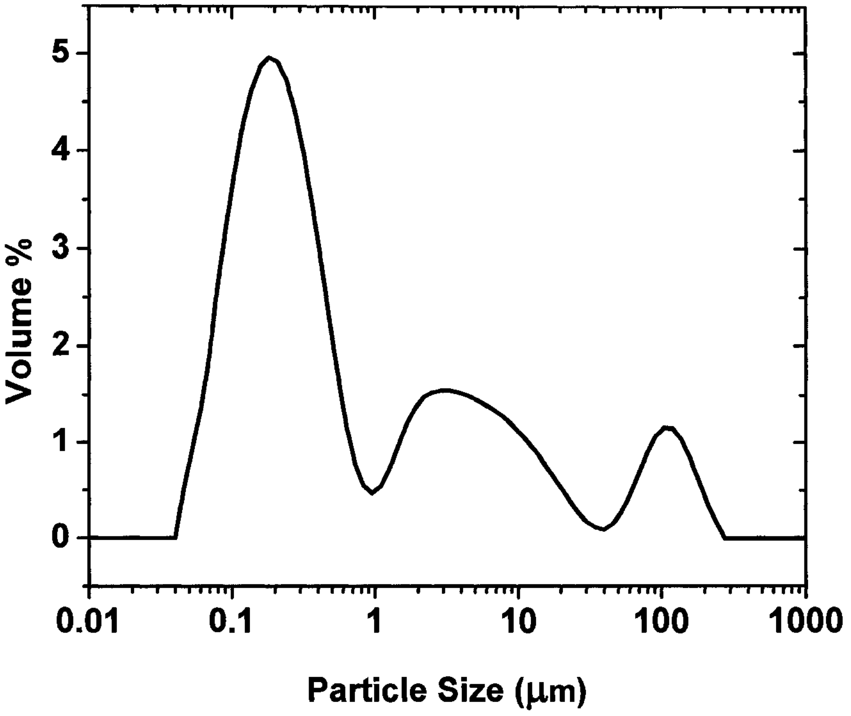
Lime Concentration (mM)	*Settling Rate (m/h)*
0	0.39
2	0.43
5	0.58
8	0.35

C6. Figure 5.13

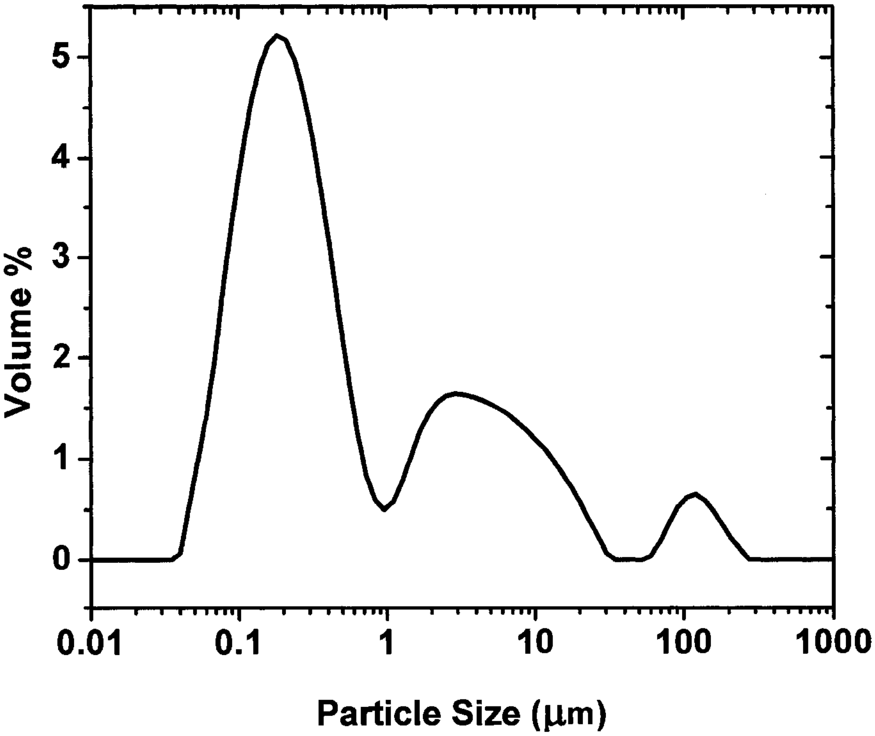
Time (min.)	*Sediment Volume (mL)*			
	32% solids (control)	**40% solids**	**50% solids**	**65% solids**
0	50	50	50	50
2	45	44	42.5	47.5
5	42	40.5	40	47
10	40	38	37.5	44
20	38	36	36	43
30	37.5	36	35.5	43
40	37	35.5	35.5	43
50	37	35.5	35	43
60	37	35	34.5	43
80	37	35	34.5	43
100	37	35	34	43

C7. Figure 5.14

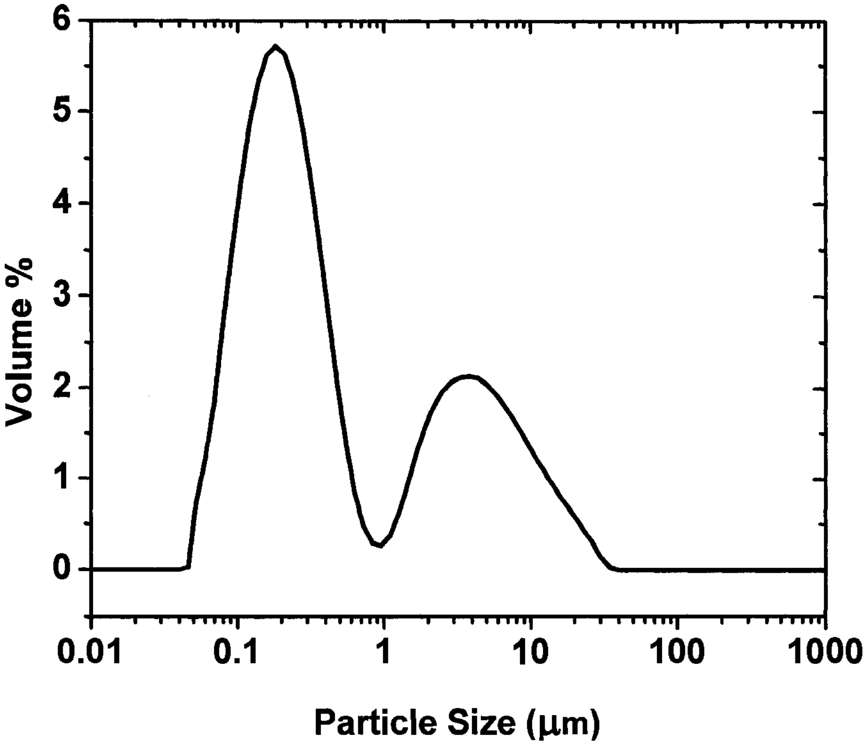
Total Solids in Slurry (%)	*Settling Rate (m/h)*
32	0.39
40	0.41
50	0.51
65	0.15



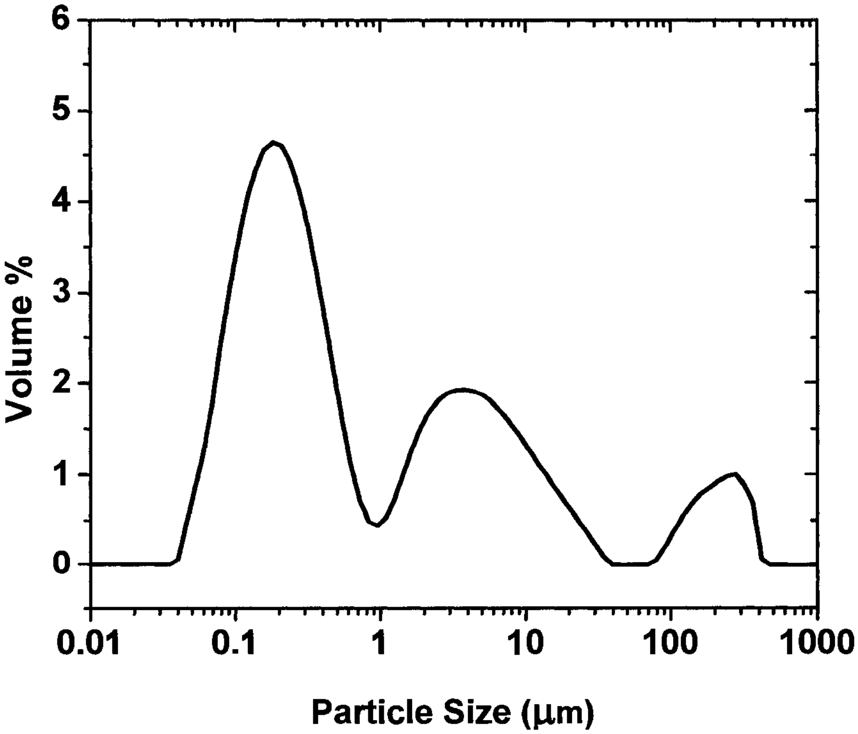
C8. PSD of fine solids in supernatant after addition of 80 ppm Magnafloc 1011



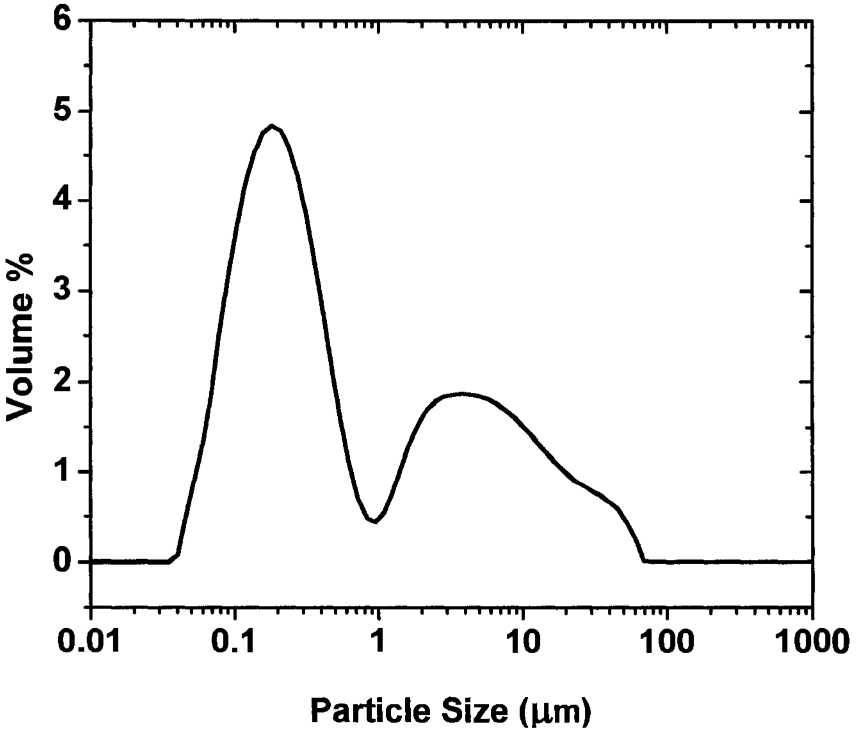
C9. PSD of fine solids in supernatant after pretreating with 2 mM Lime prior to addition of 80 ppm Magnafloc 1011



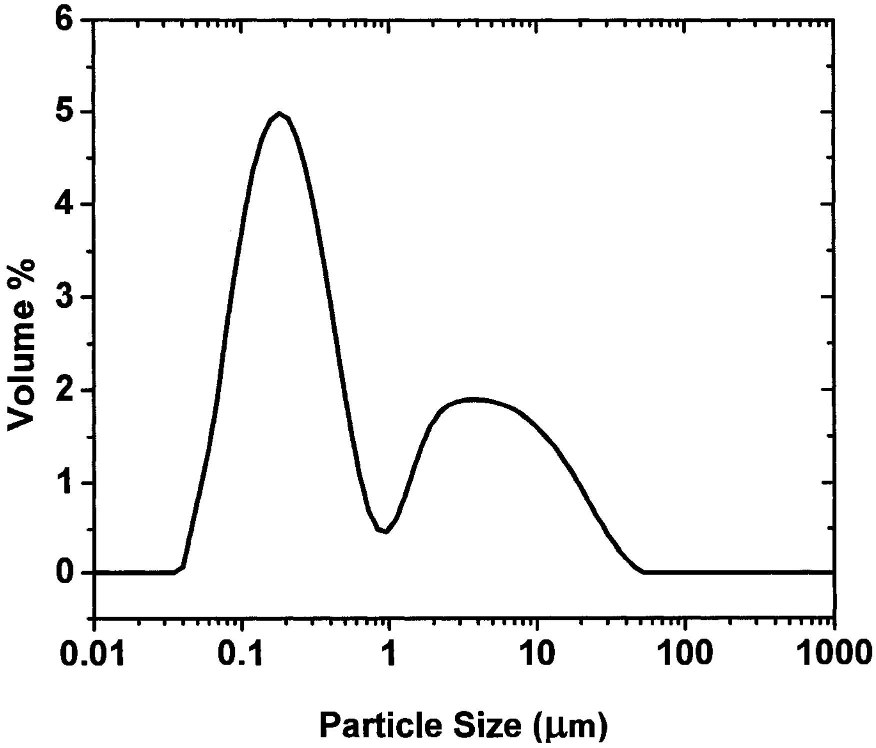
C10. PSD of fine solids in supernatant after pretreating with 5 mM Lime prior to addition of 80 ppm Magnafloc 1011



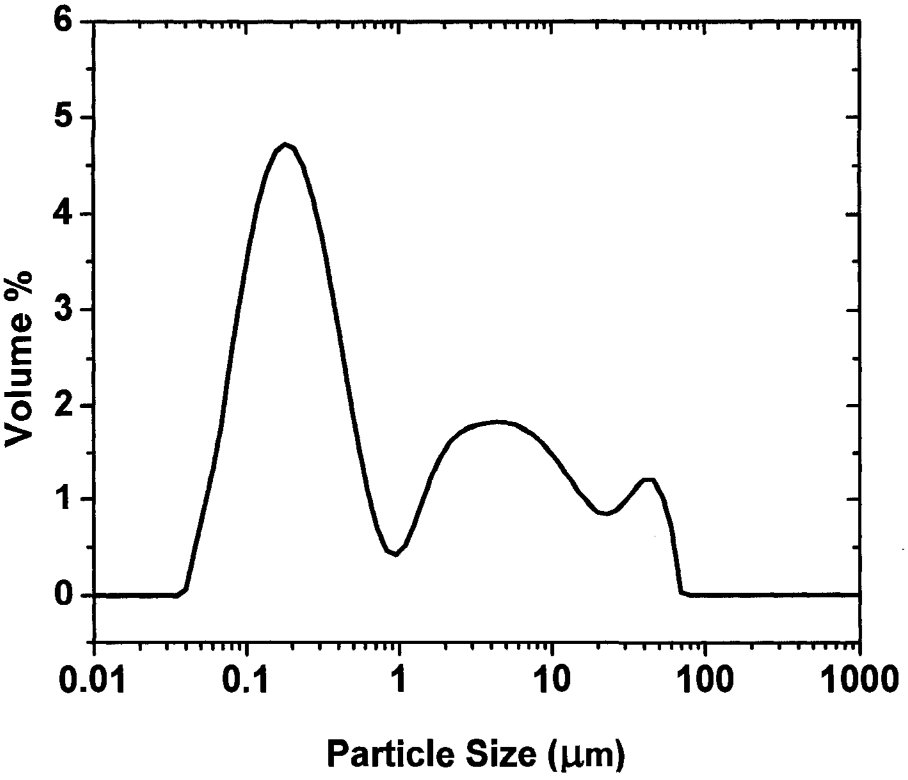
C11. PSD of fine solids in supernatant after pretreating with 8 mM Lime prior to addition of 80 ppm Magnafloc 1011



C12. PSD of fine solids in supernatant after coarse sands addition (MFT + 80 ppm Magnafloc 1011 + **40%** total solids)



C13. PSD of fine solids in supernatant after coarse sands addition (MFT + 80 ppm Magnafloc 1011 + **50%** total solids)



C14. PSD of fine solids in supernatant after coarse sands addition (MFT + 80 ppm Magnafloc 1011 + **65%** total solids)