Flocculation and dewatering of kaolinite suspensions and oil sands mature fine tailings using dual polymers

by

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Abstract

The development of a method to consolidate and dewater Athabasca oil sands mature fine tailings (MFT) is one of the major challenges facing Alberta's oil sands industry. This thesis presents studies performed on the flocculation and dewatering of kaolinite suspensions (the major clay component in MFT) and Athabasca MFT using a combination of two polymers in series. The first additives used were a low molecular weight (LMW) anionic lignin-based polymer (lignosulfonate) and four LMW cationic cellulose-based polymers (Celquat). The second additive used was a HMW linear PAM based polymer (A3335). The performance of the dual polymer systems was compared to that of using A3335 alone. Performance of the treatments was assessed based on real-time monitoring of floc size growth and fines capture using a Focused Beam Reflectance Measurement (FBRM) particle size analyzer, net water release, supernatant clarity, and capillary suction time (CST) measurements on the flocculated mixtures.

A dual polymer system consisting of lignosulfonate as the first additive followed by A3335 was found to perform best for MFT flocculation and dewatering, reducing the CST of MFT by over 50%. A dual polymer system of Celquat followed by A3335 performed best on kaolinite suspensions. In both MFT and kaolinite suspensions, the dual polymer treatments performed better than single polymer treatment. The beneficial effect of lignosulfonate together with A3335 has been attributed to its ability to interact with the residual bitumen in MFT. The study shows that dual polymer flocculation poses considerable advantages over single polymer flocculation, and has the potential to be a viable method to treat MFT from Alberta's oil sands industry.

Preface

Chapter 4 of this thesis has been presented at the Paste 2014 conference (the 17th annual international seminar on paste and thickened tailings) held in Vancouver, BC, in June 2014 as M. H. Haroon, X. Tan and Q. Liu, "Flocculation and Dewatering of Clay Suspension Using Dual Polymer Flocculants".

Chapter 5 of this thesis is being prepared for submission to the journal Energy & Fuels, as M.H. Haroon, X. Tan and Q. Liu, "Floc Size Growth and Water Release During Treatment of Mature Fine Tailings Using Dual Polymers".

In both chapters M.H. Haroon was responsible for the data collection and analysis as well as the manuscript composition. X. Tan contributed to concept formation and manuscript edits, and Q.Liu was the supervisory author and was also involved with concept formation, guidance and manuscript edits.

The remainder of this thesis has not been published elsewhere. The thesis is an original work by M. H. Haroon, with guidance and edits by both X. Tan and Q. Liu.

Dedication

This thesis is dedicated to my parents, Dr. Muhammad Yusuf Haroon and Mrs. Tahsina Sayeed. Without your love, effort and support I would never have achieved any success in life.

Acknowledgements

First of all I offer my sincere gratitude to my supervisor Dr. Qi Liu and advisor Dr. Xiaoli Tan, for their excellent and continued guidance throughout the course of my studies and research at the University of Alberta. Their support and training played a crucial part in my academic experience and ability to complete this research project.

Thanks to Jeremiah Bryksa and Lisa Brandt for their training, technical support in the laboratory, and for providing me with the supplies required for my work. Thanks also to Syncrude for providing the MFT and some of the materials used in this thesis.

I am grateful to the Institute for Oil Sands Innovation (IOSI) for funding my studies, and the Department of Chemical and Materials Engineering for providing an engaging environment for graduate studies and research.

Lastly but most importantly of all, I would like to express my gratitude to God, without whose blessings none of this would have been possible.

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LIST OF ABBREVIATIONS

AER – Alberta Energy Regulator

AENV – Alberta Environment

CST – Capillary Suction Time

CSS – Cyclic Steam Stimulation

DDA – Dedicated Disposal Area

ERCB – Energy Resources Conservation Board

ESRD – Environment and Sustainable Resource Development

FBRM – Focused Beam Reflectance Measurement

FFT – Fluid Fine Tailings

HMW – High Molecular Weight

HPAM – Hydrolyzed Polyacrylamide

LMW – Low Molecular Weight

MFT – Mature Fine Tailings

NEB – National Energy Board

PAM - Polyacrylamide

QCM-D – Quartz Crystal Microbalance – Dispersion

SAGD – Steam Assisted Gravity Drainage

SEM – Scanning Electron Microscopy

SRF – Specific Resistance to Filtration

Chapter 1 - Introduction

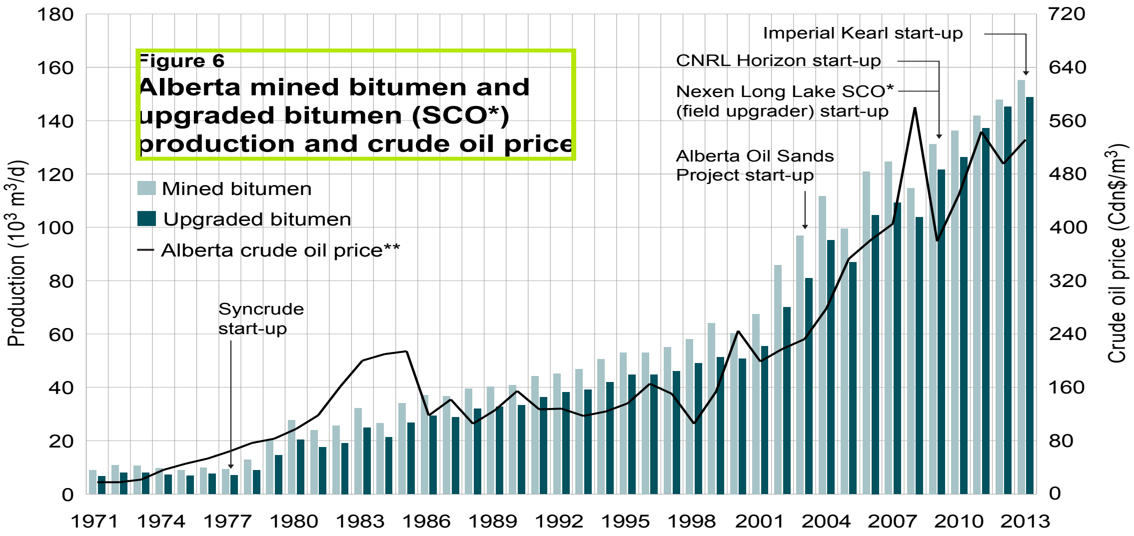
1. Introduction

1.1 Introduction to Alberta’s Oil Sands

Alberta's oil sands are the third-largest proven crude oil reserve in the world (Alberta Energy, 2014), with an in-place reserve of around 293 billion cubic metres (1.84 trillion barrels). Of the total reserves, 26.56 billion cubic metres (167.2 billion barrels) are currently recoverable using existing mining and in-situ technology, based on information provided by Alberta Energy Regulators as of December 31, 2013 (AER, 2014). At the current rate of oil consumption of about 1.5 million barrels per day, this resource should be able to meet Canada’s crude oil needs for several centuries to come.

Bitumen is recovered from oil sands deposits using either open-pit mining or in-situ technology. The method used to recover bitumen depends on the depth of the deposit. Within the 381,000 square kilometres of boreal forest in Alberta, about 90,000 square kilometres contain active oil sands deposits, distributed in three principle areas: Athabasca, Cold Lake and Peace River. Of that, only 4,800 square kilometres (about 5%) is close enough to the surface to be mined (AER, ‘Spotlight on oil sands’, 2014; Chalaturnyk et al, 2002).

In 2013, Alberta oil sands operation accounted for 76% of Canada’s oil and equivalent production, with bitumen representing 56% of the total. Alberta produced 357 million barrels from mining methods and 405 million barrels from in situ methods, totalling 761 million barrels, equivalent to 2.1 million barrels per day. Bitumen production from mining and in-situ projects increased by 5% and 12%, respectively, resulting in an overall bitumen production increase of 8% compared to 2012 (AER, 2014).



* Synthetic crude oil.
** Source: Canadian Association of Petroleum Producers *Statistical Handbook*.

Figure 1.1 – Mined and upgraded Alberta bitumen and Crude oil price from 1971 – 2013 (AER, 2014)

Total bitumen production is projected to reach 4.1 million barrels per day by 2023, with mined bitumen accounting for 1.7 million barrels per day. Over the same period, mined bitumen is projected to continue to be the primary source of crude bitumen to be upgraded in Alberta. (AER, 2014) With rising geopolitical tensions in oil-producing countries, particularly in the Middle-East, the price of crude oil can be expected to continue increasing, further establishing the importance of the oil sands to the Canadian economy.

North of Fort McMurray, at the Athabasca oil sands, crude bitumen occurs near the surface and can be recovered by open-pit mining (AER, ‘ST98’, 2014). In this method, overburden is removed, oil sands ore is mined, and bitumen is extracted from the mined material in large facilities using the hot water extraction process, also known as the Clark Process (Clark, 1939; Clark and Pasternack, 1932). At greater depths, it is not economical to recover the bitumen by mining. In such cases, in situ methods are employed. Cyclic steam stimulation (CSS) and steam-assisted gravity drainage (SAGD) are the two main methods used. The reservoir is heated using injected steam to reduce the viscosity of the bitumen, allowing it to flow to a vertical or horizontal wellbore.

Figure 1.2 – Map of Alberta showing total oil sands deposits and surface mineable area (AER, Spotlight on oil sands)

Production of bitumen from Alberta's oil sands began with the start-up of Great Canadian Oil Sands (Suncor) in 1967. As of March 2013, there are nine oil sands mining projects and over 50 in-situ thermal projects in Alberta (AER, 'Spotlight on oil sands', 2014). The total number of projects including those not yet approved through the regulatory process is currently close to 200 (Alberta Energy, 'Oil sands project map', 2014).

1.2 Oil Sands and the Bitumen Extraction Process

Crude bitumen is extra heavy oil that in its natural state does not flow to a well. Oil sands are a mixture of bitumen, mineral matter and water in varying proportions. The bitumen content of Alberta oil sands ranges from 0-19 wt%, and is 12 wt% on average. The water content increases as bitumen content decreases, and is 3-6 wt%. The balance is mineral content, predominantly quartz, silts and clay (Chalaturnyk et al, 2002).

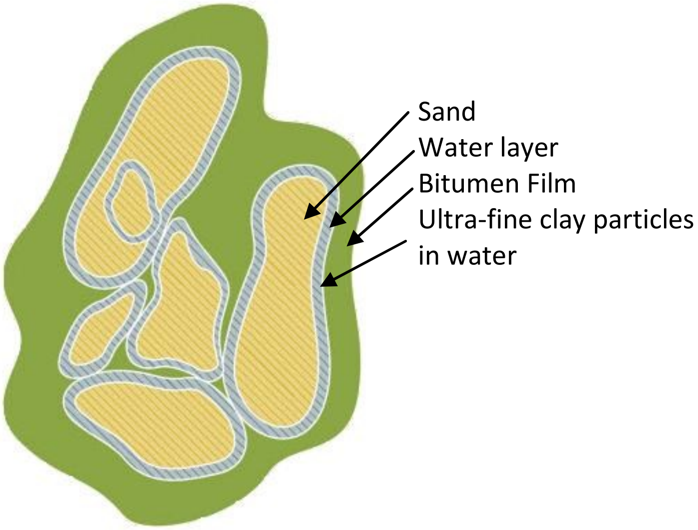


Figure 1.3 – Composition and structure of oil sands (Alberta Energy, 2014)

Bitumen is extracted from mined oil sands using the Clark hot water process, with some variations and differences in detail. The oil sands are mined in open-pit mines using trucks and shovels. The mined oil sands are crushed and mixed with process water and caustic soda. The conditioned oil sands slurry is then introduced to hydrotransport pipelines or tumblers, where further size reduction occurs under shear. This liberates bitumen from the sand grains. Air is then introduced, which attaches to the bitumen, causing the aerated bitumen to float to the top of large gravity separation vessels. The aerated bitumen froth is skimmed off from the slurry. The coarse sands settle out and are removed as tailings. Un-aerated bitumen remaining in the slurry is recovered using self-aerated mechanical flotation cells and tails oil recovery vessels, or cyclo-separators.

The recovered bitumen froth typically contains 60% bitumen, 30% water and 10% solids (Masliyah et al, 2004). The froth is de-aerated and mixed with solvents, either naphtha or a paraffinic diluent. The addition of a solvent increases the density difference between the bitumen and the water, facilitating separation, while also reducing the bitumen viscosity. The solids and water are then separated from the bitumen using inclined plane settlers, cyclones or centrifuges. This mixture of diluent and bitumen, also known as dilbit, is then ready for upgrading to synthetic crude oil.

The remaining mixture of water, sand, fine clays and residual hydrocarbons is removed as tailings. The tailings stream is sent to tailing ponds for solid-liquid separation. The coarse solids settle out quickly to form beaches, and the clarified water is recycled back to the process. The remaining fine tails of 6-10 wt% solids accumulate in the tailings ponds, settling quickly to 20 wt% solids. These fluid fine tails then settle over the course of a few years to about 30 wt% solids, known as mature fine tailings (MFT). MFT forms a very stable gel-like structure that has a very slow consolidation rate and remains in a fluid state for decades. Figure 1.4 shows a generalized scheme of the hot water extraction process. The accumulation of the very slow settling MFT is currently one of the major environmental liabilities of the Alberta oil sands operations.

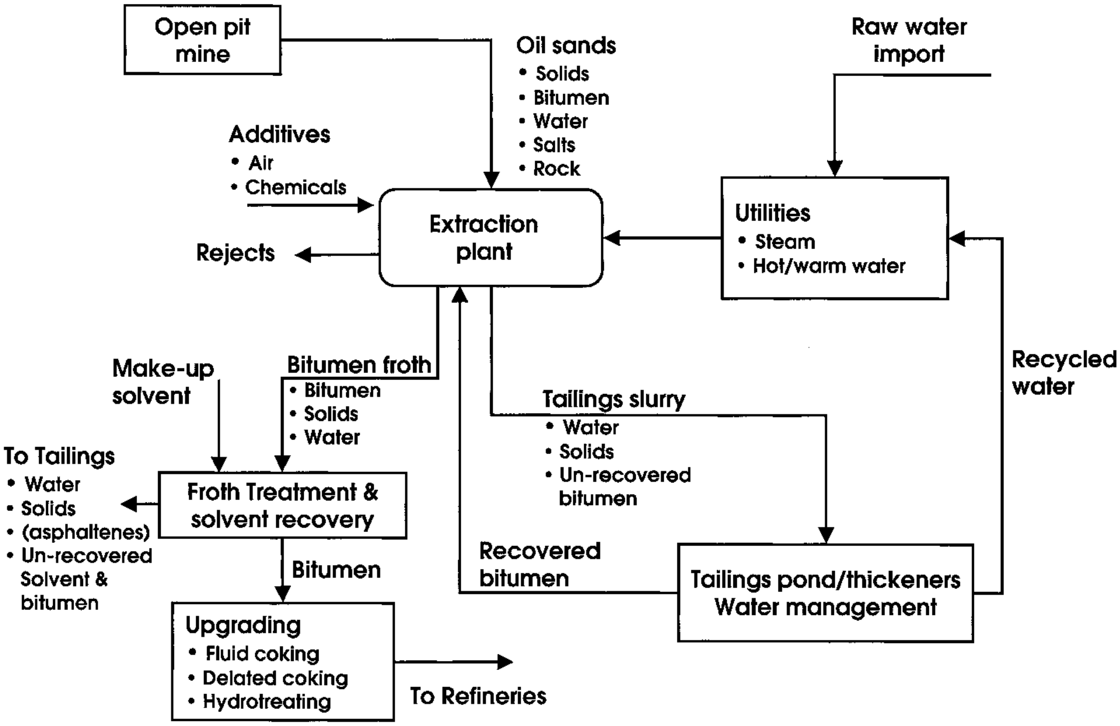


Figure 1.4 – Generalised scheme of the hot water extraction process (Masliyah et al, 2004)

1.3 Oil Sands Tailings

1.3.1 Composition and nature

MFT has a solids content that ranges from 30-40 wt% and a residual bitumen content of 1-3%, with the balance made up of water. The solid materials are mainly fine clays, with over 90% of the solids below 44 μm in diameter (Wang et al, 2014). The major clay components in the Alberta oil sands are kaolinite (40-70 wt%), illite (28-45 wt%) and montmorillonite (1-15 wt%)

(Chalaturnyk et al, 2002). As such, kaolinite and illite form the majority of the fine clays in MFT. The exceptional stability of MFT can be attributed to the gel-like structures formed by the fine clays in water.

1.3.2 Production and accumulation of tailings

The tailings produced as a waste product of the hot water extraction process pose a major environmental and public relations problem for the oil sands industry. Consolidation of untreated MFT is estimated to take thousands of years.

Tailings ponds currently cover over 180 square kilometers of land in Alberta (AESRD, 2014). About 3.3 cubic meters of tailings is discharged to the tailings ponds per barrel of bitumen produced. Of these tailings, 1.5 cubic meters will eventually accumulate as fluid fine tailings or mature fine tailings after supernatant recovery (Masliyah et al, 2011). According to recently published figures released by the Alberta Energy Regulator (AER 'ST98', 2014), 357 million barrels of bitumen were produced from surface mining activities in 2013 – this amounts to an increase in fluid fine tailings deposits of almost 540 million cubic meters in 2013 alone. With mined bitumen expected to be the primary source of upgraded bitumen in Alberta for the next ten years (AER, 'ST98', 2014), the volume of tailings is expected to grow at an increasing rate. The volume of the fluid tailings is forecasted to grow to over 1.2 billion cubic meters by 2020, and to stabilize at 1.3 billion cubic meters in 2060 (Houlihan and Hale, 2011).

1.3.3 Risks associated with tailings ponds

Tailings contain toxic materials such as naphthenic acids, phenolic compounds, polycyclic aromatic hydrocarbons, ammonia, and trace metals such as mercury (Nix and Martin, 1992). Oil sands tailings ponds have been found to be acutely toxic to wildlife and aquatic organisms (Scarlett et al, 2012; Royal Society of Canada 2010; Rogers et al, 2002) in surrounding areas, with naphthenic acids in particular considered to be one of the most significant contaminants associated with tailings ponds. The Pembina institute compiled data regarding toxic materials disposed of in tailings ponds (from the National Pollutant Release Online Inventory, accessible at: http://www.ec.gc.ca/pdb/websol/querysite/query_e.cfm) for CNRL's Horizon Mine, Syncrude's Mildred and Aurora Mines, Shell's Muskeg River Mine and Suncor Mines for 2010. They reported over 300 tonnes of arsenic, 178 tonnes of benzene, 756 tonnes of lead, 0.8 tonnes of mercury, 1.2 tonnes of toluene and 342 tonnes of polyaromatic hydrocarbons (Pembina Institute, 2014).

Although tailings ponds are typically lined with geomembranes to prevent seepage, studies have suggested that seepage does occur (Frank et al. 2014). In any case, the seepage from the tailings ponds into the surrounding environment and groundwater poses significant risks to the environment. The health effects on migrating birds that land in tailings ponds have been widely publicized, and although most tailings ponds contain deterrent systems, this poses a risk that affects public perception.

The large quantities of water required to extract bitumen from mined oil sands is another environmental issue of concern. Around 2.5 – 4 barrels of fresh water are required to produce a barrel of bitumen (NEB, 2013), and the Athabasca river is the main source of fresh water for mining operations.

1.3.4 Directive 074: Tailings performance criteria and requirements for oil sands mining schemes

In 2009, the Energy Resource Conservation Board (ERCB) (now the Alberta Energy Regulator) passed Directive 074, establishing performance criteria and requirements for oil sands tailings. Among other requirements, Directive 074 stipulates that by July 1, 2012, at least 50% of the fines present in the oil sands feed must be disposed of in dedicated disposal areas (DDA) in order to reduce tailings pond volumes. The DDAs must be formed in a manner that ensures trafficable deposits. A minimum undrained shear strength of 5 kPa for material deposited in the previous year was specified, and material that does not meet the shear strength criteria must be removed or remediated. The material deposited must also be ready for reclamation within 5 years of cessation of active deposition, and within this period must have a minimum undrained shear strength of 10 kPa to allow for a trafficable surface layer.

Directive 074 requires that companies submit annual compliance reports. As of 2013, despite committing significant resources towards tailings management, industrial operators have not been able to meet the Directive 074 criteria (ERCB, 2013). Therefore there is currently increased pressure to develop an industrially and economically feasible process to dewater the fresh and legacy fine tailings to meet the requirements of the directive.

1.4 Current industrial tailings management practices

Tailings management processes that operate commercially at full scale have been detailed in this section. Less developed technologies have also been mentioned.

1.4.1 Sedimentation/Self weight consolidation

This process uses natural dewatering processes that use the force of gravity to separate the suspended solids from the tailings stream. The tailings are pumped directly to the tailings ponds and allowed to dewater, while the supernatant is decanted and recycled back to the extraction process. This is a low-cost and low-maintenance method, and effective for widely varying feed characteristics. However, the method requires vast areas, often requiring engineered dams. The process is extremely slow and only results in partial dewatering. Although this method has been used for 40 years in the oil sands industry, understanding of the fundamentals of densification of MFT remains poor (BGC Engineering, 2010).

1.4.2 Thickened Tailings/Paste technology

The thickened tailings technology involves the addition of chemicals to aid in flocculation of the fine solids in the tailings, resulting in the settling of suspended fines. The process takes place in a thickener, and releases water that is suitable for reuse in the extraction process. A rake mechanism in the thickeners transports bed materials to the underflow, assists with dewatering and also scrapes away deposits from the thickener base. The faster settling of the fines results in a more concentrated solids stream that requires less land area for deposition. Normal thickener processing produces slurries with around 30 wt% solids. The residence time in a thickener to achieve this solid content is around half an hour, whereas gravity settling takes several years to achieve the same solids content.

The thickened tailings process targets new fines in the tailings streams, and can quickly recover some of the process water with its contained heat (reducing the energy requirements to recycle the water back to the process). The densified tailings with higher solids content can be deposited with less land disturbance. However, the resulting material requires further treatment, and the thickened tailings process does not address the legacy MFT (BGC Engineering, 2010). In addition, polymers are often expensive and may cause quality issues in the water recycled back from the tailings.

1.4.3 Consolidated Tailings (CT) Process

The consolidate tailings process (also known as the composite tailings process) involves mixing MFT with the coarse sand from the tailings cyclone underflow and gypsum to create a non-segregating slurry. The slurry is then discharged into a tailings pond to form a soft deposit that is capable of meeting various landscape performance goals. The CT process produces slurries with around 20% fines (and 60% solids overall). The CT process is relatively low cost and has been implemented at a large scale since 1995, when Suncor was the first to apply the process on a commercial scale. The process also deals with legacy MFT, and the slurry consolidates over a relatively short time.

However, despite many years of commercial use, operators experience difficulty in making CT with consistent specifications, given the variability of the feed. The process requires large, expensive containment, has low energy efficiency, and requires large amounts of sand. External sources of sand would have to be used to address the legacy MFT. The CT process also produces additional MFT from the cyclone overflow (BGC Engineering, 2010). In addition, the gypsum dosage required is quite high, causing water-quality issues in the recycled water such as the buildup of calcium and sulphate ions that negatively affect bitumen extraction (MacKinnon et al, 2001).

1.4.4 Other methods

These methods are primarily in the advanced research stage and have shown promise in MFT treatment in recent years, including physical processes such as centrifugation, natural processes such as Rim Ditching where a crust is allowed to form on the MFT surface, accelerating further dewatering, or the Freeze/Thaw method, where thin layers of MFT are allowed to freeze in the winter and thaw in the following summer, developing a fissured structure that quickly drains when thawed. Other processes include In-line Thickened Tailings, a process piloted by Suncor that involves the in-line addition of coagulants to the high fines content cyclone overflow tailings.

1.5 Problem Statement

Unless a major global shift towards energy sources other than crude oil occurs, the world will likely continue to be dependent on crude oil to meet its growing energy needs for the next few centuries. As the third largest proven reserve in the world after Saudi Arabia and Venezuela, the development of Alberta's oil sands is expected to play a vital role in Canada's economy for the foreseeable future. Efforts continue to increase Alberta's access to foreign markets, and the demand for Alberta bitumen is expected to continue to increase.

Mined oil sands are predicted to be the major source of upgraded bitumen for the coming decade, and the volume of MFT in Alberta is expected to grow at an increasing rate to over 1.2 billion cubic meters by 2020. Extensive investment and research into processes to address the MFT deposits has resulted in the development of several technologies. None of these processes have proved economically feasible or robust enough to adequately address the issue of MFT at this point in time.

However, the usage of thickeners and flocculants has resulted in much quicker settling of the fluid fine tailings to form MFT, allowing rapid partial dewatering of warm water that can be recycled.

The studies presented in this thesis were aimed towards tailings management using polymer flocculants. The ultimate goal is to develop a robust and economical process that creates consolidated deposits from MFT that meet the criteria set out in Directive 074, allowing for reuse of the trapped water and accelerated reclamation of land occupied by tailings ponds.

1.6 Thesis Objectives

The objective of this thesis is to study the consolidation and dewatering of MFT using a dual polymer system consisting of novel biodegradable polymers. The thesis is divided into chapters that follow the various stages undertaken in the study.

Chapter 2 is a review of literature on flocculation of MFT and clay suspensions using polymeric flocculants. This chapter presents basic aspects of flocculation, particle interactions and FBRM particle size measurements. Chapter 3 provides a summary of preliminary experiments performed in order to screen experimental methods.

Chapter 4 is based on a paper that was presented at the Paste 2014 conference (the 17th annual international seminar on paste and thickened tailings) held in Vancouver, BC, in June 2014. This chapter presents studies on dual polymer flocculation of kaolinite suspensions, the major clay component present in MFT. The goal of this study was to obtain better insight into flocculation performance of the dual polymer system in clay suspensions, with the intent of gaining insight into MFT flocculation. Chapter 5 is a paper on the studies carried out on dual polymer flocculation of Athabasca MFT. In both chapter 4 and 5, the performance of the polymer treatments was assessed using various criteria such as fines capture, floc size growth, net water release, capillary suction time (CST) and released water clarity. The mechanisms behind the flocculation were studied and explained based on the experimental results, and the performance of the dual polymer systems was compared to that of single polymer treatments.

Chapter 6 concludes the thesis, presenting the major findings of chapters 4 and 5, and providing a short discussion on the results of the two studies. Suggestions for future studies to strengthen key knowledge gaps are also provided.

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Chapter 2 – Literature Review

2. Literature Review

2.1 MFT Composition

As mentioned earlier, MFT has a solids content that ranges from 30-40 wt% and a residual bitumen content of 1-3%, with the balance made up of water. The solid materials are mainly fine clays, with over 90% of the solids below 44 µm in diameter (Wang et al, 2014). The major clay components in the Athabasca oil sands are kaolinite (40-70 wt%), illite (28-45 wt%) and montmorillonite (1-15 wt%) (Chalaturnyk et al, 2002). As such, kaolinite and illite form the majority of the fine clays in MFT. MFT also contains small amounts of smectite and other materials, although these materials are not present in significant quantities, and may not be found in certain samples.

2.2 MFT Structure and stability

The exceptional stability of MFT has commonly been attributed to the clay components present. Yong and Sethi (1978) attributed the high water holding capacity of MFT to the swelling characteristics of smectite. Montmorillonite also shows swelling characteristics (Chalaturnyk et al, 2002). Kaolinite structure contains repeating units of an octahedral aluminum–hydroxyl sheet bonded to the tetrahedral silicon–oxygen sheet, as illustrated in Fig. 1 (Konan et al., 2007) whereas for montmorillonite and illite, the octahedral Al–OH sheet is sandwiched between two tetrahedral Si–O sheets. Clays have a large surface area to volume ratio that facilitates interactions between themselves (Wang et al, 2014).

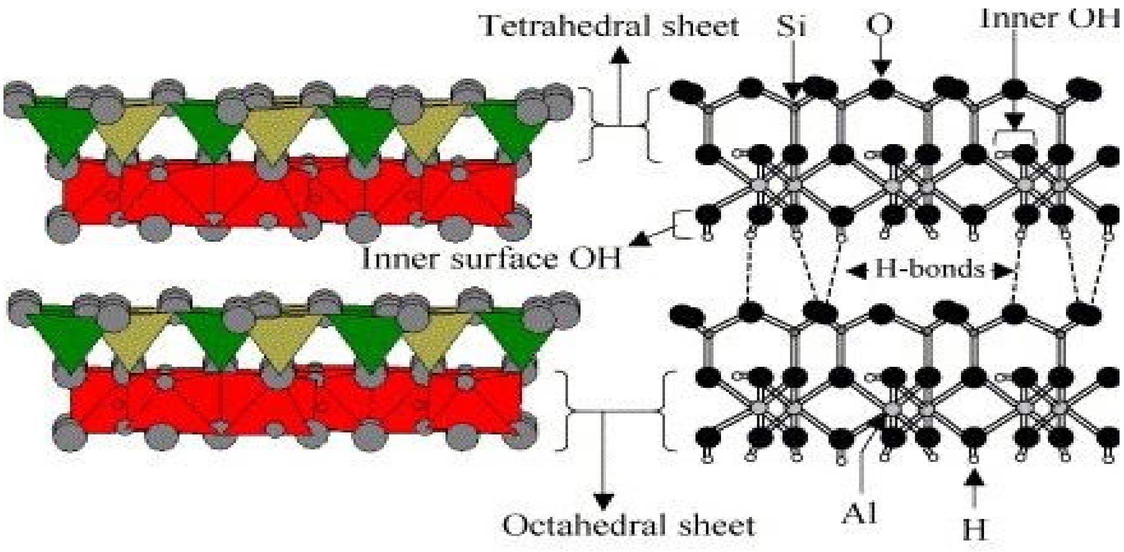

Figure 2.1 – Structure of kaolinite unit layers (Konan et al, 2007)

The charge present on clay particles in water is dependent on the suspension pH, and the charge can be different on their edges from that on their faces. The charge on the edges of clays can also have a charge opposite to that on the clay faces. In such cases, clay edges and faces attach to one another, forming a porous "house of cards" structure that can result in the gelation of the suspension (van Olphen, 1963). Kotlyar et al (1995) performed a study to characterize the different size fractions present in MFT and their properties, and also found that the ultrafine solids (<0.3 μm) in MFT form gels that give MFT its structure and impede consolidation.

SEM images obtained by Mikula et al (1993) show bitumen present as free droplets of 1 to 10 μm in size in MFT. They found that the bitumen also contaminates the edges of clays, possibly contributing to the tailings structure. Scott et al (1985) and Suthaker and Scott (1996) found that residual bitumen decreases the hydraulic conductivity of MFT, by blocking the pore spaces between particles, thus impeding water release and hindering consolidation, as shown in Figure 2.2.

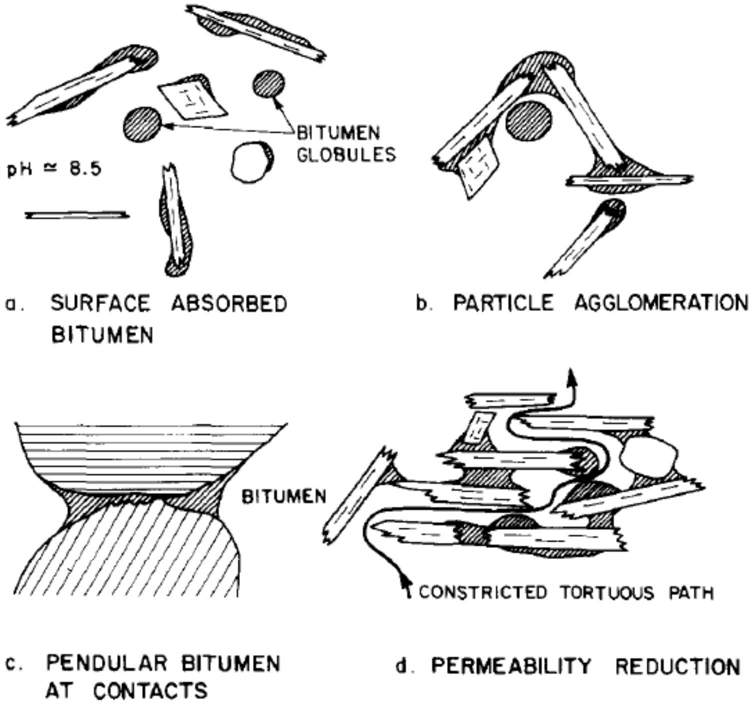

Figure 2.2: Effect of bitumen in MFT on settling and permeability (Scott et al, 1985)

2.3 Flocculation

The objective of this thesis project is to study the dual polymer flocculation of MFT. Polymer flocculation is an effective means of solid-liquid separation that involves bringing small particles together to form larger aggregates. It is useful to draw a distinction between flocculation and coagulation at this point. Although different studies have used the terms interchangeably, in this study coagulation refers to i) the process of reducing electrical double layer forces between particles, allowing attractive van der Waals forces to dominate, and ii) agglomeration as a result of surface charge neutralization. Flocculation refers to the process where particles are brought together to form large aggregates by bridging with HMW polymers, and can involve bringing together small aggregates formed by coagulation.

2.3.1 Bridging mechanism

In bridging flocculation, the polymer adsorbs onto two or more particles and bridges them together (Xu and Hamza, 2003). This method requires that sufficient unoccupied surface area of the particles be available for polymer adsorption. The polymer must have a high molecular weight in order for the polymer chain to extend past the electrostatic barrier of the particles in order to minimize the double layer repulsion between the particles. Therefore the dosage of polymer is important: too low a dosage will not be able to adequately bridge the particles in suspensions, while excess dosage will result in complete particle coverage, and reduce access to attachment sites, resulting in steric stabilization of the suspension, as shown in Figure 2.3 (Tridib et al, 2006). This suggests that an optimum dosage of polymer flocculant exists.

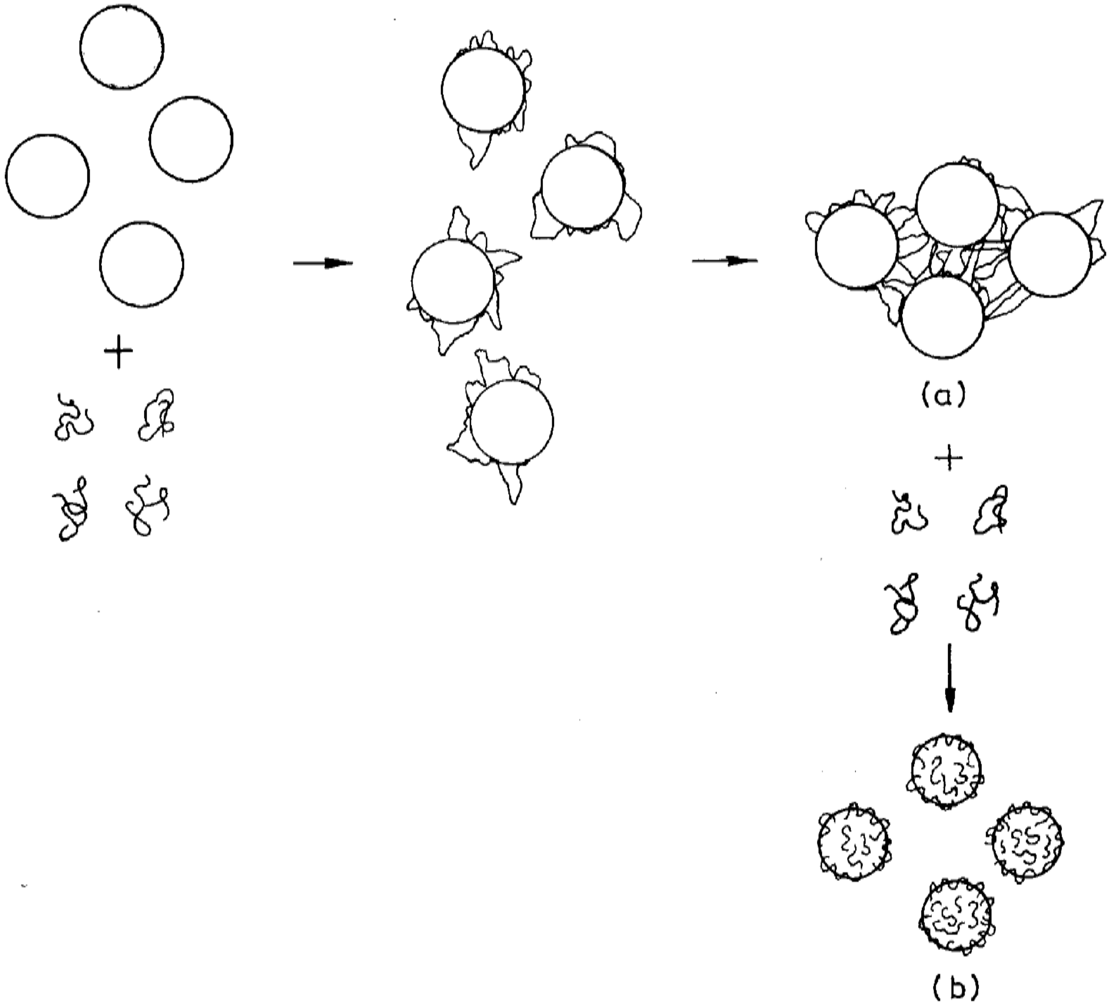

Figure 2.3 – Schematic illustration of (a) bridging flocculation and (b) steric stabilization as a result of overdosage (Tridib et al., 2006)

2.3.2 Surface charge neutralization

This mechanism involves the reduction of the magnitude of the surface charge on the particles in the suspension, reducing the energy required to agglomerate the particles. This usually involves the addition of charged particles of opposite charge to the net charge on the particles. Charged ions are also often used. Particle coagula formed by this mechanism are usually small and loosely bound, and more susceptible to breakage upon application of shear (Tridib et al, 2006).

2.3.3 Electrostatic patch mechanism

A combination of charge neutralization and bridging flocculation is often used, where the suspension is treated with highly charged ions or a LMW high charge density polymer that causes highly charged patches on particle surfaces. The HMW bridging flocculant is then added, and the flocculant and free particles in the suspension can then attach to the highly charged patches on the particle surfaces. This combination of charge patch formation and bridging is known as the electrostatic patch mechanism, first described by Gregory (1973).

2.4 Factors that affect flocculation

Some of the major factors that affect flocculation are outlined briefly in this section.

2.4.1 Polymer dosage

As discussed earlier, the dosage of the flocculants added has a significant effect on the efficiency of flocculation. A low polymer dosage may not be sufficient to neautralise the surface charges or bridge the fine particles in the suspension, while excessive polymer dosage may result in restabilisation of the suspension. For flocculation, Gregory (1988) suggested optimum performance can be achieved when half of the particle surface is covered with polymer.

2.4.2 Polymer weight and size

Polymers with higher molecular weights perform better as bridging flocculants. Polymers with higher molecular weights result in flocs with larger radius, improving collision efficiency, which results in higher flocculation rate (Tridib et al, 2006). The size and polymer structure also play an important role, with more branched polymers providing greater surface area for particle attachment.

2.4.3 Agitation and mixing

Agitation plays an important role in polymer flocculation. The agitation should be sufficient to result in efficient mixing of the flocculant and the particles in the suspension. However, excessive agitation can result in floc breakage. Therefore an optimum agitation rate that enhances mixing while minimizing floc breakage is desirable.

2.4.4 pH of the suspension

The surface charge of the particles in the suspension is affected by pH. The charge present on the polymer chain is also affected by pH, as the degree of ionization of the polymer changes with pH. The pH can also affect the conformation of the adsorbed polymers on the particles surface. The efficiency of coagulation/flocculation is therefore pH dependent.

2.4.5 Conformation of the adsorbed polymers on particle surfaces

The polymer conformation on particle surfaces is dependent on the polymer's chemical structure, charge density (and hence pH) and molecular weight. Yu et al (2006) found that highly charged cationic polymers tend to adsorb on to the kaolinite particle surface in a flat configuration. As a result, once the polymers with a higher charge density are adsorbed, the resultant particles have smaller polymer "loops" and "tails", whereas the resultant particles from the addition of the lower charge density polymers have "loops" and "tails" that are further extended from the kaolinite surfaces. The latter case would allow more effective bridging upon the addition of the HMW anionic polymer, resulting in larger final floc sizes.

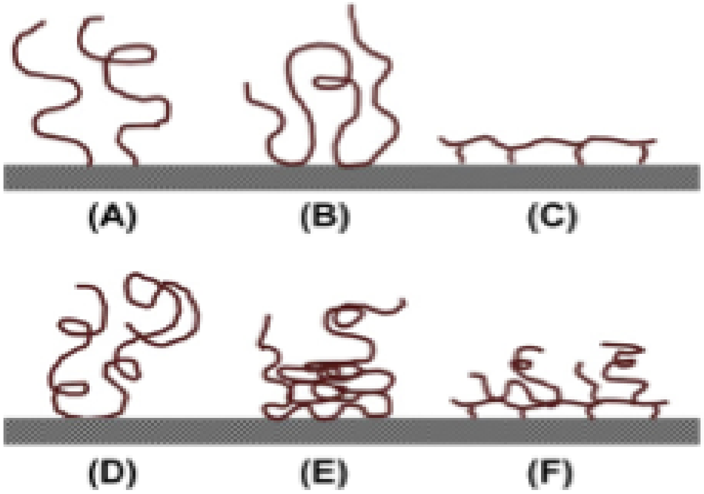

Figure 2.4– Possible conformations of adsorbed polymeric flocculants (Alagha et al, 2013)

Figure 2.4 shows the possible conformations of adsorbed polymeric flocculant on a solid/water interface. (A) represents single point attachment, (B) loop adsorption, (C) flat multiple site attachment, (D) random coil, (E) nonuniform segment distribution, and (F) multilayer adsorption (Alagha et al, 2013, Wang et al, 2014). Weak attraction between a hydrophilic polymer and clay surface results in the polymer chain extending away from the surface, such as for (A), (B) and (D). Strong polymer-surface interactions and relatively hydrophobic polymers result in flat conformations such as (C) and (F). A high level of polymer self-interaction results in a conformation such as (E). Polymers with a high chain stiffness (e.g. highly charged polymers) will resist changes to their conformation, as in the case of (A) and (C).

According to Wang et al (2014), in order for a polymer to quickly capture fines in a suspension, it is desirable for interactions between the polymer and the fines surface to be weakly attractive (in order to prevent stearic stabilization, reducing collision efficiency), hydrophilic in nature (to extend into the solution increasing adsorption area), low self-interaction and a moderate chain stiffness (to balance floc strength and re-flocculation ability).

2.4.6 Residual bitumen in MFT

Long et al (2006) studied the interactions between polyacrylamide and oil sands particle surfaces using a technique called single molecule force spectroscopy to determine the attachment force between polyacrylamide molecules and model oil sand surfaces, including silica, mica (representing clays) and bitumen. They found that both the attachment energy and the probability of attachment for polyacrylamide were lower with bitumen than the other surfaces. Klein et al (2013) studied the effect of the residual bitumen concentration in oil sands tailings on flocculation using a HMW Hydrolized polyacrylamide (HPAM) polymer. They found that reducing the residual bitumen concentration improves flocculation down to a bitumen concentration of 0.18 wt%. Below 0.18 wt% bitumen content, there is a reduction in flocculation efficiency. These findings suggest the existence of an optimum bitumen concentration in MFT for flocculation using polyacrylamides.

2.5 Types of additives used

Polymer flocculants can be made of a variety of chemical compounds and their properties can be tailored based on the needs of the flocculation process.

2.5.1 Synthetic polymers

Common synthetic industrial flocculants include polyacrylamides (PAM), polyethylene oxide (PEO) and polydiallyldimethylammonium chloride (PDADMAC) (Tridib et al, 2006). Synthetic polymers have been found to be more effective than natural polymers for flocculation purposes, as they can be tailored to particular applications, and produce rapid flocculation (Tridib et al, 2006). However, a drawback of synthetic polymers such as polyacrylamide is that they are easily degraded by shear forces (Krishnamoorti et al, 2010). In addition, synthetic polymers are typically expensive.

Polyacrylamides are often co-polymerised with other monomers and cations in order to introduce ionic character to the non-ionic polyacrylamide. Hydrolysed PAM is often used.

2.5.2 Inorganic additives

Inorganic additives are also commonly used as coagulants (Long et al, 2006; Sworska et al, 2000). These are typically metal ions with a high valence, such as Al^{3+}, Cu^{2+} and Fe^{3+}. As these ions follow the charge neutralization mechanism, the coagula formed are small and susceptible to breakage upon application of shear.

2.5.3 Natural Polymers

Natural polymers are another category of polymer used for flocculation purposes. These polymers are often polysaccharides-based (similar to those used in the pulp & paper industry) and are non-toxic and biodegradable/biocompatible. As noted earlier, an issue caused by the CT process for MFT processing is the residual chemical content in the recycled water. Natural polymers have an advantage in being low cost, and are typically shear-resistant (Krishnamoorti et al, 2010).

This study focuses on the use of a combination of cellulose and lignin based natural polymers and a PAM based polymer in order to flocculate MFT.

2.6 Previous studies on MFT and clay suspension flocculation

2.6.1 Studies on clay suspensions

Most of the studies on the flocculation of clay suspensions have focused on the use of a single high molecular weight polymer (e.g., Besra et al, 2004; Kage et al, 1988; Yu et al, 2006). High molecular weight polyelectrolytes operate through a bridging mechanism and form large flocs that are loosely packed and relatively shear resistant. The higher strength of these flocs is advantageous for filtration purposes, as they are less likely to degrade under the applied shear. The loose structures also result in fast dewatering; however it has been shown that HMW polymers result in higher water content in the settled beds (Besra et al, 2004). The high charge-density LMW polymers bring about aggregation via a charge neutralization mechanism, resulting in destabilization of the clay suspension. The resultant flocs are smaller in size leading to denser settled beds with lower water content; however, it has been found that the filtration rates of the settled beds are slow, and the resultant turbidity of the supernatant in such cases is relatively high (Besra et al, 2004; Petzold et al, 2002).

Recent studies on the use of dual polymer systems have proven to be advantageous over the use of a single polymer alone; Petzold et al (2003) found that the use of a LMW cationic polyelectrolyte followed by a HMW anionic polymer flocculant produced clearest supernatant in clay suspensions and natural waste waters from gravel pits. Yoon and Deng (2004) found that using a LMW polymer followed by a HMW polymer on clay suspensions produced better reflocculation after application of shear than using a single polymer. Glover et al (2004), studying the flocculation of alumina fines, found that the use of a LMW polymer followed by HMW polymer produced a settled bed with lower water content than by using a single HMW polymer alone, with the best results being observed when the LMW and HMW polymers used are of opposite charge.

2.6.2 Studies on MFT

The majority of the studies carried out in the past on the dewatering of MFT have focused on the use of a single polymer (Wang et al, 2010; Xu et al, 2008; Long et al, 2006; Sworska et al, 2000;). The positive effect of pretreatment of MFT with divalent cations on the flocculation performance has been well studied. Sworska et al (2000) found that pretreating the MFT with divalent cations resulted in clearer supernatants after flocculation. They used a HMW medium charge anionic copolymer of acrylamide and acrylate, such as Magnafloc 1011, and found the flocculation performance to be dependent on the pH of the MFT, with the optimum pH shifting upon the addition of Mg^{2+} ions. The flocculation performance was also found to be dependent on mixing conditions. Long et al (2006) found that the addition of divalent ions to MFT induced adhesion between fine particles, and suggested a synergistic relationship between the HMW flocculant and divalent ions.

Recent studies on the use of dual polymer flocculation for sewage treatment and the pulp and paper industry have shown promise over the use of a single polymer (Lee et al, 2001; Senthilnathan and Sigler, 1993). Similar promise has also been shown in dual polymer treatments carried out on MFT. Yuan and Shaw (2007) carried out an extensive study on the use of combinations of coagulation (C) and flocculation (F) to dewater the MFT, and observed that certain combinations, such as F-C, F-C-F, etc., worked better than the others. Watson et al. (2010) found that combining the use of a very low molecular weight (VLMW) anionic polymer and a high molecular weight (HMW) polymer flocculant on MFT resulted in higher average particle size and solids content in the settled beds, in addition to faster dewatering. However, very few such studies have been carried out to understand the mechanisms and kinetics of a dual polymer system.

2.7 The use of cellulose and lignin derived polymers

Bensebaa et al (2000) in their characterization study on organic coated solids in Athabasca bitumen found that the ultrafine inorganic solids in bitumen and tailings is coated with toluene insoluble organic matter with contributions from both humic and asphaltene like components. They found the coverage to be patchy rather than continuous, and suggested that this organic coating contributes to the ability of the solids to stabilize fine water emulsions. Lignin and the organic bitumen residues present in tailings streams share common humic chemical structures and lineage (Shevchenko & Bailey, 1996).

The beneficial effects of lignosulfonates and other lignin derivatives in enhanced oil recovery is well documented. Hong et al (1987) suggested that the lignosulfonates behaved as sacrificial adsorbates, adsorbing irreversibly to reservoir rock surfaces, while Novosad (1984) attributed the enhancement of oil recovery to the interfacial effects of the lignosulfonates. Lignosulfonates have also been applied as soil hardening agents (Kojima & Danchia, 1977). The common lineage and strong interaction with rock surfaces suggests the potential for strong interfacial activity between lignosulfonates and bitumen and clay surfaces.

In addition, experimental and simulation studies both suggest strong interaction between lignin and cellulose in water (Houtman & Atalla, 1995). In the chemical pulping process, the porosity of the pulp suspension decreases as the lignin is removed (Andreasson et al, 2003). It is anticipated that the use of a combination of lignin and cellulose may be analogous to this process in reverse, forming a high porosity fibrous structure that would be easy to dewater and filter.

Figure 2.5 shows the polymers used in this thesis along with their molecular weights and monomers.

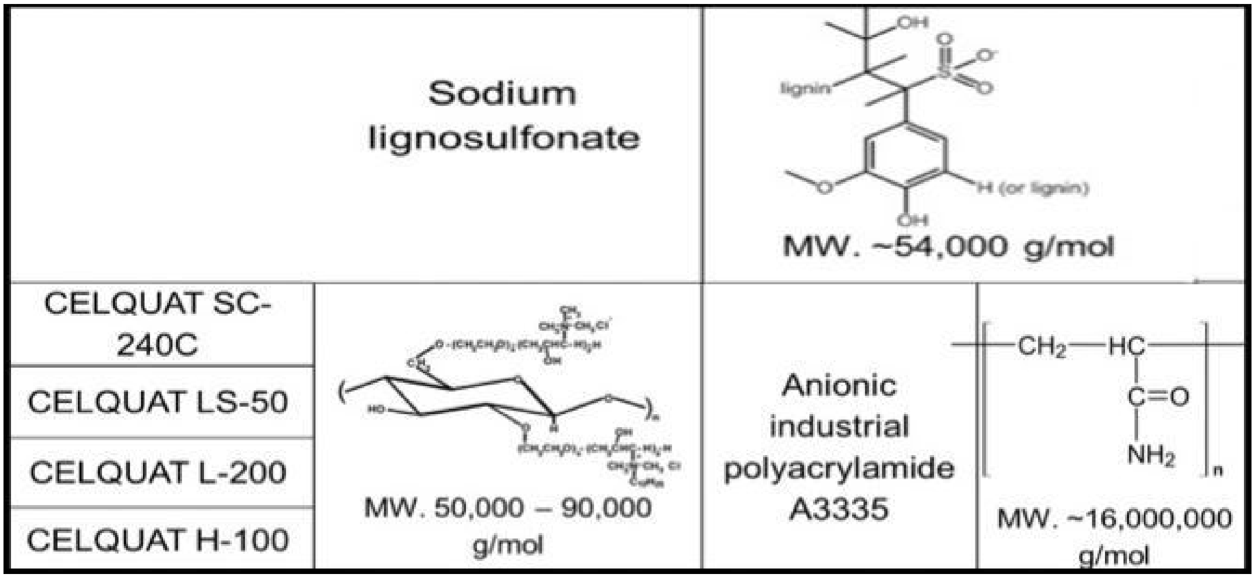

Figure 2.5 – Polymers used in this study

2.8 Focused Beam Reflectance Measurement (FBRM) Method

FBRM probes allow in-situ measurements of particle size distributions in real time, over a wide range of solids concentrations. In this method, a rotating laser beam is focused at the external surface of a sapphire glass window, and scanned at a fixed speed across the suspension. The backscattered light is then reflected back to a detector; since the velocity of the scanning laser is known, multiplying this with the time lag between laser emission and detection results in a characteristic measurement of particle geometry known as the chord length. Thousands of measurements can be taken during each measurement interval, and from the data, the total counts, counts for specific size ranges, mean and median chord lengths can be calculated, allowing the kinetics of the flocculation process to be followed in real time.

The FBRM software allows the chord lengths recorded to be presented using an unweighted distribution, or using a square weighted distribution. The square weighted distribution is achieved using the following equation:

$$n_{i,2} = n_i M_i^2 \qquad (2.1)$$

Where n_i and $n_{i,2}$ are the counts and square-weighted counts respectively, and M_i is the chord length. The mean of the square weight distribution can be derived using the following equation (Senaputra et al., 2013):

$$Mean\ chord\ length = \frac{\sum_{i=1}^{k} n_i M_i^3}{\sum_{i=1}^{k} n_i M_i^2} \qquad (2.2)$$

It is clear from equations (2.1) and (2.2) that the square weighted distribution is more sensitive to larger particles than the unweighted distribution, which is more likely to produce more accurate results regarding the fine particles. Although the FBRM does not provide exact particle sizes, the square weighted chord lengths from FBRM measurements have been found to be comparable to conventional particle sizing techniques (Heath et al, 2002). FBRM measurements allow for reliable characterization and monitoring of flocculation processes in real time. Unlike image analysis techniques, FBRM measurements do not require sampling or dilution that could alter the floc structures.

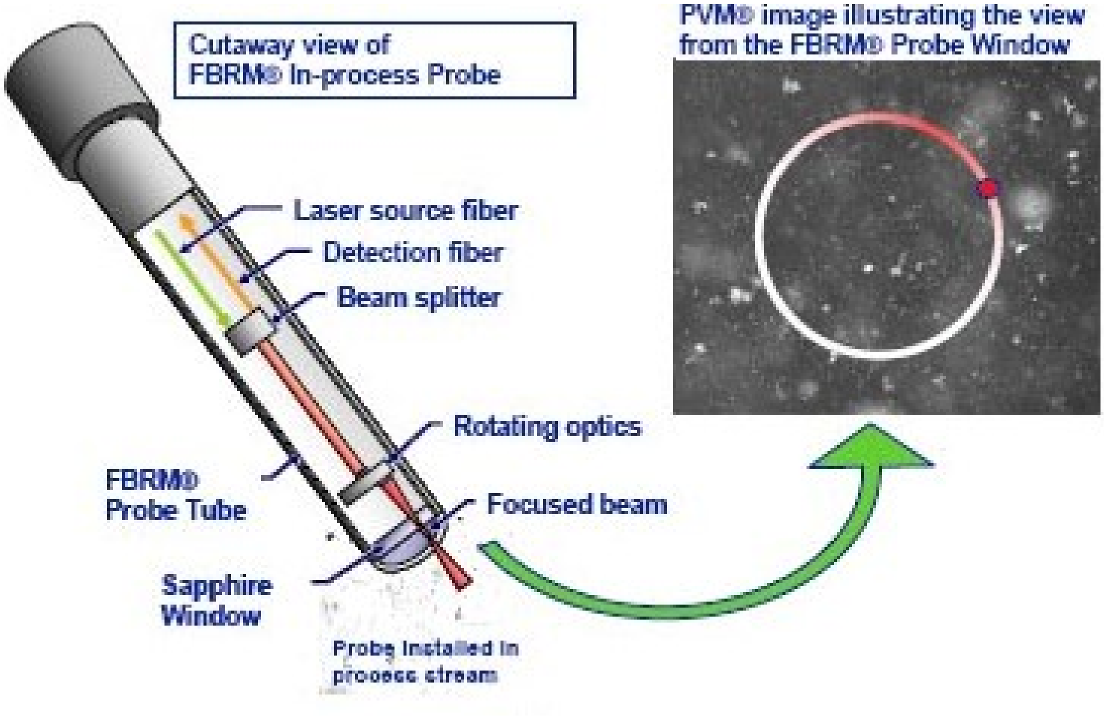

Figure 2.6 – FBRM probe and operation principle (Mettler Toledo, 2014)

2.8.1 Use of FBRM in flocculation monitoring

Senaputra et al (2013) and Yoon and Deng (2004) used FRBM to monitor flocculation performance in clay suspensions. Thapa et al (2009) and Blanco et al (2002) used FBRM to study the flocculation of sewage sludge and paper manufacturing processes respectively. Blanco et al (2002) found FBRM to be a useful tool to monitor the floc evolution under the influence of shear forces and reflocculation processes.

Klein et al (2013) used FBRM to measure the mean floc size of the particles during the flocculation of MFT using a HMW HPAM polymer. Zhu et al (2011) in their study on the role of dissolving carbon dioxide in the densification of oil sands tailings used FBRM to measure the particle size distribution of the slurries. The use of FBRM in MFT flocculation monitoring is relatively rare so far.

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Chapter 3 – Preliminary Experimental Studies

3. Preliminary Experimental Studies

A number of preliminary experimental runs were carried out on the kaolinite suspensions and the MFT sample in order to select the right experimental conditions. This section outlines the relevant experiments carried out and the results obtained.

3.1. Studies on kaolinite

3.1.1 Kaolinite preparation

Kaolinite was obtained from Wards Natural Sciences, USA. The kaolinite clay was mixed with Edmonton tap water to produce a slurry. The slurry was then treated using a 1” diameter laboratory hydrocyclone to reject the coarse fractions and collect the overflow as kaolinite test sample. The overflow slurry contained only the kaolinite particles below 20 μm. Edmonton tap water has a low hardness, with Ca^{2+} ion concentration of 48 mg/L (1.2×10^{-3} M), resulting in a $CaCO_3$ hardness of 120 ppm. The water also has an Mg^{2+} and Na^{+} ion concentration of 12.8 and 9.51 mg/L (5.3×10^{-4} and 4.13×10^{-4} M) respectively, and trace amounts of other cations. The cyclone overflow slurry was used as the stock suspension from which the test suspensions were prepared, at the same time. The kaolinite suspensions were used at natural pH, around 6.9. The kaolinite suspensions were prepared at 0.5 wt% kaolinite. The flocculation tests were carried out in a special stainless steel baffled container, with the following dimensions: Internal diameter: 110 mm; internal height: 160 mm; 4 baffles with length x width x height: 130 x 10 x 10 mm; total internal volume of the cylinder: 1.5 liters (figure 3.1). The polymers used were all prepared at a concentration of 0.4 wt%.

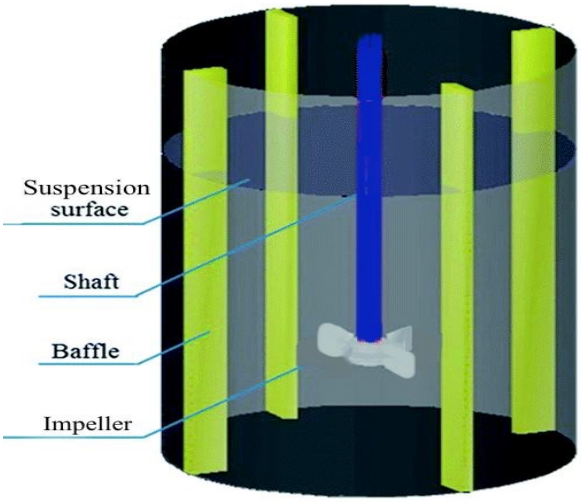

Figure 3.1 – Schematic representation of the baffled steel container and impeller used

3.1.2 Effect of metal cations present in Edmonton tap water on kaolinite flocculation

The presence of ions in water is known to affect the flocculation and settling characteristics of clay systems. Kaya et al (2006) studied the effect of ionic strength and pH on the settling characteristics of Kaolinite suspensions. They found that at high ionic concentrations, kaolinite suspensions settle in a coagulated form, due to the formation of positive charges on the edges of the kaolinite particles. According to their results, at pH 7, kaolinite settles in the coagulated form at Na^+ and Ca^{2+} concentrations of $1x10^{-2}$ M, while settling in the dispersed form at concentrations of $1x10^{-4}$ M. The concentration of Ca^{2+} and Na^+ in the suspensions brought in with the Edmonton tap water used in this study was far below $1x10^{-2}$ M, making coagulated settling unlikely without the addition of coagulant. Peng and Di (1994) found that the presence of $1x10^{-3}$ M Ca^{2+} can reduce flocculation efficiency for kaolinite suspension treated with 5 ppm of a high MW anionic polyacrylamide flocculant due to the adsorption of Ca^{2+} ions on the active sites of the flocculant. In this study, as the dosage of polymer used (270 ppm) is significantly higher than the polymer dosage used by Peng and Di (1994) (5 ppm), site blocking is unlikely to considerably affect the flocculation efficiency. Divakaran and Pillai (2001) studied the effect of Mg^{2+} and Ca^{2+} ions at similar concentrations present in the suspensions used in this study, on the flocculation of kaolinite using chitosan, a biopolymer obtained by deacetylation of chitin, and found that there is no effect on the results when compared to the suspensions produced using distilled water. Lastly, the test suspensions produced from the stock solution were all prepared at the same time, removing the effect of water composition variations. Thus, the effect of cations from the tap water on kaolinite flocculation is excluded.

3.1.3 Agitation speed

The kaolinite suspensions were stirred using a Heidolph RZR 2052 electronic stirrer and a 3 blade axial-flow impeller (blade height – 2.5 cm) of 60 mm diameter, with the impeller immersed such that the bottom of the tips were 1.7 cm from the base of the steel container.

Tests were carried out in order to determine the optimum agitation speed. The desirable agitation speed would have to be high enough in order to keep the flocculated particles in suspension to allow measurements of the sizes of the flocs formed, while also minimizing floc breakage. The kaolinite suspensions were flocculated and agitated at speeds ranging from 100 rpm to 400 rpm, at 100 rpm intervals, and the flocculation monitored using

FBRM. The counts of particles was plotted against the square weighted chord lengths for the suspension at each speed, and the counts of particles in the suspension were measured, for particular size ranges and for the suspension overall. Figures 3.2 and 3.3 show the FBRM measurements of the counts of particles against the chord length at different times for agitation at 200 rpm and 400 rpm respectively. These figures show the particle size distribution upon flocculation and agitation. The HMW PAM based flocculant A3335 was added at 00:01:40 in each case. The square weighted measurements are presented along with the unweighted measurements for comparison. The measurements obtained at 100 rpm and 300 rpm agitation are presented in figures A.1 and A.2 in the Appendix respectively.

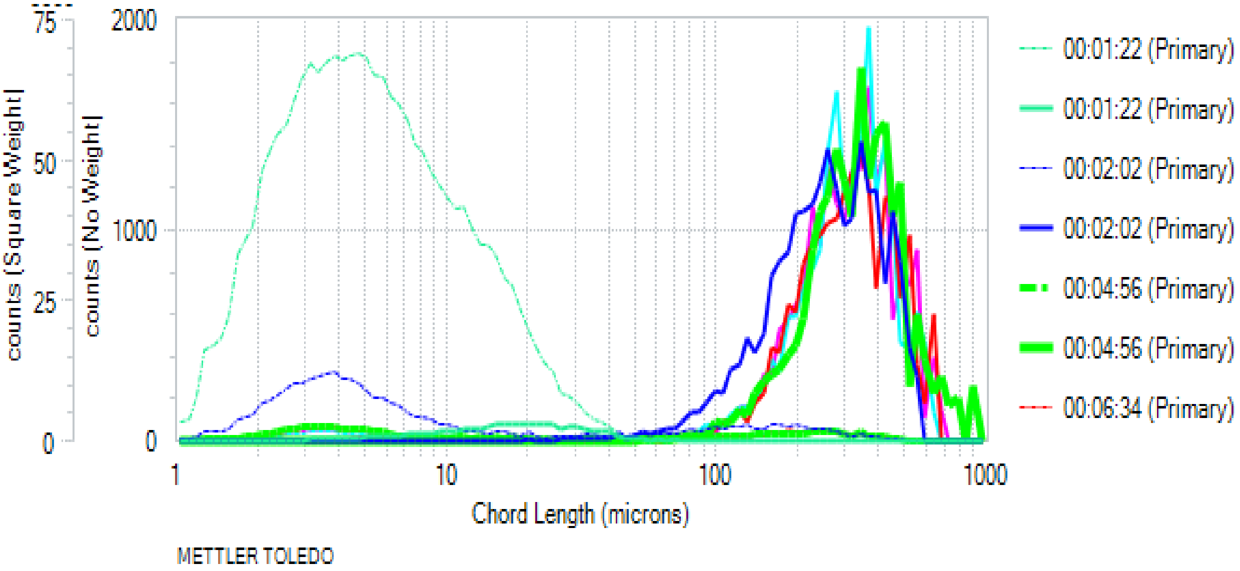

Figure 3.2: Counts of particles against chord length using the no weight method (dotted lines) and square weight method (solid lines) at 200 rpm stirring.

The square weighted measurements are more sensitive to larger particles (a function of the square of the particle size squared), while the unweighted weight method is more sensitive to smaller particles.

After flocculation, the square weighted measurements show large peaks at higher chord lengths throughout the experiment as shown in Figure 3.2. This indicates that the fine particles are flocculated to form large flocs of around 400 μm diameter, and the flocculated particles remain suspended at 200 rpm stirring (and are hence still detected by the FBRM probe). There is no visible shift in the chord length peak as time progresses, nor a considerable change in the counts of particles.

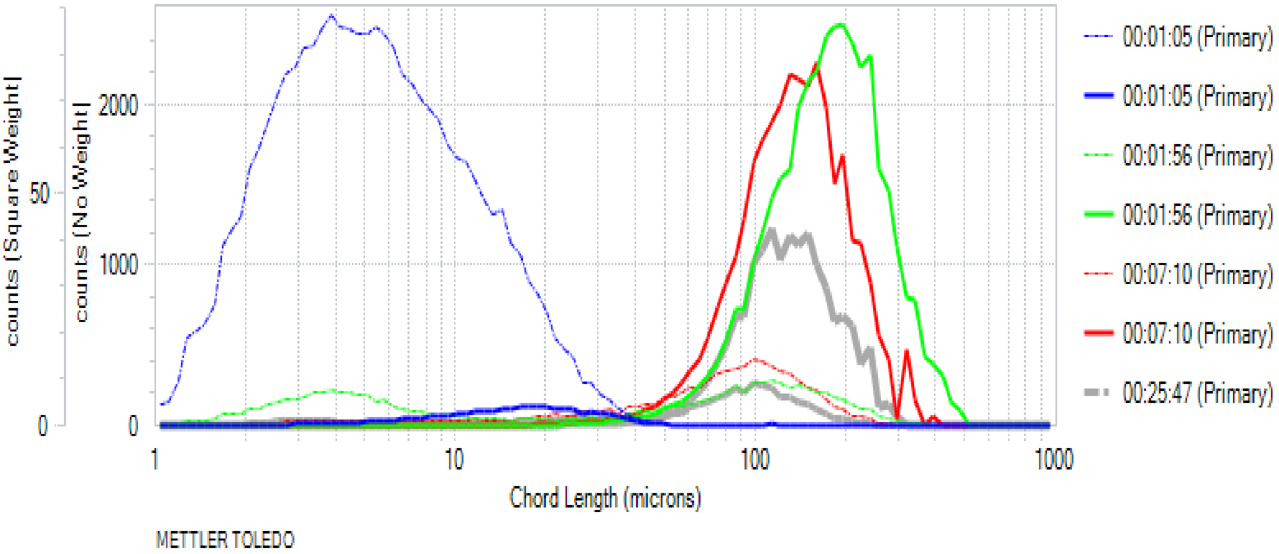

Figure 3.3: Counts of particles against chord length using the unweighted method (dotted lines) and square weight method (solid lines) at 400 rpm stirring.

The square weighted measurements in figure 3.3 once again show large peaks at higher chord lengths throughout the experiment, as the flocculated particles also remain suspended at 400 rpm stirring. However, as the experiment progressed, the square weight peaks shifted visibly to the left, along with a corresponding decrease in counts, indicating floc breakage.

FBRM measurements of the change in the overall counts during the same experiments show a noticeable increase in the counts of particles upon continued agitation at 400 rpm after flocculation. Measurements of specific particle size regime showed an increase in the counts of the 10-150 μm size particles upon flocculation, and a corresponding decrease in the number of particles in 150-1000 μm size range, at 300 and 400 rpm agitation. This effect can be seen in figures A.3(a) – (d) in the Appendix. Agitation at 100 rpm was not sufficient to keep the flocculated particles in suspension. Agitation at 200 rpm was therefore selected for further studies as the flocculated particles remain in suspension and do not show noticeable breakage at this speed. Yoon and Deng (2004) on their study on the flocculation and reflocculation of clay particles used an agitation speed of 300 rpm for the flocculation stage using HMW PAM polymers.

3.1.4 Control experiments on dual polymer flocculation

A number of experiments involving FBRM measurements of water agitated at 200 rpm, with and without addition of the polymers tested were carried out. Such tests were carried out for the polymers individually and the dual polymer combinations used in the studies in chapters 4 and 5. The change in counts and particle size were measured for each of these tests. Other than a small increase in counts detected upon addition of polymer to the water, the results of the control experiments were very different from the results obtained in the tests carried out on kaolinite suspensions (or MFT). This is also backed up by visual observations of kaolinite flocculation.

Tests were also carried out to determine whether kaolinite suspensions flocculate without polymer addition at various suspension pH, and no results of note were obtained at or near the pH used in this thesis.

3.2. Studies on MFT

3.2.1 MFT Characterization

The MFT used was from the Athabasca region, and provided by Syncrude. The particle size distribution of the unflocculated MFT was measured using a Malvern Mastersizer 3000, a laser diffraction particle size analyzer. The particle size distribution was measured under various conditions, including agitation at high rpm and sonication. The results of these measurements are shown in Figure 3.4.

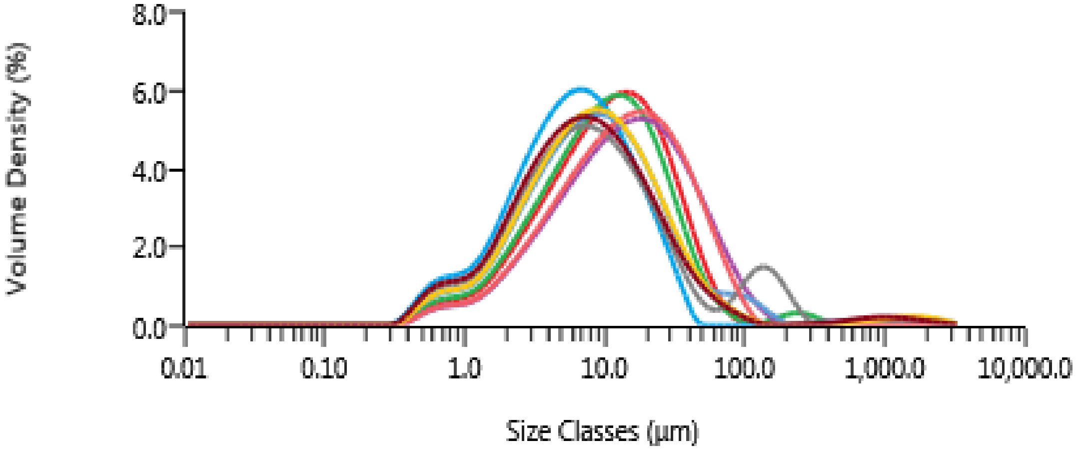

Figure 3.4 – Particle size distribution of MFT (various agitation conditions)

The results show that the majority of the MFT particles are around 10-20 μm in size. Under high agitation speeds and sonication, the average particle size can be as small as 6 μm. The mean d(50) of the un-sonicated MFT particles was found to be 9.54 μm, with a standard deviation of 2.86 μm.

The composition of the MFT was found using the Dean-Stark method. The MFT had a solids content of 36.0%, bitumen content of 2.6% and water content of 61.4%. The MFT was used without any pre-processing, at natural pH.

3.2.2 Agitation speed during flocculation

The flocculation performance of MFT under a range of agitation speeds was tested in order to determine the agitation speed for further tests. The desired agitation speed should ensure proper mixing of polymer and MFT, while minimizing floc breakage. The MFT was flocculated using the HMW PAM based flocculant A3335 for a range of agitation speeds from 400-800 rpm at 200 rpm intervals. The flocculation performance was assessed based on the change in floc size (from FBRM measurements) and water release after 24 hours of settling. Figures 3.5 and 3.6 show the FBRM results at 600 rpm and 800 rpm agitation respectively. 200 ppm (based on MFT solids content) of A3335 was added at 2 minute in each case. A polymer dosage of 200 ppm was enough to determine flocculation performance using FBRM. The solid lines and dotted lines represent the square weighted and unweighted measurements respectively. The results for 400 rpm agitation are shown in figure A.4 in the Appendix.

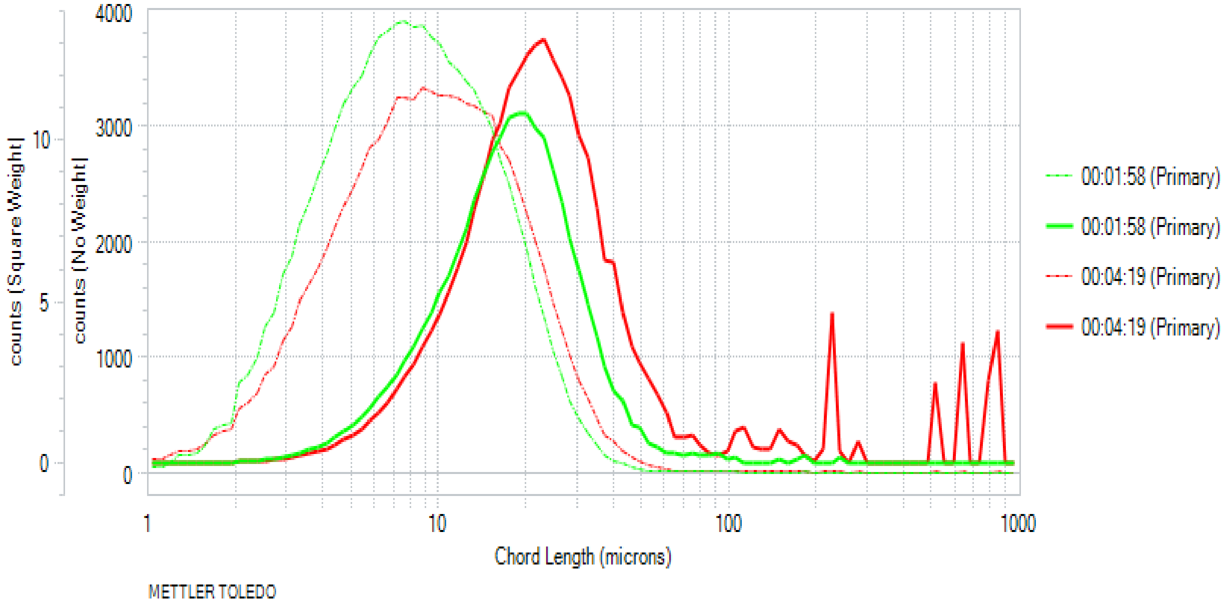

Figure 3.5 – Counts vs chord length for MFT flocculation at 600 rpm stirring

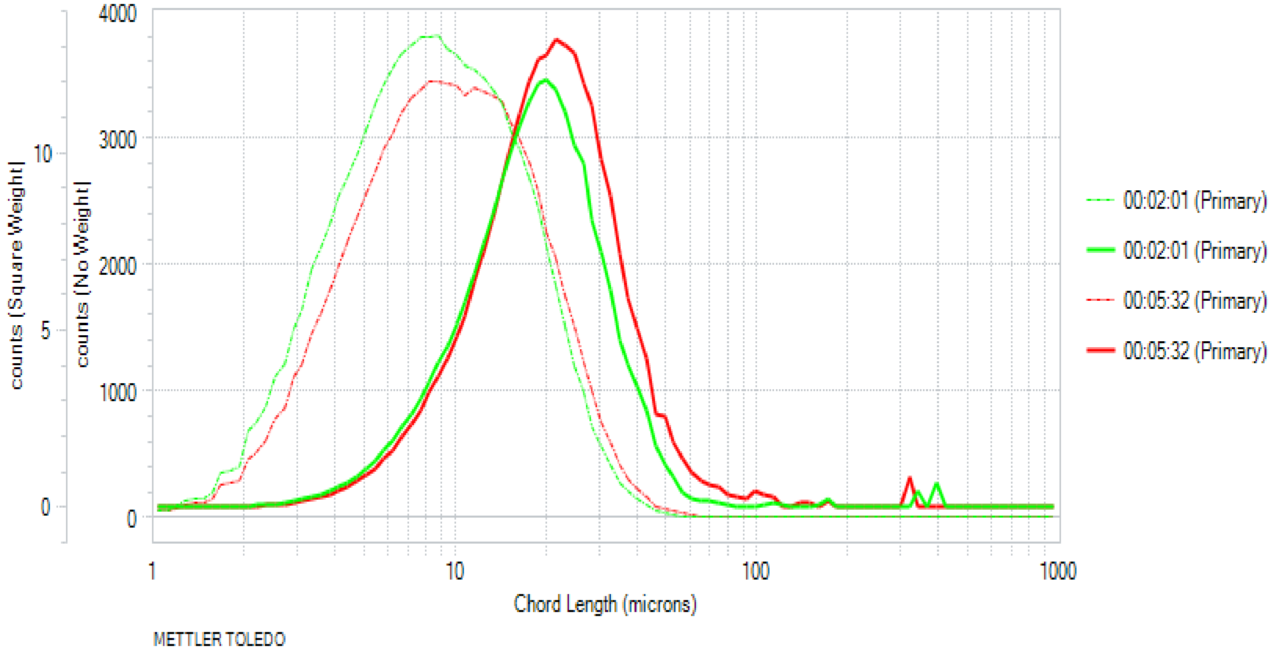

Figure 3.6 – Counts vs chord lenth for MFT flocculation at 800 rpm

The results show that at 600 rpm, flocculation results in an increase in the square weighted particle size. The peak of the particle size distribution shifts noticeably to the right and the counts increases, indicating a higher number of larger particles or flocs. At the same time, the unweighted distribution shows a noticeable decrease in fine particles. The small individual peaks at larger chord lengths indicate the formation of a small number of very large flocs. Figure 3.6 shows a slighter shift to the right for the square weighted distribution. Similarly, the decrease in counts of the fine particles is also less noticeable. The individual peaks at larger chord lengths are also absent, with only one small peak at around 300 μm. This indicates fewer fines being captured to form large flocs than for 600 rpm agitation. The results for 400 rpm agitation were similar to those at 800 rpm. However, the square weighted measurements appear to show no increase in particle size.

The flocculated suspensions were allowed to settle in 2000 ml measuring cylinders for 24 hours. At the end of this period, the MFT agitated at 400 and 600 rpm released the most water. 600 rpm was chosen as the agitation speed for further studies on MFT due to the better fines capture and water release at this speed. Other studies on MFT flocculation have used similar agitation speeds – Munoz et al (2010) studied the effect of mixing time on undiluted MFT flocculation and dewatering at 600 rpm agitation. Wang et al (2010) used an agitation speed of 500 rpm prior to flocculant addition followed by 350 rpm after the addition of flocculant to the MFT. However, they studied fluid tailings with relatively low solids content. Klein et al (2013) also used a similar 500 rpm/350 rpm procedure. Once again, the solids content of the MFT was diluted to 10 wt%. As expected, lower agitation speeds are required to ensure proper polymer mixing for MFT test suspensions with lower solids content.

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Chapter 4 - Flocculation and Dewatering of Clay Suspension Using Dual Polymer Flocculants

4. Flocculation and Dewatering of Clay Suspension Using Dual Polymer Flocculants

Abstract

The accumulation of mature fine tailings (MFT) in Alberta's oil sands industry poses serious environmental issues. Besides water, MFT consists of 1-3 wt% hydrocarbons (residual solvents and bitumen) and 30-40 wt.% clays and minerals which are mostly below 44 µm in size. The major clay minerals in MFT are kaolinite and illite. Without physical and/or chemical treatment the MFT remains suspended in the tailings ponds indefinitely. A promising practice to treat MFT for faster water release is to use polymer flocculants. The majority of studies carried out on the dewatering of MFT in the past have focused on the use of a single polymer. However, recent studies on the use of dual polymers in sewage treatment and pulp & paper industries, where two polymers are added in sequence to manipulate floc size and porosity, have shown significant benefits over the use of a single polymer with higher dewatering rates, higher solids content of the settled sludge and lower polymer dosages. Researchers have also studied the combinations of flocculation and coagulation of oil sands tailings resulting in better supernatant clarity and faster settling rates.

In this study we investigated the use of dual polymers on the flocculation and dewatering of kaolinite suspensions (< 20 µm) with the objective of tuning the properties of the sediments for fast and maximum water release during post-flocculation treatment. The first polymer (polymer A) was used sequentially with a second polymer (polymer B). The flocculation and dewatering performance of these dual polymers were assessed in terms of floc size, floc strength, settling rate, net water release, settled floc density, and dewatering performance using bench jar tests, Focused Beam Reflectance Measurements (FBRM) and Capillary Suction Timer (CST). The kinetics of floc formation and the mechanisms of flocculation and dewatering were discussed.

4.1. Introduction

It has been estimated that there are around 1.7 trillion barrels of bitumen in the oil sands reserves in Northern Alberta, Canada (Alberta Energy, 2012). In the current water based commercial oil sands extraction process, the bitumen is recovered from the oil sands slurry by flotation using aeration; while the tailings (a mixture of water, sand, clay and residual bitumen) are discharged into tailings ponds, where the coarse solids settle out quickly, leaving a stable suspension often referred to as mature fine tailings (MFT). More than 3 m^3 of tailings are generated per barrel of bitumen produced (Xu et al, 2008). Besides water, MFT typically contains around 30-40 wt% solids, mostly clays and trace minerals, and around 1-3 wt% bitumen. The major clay components in MFT are kaolinite and illite, with the majority of the particles below 44 μm in size. Without chemical or physical treatment, the MFT remains suspended in the tailings ponds indefinitely, where the trapped water cannot be recycled. Moreover, the continuing accumulation of MFT is cause for great economical and environmental concern. It is estimated that at current production rates, the accumulated volume of MFT will increase to over one billion m^3 by 2020 (Long et al., 2006). Currently, MFT is processed by the addition of gypsum and blending with coarse sands, through a process known as the composite tailings (CT) technology. Although satisfactory for tailings treatment, this method requires a relatively long time, and a negative effect of the chemicals remaining in the process water as a result of the treatment has been observed in pilot tests (Long et al., 2006). Other methods employed for tailings treatment include beaching, mature fine tailings drying, tailings thickening and drying, MFT centrifugation and drying, accelerated dewatering and water-capped MFT – most of the techniques have been rejected as they lack economical or technical feasibility (Fair, 2011). Therefore the development of an effective method for the treatment of MFT is of the utmost importance.

The majority of the studies carried out in the past on the dewatering of MFT have focused on the use of a single polymer (Wang et al., 2010; Xu et al., 2008; Long et al., 2006; Sworska et al., 2000;). However, recent studies on the use of dual polymer flocculation for sewage treatment and the pulp and paper industry have shown promise over the use of a single polymer (Liu et al., 2001; Senthilnathan and Sigler, 1993). Similar promise has also been shown in dual polymer treatments carried out on MFT. Yuan and Shaw (2007) carried out an extensive study on the use of combinations of coagulation (C) and flocculation (F) to dewater the MFT, and observed that certain combinations, such as F-C, F-C-F, etc., worked better than the others. Watson et al. (2010) found that combining the use of a very low molecular weight (VLMW) anionic polymer and a high molecular weight (HMW) polymer flocculant resulted in higher average particle size and solids content in the settled beds, in addition to faster dewatering. However, very few such studies have been carried out to understand the mechanisms and kinetics of a dual polymer system.

The exceptional stability of the MFT slurry is due to the clay components, the majority of which is kaolinite. Therefore in order to obtain a proper understanding of the mechanism of a dual polymer system it is useful to simulate the MFT slurry using a kaolinite suspension. Most of the studies on the flocculation of clay suspensions have focused on the use of a single high molecular weight polymer (Besra et al., 2004; Kage et al., 1988; Yu et al., 2006). High molecular weight polyelectrolytes operate through a bridging mechanism and form large flocs that are loosely packed and relatively shear resistant. The higher strength of these flocs is advantageous for filtration purposes, as they are less likely to degrade under the applied shear. The loose structures also result in fast dewatering; however it has been shown that HMW polymers result in higher water content in the settled beds (Besra et al., 2004). The high charge-density LMW polymers bring about aggregation via a charge neutralization mechanism, resulting in destabilization of the clay suspension. The resultant flocs are smaller in size leading to denser settled beds with lower water content; however, it has been found that the filtration rates of the settled beds are slow, and the resultant turbidity of the supernatant in such cases is relatively high (Besra et al., 2004; Petzold et al., 2002).

Recent studies on the use of dual polymer systems have proven to be advantageous over the use of a single polymer alone; Petzold et al. (2003) found that the use of a LMW cationic polyelectrolyte followed by a HMW anionic polymer flocculant produced clearest supernatant in clay suspensions and natural waste waters from gravel pits. Yoon and Deng (2004) found that using a LMW polymer followed by a HMW polymer on clay suspensions produced better reflocculation after application of shear than using a single polymer. Glover et al. (2004), studying the flocculation of alumina fines, found that the use of a LMW polymer followed by HMW polymer produced a settled bed with lower water content than by using a single HMW polymer alone, with the best results being observed when the LMW and HMW polymers used are of opposite charge.

Cellulose based polymers (similar to those used in the pulp & paper industry) are non-toxic and biodegradable. As noted earlier, an issue caused by the CT process for MFT processing is the residual chemical content in the water. Synthetic polymers have been found to be more effective than natural polymers for flocculation purposes, as they can easily be tailored to particular applications. However, a drawback of synthetic polymers such as polyacrylamide is the fact that they are easily degraded by shear forces. Natural polymers have an advantage in being low cost, and being shear-resistant (Krishnamoorti et al., 2010). The application of lignosulfonates as sacrificial agents in enhanced oil recovery is well documented, due to the strong adhesion of lignosulfonates with soil and clays (Hong et al., 1987). This implies that the lignosulfonate may interact strongly with the fine clays in the tailings, despite being a dispersant in nature.

Most studies on the flocculation of clay suspension assess performance in terms of settling rates, settled bed solids content and dewatering rate, and turbidity of the resultant supernatant. One method commonly used to assess the extent of flocculation is Photometric Dispersion Analysis (PDA). This method allows the user to observe whether flocculation or dispersion is occurring in the suspension upon addition of flocculant, but does not provide any information regarding the size of the flocs formed (other than relative increase or decrease) or the resultant particle size distribution. The challenge in such studies is to obtain reliable characterization under relevant conditions. Image analysis techniques require sampling and may require dilution that could alter the floc structures. Recently, Focused Beam Reflectance Measurement (FBRM) has been found to be a useful tool to monitor flocculation performance in clay suspensions (Senaputra and Jones, 2013; Yoon and Deng, 2004), sewage sludge (Thapa et al., 2009) and paper manufacturing processes (Blanco et al., 2002).

FBRM probes allow in-situ measurements of particle size distributions in real time, over a wide range of solids concentrations. In this method, a rotating laser beam is focused at the external surface of a sapphire glass window, and scanned at a fixed speed across the suspension. The backscattered light is then reflected back to a detector; since the velocity of the scanning laser is known, multiplying this with the time lag between laser emission and detection results in a characteristic measurement of particle geometry known as the chord length. Thousands of measurements can be taken during each measurement interval, and from the data, the total counts, counts for specific size ranges, mean and median chord lengths can be calculated, allowing the kinetics of the flocculation process to be followed in real time.

The FBRM machine allows the chord lengths recorded to be presented using an unweighted distribution, or using a square weighted distribution. The square weighted distribution is achieved using the following equation:

$$n_{i,2} = n_i M_i^2 \qquad (4.1)$$

Where n_i and $n_{i,2}$ are the counts and square-weighted counts respectively, and M_i is the chord length. The mean of the square weight distribution can be derived using the following equation (Senaputra et al., 2013):

$$Mean\ chord\ length = \frac{\sum_{i=1}^{k} n_i M_i^3}{\sum_{i=1}^{k} n_i M_i^2} \qquad (4.2)$$

It is clear from equations (4.1) and (4.2) that the square weighted distribution is more sensitive to larger particles than the unweighted distribution, which is more likely to produce more accurate results regarding the fine particles. Although the FBRM does not provide exact particle sizes, the square weighted chord lengths from FBRM measurements have been found to be comparable to conventional particle sizing techniques (Heath et al., 2002).

This paper focuses on the use of a dual polymer system consisting of various combinations of cellulose-based, LMW cationic polymer coagulant/LMW anionic natural polymer and an industrially used HMW anionic polymer to dewater clay suspensions. The flocculation and dewatering performance was assessed in terms of floc size and strength, net water release, filterability of the settled beds through capillary suction time (CST) measurements, FBRM measurements to study the flocculation process in real time to obtain a better understanding of the mechanism and kinetics of flocculation. The performance of the dual polymer system was also compared to that of a single HMW polymer. It is expected that the results of this study will provide insight into the application of such a system for the dewatering of MFT, the results of which will be presented in a future report.

4.2. Materials and Methods

4.2.1 Materials

Kaolinite was obtained from Ward's Natural Sciences, USA. The kaolinite was mixed with Edmonton tap water to form a slurry, which was then processed using a 1" diameter laboratory hydrocyclone to remove any particles over 20 µm in size. A stock suspension of kaolinite was prepared for testing. Edmonton tap water has a low hardness, with Ca^{2+} ion concentration of 48 mg/L ($1.2x10^{-3}$ M), resulting in a $CaCO_3$ hardness of 120 ppm. The water also has an Mg^{2+} and Na^{+} ion concentration of 12.8 and 9.51 mg/L ($5.3x10^{-4}$ and $4.13x10^{-4}$ M) respectively, and trace amounts of other cations. The test kaolinite suspensions were used at natural pH (around 6.9), and were prepared from the stock suspension at the same time.

The four cationic polymer coagulants (hereafter referred to as B1, B2, B3 and B4) were obtained from AkzoNobel. The coagulants used had an average molecular weight ranging from 60,000 to 80,000 g/mol (determined by gel permeation chromatograph – the chromatograms are presented in the appendix) and were hydroxyl-ethyl cellulose polymers grafted with different ratio of PDADMAC, resulting in different charge density and distribution along the polymer chains. The LMW anionic polymer (referred to in this paper as A) was obtained from Sigma Aldrich, and had an average molecular weight of 52,000 g/mol. The HMW anionic polymer (referred to as C) was obtained from industry, with an average molecular weight of 17×10^{6} g/mol, and no further information regarding the structure of the polymer has been provided.

Table 4.1 – Molecular weights of the tested polymers

Polymer	Average Molecular Weight (g/mol)
A	52,000
B1	61,370
B2	46,010
B3	82,580
B4	66,470
C	17×10^6

4.2.2 Flocculation

The flocculation tests were carried out in a special stainless steel baffled container, with the following dimensions: Internal diameter: 110 mm; internal height: 160 mm; 4 baffles with length x width x height: 130 x 10 x 10 mm; total internal volume of the cylinder: 1.5 liters.

A kaolin stock solution containing 9.67 wt% solids was prepared using Edmonton tap water. The stock solution was diluted to produce sample suspensions of 0.5 wt% for FBRM testing and 0.4 wt% for water release, CST testing on settled beds and turbidity measurements of the resultant supernatant. The model 319 multi-purpose CST apparatus (Triton Electronics Ltd. U.K) was used to measure capillary suction time of flocs using an 18 mm diameter cylindrical funnel. Standard Whatman No. 17 filter paper was used. The polymer solutions were prepared at a concentration of 0.4 wt% using distilled water, and stirred for 24 hours prior to testing.

The stirrer used for testing was a Heidolph RZR 2052 electronic stirrer and a 3 blade axial-flow impeller (blade height – 2.5 cm) of 60 mm diameter, with the impeller immersed such that the bottom of the tips were 1.7 cm from the base of the steel container. Polymer solutions were added to the suspension using 1.0 mL syringes.

4.2.2.1 FBRM Measurements

The FBRM unit used was a Mettler-Toledo G-400. The probe was inserted at the same depth and in the same position for each test. The smallest sampling interval (2 s) was used for best resolution of results.

Initial testing using FBRM on flocs produced by the use of single HMW polymer showed that 200 rpm was the optimum stirring speed for flocculation tests, which was vigorous enough to keep the resultant flocs in suspension without causing significant floc breakage.

For single polymer tests, 600 mL of 0.5 wt% kaolinite suspension was stirred at 200 rpm for 90 s, and then the polymer was added. The suspension was stirred at 200 rpm for another 510 s, for a total time of 600 s. For dual polymer tests, 600 mL of 0.5 wt. % kaolinite suspension was stirred at 200 rpm for 60 s, then the first polymer was added. The suspension was stirred for another 300 s, after which the second polymer was added, and the suspension stirred for a further 300 s for a total time of 660 s. The polymer dosage used was 270 g/t of each polymer, based on the solids content of the kaolinite suspension.

4.2.2.2. Settling and dewatering tests

Around 190 mL of 0.5 wt% kaolinite suspension was added to the baffled steel container in each test. The first polymer was added to the suspension and stirred at 200 rpm for 30 s before being transferred to a 250 mL graduate cylinder. In cases where a second polymer was used, the second polymer was then added, the cylinder covered, and the cylinder turned over 5 times. The cylinder was then set down to do settling measurements, when possible. After 24 h the settled bed volume was noted and the supernatant siphoned off for turbidity measurements using a VWR Scientific Turbidity Meter. CST tests were performed on the settled beds using a Triton Electronics Type 319-Multi CST meter, using 7 x 9 cm CST paper, also obtained from Triton Electronics. Again, the polymer dosage used was 270 g/t, based on the solids content of the kaolinite suspension.

4.3 Results and Discussion

4.3.1 Particle size distributions and real time flocculation monitoring using FBRM

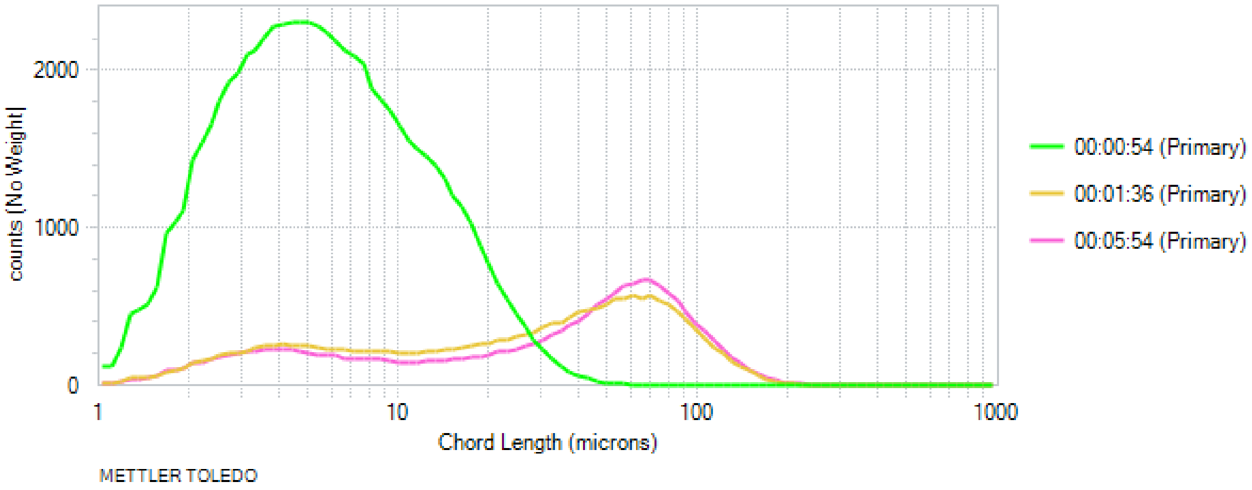

Figure 4.1 – Counts vs Chord length (unweighted) for kaolinite suspension with B1 added at 01:30.

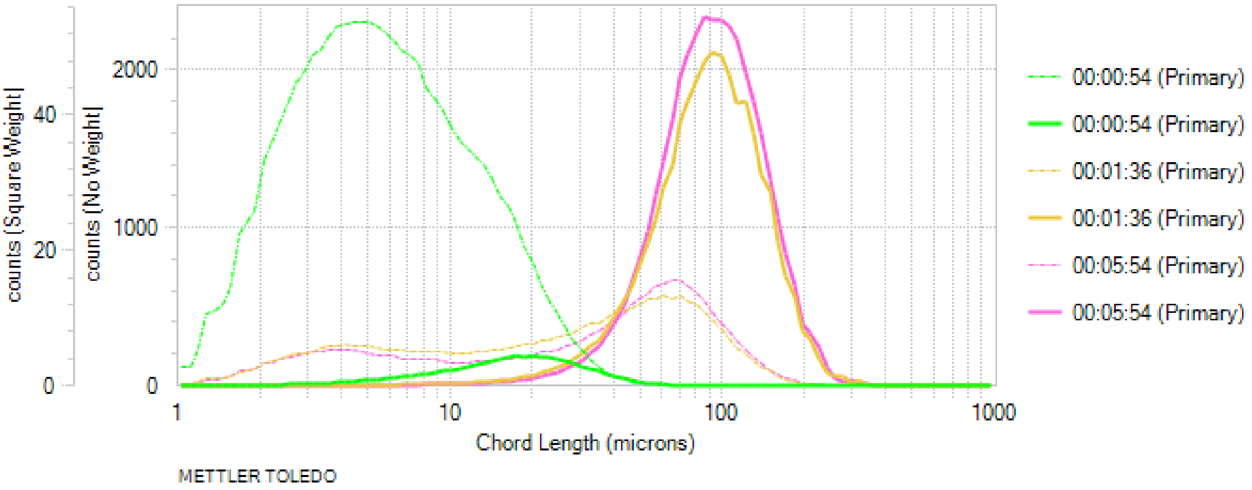

Figure 4.2 – Counts vs Chord length (square weighted) for kaolinite suspension with B1 added at 01:30.

The four cationic polymer coagulants were tested on the kaolinite suspension, in order to understand the mechanism by which the coagulants interact with the clay particles. Figures 4.1 and 4.2 show the counts recorded by the FBRM at different time points in the test using B1, plotted against the chord length. The dotted lines in Figure 4.2 represent the unweighted distribution, included for comparison. The results for the other polymers were very similar, as shown in figures A.9 - A.11 in the appendix. In each case the unweighted chord length of kaolinite is in the range of 1 – 30 µm, with most particles being around 5 µm. Upon addition of the cationic coagulants, the unweighted chord length of kaolinite shows a clear bimodal distribution with a lower peak around 5 µm representing un-flocculated kaolinite, and a higher peak around 30 µm as a result of the flocculated kaolinite. The decrease in the counts in the fine size region also indicates flocculation of the particles. On the other hand, square weighted chord length shows a monomodal size distribution from the peak at 20 µm prior to addition of polymers to the peak at 80 µm after polymer addition. The square weighted distribution was used to determine the particle size distribution of kaolinite flocs since it is more sensitive to larger particles and flocs than the unweighted distribution. The results of chord length distribution with polymer addition were summarised in Table 4.2. Of the four coagulants, B1 and B2 possess the smallest average molecular weights, however, the largest aggregates are formed by B1, followed by B2. B3 and B4 produce smaller aggregates, and also produce fewer aggregates in number. The aggregates produced by B3 and B4 undergo significant breakage under the applied shear, suggesting weaker flocs possibly due to weaker interactions between the polymers and the kaolinite particles. This may indicate that the charge density of the cationic polymers through a charge neutralisation mechanism plays an important role in their aggregation performance.

Table 4.2 – Initial and final peak sizes in the particle size distribution of kaolinite treated using different polymers

Polymer	Initial peak size (µm) (unweighted)	Initial peak size (µm) (square weighted)	Peak size after flocculation (µm) (unweighted)	Peak size after flocculation (µm) (Square weighted)
B1	5	20	70	80
B2	5	20	60	80
B3	5	20	30	60
B4	5	20	30	60
C	5	20	200	400

Figures 4.3 and 4.4 show the count vs. chord length distribution for HMW anionic polymer C. In this case the aggregates formed are much larger, with most of the aggregates formed at around

400 µm, likely due to the bridging mechanism that occurs as a result of the high molecular weight of the polymer. As expected, these flocs were not degraded by the application of shear indicating stronger flocs were formed.

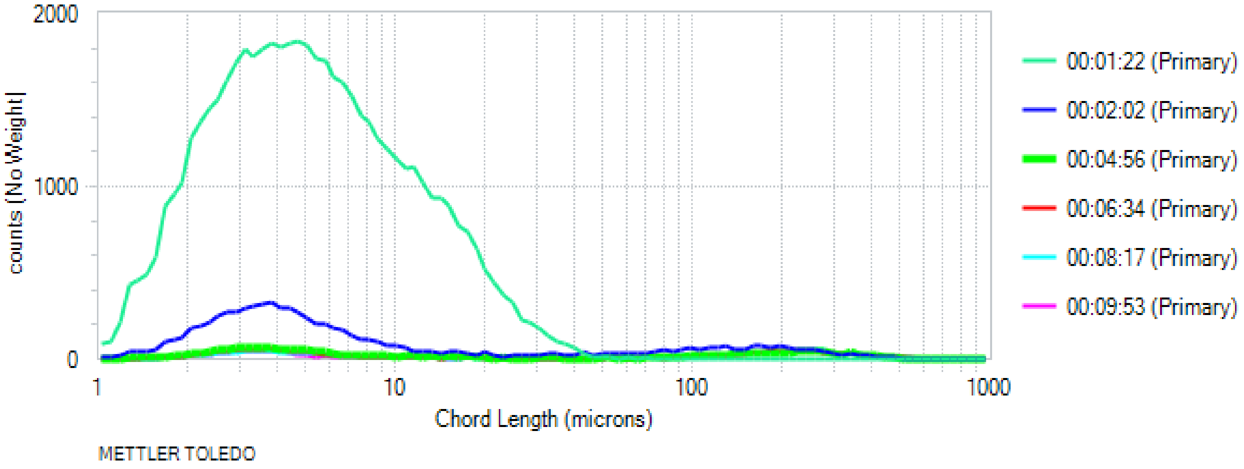

Figure 4.3 – Counts vs Chord length (unweighted) for kaolinite suspension with C added at 02:00.

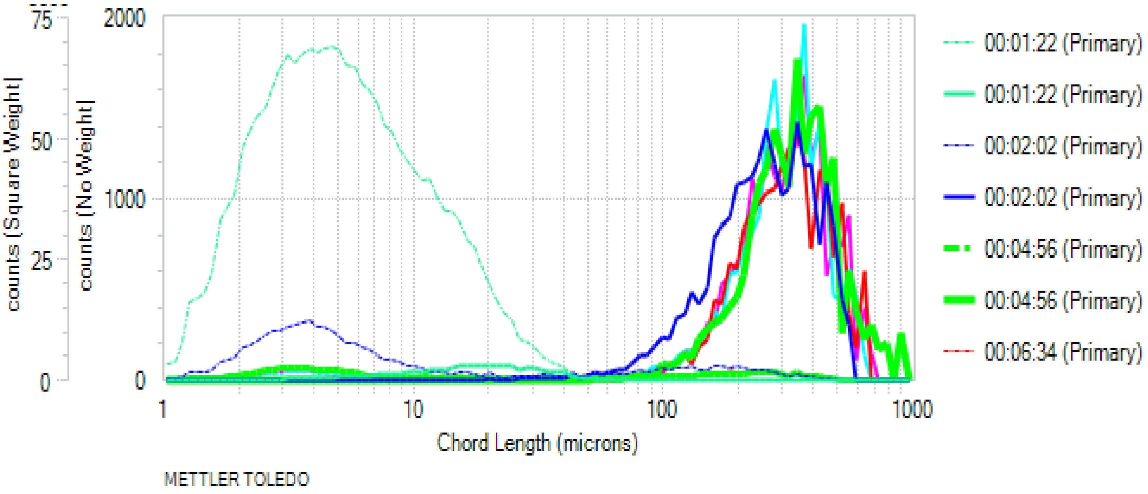

Figure 4.4 – Counts vs Chord length (square weighted) for kaolinite suspension with C added at 02:00.

Figure 4.5 shows the variation of the mean sizes of the particles in the kaolinite suspension with time upon flocculation using different polymer combinations. It is clear that the dual polymer combinations produce larger final flocs than using the HMW polymer alone. The line marked 'C double' represents the HMW polymer being introduced twice (at 270 g/t each time) to check if the larger floc sizes obtained using the dual polymer systems was due to a higher polymer dosages. The results show that the properties of the first LMW polymer has an effect on the final floc size – the suspensions treated with B3 and B4 produce larger final flocs than those treated with B1 and B2. In the cases of the single polymer addition, B1 and B2 produced larger aggregates that were stronger and more resistant to shear, while B3 and B4 produced smaller aggregates that showed greater degradation as a result of shear application. This was attributed to the weaker nature of the interactions between polymers B3 and B4 and the kaolinite particles. However, the combination of B4 + C results in the largest floc size among all the polymer pairs, indicating the polymer B4 modified kaolinite particles have better ability to form large final floc sizes. It is known that the polymer conformation on surface is dependent on the polymer's chemical structure, charge density and molecular weight. Yu et al. (2006) found that highly charged cationic polymers tend to adsorb on to the kaolinite particle surface in a flat configuration. As a result, once the polymers with a higher charge density are adsorbed, the resultant particles have smaller polymer "loops" and "tails", whereas the resultant particles from the addition of the lower charge density polymers have "loops" and "tails" that are further extended from the kaolinite surfaces. The latter case would allow more effective bridging upon the addition of the HMW anionic polymer, resulting in larger final floc sizes. The use of a dual polymer system (high charge density LMW polymer followed by a HMW polymer) results in a combination of charge patch formation and bridging, as explained by the electrostatic patch model introduced by Gregory (1973). The net residual charge of a high charge density polymer patch on the particle surface can attach to a bare portion of an oppositely charged particle, which seems to cause the formation of more compact flocs. Sengupta et al. (1997) tested the flocculation of kaolinite suspensions using a high MW cationic polyacrylamide, Percol 753 and found the peak floc size obtained for a similar suspension using 625 g/t polymer to be around 300 µm, which then decreased to around 200 µm after 15 minutes of stirring at 500 rpm. Yu et al. (2006) found the maximum floc sizes obtained for kaolinite flocculation using LMW cationic PDADMAC and HMW cationic acrylamide copolymer to be around 100 µm and 150 µm respectively. It can be seen that the B1 and B2 polymers used in this study produce flocs of similar size as those produced by LMW PDADMAC. Yoon and Deng (2004) studied the flocculation of kaolinite suspensions using a dual cationic polymer system of LMW PDADMAC and HMW CPAM. The highest floc sizes observed using their dual polymer flocculation was around 400 µm, compared with 35 µm and 350 µm for single polymer flocculation using PDADMAC and CPAM respectively. Our results align well with the reported values, and it is worth noting that all of the dual polymer systems used in this study produce peak floc sizes greater than 400 µm in size, demonstrating strong flocculation performance.

The addition of the anionic LMW polymer dispersant A does not produce any aggregation behavior, as expected. However, it is apparent from the results that the final floc size obtained through the use of A as the first additive followed by the addition of C is slightly larger than that obtained through the use of C alone. It is suggested that the dispersant A affects the structure of the bridged final flocs, resulting in a looser arrangement and larger floc sizes.

The lines 'C' and 'C double' in Figure 4.5 show that the larger floc sizes obtained through employing a dual polymer system are not a result of the polymer concentration alone. Doubling the concentration of polymer C added to the suspension resulted in a final floc size increase of around 10%, still lower than the lowest mean size obtained from the dual polymer systems.

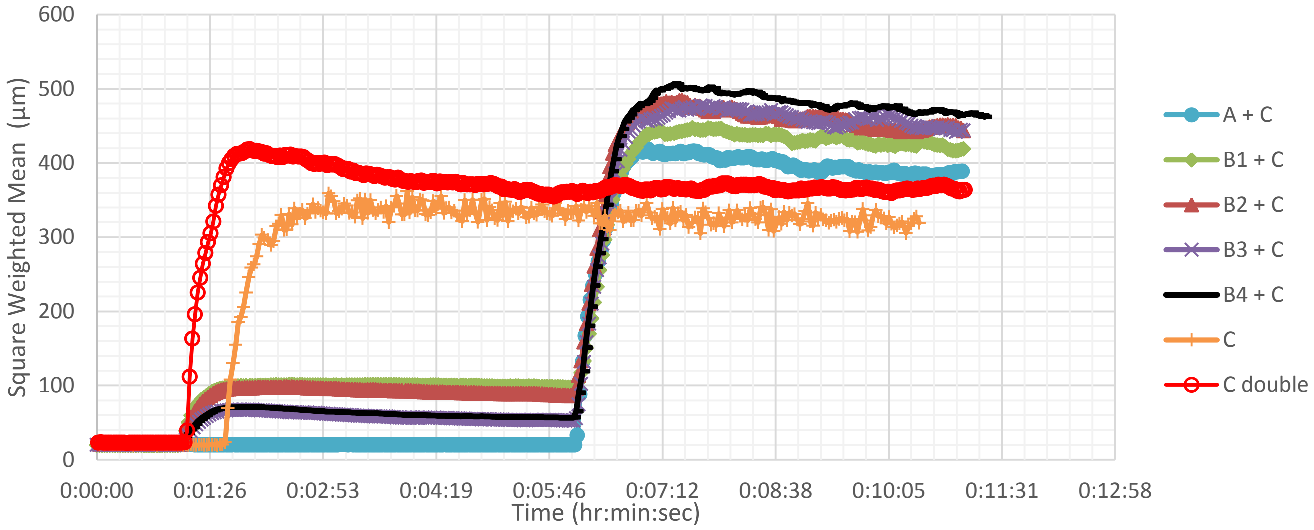

Figure 4.5 – Mean size of the particles in suspension upon flocculation by different polymer combinations

Figure 4.6 and Table 4.3 show the variation of the number of fine particles (<44 µm) over time in the suspensions with the different polymer combinations. The initial fines content of the suspensions was around 62,000 ± 10%. The combinations of the different cationic LMW polymers and the anionic HMW polymer appear to produce similar results with regards to final fines content in the suspension. The difference in the initial fines content of the suspensions makes up for most of the difference in the remaining fines; the suspensions treated with B1 and B4 initially had around 5% higher fines content than those treated with B2 and B3. However, the suspension treated with B1 shows a considerably higher final fines content, even after accounting for this difference. Out of the five dual polymer systems, the combination of B2 and C performs the best, followed by A and C. The suspensions treated with C alone possess a considerably lower final fines content than those treated with the combinations of B and C. However, this could be due to the considerably lower initial fines content of the suspensions treated using C alone. For the single polymer system, doubling the concentration of C almost halves the remaining fines in the solution. However, considering the actual counts of the fines removed from the solution, the single polymer systems showed significantly lower fines capture than the dual polymer systems, even though the polymer dosage was the same in each case.

Table 4.3 – Initial and final fines contents of suspensions treated with different polymer combinations

Polymer System	Initial Fines Content (counts)	Final Fines Content (counts)	Fines removed	% fines remaining
A + C	63,788	1,170	62,618	1.8
B1 + C	69,522	7,627	61,895	11.0
B2 + C	65,458	1,187	64,271	1.8
B3 + C	64,610	2,627	61,983	4.1
B4 + C	69,778	4,056	65,722	5.8
C	55,005	823	54,182	1.5
C double	57,678	442	57,236	0.8

While it is known that the use of a single LMW high charge density polymer results in less efficient fines capture, and fines capture is more dependent on molecular weight of the polymer than charge density, Petzold et al. (2004) found that there is an optimum charge ratio between dual polymer systems of opposite charge that results in the lowest resultant solids content in the supernatant of kaolinite suspension. Although charge ratios between the oppositely charged polymers were not assessed in this study, it is possible that the B2 + C system came closest to the optimum charge ratio, resulting in the best dual polymer performance. In the next section of the paper, results of turbidity measurements on the resultant supernatants are presented for the different polymer systems, which will allow a better comparison to be made with regards to the performance of the different systems.

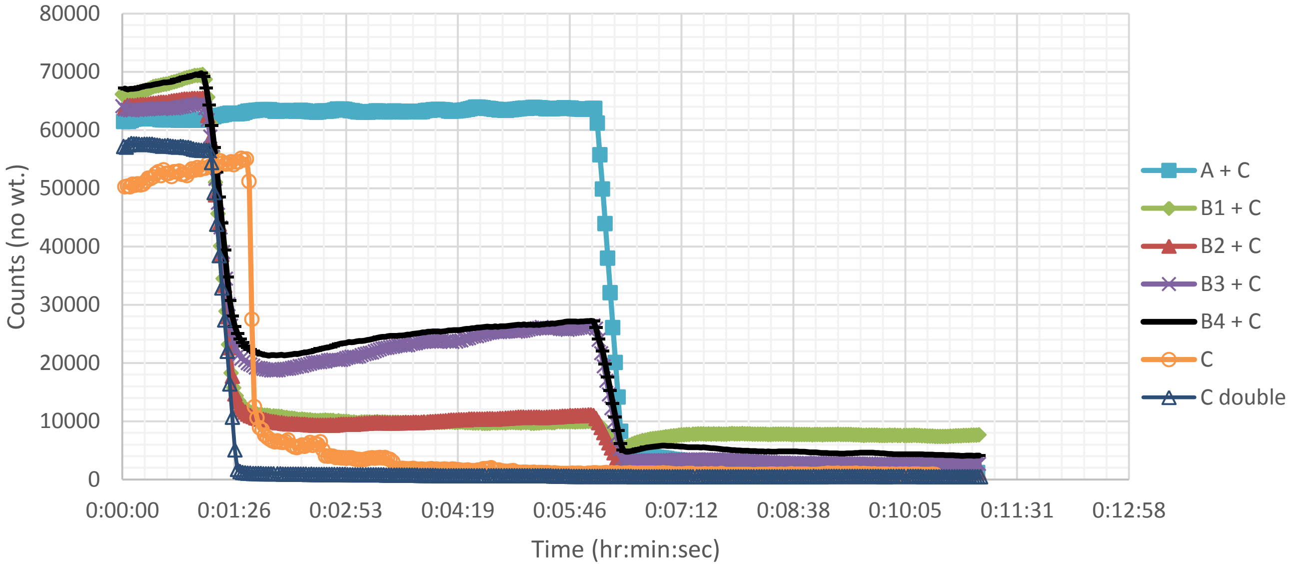

Figure 4.6 – Variation in the unweighted counts of particles below 44 µm upon flocculation using different polymer combinations

Figure 4.7 shows the variation in the number of particles larger than 44 µm in the suspension over time for the various polymer combinations used.

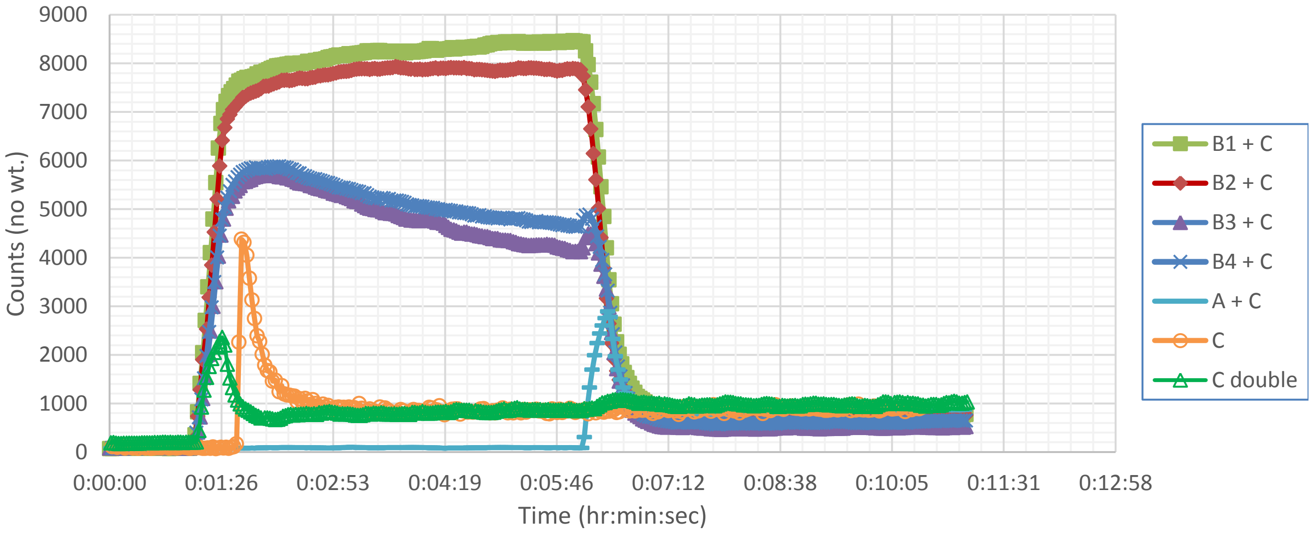

Figure 4.7 – Variation in the unweighted counts of particles above 44 µm upon flocculation using different polymer combinations

Figures 4.5, 4.6 and 4.7 also provide some information regarding the kinetics of the aggregation process. It can be seen that for the dual polymer system, the initial flocs formed by the addition of the cationic LMW polymers are in the size range 60-100 µm. These initial flocs are then bridged by the addition of the HMW anionic polymer to form larger flocs in the 400 – 500 µm size range. For example, for the suspension treated with B4, the initial flocs are around 60 µm, with a final floc size of around 500 µm upon addition of the HMW polymer C. This would imply aggregation of an average of 8 smaller flocs to form the final flocs. However, this will not always be the case, as some remaining fines are likely to be bridged along with the primary flocs. Also, it is apparent from the figures that some floc breakage occurred in the final flocs upon application of shear. For the single polymer system, however, the final floc size is reached early on, as a result of the aggregation of fines through the bridging mechanism. The flocs formed in this way are more shear resistant, as apparent from the results, due to the strong physical interaction between the polymer and the particles. Figure 4.7 shows that as the HMW polymer C is added to the suspension (alone, or with A), an increase in the count of particles above 44 µm is observed immediately, followed by a slow decrease of counts within a minute, after which the counts remains constant. On the other hand, the pairs of B1-B4 show a stepwise change of counts. For instance, B1 produces a large number of flocs larger than 44 µm that are shear resistant. B2 also produces a large number of such particles, but floc breakage and immediate reflocculation may be occurring, as suggested by the small decrease in the number of particles above 44 µm in size, accompanied by the increase in the number of particles below 44 µm (Figure 4.6) while maintaining almost the same mean floc size (Figure 4.5). Yoon and Young (2004) found that reflocculation is a function of the charge density of the polymer. The difference between C or A+C and B1-B4 + C combinations implies that the flocculated particles are possibly easier to bridge at the second stage than the fine particles, up to a certain size range. This could easily be explained by the larger size and increased exposed surface in the aggregated particles for bridging. All five dual polymer systems produce final flocs that degrade upon application of shear, with the effect being most pronounced in the system using B4. The floc breakage seen for the dual polymer systems appears to occur within the primary flocs (the aggregates formed by charge neutralisation), releasing fine clay particles, rather than breakage of the bridges between the primary flocs, as HMW polymers are known to produce stronger flocs than LMW polymers (Thapa et al., 2009). Interestingly, the system using a combination of dispersant A and C also shows degradation of the final flocs, which could be a result of the looser floc structure that was suggested earlier.

4.3.2 Effect of the metal cations present in tap water on kaolinite flocculation

The presence of ions in water is known to affect the flocculation and settling characteristics of clay systems. Kaya et al. (2006) studied the effect of ionic strength and pH on the settling characteristics of Kaolinite suspensions. They found that at high ionic concentrations, kaolinite suspensions settle in a flocculated form, due to the formation of positive charges on the edges of the kaolinite particles. According to their results, at pH 7, kaolinite settles in the flocculated form at Na^+ and Ca^{2+} concentrations of $1x10^{-2}$ M, while settling in the dispersed form at concentrations of $1x10^{-4}$ M. The concentration of Ca^{2+} and Na^+ in the suspensions brought in with the Edmonton tap water used in this study was far below $1x10^{-2}$ M, making flocculated settling unlikely without the addition of flocculant. Peng and Di (1994) found that the presence of $1x10^{-3}$ M Ca^{2+} can reduce flocculation efficiency for kaolinite suspension treated with 5 ppm of a high MW anionic polyacrylamide flocculant. due to the adsorption of Ca^{2+} ions on the active sites of the flocculant. . In this study, considering the dosage of polymer used (270 ppm) is significantly higher than the polymer dosage used by Peng and Di (1994) (5 ppm), site blocking is unlikely to considerably affect the flocculation efficiency. Divakaran and Pillai (2001) studied the effect of Mg^{2+} and Ca^{2+} ions at similar concentrations present in the suspensions used in this study, on the flocculation of kaolinite using chitosan, a biopolymer obtained by deacetylation of chitin, and found that there is no effect on the results when compared to the suspensions produced using distilled water. Lastly, the test suspensions produced from the stock solution were all prepared at the same time, removing the effect of water composition variations. Thus, the effect of cations from the tap water on kaolinite flocculation is excluded.

4.3.3. Capillary suction time, turbidity of supernatant and water release

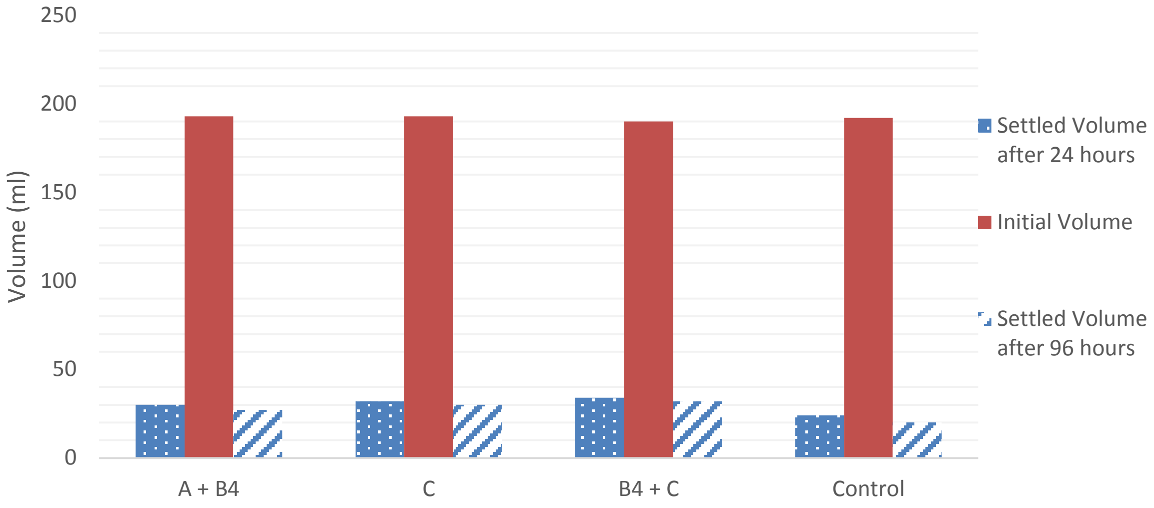

Figure 4.8 – Initial and settled volumes of the suspension after 24 and 96 hours of settling

Figure 4.8 shows the initial and final settled volumes of the kaolinite suspension treated with different polymer combinations after 24 and 96 hours of settling. Comparing the volumes and CST results after 24 hours and 96 hours provides an idea regarding the strength of the settled beds and whether or not there is any further flocculation or breakage that occurs over this time period. It is seen that in all cases, the volume of the settled bed was almost the same after 24 and 96 hours, with a small decrease in each case. The lowest settled bed volume (and hence most tightly packed bed) was obtained without any polymer addition – however, the kaolinite took the longest time to settle. The system treated with a combination of A and B4 produced almost as dense a settled bed, as the mechanism of aggregation in this case was charge neutralisation, forming smaller and denser flocs compared to the systems treated with polymer C (either alone or with an initial coagulant), in which the final flocs are formed by bridging, producing larger and looser flocs and hence settled beds.

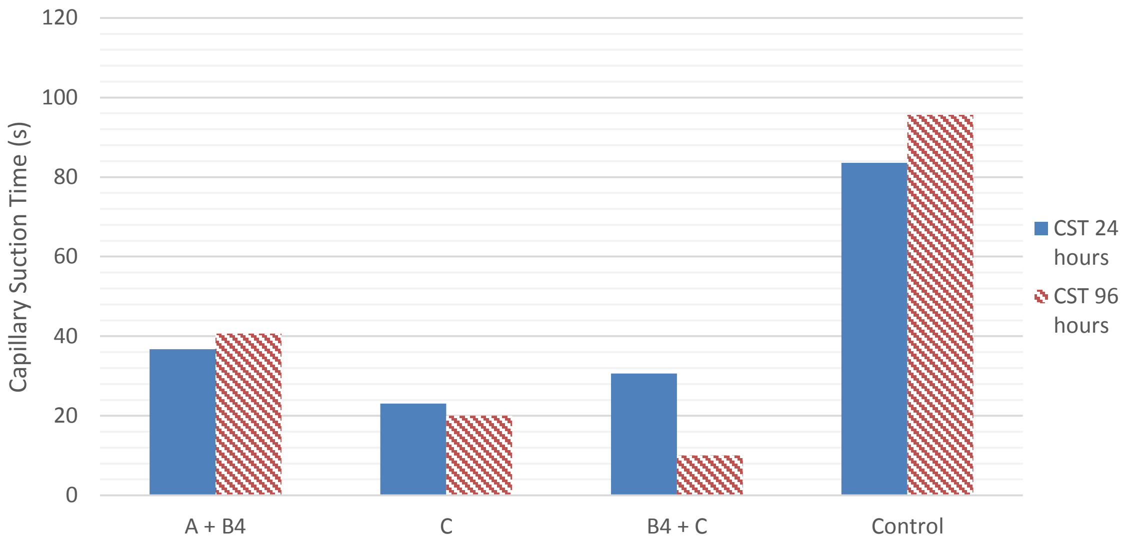

Figure 4.9 – Capillary suction time of the settled beds after 24 and 96 hours

Figure 4.9 shows the capillary suction times (CST) of the flocculated kaolinite after 24 hours and 96 hours of settling respectively. In every case, the untreated kaolinite suspension produced a settled bed with a very high CST. The system treated with A and B4 produced a settled bed with a CST lower than half of the control. After 24 hours of settling, the CST of the systems treated with A+B4, and B4+C were comparable, with the latter having a lower CST of 30.6 s, compared to 83.6 s for the untreated kaolinite. The system treated with C alone produced the lowest CST (23.1 s) after 24 hours. However, after 96 hours of settling, the CST of the systems treated with B4+C significantly decreased to 10.1 s, while the other polymer pairs show a slight change. It was mentioned earlier that the LMW cationic polymers show strong reflocculation characteristics, whereas in the other cases, the flocs broken under the pressure of settling and filtration would release fines that would cause the CST to increase, the presence of the LMW polymer could be responsible for removing these free fines. The slight decrease in the CST of the system treated with C alone may simply be due to the settling of the free fines within the porous settled bed. The control bed and the bed produced by treatment with A and B4 showed an increase in the CST after 96 hours, as the particles and relatively smaller flocs were more tightly packed. Compared to the CST values obtained by Sengupta et al. (2007) using a HMW cationic PAM polymer, the CST obtained for our systems are relatively higher – they obtained a CST of 13.3 s at peak floc size using a stirring speed of 300 rpm. However, the lower CST could be attributed to the higher stirring speed (indeed in their study, they found the CST decreased as agitation speed increased) and the period of time allowed for settling.

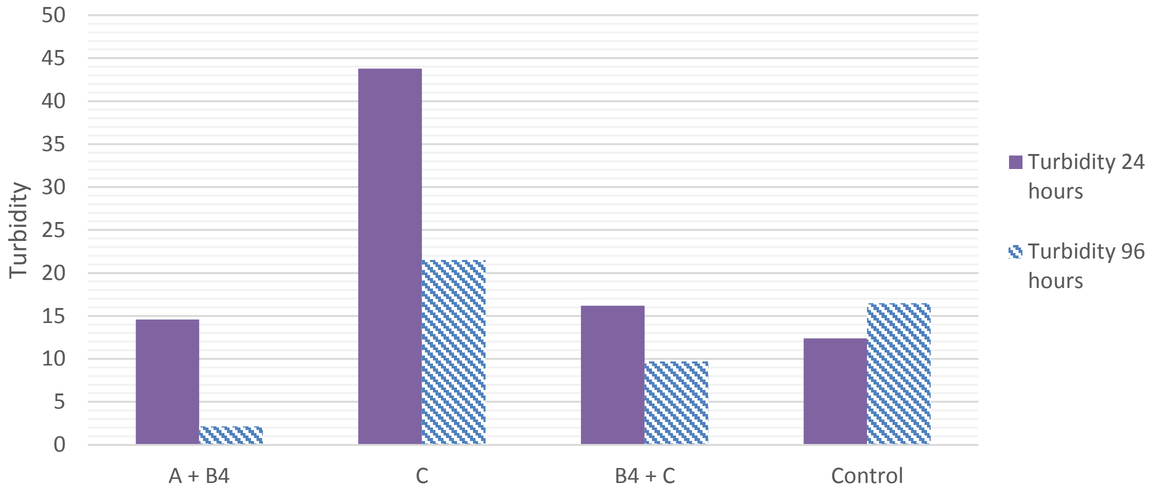

Figure 4.10 – Turbidity of the supernatant after 24 and 96 hours of settling

Figure 4.10 shows the turbidity of the resultant supernatants after 24 and 96 hours of settling. The highest turbidity is seen in the supernatant resulting from treatment with C alone, after both 24 and 96 hours. This result aligns well with the results in the earlier sections on fines capture, where it was found that dual polymer systems removed greater number of fines from the suspension than using C alone (Table 4.3). The dual polymer systems A+B4, and B4+C, produce supernatants with considerably lower turbidity. After 24 hours of settling, the untreated control suspension produces the supernatant with the lowest turbidity. However, after 96 hours of settling, it can be seen that the dual polymer systems produce supernatants with even lower turbidity, with the most marked decrease seen in the suspension treated with A and B4. While the mechanism behind the fines removal over this extended period of time is not fully understood for this system, it is clear that the oppositely charged A and B4 produce a synergistic effect in producing a clear supernatant. The lowest turbidity of supernatant achieved by Sengupta et al. (1997) using HMW CPAM on a similar kaolinite suspension was around 40 NTU, using an agitation speed of 500 rpm. Their results also suggested that decreasing the agitation speed during flocculation resulted in increased residual turbidity in the supernatant. Yu et al. (2006) found that the lowest turbidity achieved in the supernatant of a dilute (100 mg/L) kaolinite suspension flocculated using LMW PDADMAC or HMW cationic polyacrylamide copolymer was around 45 NTU. With the exception of the single polymer system using C, all the systems tested in this study perform considerably better than the aforementioned examples. The dual polymer systems exhibit significantly better fines capture characteristics than the systems treated with a single HMW anionic polymer, and this finding is similar to that of Petzold et al. (2001), as mentioned earlier in this paper.

4.4. Conclusions

1. The use of a dual polymer system consisting of a cationic LMW coagulant and an anionic HMW flocculant results in better fines removal performance (and hence low turbidity of supernatant) compared to the use of a single HMW polymer, while exhibiting similarly fast settling rate.
2. After 24 hours settling, the dual polymer system results in settled beds with a similar CST to that produced by a single HMW polymer, resulting in fast water release characteristics. Over an extended period of time, the CST of the bed produced using the dual polymer system is even lower than that produced by the single HMW polymer.
3. The cellulose based cationic LMW polymers have been found to be effective primary additives.
4. The addition of anionic dispersant A along with a LMW cationic polymer produces the lowest turbidity in the supernatant, but results in a slow settling rate and relatively high CST.
5. The use of the FBRM method allows effective in-situ monitoring of flocculation processes, providing insight into the mechanisms and kinetics of the flocculation processes.

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Chapter 5 - Floc Size Growth and Water Release during Treatment of Oil Sands Mature Fine Tailings Using Dual Polymers

5. Floc Size Growth and Water Release during Treatment of Oil Sands Mature Fine Tailings Using Dual Polymers

Abstract

The accumulation of mature fine tailings (MFT) in Alberta's oil sands industry poses serious environmental issues. Without physical and/or chemical treatment the MFT remains suspended in the tailings ponds indefinitely. In this study we investigated the use of dual polymers on the flocculation and dewatering of MFT with the objective of tuning the properties of the sediments (floc size, porosity, etc.) for fast and maximum water release during post-flocculation treatment. The first polymer was used sequentially with a second polymer. The flocculation and dewatering performance of these dual polymers were assessed in terms of floc size, floc strength, net water release, fines capture and dewatering performance using Focused Beam Reflectance Measurements (FBRM) particle size analyzer, dewatering sieves, and Capillary Suction Timer. The kinetics of floc formation and the mechanisms of flocculation and dewatering were discussed. The role of polymer interaction with residual bitumen in the MFT was also studied.

5.1. Introduction

It has been estimated that there are around 1.7 trillion barrels of bitumen in the oil sands reserves in Northern Alberta, Canada (Alberta Energy, 2012). In the current water based commercial oil sands extraction process, the bitumen is recovered from the oil sands slurry by flotation using aeration; while the tailings (a mixture of water, sands, clay and residual bitumen) are discharged into tailings ponds, where the coarse solids settle out quickly, leaving a stable suspension referred to as mature fine tailings (MFT). More than 3 m^3 of tailings are generated per barrel of bitumen produced (Xu et al., 2008). Of these tailings, 1.5 m^3 will eventually accumulate as MFT or fluid fine tailings after supernatant recovery (Masliyah et al., 2011). Besides water, MFT typically contains around 30-40 wt% solids, mostly clays and trace minerals, and around 1-3 wt% bitumen. The major clay minerals in MFT are kaolinite and illite, with the majority of the particles below 44 μm in size. Without chemical or physical treatment, the MFT remains suspended in the tailings ponds indefinitely, where the trapped water cannot be recycled. Moreover, the continuing accumulation of MFT is cause for great economic and environmental concerns. It is estimated that at current production rates, the accumulated volume of MFT will increase to over one billion m^3 by 2020 (Long et al., 2006). Currently, one of MFT treatment methods is the addition of gypsum and blending with coarse sands, through a process known as the composite tailings (CT) technology. This method requires a relatively long time, and a negative effect of the chemicals remaining in the process water as a result of the treatment has been observed in pilot tests (Long et al., 2006). Other methods employed for tailings treatment include beaching, MFT drying, tailings thickening and drying, MFT centrifugation and drying, accelerated dewatering and water-capped MFT – most of the techniques have been rejected as they lack economical or technical feasibility (Fair, 2011). Therefore the development of an effective method for the treatment of MFT is of the utmost urgency.

The majority of the studies carried out in the past on the dewatering of MFT have focused on the use of a single polymer (Wang et al., 2010; Xu et al., 2008; Long et al., 2006; Sworska et al., 2000). However, recent studies on the use of dual polymer flocculation for sewage treatment and in the pulp and paper industry have shown promise over the use of a single polymer (Lee et al., 2001; Senthilnathan and Sigler, 1993). Petzold et al. (2003) found that the use of a low molecular weight (LMW) cationic polyelectrolyte followed by a high molecular weight (HMW) anionic polymer flocculant produced the clearest supernatant in clay suspensions and natural waste waters from gravel pits. Yoon and Deng (2004) found that using a LMW polymer followed by a HMW polymer on clay suspensions produced better re-flocculation after application of shear than using a single polymer. The positive effect of pretreatment of MFT with divalent cations on the flocculation performance is well known. Sworska et al. (2000) found that pretreating the MFT with divalent metal cations resulted in clearer supernatants after flocculation. Long et al. (2006) found that the addition of divalent ions to MFT induced adhesion between fine particles, and suggested a synergistic relationship between the HMW flocculant and the divalent ions. Similar results have also been reported in dual polymer treatments carried out on MFT. Yuan and Shaw (2007) carried out an extensive study on the use of combinations of coagulation (C) and flocculation (F) to dewater the MFT, and observed that certain combinations, such as F-C, F-C-F, etc., worked better than the others. Watson et al. (2010) found that combining the use of a very low molecular weight (VLMW) anionic polymer and a HMW polymer flocculant resulted in higher average particle size and solids content in the settled beds, in addition to faster dewatering. However, very few such studies have been carried out to understand the mechanisms and kinetics of a dual polymer system.

High molecular weight polyelectrolytes operate through a bridging mechanism and form large flocs that are loosely packed and relatively shear resistant. The higher strength of these flocs is advantageous for filtration purposes, as they are less likely to degrade under the applied shear.

The loose structures also result in fast dewatering; however it has been shown that HMW polymers result in higher water content in the settled beds (Besra et al., 2004). The high charge-density LMW polymers bring about aggregation via a charge neutralization mechanism, resulting in destabilization of the clay suspension. The resultant coagula are smaller in size leading to denser settled beds with lower water content; however, it has been found that the filtration rates of the settled beds are slow, and the resultant turbidity of the supernatant in such cases is relatively high (Besra et al., 2004; Petzold et al., 2002).

Cellulose based polymers (similar to those used in the pulp & paper industry) are non-toxic and biodegradable. As noted earlier, an issue caused by the CT process for MFT processing is the residual chemical content in the water. Synthetic polymers have been found to be more effective than natural polymers for flocculation purposes, as they can easily be tailored to particular applications. However, a drawback of synthetic polymers such as polyacrylamide is the fact that they are easily degraded by shear forces. Natural polymers have an advantage in being low cost, and shear-resistant (Krishnamoorti et al., 2010). Lignosulfonate is a water-soluble by-product of the sulphite pulping process (Lebo et al., 2000). The application of lignosulfonates as sacrificial agents in enhanced oil recovery is well documented, due to the strong adhesion of lignosulfonates with soil and clays (Hong et al., 1987). This implies that the lignosulfonate may interact strongly with the fine clays in the tailings. An advantage of such biomass-derived polymers is that they are biodegradable/biocompatible and do not pose problems during mine reclamation or disposal of the solid waste streams.

Most studies on the flocculation of MFT assess performance in terms of settling rates, settled bed solids content and dewatering rate. The challenge in such studies is to obtain reliable characterization under relevant conditions. Image analysis techniques require sampling and may require dilution that could alter the floc structures. Recently, Focused Beam Reflectance Measurement (FBRM) has been found to be a useful tool to monitor flocculation performance in clay suspensions (Senaputra and Jones, 2013; Yoon and Deng, 2004), sewage sludge (Thapa et al., 2009) and paper manufacturing processes (Blanco et al., 2002). Klein et al. (2013) used FBRM to measure floc size during the flocculation of MFT using a HMW HPAM polymer; however, the use of FBRM for MFT flocculation is still relatively uncommon.

FBRM probes allow in-situ measurements of particle size distributions in real time, over a wide range of solids concentrations. In this method, a rotating laser beam is focused at the external surface of a sapphire glass window, and scanned at a fixed speed across the suspension. The backscattered light is then reflected back to a detector; since the velocity of the scanning laser is known, multiplying this with the time lag between laser emission and detection results in a characteristic measurement of particle geometry known as the chord length. Thousands of measurements can be taken during each measurement interval, and from the data, the total counts, counts for specific size ranges, mean and median chord lengths can be calculated, allowing the kinetics of the flocculation process to be followed in real time.

The FBRM particle size analyzer allows the chord lengths recorded to be presented using an unweighted distribution, or using a square weighted distribution. The square weighted distribution is obtained using the following equation:

$$n_{i,2} = n_i M_i^2 \qquad (5.1)$$

Where n_i and $n_{i,2}$ are the counts and square-weighted counts respectively, and M_i is the chord length. The mean of the square weight distribution can be derived using the following equation (Senaputra et al., 2013):

$$Mean\ chord\ length = \frac{\sum_{i=1}^{k} n_i M_i^3}{\sum_{i=1}^{k} n_i M_i^2} \qquad (5.2)$$

It is clear from equations (5.1) and (5.2) that the square weighted distribution is more sensitive to larger particles than the unweighted distribution, which is more likely to produce more accurate results regarding the fine particles. Although the FBRM does not provide exact particle sizes, the square weighted chord lengths from FBRM measurements have been found to be comparable to conventional particle sizing techniques (Heath et al., 2002).

This paper focuses on the use of a dual polymer system consisting of various combinations of cellulose-based, LMW cationic polymer coagulant/LMW anionic natural polymer and an industrially used HMW anionic polymer to dewater MFT, with particular focus on the LMW anionic polymer and HMW anionic polymer pair. The flocculation and dewatering performance was assessed in terms of floc size and strength, net water release, filterability of the settled beds through capillary suction time (CST) measurements and FBRM measurements to study the flocculation process in real time to obtain a better understanding of the mechanism and kinetics of flocculation. The performance of the dual polymer system was also compared to that of a single HMW polymer. The mechanisms of flocculation were discussed based on the results.

5.2. Materials and methods

5.2.1 Materials

The MFT used was from the Syncrude tailings pond in Athabasca region. The MFT had a solids content of 36.0%, bitumen content of 2.6% and water content of 61.4% by using the Dean-Stark method. The MFT was used without any dilution or pre-processing, at natural pH. The mean ($d_{(50)}$) of the MFT particles was 9.5 μm with a standard deviation of 2.9 μm, tested under different agitation conditions using a Malvern Mastersizer 3000 laser diffraction particle size analyser. The bulk MFT sample was homogenized and divided into 1000 g sample sizes, stored in air-tight buckets.

The two cationic polymer coagulants (Celquat H100 and SC240c respectively) were obtained from Akzo Nobel. The coagulants used had an average molecular weight ranging from 60,000 to 80,000 g/mol (determined by gel permeation chromatograph, with individual chromatograms shown in Figures A.5 – A.8 in the appendix) and were hydroxyl-ethyl cellulose polymers grafted with different ratio of PDADMAC, resulting in different charge density and distribution along the polymer chains. The LMW anionic polymer, a sodium salt of Lignosulfonic acid (hereafter referred to as lignosulfonate) was obtained from Sigma Aldrich, and had an average molecular weight of 52,000 g/mol. The HMW anionic polymer A3335 is a HMW linear commercial flocculant manufactured by SNF, with an average molecular weight of 17×10^6 g/mol, and no further information regarding the structure of the polymer has been provided. In the interest of readability and brevity, the polymers will be referred to as A, B1, B4 and C in this paper, as shown in the parenthesis in Table 5.1.

Table 5.1 – Molecular weights of the tested polymers

Polymer	Average molecular weight (g/mol)
Lignosulfonate (A)	52,000
Celquat H100 (B1)	61,370
Celquat SC240c (B4)	66,470
A3335 (C)	17×10^6

Experimental agitation cells were washed using Edmonton tap water. Edmonton tap water has a low hardness, with Ca^{2+} ion concentration of 48 mg/L (1.2×10^{-3} M), resulting in a $CaCO_3$ hardness of 120 ppm. The water also has an Mg^{2+} and Na^{+} ion concentration of 12.8 and 9.51 mg/L (5.3×10^{-4} and 4.13×10^{-4} M) respectively, and trace amounts of other cations.

5.2.2. Flocculation

The flocculation tests were carried out in a special stainless steel baffled container, with the following dimensions: Internal diameter: 110 mm; internal height: 160 mm; 4 baffles of length x width x height: 130 x 10 x 10 mm; total internal volume of the cylinder: 1.5 liters. The stirrer used for testing was a Heidolph RZR 2052 electronic stirrer and a 3 blade axial-flow impeller (blade height – 2.5 cm) of 60 mm diameter, with the impeller immersed such that the bottom of the tips were 1.7 cm from the base of the steel container.

A model 319 multi-purpose Capillary Suction Timer (Triton Electronics Ltd. U.K) was used to measure capillary suction time (CST) of flocs using an 18 mm diameter cylindrical funnel and standard filter paper obtained from Triton Electronics Ltd.

The HMW polymer C solutions were prepared at a concentration of 0.8 wt%, and the LMW polymers (A, B1 and B4) were prepared at a concentration of 2.0 wt%, using distilled water in each case. The polymer solutions were prepared 24 hours prior to testing.

5.2.2.1. FBRM measurements

The FBRM unit used was a G400 with a 91 mm fixed probe (Mettler Toledo, Columbia, MD). The probe was inserted at the same depth and in the same position for each test. The smallest sampling interval (2 s) was used for best resolution of results.

Initial testing using FBRM on flocs produced by the use of single HMW polymer showed that 600 rpm was the optimum stirring speed for flocculation tests, vigorous enough to keep the resultant flocs in suspension without causing significant floc breakage, and resulting in good water release and increase in particle size.

For single polymer tests, 1000 g of MFT was stirred at 600 rpm for 300 s, and then the polymer was added. The suspension was stirred at 600 rpm for another 300 s, for a total time of 600 s.

For dual polymer tests, 1000 g of MFT was stirred at 600 rpm for 120 s, then the first polymer was added. The suspension was stirred for another 180 s, after which the second polymer was added, and the suspension stirred for a further 300 s for a total time of 600 s. The polymer dosages tested ranged from 500 ppm to 2000 ppm based on the solids content of the MFT (i.e., 500 to 2000 grams of polymer per tonne of solids in the MFT). The tests were carried out in the previously mentioned baffled stainless steel container.

5.2.2.2. Settling and dewatering tests

Upon completion of the FBRM floc size measurement for each test, the MFT and polymer mixture in the baffled steel container was transferred to a 150 μm standard test brass sieve (Fischer Sci.) for dewatering, and 50 mL of the well mixed mixture was set aside for CST measurements. After 24 h the water released was collected and measured, and CST tests were performed on the 50 mL sample using the Triton Electronics Type 319 Multi-purpose CST meter, using 7 x 9 cm standard CST paper, also obtained from Triton Electronics. The water release was also noted after 48 h of dewatering.

5.2.3. Tests on lignosulfonate-bitumen interactions

For tests on the interaction of lignosulfonates and bitumen, the bitumen was extracted from the MFT samples using the Dean-Stark method, in order to accurately represent the effect of the residual bitumen in the MFT.

5.2.3.1 Glass slide and emulsion tests

In the glass slide tests, a small amount of the residual bitumen extracted from the MFT was spread evenly over glass slides, allowed to dry, and then immersed in trays containing 0.4 wt% solutions of polymer A, polymer C, and a combination of polymers A and C. Distilled water was used as a control. The slides were left immersed for 24 hours. The interaction of the polymer solutions with the dried bitumen was determined visually.

The emulsion tests involved shaking equal parts (by volume) bitumen/toluene mixture and a 0.4 wt% solution of polymer A in an attempt to form an emulsion. The interaction of the polymer A suspension with the bitumen was determined visually.

5.2.3.2 Elemental analysis

The bitumen obtained from the MFT was dissolved in toluene and shaken with a 0.4 wt% solution of A in a separation funnel. The aqueous A phase was separated after 24 hours, and shaken with methylene chloride in a separation funnel. After a further 24 hours, the methylene chloride phase was separated and dried in a rotary evaporator. The resultant dry solids were subjected to elemental analysis using a Carlo Erba EA1108 Elemental Analyzer, to obtain the content of carbon, hydrogen, nitrogen and sulphur .

5.3. Results and discussion

5.3.1 Real time flocculation monitoring using FBRM

5.3.1.1 Flocculation using various polymer combinations

Flocculation experiments using various polymer combinations were monitored in real-time using FBRM measurements. Figure 5.1 shows the change in the mean square weighted chord length against time for these flocculation experiments. For single polymer tests, the polymer was added to the MFT after 5 minutes, with the exception of the ‘2000 ppm C’ test, where 1000 ppm C was added after 2 minutes and another 1000 ppm C was added after 5 minutes. For the dual polymer tests, the first polymer was added at 2 minutes, followed by the second polymer at 5 minutes. The results show that the largest floc size achieved was around 120 μm, using a combination of polymers A and C. Flocculation using the HMW anionic PAM based polymer C alone resulted in a maximum floc size around 90 μm using a dosage of 1000 ppm, whereas the maximum floc size using a dosage of 2000 ppm C was around 70 μm indicating overdosage may have occurred. The addition of LMW anionic polymer A alone resulted in no increase in the floc size. The combinations of oppositely charged LMW polymers ‘A+B1’ and ‘A+B4’ produced no significant increase in floc size.

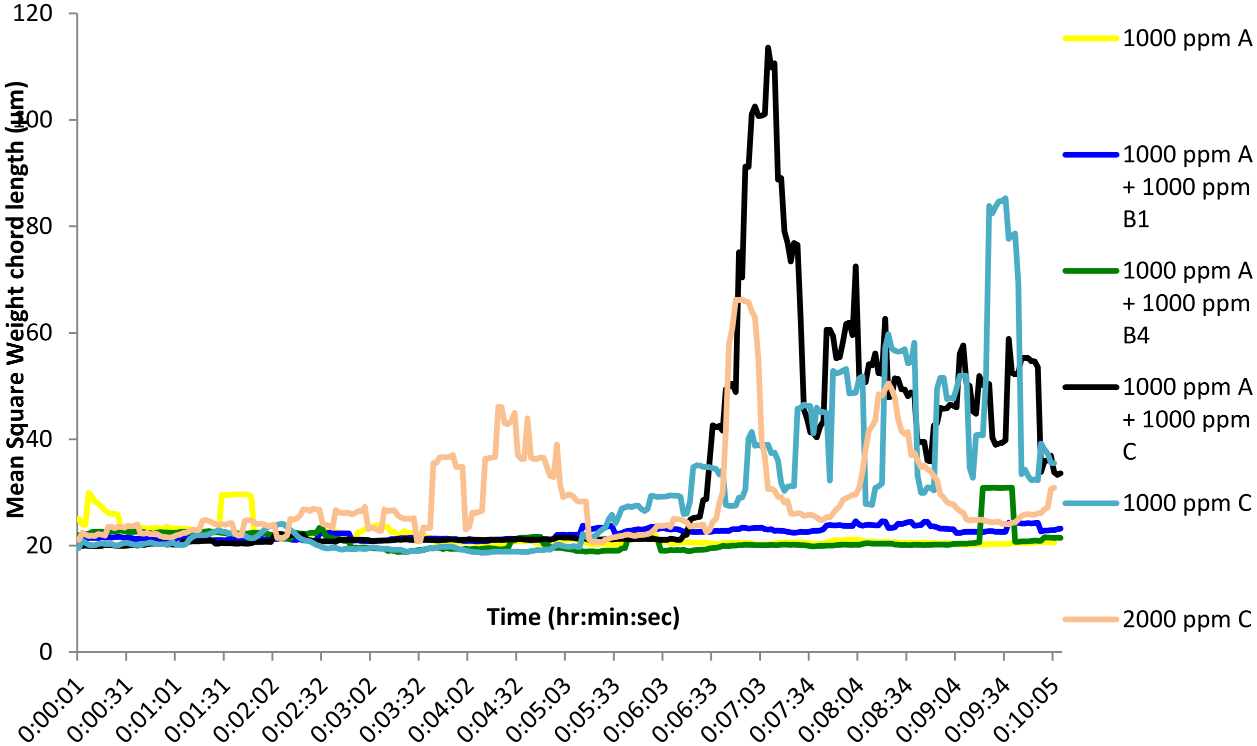


Figure 5.1 - Change in floc size upon flocculation with different polymer combinations.

Klein et al. (2013) studied the flocculation of laboratory oil sands extraction tailings using a HMW HPAM polymer and FBRM. The maximum floc size obtained for a sample of tailings with bitumen content of 0.45% was found to be 280 µm, considerably larger than the maximum floc size obtained in this study. However, they found that as bitumen content of the MFT increased to over 0.45 wt%, the flocculation efficiency dropped considerably. In Klein et al.'s study the MFT was also diluted to 10 wt% with process water prior to use, whereas in the present work the MFT was used without dilution so it contained 36 wt% solids. Watson et al. (2011) used a light scattering technique to measure the particle size distribution of oil sands process tailings upon flocculation using a VLMW polymer followed by a HMW polymer, which were both polyacrylamide/co-acrylate mixtures, and found that the majority of the flocculated particles were around 100 µm in size. They provided no information or characterization of the MFT used in the study. Due to the lack of flocculation studies employing real-time monitoring methods such as FBRM, it is difficult to obtain comparisons between other studies and the results presented; however the results of the aforementioned studies align well with those presented in this paper.

Typically the mechanism involved in dual polymer flocculation can be explained using the electrostatic patch model (Gregory, 1973) together with bridging flocculation. The net residual charge of a high charge density polymer patch on the particle surface can attach to a bare portion of an oppositely charged particle. A high charge density LMW polymer is usually used as the primary polymer, followed by a HMW secondary polymer (Yoon & Deng, 2004; Watson et al., 2010). The electrostatic patch model however, does not explain the mechanism for the polymer combination 'A + C', as polymer A is in theory a dispersant and not a coagulant. The improved flocculation using polymer C on MFT pretreated with polymer A is likely due to the interactions of polymer A, an anionic LMW lignin derivative, with the residual bitumen in the MFT.

In their characterization study on organic coated solids in Athabasca bitumen, Bensebaa et al. (2000) found that the ultrafine inorganic solids in bitumen and tailings are coated with toluene insoluble organic matter, possibly contributed from both humic and asphaltene like components. They found the coverage to be patchy rather than continuous, and suggested that this organic coating contributes to the ability of the solids to stabilize water-in-oil emulsions. Klein et al. (2013) studied the effect of the residual bitumen concentration in oil sands tailings on flocculation using a HMW HPAM polymer. They found that reducing the residual bitumen concentration improves flocculation down to a bitumen concentration of 0.18 wt%. Below 0.18 wt% bitumen, there is a reduction in flocculation efficiency. The study also showed that the HPAM polymer preferentially adsorbed on clays rather than on bitumen and sand particles, as shown by a QCM-D study. The bitumen content of the MFT used in this study was 2.6 wt%, significantly higher than 0.18 wt%. Therefore, the flocculation efficiency may be lower.

The beneficial effects of lignosulfonates and other lignin derivatives in enhanced oil recovery are well documented. Hong et al. (1987) suggested that the lignosulfonates behaved as sacrificial adsorbates, adsorbing irreversibly on reservoir rock surfaces, while Novosad (1984) attributed the enhancement of oil recovery to the interfacial effects of the lignosulfonates, behaving as co-surfactants rather than adsorbing on to rock surfaces. While Hong et al. (1987) and Novosad (1984) suggested different explanations for the beneficial effects of Lignosulfonate in enhanced oil recovery, these studies suggest that lignosulfonate may have the ability to interact with either the clay particles or the residual bitumen present in the MFT. Lignosulfonates have also been applied as soil hardening agents (Kojima & Danchia, 1977). Lignin and the organic bitumen residues present in oil sands tailings streams also share common humic chemical structures and lineage (Shevchenko & Bailey, 1996), suggesting potential for strong interfacial activity between lignosulfonates and bitumen and clay surfaces.

It is suggested that Polymer A interacts with the residual bitumen in the MFT, exposing the clay particle surface to further interaction with the HMW polymer (which possibly has a greater affinity to the clay surface according to Klein et al. (2013)). Polymer A is a dispersant by nature, and FBRM measurements suggest that it disperses the MFT as shown in Figure 5.2, where the counts of fine particles increase substantially with addition of A. Its effectiveness may be attributed to its interaction with the residual bitumen. The MFT that was dispersed by polymer A produced loose and large flocs when further treated with HMW polymer C. It is likely that these large and loosely arranged flocs would result in fast dewatering. This hypothesis fits with the observed weakness of the flocs from the results - the flocs appear to break fairly easily upon shear, as shown by the decrease in the mean square weighted floc sizes upon continued agitation in Figure 5.1 The MFT dispersed using polymer A appears to have better mixing characteristics, as the peak floc size obtained using polymer C in the dual polymer treatment occurs within 2 minutes of the addition of polymer C, whereas for the polymer C alone, the peak floc sizes occur at around 4 minutes after addition.

The larger floc sizes observed using the combination of polymers A and C are not solely an effect of using a higher polymer dosage/concentration. This becomes apparent when comparing the dual polymer results with those obtained using a 2000 ppm polymer C dosage (which clearly results in an overdose).

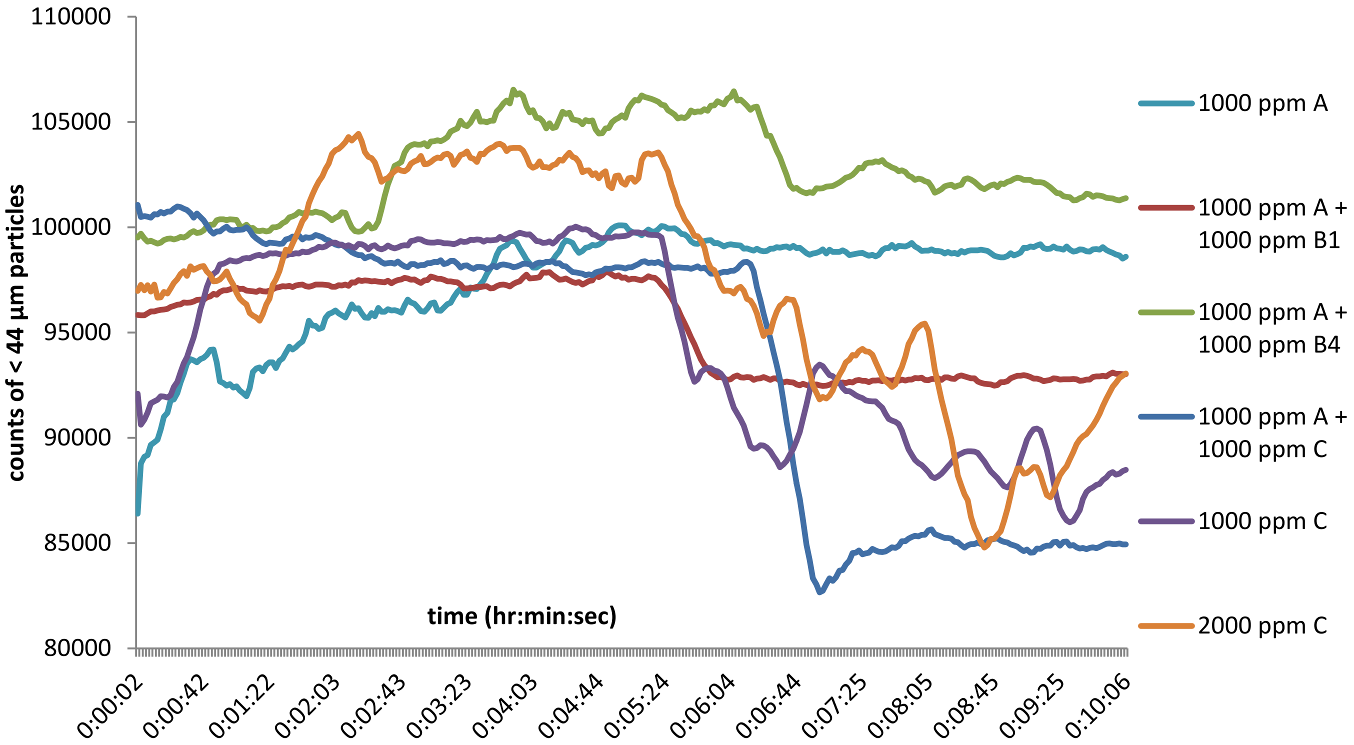


Figure 5.2 – Change in counts of fine particles (< 44 µm) upon flocculation with various polymer combinations

Figure 5.2 shows the change in the counts of fine particles (<44 µm) upon flocculation with the polymer combinations tested. In almost every case, the counts of the <44 µm fine particles increases upon the addition of polymer A (at 00:02:00), followed by a decrease upon the addition of the secondary polymer. For better comparison, the change in the fine particle counts has been presented in Figure 5.3, against the initial fines content of around 95, 000±5000. In each test, the measured highest fines content prior to any polymer addition was considered the initial fines content, while the lowest fines content after flocculation was considered the final fines content.

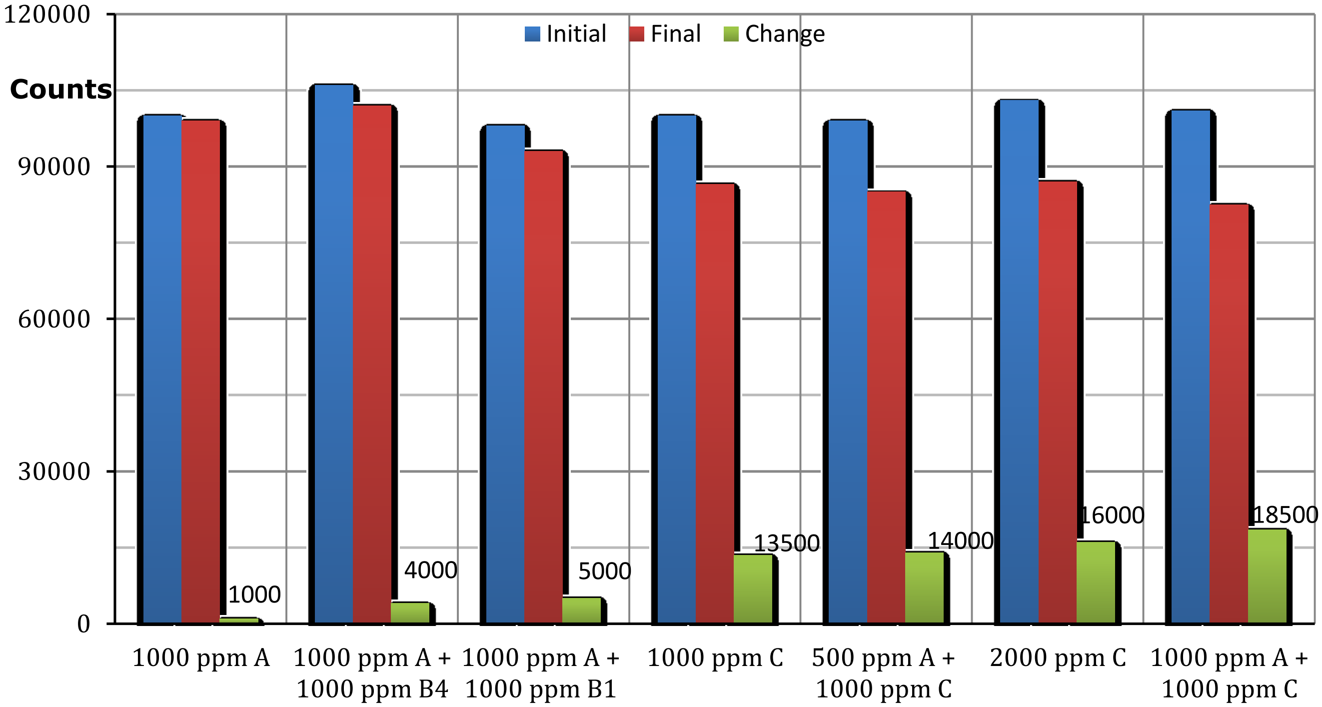


Figure 5.3 - Change in the counts of fine particles (< 44 µm) using various polymer combinations

Polymer A is essentially a dispersant, and the slight reduction in fine particle counts using polymer A is most likely due to settling over the course of the experiment. Cellulose-based cationic polymers B1 and B4 perform poorly with regards to removal of fine particles. Dual polymer treatment with A and C results in the best fines capture performance. A high dosage of polymer C alone also performs similarly. The improvement in doubling the dosage of C in the single polymer treatment is slight, less than 20%, and is likely due to the better mixing of the larger dosage in the MFT sample, due to the dilution as a result of additional water from the polymer solution. The performance of the dual polymer system is also clearly dependent on the dosage of polymer A, with an initial dosage of 1000 ppm A performing 32% better than an initial dosage of 500 ppm A. The better fines capture performance of the A + C system is possibly due to polymer A's interaction with the residual bitumen, allowing better interaction between the flocculant C and the clay particles. Dispersing the MFT using polymer A also allows for better mixing of polymer C. As a result of these two effects, the fines capture occurs within a minute of addition of polymer C in the dual polymer systems, whereas the single polymer systems take considerably longer to reach the minimum fines content (Figure 5.2). Thus the dual polymer system A + C appears to perform better with regards to fines capture for the same reasons it produces larger floc sizes, as discussed earlier.

5.3.1.2. Flocculation using various concentrations of polymers A and C

Polymers A and C were chosen for more detailed study based on their flocculation performance compared to the other polymer pairs. Figure 5.4 shows the change in the mean floc size of the particles upon flocculation using different concentrations of A and C. The concentration of A was varied between 500 ppm to 5000 ppm, and the concentration of C was varied between 1000 ppm and 2500 ppm. Greater focus has been placed on the effect of varying polymer A dosage, as polymer C is an industrially used polymer whose performance, as a HMW PAM based polymer has been well studied. The results presented earlier also show that the beneficial effects of higher polymer C dosage in this study are primarily due to the higher efficiency of mixing. Polymer C is also a more expensive polymer; therefore the development of a system that utilizes a high C dosage is not desirable.

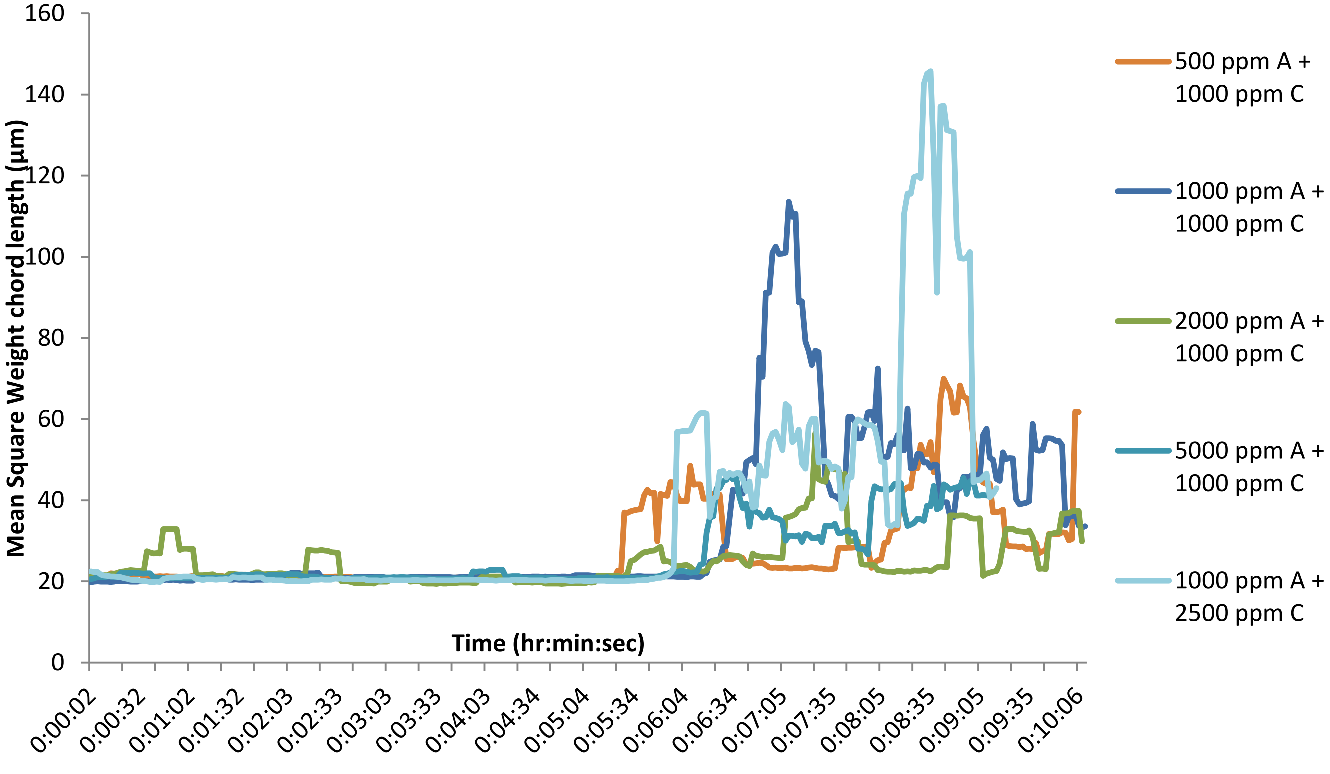


Figure 5.4 – Change in mean floc size upon flocculation with various concentrations of polymers A and C

The results show that increasing the dosage of polymer A from 500 ppm to 1000 ppm while maintaining a constant polymer C dosage of 1000 ppm results in an increase in the maximum floc size from 70 μm to 113 μm. Increasing the polymer A dosage to 2000 ppm results in a sharp drop in the maximum floc size, while increasing the polymer A dosage further to 5000 ppm results in a further decrease. The dosage of polymer C was kept constant at 1000 ppm, except for one test to verify that over dosage does not occur at 1000 ppm. Using 2500 ppm C and 1000 ppm A increases the maximum floc size to 145 μm, therefore 1000 ppm C is not an overdose.

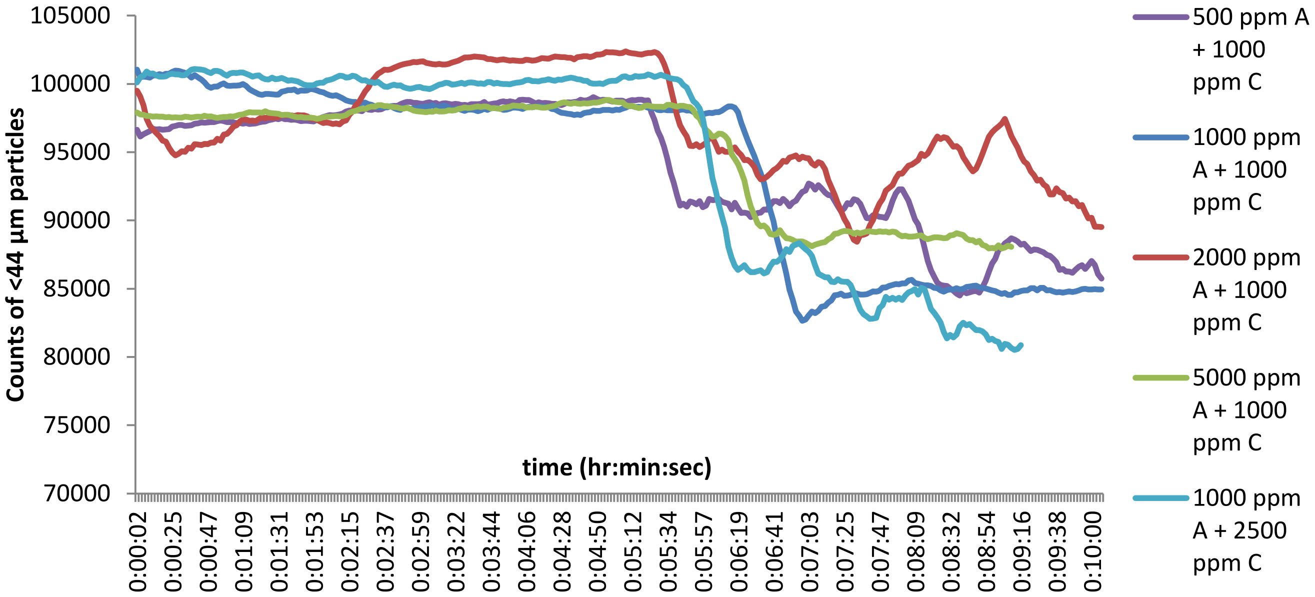


Figure 5.5 – Change in counts of fine particles (< 44 μm) using different concentrations of A and C

Figure 5.5 shows the change in the counts of fine particles (<44 μm) upon flocculation using different dosages of A and C. The fines capture follows a similar trend to the maximum floc size as seen in Figure 5.4. Increasing the dosage of polymer A from 500 ppm to 1000 ppm results in better fines capture performance, while further increases to 2000 ppm and 5000 ppm progressively decrease the number of fine particles captured. Increasing the dosage of polymer C to 2500 ppm results in better fines capture, verifying that 1000 ppm C is not an overdose. These results suggest that an optimum dosage of polymer A exists between 500 and 2000 ppm. At the higher dosages, the dispersant nature of polymer A can make flocculation and fines capture difficult for the secondary polymer, as the large number of polymer A particles are likely to be interacting with the clay particles in addition to the residual bitumen particles in the MFT, hindering access for the HMW polymer flocculant.

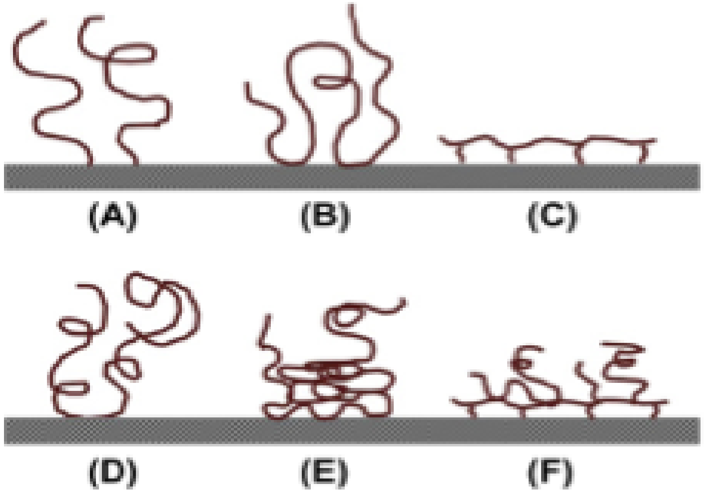


Figure 5.6 - Possible conformations HMW flocculants adsorbed on clay particles (Zecha, 1981).

Fines capture by polymer flocculants depends on the affinities between the polymer and the fines, as well as on the conformation of the adsorbed polymers. Figure 5.6 shows the possible conformations of adsorbed polymeric flocculant on a solid/water interface. (A) represents single point attachment, (B) loop adsorption, (C) flat multiple site attachment, (D) random coil, (E) nonuniform segment distribution, and (F) multilayer adsorption (Zecha, 1981; Alagha et al., 2013; Wang et al., 2014). Weak attraction between a hydrophilic polymer and clay surface results in the polymer chain extending away from the surface, such as for (A), (B) and (D). Strong polymer-surface interactions and relatively hydrophobic polymers result in flat conformations such as (C) and (F). A high level of polymer self-interaction results in a conformation such as (E). Polymers with a high chain stiffness (e.g. highly charged polymers) will resist changes to their conformation, as in the case of (A) and (C).

According to Wang et al. (2014), in order for a polymer to capture fines in a suspension, the following are desirable: 1) the interactions between the polymer and the fines are weakly attractive (in order to prevent steric stabilization), 2) the polymer is hydrophilic in nature (so that it extends into the solution increasing adsorption area), 3) the polymer has low self-interaction and a moderate chain stiffness (to balance floc strength and re-flocculation ability). Figures 5.1 and 5.4 show that the flocs formed upon dual polymer treatment are subject to breakage upon application of shear, suggesting that the interactions between polymer C and the fine particles is relatively weak. The presence of residual bitumen in the MFT, coupled with the weak nature of interaction between polymer C and the fine particles affect the efficiency of single polymer flocculation. However, the introduction of an optimum dosage of polymer A increases the efficiency of flocculation by interacting with the residual bitumen and destabilizing the suspension. This improves the flocculation efficiency for a dual polymer system by improving flocculant access to the fines and providing an environment more akin to that suggested by Wang et al. (2014) for an ideal flocculant – weak polymer-clay surface interactions, highly hydrophilic polymer and low levels of self-interaction.

5.3.2. Capillary suction time, water release and water quality

5.3.2.1 Capillary suction time (CST)

Figure 5.7 shows the capillary suction times (CST) of the MFT samples 24 hours after flocculation at various polymer concentrations. In the case of the 'MFT Untreated', the MFT was stirred at 600 rpm for 10 min without any polymer addition. The use of a dual polymer system of polymer A and polymer C results in the lowest CST, comparable to using a high dosage of polymer C alone. The dual polymer systems using polymers A and B1, and A and B4 have similar CST to untreated MFT, which is the highest. The use of polymer A alone lowers the CST of MFT by 24%. This can be attributed to the interaction of lignosulfonates with the bitumen, which seemed to improve water release from the MFT. The use of 1000 ppm polymer C alone results in a considerably higher CST than the use of an A + C system. When the dosage of polymer C is doubled to 2000 ppm however, the CST is comparable to the dual polymer system. This supports the earlier suggestion that the use of polymer A as a primary additive improves access to clay particles by the flocculant polymer C, reducing the dosage required to obtain satisfactory results. In their study on the role of mixing energy in the flocculation of MFT, Demoz and Mikula (2012) measured the CST of MFT treated with 1000 ppm polymer C. They also utilized a stirring speed of 600 rpm, for various mixing times. The longest mixing time used in that study was 5 min, which resulted in a CST around 450 s, significantly lower than the results presented in this study. However, the MFT used by Demoz and Mikula had a solids content of 21 wt%, whereas the MFT used in this study has a solids content of 36 wt%. Indeed, Demoz and Mikula found that the CST increased with increased mixing time beyond 2 min, and the total agitation time in this study was 10 min, which would cause a longer CST. Lastly, the CST measurements in that study were performed immediately after flocculation, whereas the CST measurements presented in this paper were performed after 24 hours of settling. The effect of consolidation over that period may also result in higher CST values.

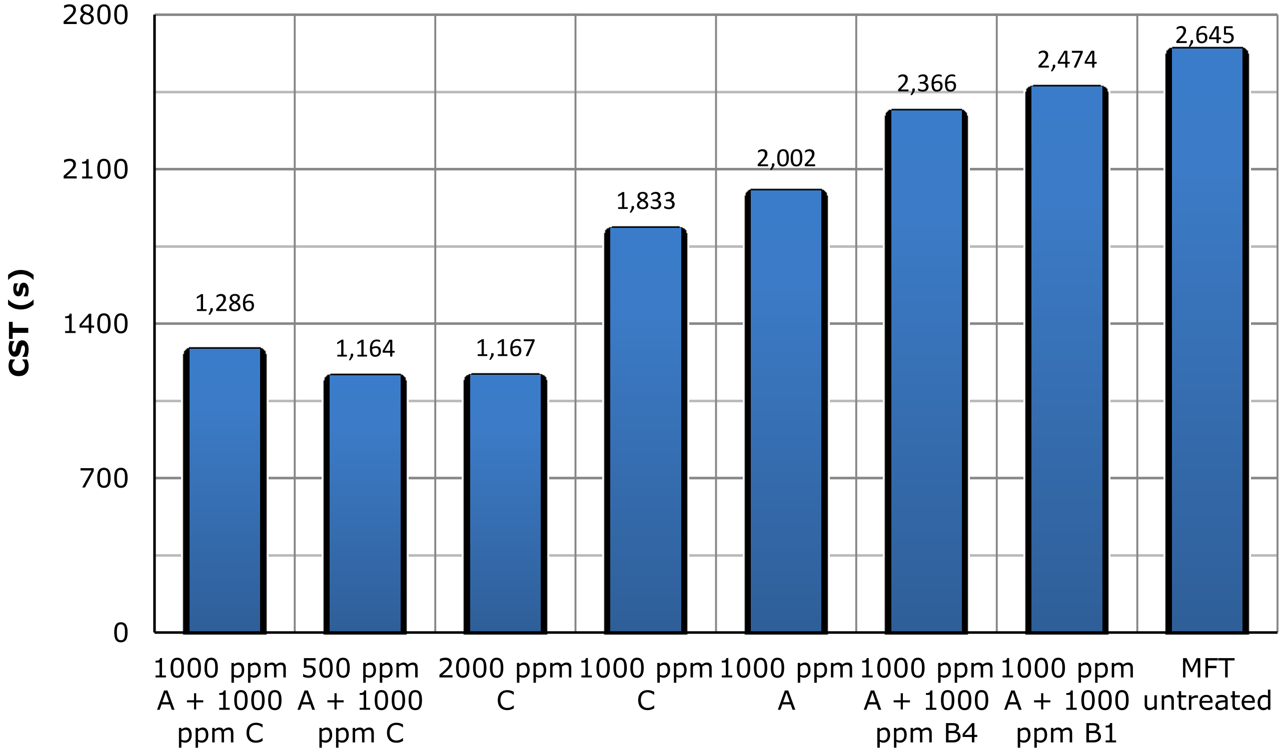


Figure 5.7 - Capillary suction time of the MFT 24 hours after flocculation

5.3.2.2 Water release and quality

Figure 5.8 shows the water added (through polymer addition) and released after 24 and 48 hours for the MFT treated with various polymer combinations. The net water release is calculated by subtracting the water added (through polymer addition) from the total water released after 24 or 48 hours. As can be seen, the dual polymer treatments perform considerably better than the single polymer treatments. Polymer A dosage of 500 ppm performs better than 1000 ppm as a primary additive, a result that supports the CST results presented earlier. However, the addition of polymer A alone prevents any dewatering from the MFT sample, a result that is interesting considering the observation that the untreated MFT releases around 5 mL water over the first 24 hours. This is likely due to the dispersion of fine particles, which shrinks the capillary channels. Demoz and Mikula (2012) measured the water released after 24 hours from MFT treated with 1000 ppm polymer C, agitated at 600 rpm for 5 min. They reported a water release of less than 50 mL, similar to the water release for the single polymer C treatment reported in this study. Demoz and Mikula (2012) found that as the agitation time was increased, the water release decreased (they measured gross water release as opposed to net water release). The water release presented in this study after a total agitation time of 10 min is therefore considerably higher, especially with dual polymer treatments. However, even for the best performing system (500 ppm polymer A + 1000 ppm polymer C), the net water release is only around 5% of the total water content of the MFT, and therefore requires much optimization.

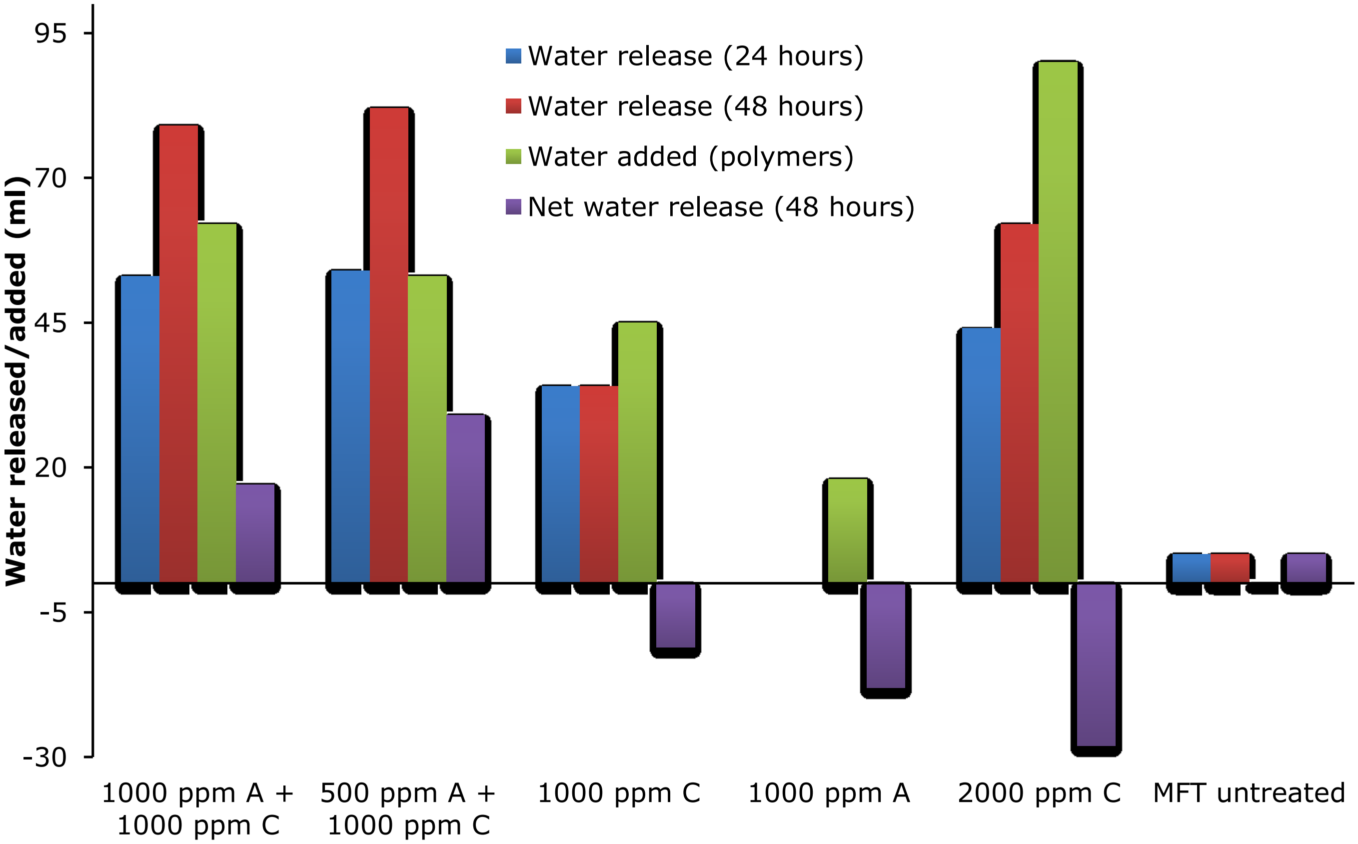
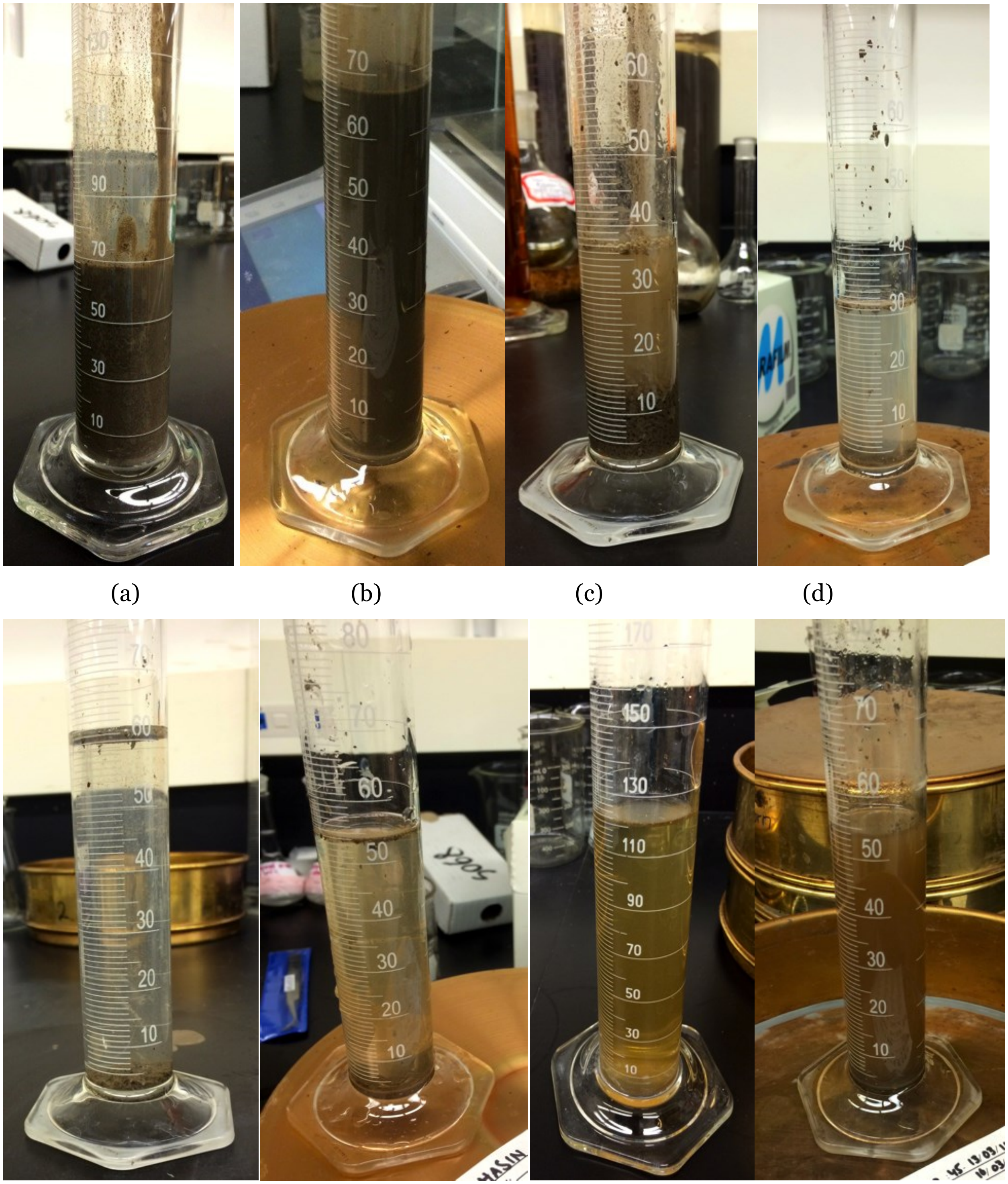


Figure 5.8 – Water release from treated MFT



(a) (b) (c) (d)

(e) (f) (g) (h)

Figure 5.9 – Water released from MFT after flocculation using various polymer combinations: (a) no polymer; (b) 1000 ppm polymer A; (c) 1000 ppm polymer A + 1000 ppm polymer B1; (d) 1000 ppm polymer C; (e) 2000 ppm polymer C; (f) 500

ppm polymer A + 1000 ppm polymer C; (g) 1000 ppm polymer A + 1000 ppm polymer C; (h) 2000 ppm polymer A + 1000 ppm polymer C.

Figure 5.9 shows the water released by the MFT samples treated with various polymers, obtained from the 150 μm sieves. Figures 5.9a and 5.9b show that there was no water release by untreated MFT and MFT treated with polymer A alone; The collected muddy water was what passed through the 150 μm sieve, and they appeared similar to the original MFT but possibly with a lower solid contents; More muddy water was collected when polymer A was used (Figure 5.9b) than from the untreated MFT (Figure 5.9a), indicating the dispersing effect of polymer A.

The water resulting from single polymer treatments (Figures 5.9d and 5.9e) is colourless, but contains visibly suspended fines, with a dosage of 2000 ppm polymer C resulting in clearer released water. In both of these cases, the released water has a thicker texture, due to the presence of free polymer. Figures 5.9f, 5.9g and 5.9h all show water released using a dual polymer treatment of polymer A and polymer C, at a fixed polymer C dosage of 1000 ppm and increasing polymer A dosage of 500, 1000 and 2000 ppm, respectively. The brownish colour is due to polymer A. The water released using a dosage of 1000 ppm A appears to possess less suspended fines than that using 500 ppm A, while the 2000 ppm A dosage results in visibly higher suspended solids. While the brownish colour may suggest the presence of free polymer A in the water, the released water is notably less viscous than those from single polymer treatment using polymer C. This observation aligns with the suggested benefit of using a dual polymer system - increased access to the fines for flocculant C to enhance supernatant clarity. Figure 5.9c shows the water released after treatment with polymer A and polymer B1. The water is muddy and contains solids that quickly settle out. The water released using a dual polymer system of A and B4 (not shown) is similar.

5.3.3. Interactions between residual bitumen and polymer A

In the foregoing discussion, the superior performance of a dual polymer system of polymer A and polymer C with regards to floc size and water release has been attributed to the interactions of polymer A with the residual bitumen in the MFT samples. The bitumen content of the MFT samples used was 2.6 wt%, measured using the Dean-Stark method. The residual bitumen content plays a significant role in the flocculation of MFT as shown by Klein et al. (2013). The use of lignosulfonates in enhanced oil recovery and as soil hardening agents is well known

(Hong et al. 1987; Novosad, 1984; Kojima and Danchia, 1977), while the common chemical structures and lineage of lignosulfonates and bitumen (Shevchenko & Bailey, 1996) suggests potential for interfacial activity between the two species. Several simple tests were performed to assess the interaction between polymer A and bitumen, the results of which are presented in this section. The bitumen used in these tests were obtained from the MFT samples using the Dean Stark method, in order to accurately account for the role of residual bitumen in results presented in this study.

The interaction of Polymer A with bitumen was tested by using two methods: attempting to form an emulsion with the bitumen extracted from the MFT, and checking the water solubility of a dry film of bitumen on a glass slide with and without polymer A. Polymer A's interaction with “clean” MFT (i.e., bitumen was removed) was also tested, and its performance as a primary flocculant for MFT evaluated. The results of these tests are presented in section 5.3.3.

5.3.3.1 Glass slide and emulsion tests

The glass slide tests were carried allowed a visual determination of the interaction between the bitumen obtained from the MFT and the polymer suspensions. It was expected that polymers capable of surface interactions with bitumen would result in bitumen dissolution. Figure 5.10 shows the experimental setup at the start (top) and the end (bottom) of the test.

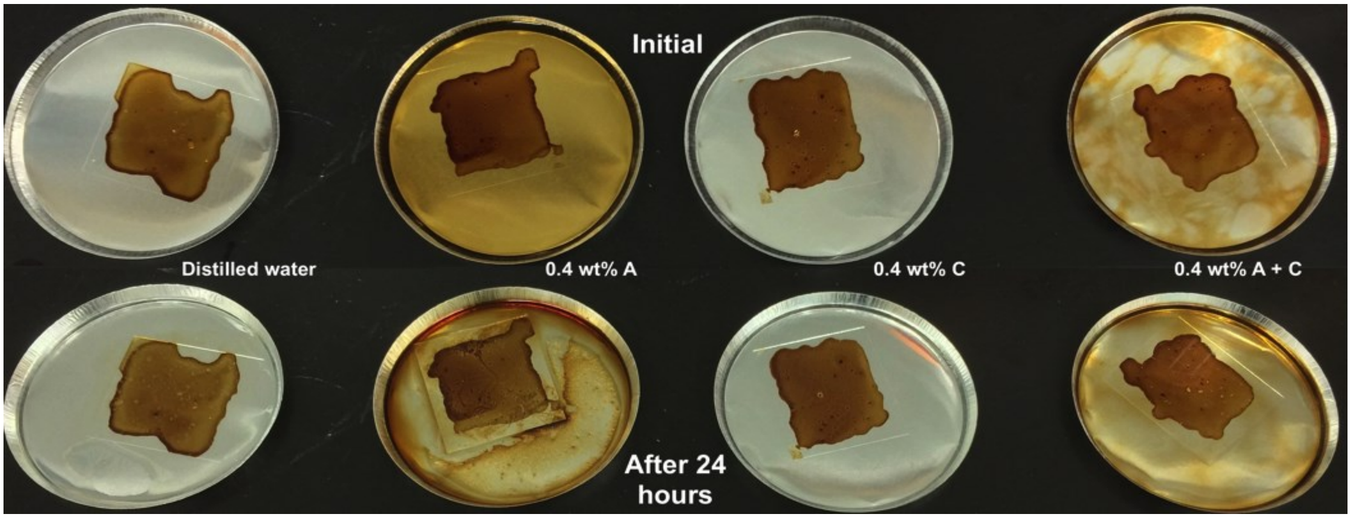


Figure 5.10 – Glass slide test for bitumen-lignosulfonate interactions at the start (top) and end (bottom) of the experiment

After 24 hours, only the glass slide immersed in polymer A shows considerable dissolution of bitumen. The slide immersed in a mixture of A and C shows some degree of bitumen dissolution, while distilled water and polymer C show no interaction with the bitumen.

The possible interactions between polymers and residual bitumen were also tested by emulsion tests. Figure 5.11 shows the result of the test, compared to a similar test performed on bitumen/toluene mixture and distilled water.

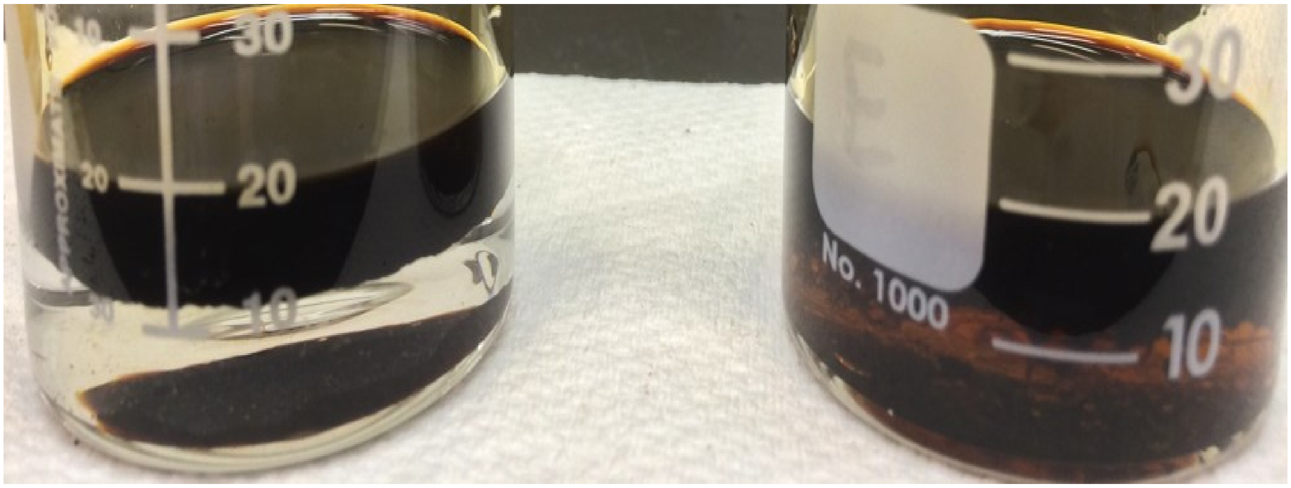


Figure 5.11 - Emulsion test. Left: bitumen in toluene/distilled water; Right: bitumen in toluene/polymer A solution.

Figure 5.11 shows that a rag layer forms between the phase of polymer A solution and bitumen solution, where a significant migration of bitumen to the water phase was observed when the water contained 0.4% polymer A. The distilled water test shows two distinct layers as expected without bitumen migration. These two simple tests show that polymer A does indeed posses the ability to interact with the residual bitumen in MFT.

5.3.3.2 Elemental analysis

The bitumen obtained from MFT was dissolved in toluene and mixed with a polymer A solution. The aqueous phase was collected after 24 hours and mixed with methylene chloride to dissolve the organic matter. The methylene chloride phase was dried after 24 hours, and the resultant dry solids were subjected to elemental analysis. Table 5.2 shows the results of the elemental analysis, and compares the results of the solids with dry polymer A.

Table 5.2 – Elemental analysis of solids obtained by separation and polymer A, compared to that of bitumen.

	% Nitrogen	%Carbon	%Hydrogen	%Sulfur
Average of solid sample	0.36	36.28	3.10	5.58
Average of Polymer A	0.33	40.49	4.44	4.35
Bitumen (Selucky et al, 1976)	0.40	83.15	10.30	4.58

Although the sulphur and nitrogen contents are similar to that of bitumen in oil sands (Selucky et al, 1976; Hitchon, 1993), the carbon contents were significantly lower than that of bitumen. It is possible that the materials that migrated to the aqueous phase in the presence of polymer A were a mixture of organic and inorganic matters, such as bitumen-coated fine clays or materials similar to kerogen, humic substances, etc. Further characterization of these materials and the interactions between lignosulfonate and bitumen need to be carried out.

5.3.3.3 Dual polymer flocculation of MFT with bitumen removed

An MFT sample was treated using the Dean-Stark method to remove the bitumen, after which the solids were re-dissolved in distilled water according to a solids weight percent of 35 wt%. The sample was then subjected to dual polymer treatment using 1000 ppm each of polymers A and C at 0.4 wt% each, at 600 rpm. Polymer A was added at 02:00, polymer C at 05:00 and the stirring stopped at 07:30.

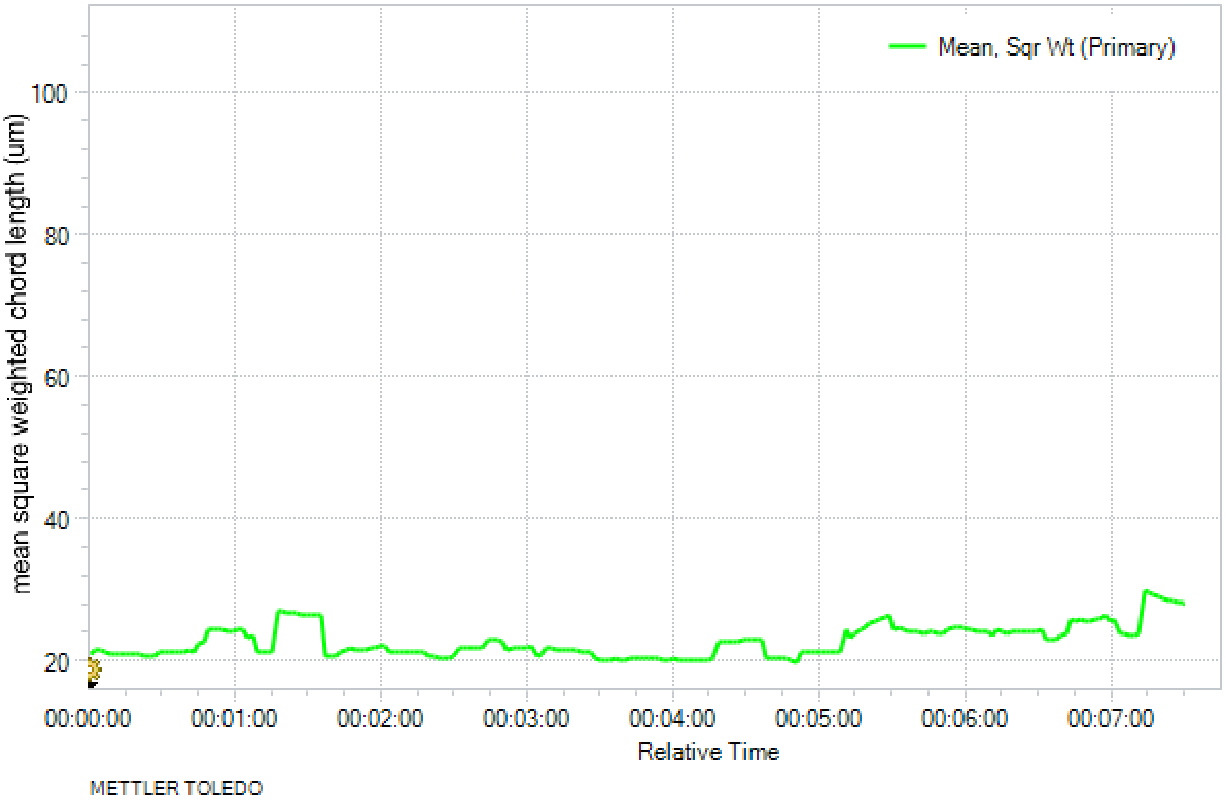


Figure 5.12 – Change in mean square weighted chord length upon flocculation of MFT with bitumen removed

Figure 5.12 shows the change in the mean square weight chord length of the MFT particles upon flocculation using a combination of polymers A and C. It is clear that the removal of bitumen from the MFT reduces the flocculation efficiency considerably. This agrees with the findings of Klein et al. (2013), who found that a reduction of bitumen content in MFT beyond 0.18 wt% reduces flocculation efficiency using a HMW anionic HPAM flocculant.

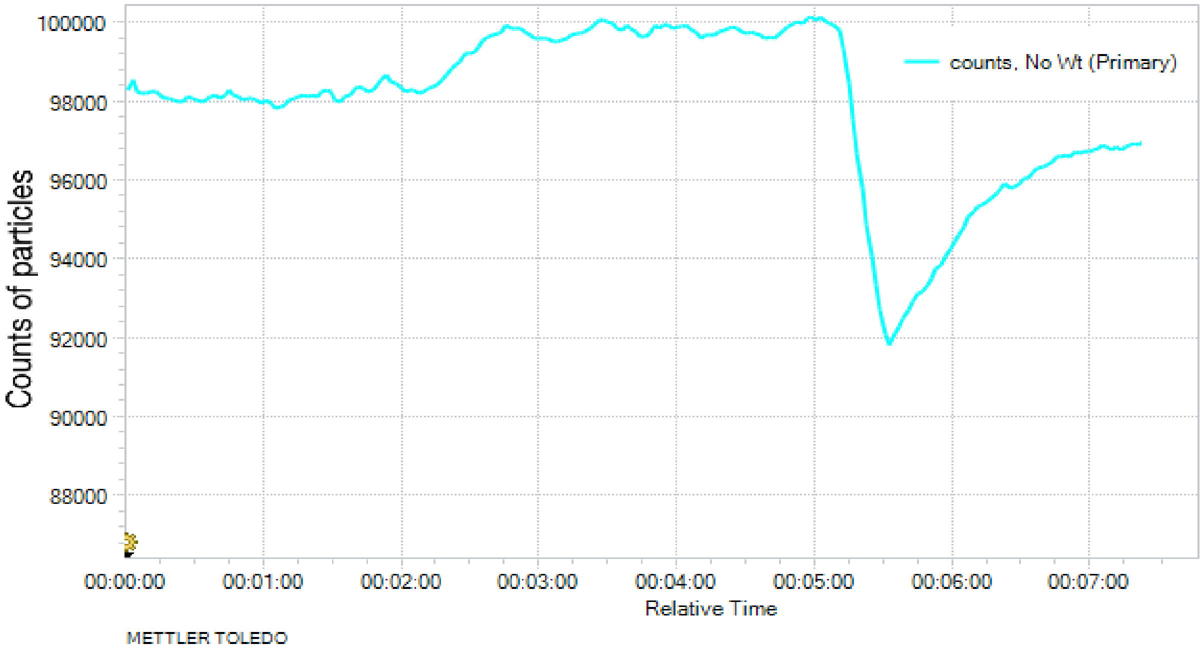


Figure 5.13 – Change in overall counts of particles upon addition of polymers A and C

Figure 5.13 shows the overall change in counts of particles in the MFT with bitumen removed upon addition of the polymers A and C. The interesting observation from Figure 5.13 is the increase in counts of particles upon addition of polymer A. Figure 5.14 shows that the majority of these dispersed particles are below 10 μm in size.

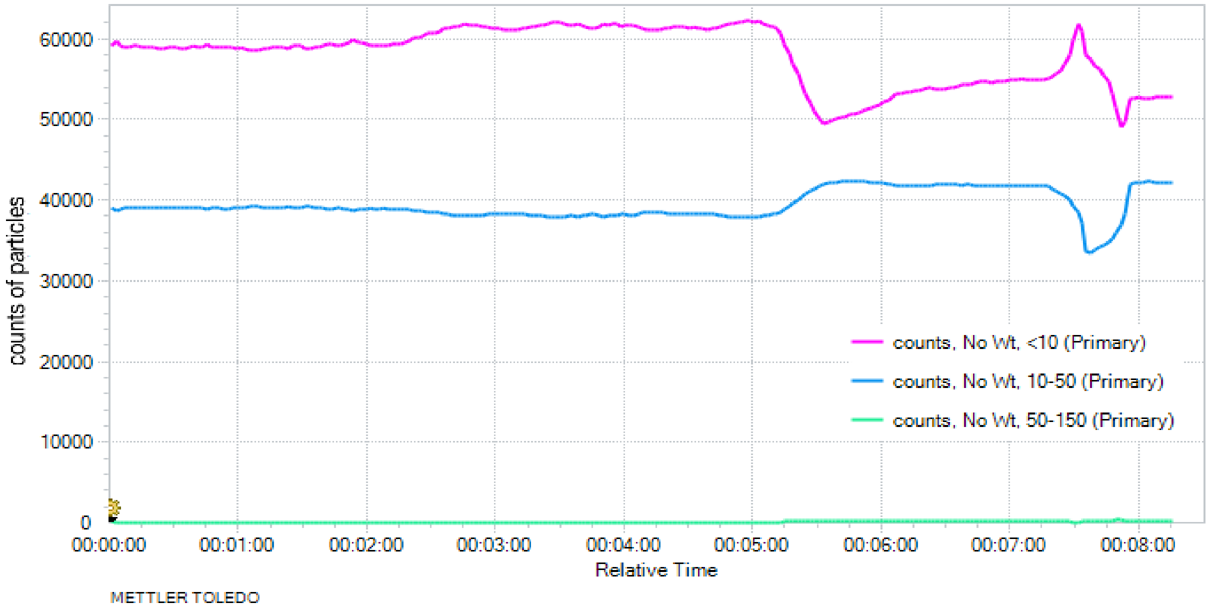


Figure 5.14 – Change in counts of particles below 150 μm in size upon addition of polymers A and C

It is useful to compare the results to Figure 5.5, where such an increase occurs for a dosage of 2000 ppm polymer A but not for the lower dosages. This suggests that in the regular MFT, some of the polymer A interacts with the residual bitumen, with the remainder acting as dispersant for the fine clays. In the case of the bitumen-free MFT, all of the polymer A can behave as a dispersant, resulting in a more noticeable increase in counts. While addition of polymer C reduces the overall counts, the reduced flocculation efficiency results in flocs that are easily broken, as shown by the subsequent increase in counts.

5.4. Conclusions

The use of dual polymers for the flocculation and dewatering of MFT was investigated using a combination of biomass derived LMW polymers and an industrially used HMW PAM based polymer. The dual polymer systems were compared to the use of a single HMW polymer alone. The flocculation and dewatering performance was assessed using real-time FBRM monitoring of floc size and fines capture, water release and quality and CST measurements. Experiments were also carried out to investigate the interaction of the lignosulfonate with the residual bitumen in MFT. The major findings of this study are summarized below:

1. The use of a dual polymer system consisting of LMW anionic lignosulfonate polymer and anionic HMW PAM based flocculant A3335 results in better fines capture performance compared to the use of A3335 alone for MFT flocculation.
2. After 24 hours settling, the dual polymer combination of lignosulfonate and A3335 resulted in lower capillary suction time (CST) than that from single polymer treatments using A3335, with comparable CST observed only at high A3335 dosages.
3. The dual polymer treatment of lignosulfonate and A3335 produced considerably higher net water release (and clearer water) compared to single polymer treatment using A3335.
4. The lignosulfonate (polymer A) likely interacts with the residual bitumen present in the MFT, improving access to fine particles for the HMW flocculant A3335 and increasing the flocs strength.
5. An optimum dosage of lignosulfonate for best CST, water release and fines capture exists, possibly between 500 and 1000 ppm. Overdosage occurs at a dosage of 2000 ppm and above.
6. The use of the FBRM method allows effective in-situ monitoring of flocculation of MFT, providing insight into the mechanisms and kinetics of the flocculation processes.

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Chapter 6 – Conclusions

6. Conclusions

6.1 Major findings

The major findings from the studies on kaolinite suspensions and MFT are listed in this section.

6.1.1 Dual polymer studies on kaolinite suspensions

a. The use of a dual polymer system consisting of a cationic LMW Cellulose based coagulant (Celquat) and an anionic HMW PAM based flocculant (A3335) results in better fines removal performance (and hence low turbidity of supernatant) compared to the use of A3335 alone, while exhibiting similarly fast settling rate.
b. After 24 hours settling, the dual polymer system results in settled beds with a similar CST to that produced by a A3335 alone, resulting in fast water release characteristics. Over an extended period of time, the CST of the bed produced using the dual polymer system is even lower than that produced by the single HMW polymer.
c. The cellulose based Celquat polymers have been found to be effective primary additives.
d. The addition of lignosulfonate (an anionic dispersant) along with a LMW Celquat polymer results in the lowest turbidity of the supernatant, but also results in a slow settling rate and relatively high CST.
e. The use of the FBRM method allows effective in-situ monitoring of kaolinite flocculation processes, providing insight into the mechanisms and kinetics of the flocculation processes.

6.1.2 Dual polymer studies on MFT

a. The use of a dual polymer system consisting of LMW anionic lignosulfonate polymer and anionic HMW PAM based flocculant A3335 results in better fines removal performance compared to the use of A3335 alone for MFT flocculation.
b. After 24 hours settling, the dual polymer combination of lignosulfonate and A3335 resulted in lower capillary suction time (CST) than that from single polymer treatments using A3335, with comparable CST observed only at high A3335 dosages.
c. The dual polymer treatment of lignosulfonate and A3335 produced considerably higher net water release (and clearer water) compared to single polymer treatment using A3335.
d. The lignosulfonate polymer likely interacts with the residual bitumen present in the MFT, improving access to fine particles for the HMW flocculant A3335.

e. An optimum dosage of lignosulfonate for best CST, water release and fines capture exists, possibly between 500 and 1000 ppm. Overdosage occurs at a dosage of 2000 ppm and above.
f. The use of the FBRM method allows effective in-situ monitoring of flocculation of MFT, providing insight into the mechanisms and kinetics of the flocculation processes.

6.2 Discussion on major findings

The results of the experiments presented in chapters 4 and 5 show some interesting differences. The experiments on kaolinite in chapter 4 were carried out in order to understand the mechanism of flocculation using dual polymer systems. It was hoped that these studies would also provide some insight into dual polymer flocculation of MFT, as kaolinite is the major clay component in MFT.

Dual polymer systems consisting of a cationic LMW cellulose based coagulant (Celquat) and a HMW PAM based flocculant (A3335, also referred to as C) were found to perform better than single polymer treatment using A3335 alone. The performance was assessed based on fines removal performance, turbidity of the supernatant, CST and real time monitoring of flocculation using the FBRM technique.

It was suggested that the dual polymer flocculation of kaolinite suspensions can be explained by the electrostatic patch model (Gregory, 1973). The Celquat additives appeared to aggregate particles into loose small flocs through charge neutralization. These small flocs were then bridged by the HMW A3335 flocculant. The coagulant Celquat SC240c (referred to as B4) appeared to produce the loosest primary flocs. Although these flocs were more prone to breakage upon application of shear, upon addition of the A3335 flocculant, the secondary flocs produced were large and loosely packed, enhancing dewatering rates. The results obtained for floc size, CST and turbidity were compared with those from other studies and were found to perform better or to be comparable under relevant conditions.

Other than producing the lowest supernatant turbidity when used in combination with Celquat SC240c, the use of lignosulfonate (also referred to as A) did not appear to produce any beneficial results in terms of floc size, settling rates or CST, and was therefore not considered to perform well as a primary additive. The lignosulfonate behaved as a dispersant and did not form the porous fibrous network when used in combination with Celquat polymers as hoped for based on the sulphite paper pulping process.

Chapter 5 presented the work performed on dual polymer flocculation of MFT. The results show that a dual polymer treatment consisting of lignosulfonate followed by A3335 performed better than a single polymer treatment of A3335 alone. This performance was assessed based on fines capture and flocculation monitoring using the FBRM technique, CST measurements of the settled beds and water release using standard test sieves. The dual polymer system was found to produce large and loose flocs, enhancing dewatering.

It was suggested that the lignosulfonate interacts with the residual bitumen present in the MFT, improving access to fine particles for the HMW flocculant A3335. Studies that suggested possible interaction of lignosulfonate with bitumen were cited (Novosad, 1984; Shevchenko and Bailey, 1996). A mechanism of dual polymer flocculation occurring for this system was suggested based on the experimental results and literature on MFT and clay flocculation. The interaction of lignosulfonate with the residual bitumen from the MFT tested was investigated using a series of tests. Visual tests strongly indicate that the lignosulfonate possesses the ability to interact with bitumen. However, the elemental analysis performed was inconclusive.

The optimum dosage range for lignosulfonate was suggested to be between 500 and 1000 ppm (based on MFT solids content). Overdosage was found to occur at 2000 ppm. An A3335 dosage of 2000 was also found to be an overdosage.

The celquat polymers were found to be ineffective for use as first additives in MFT, with dual polymer systems consisting of celquat additives followed by A3335 resulting in very low fines capture and similar CST to untreated MFT. The effectiveness of lignosulfonate and lack thereof of Celquat polymers as first additives in MFT has been attributed to the presence of residual bitumen in the MFT. Literature has been cited on the negative effects of residual bitumen on MFT flocculation, and the preferential adsorption of HMW flocculants on clay surfaces rather than bitumen or sand surfaces (Klein et al, 2013). The MFT used in this study was from the Athabasca region, and had a relatively high residual bitumen content of 2.59%.

The FBRM technique was found to be a useful real-time flocculation monitoring tool for both kaolinite and MFT flocculation. The technique allows the measurement of particle size distributions and fines capture, providing insight into the mechanisms involved in the flocculation processes.

6.3 Suggested further study

A number of knowledge gaps still exist on the dual polymer flocculation of MFT using a combination of lignosulfonate and A3335. Most importantly, the nature of the interactions between lignosulfonate and the residual bitumen in MFT requires further study in order to be fully understood. Future studies may involve the Quartz Crystal Microbalance – Dispersion (QCM-D) method in order to gain insight into the strength of interaction between bitumen and lignosulfonate. Scanning Electron Microscopy (SEM) images of the MFT treated with lignosulfonate and A3335 should provide information regarding the changes occurring and structures formed during dual polymer treatment.

Specific Resistance to Filtration (SRF) studies on the flocculated MFT would provide useful information on the filterability of the settled beds that would be required to evaluate the industrial feasibility of this method of treating MFT.

Other areas of interest for further study include the optimum dosage of the polymers used (while the experiments presented in this thesis managed to provide a range, further studies could provide specific optimum dosages), optimum agitation speed and possibly changes to pH. While dual polymer treatments have been shown to result in better water release than single polymer treatments, the net water release is still only a small fraction of the total water trapped in the MFT, and better further studies on dewatering are required.

Although the LMW cationic Celquat polymers at low dosage were ineffective as first additives in the dual polymer treatment of MFT, the use of a dual polymer system of a Celquat polymer and a HMW flocculant may perform well if preceded either at high dosage or by a pre-treatment stage of the MFT using lignosulfonate. Lastly, the HMW flocculant A3335 used in this study was an unbranched PAM based polymer. The use of branched HMW flocculants may also show better flocculation performance, and one polymer of particular interest may be branched HMW polyacrylamide.

6.4 Summary

The objective of this thesis was to study the consolidation and dewatering of MFT using dual polymer flocculation. The first additives used were biomass derived and biodegradable – four LMW cationic cellulose-based Celquat polymers, and a LMW anionic lignosulfonate. The flocculant used was a HMW anionic PAM based polymer A3335. In the first stage of this study, the dual polymer treatment was carried out on kaolinite suspensions in order to better understand the mechanisms and kinetics of flocculation, and to gain insight into MFT flocculation as kaolinite is the major clay component of MFT. The second stage was the dual polymer treatment of MFT using the same polymers. The performances of the treatments were assessed in terms of floc size and fines capture, monitored in real time using the FBRM technique, water release and quality and CST of the flocculated mixtures. The performance of the dual polymer treatments was also compared to that of a single HMW polymer, A3335 alone.

A dual polymer combination of Celquat coagulant and A3335 flocculant was found to perform best for kaolinite suspensions, with Celquat SC240c performing the best out of the four. However, the use of a dual polymer combination of lignosulfonate followed by A3335 resulted in the best fines capture, dewatering and CST performance for MFT. Mechanisms for the dual polymer flocculation of kaolinite and MFT were suggested based on experimental results and literature. The beneficial effect of using lignosulfonate as a first additive was attributed to its interaction with the residual bitumen in MFT. Tests were carried out that strongly indicate lignosulfonate possesses the ability to interact with the residual bitumen. The use of FBRM in MFT flocculation monitoring is relatively novel, and has proved useful in this study. Knowledge gaps and further studies to account for these gaps were identified and experimental techniques were suggested.

In both MFT and kaolinite suspensions, dual polymer treatment using a LMW additive and a HMW flocculant performed better than a single polymer treatment using HMW polymer alone. The benefits in MFT included better fines capture, increased water release and clarity and lower CST. Further study into the nature of interaction of lignosulfonate and MFT, and the use of different HMW flocculants is required. The results from this work suggest great potential for the use of a dual polymer system consisting lignosulfonate and a HMW flocculant to treat MFT. Further research could result in the development of a process that allows accelerated consolidation and dewatering of fresh and legacy MFT, allowing reuse of trapped water with little negative effect on the environment. Such a process would prove invaluable to tailings management and the oil sands mining industry as whole for the foreseeable future.

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Appendix

Appendix

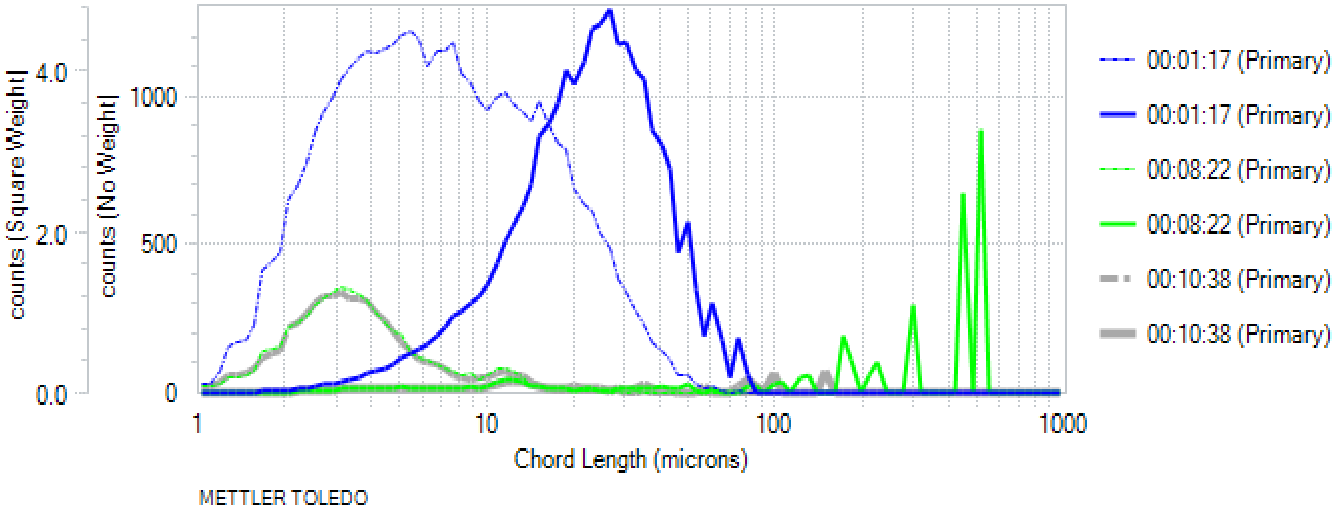


Figure A.1 - Counts of particles against chord length using the no weight method (dotted lines) and square weight method (solid lines) for kaolinite flocculation at 100 rpm stirring.

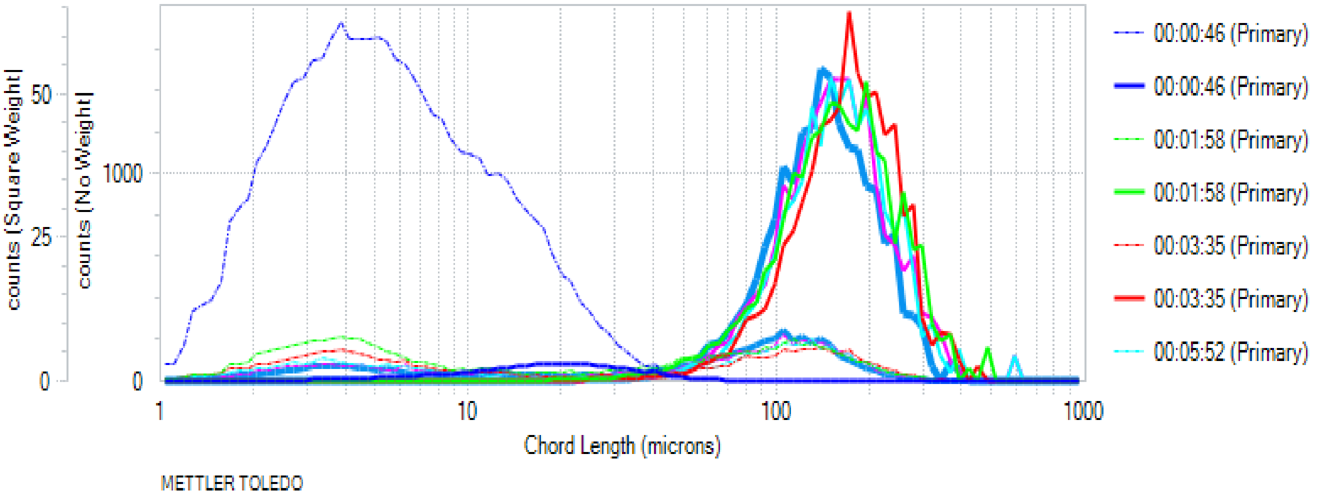


Figure A.2 - Counts of particles against chord length using the no weight method (dotted lines) and square weight method (solid lines) for kaolinite flocculation at 300 rpm stirring.

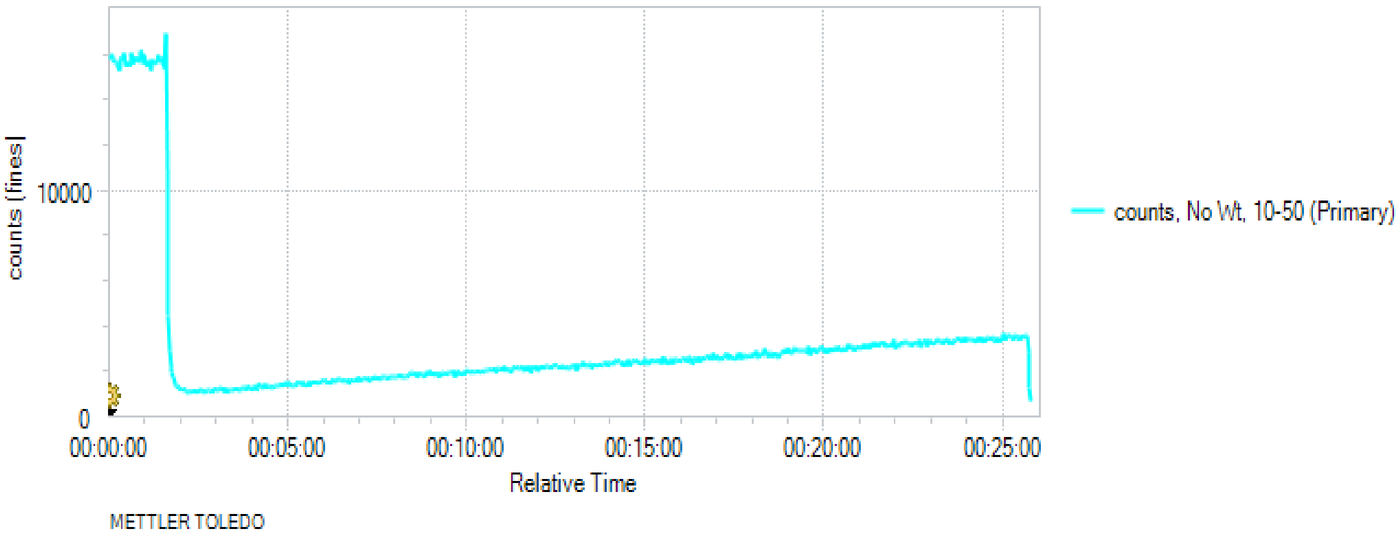


Figure A.3(a) - Counts of particles of size 10-50 μm against time for kaolinite flocculation at 400 rpm. A3335 added at 01:40.

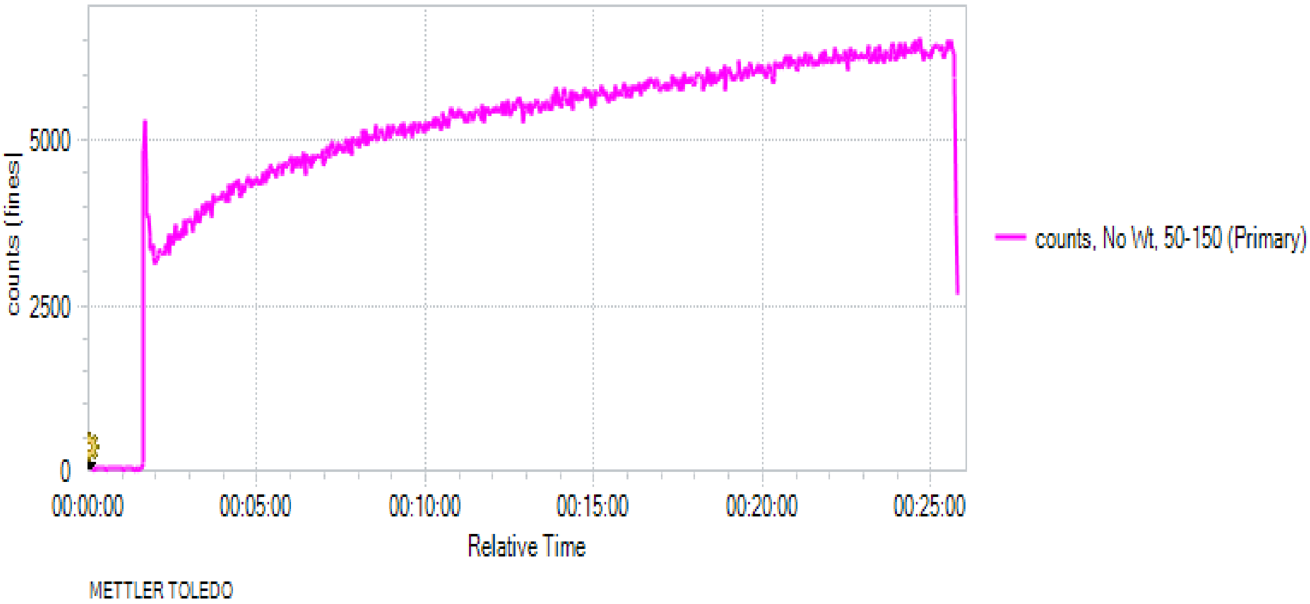


Figure A.3(b): Counts of particles of size 50-150 μm against time for kaolinite flocculation at 400 rpm. A3335 added at 01:40.

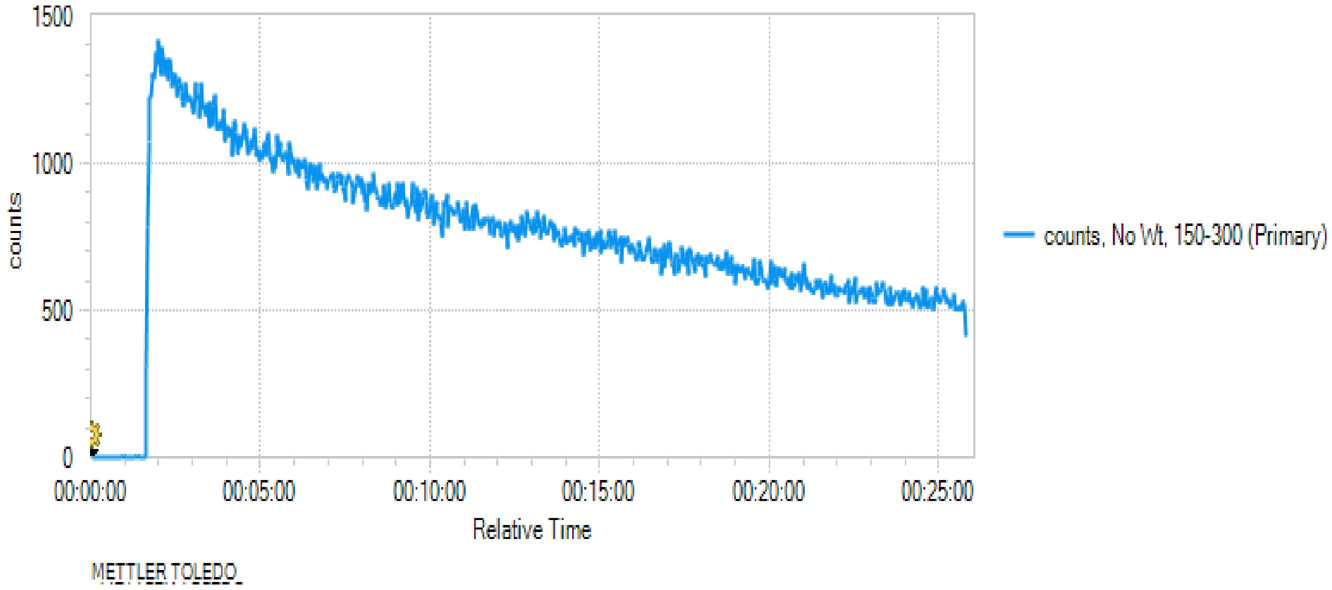


Figure A.3(c): Counts of particles of size 150-300 µm against time for kaolinite flocculation at 400 rpm. A3335 added at 01:40.

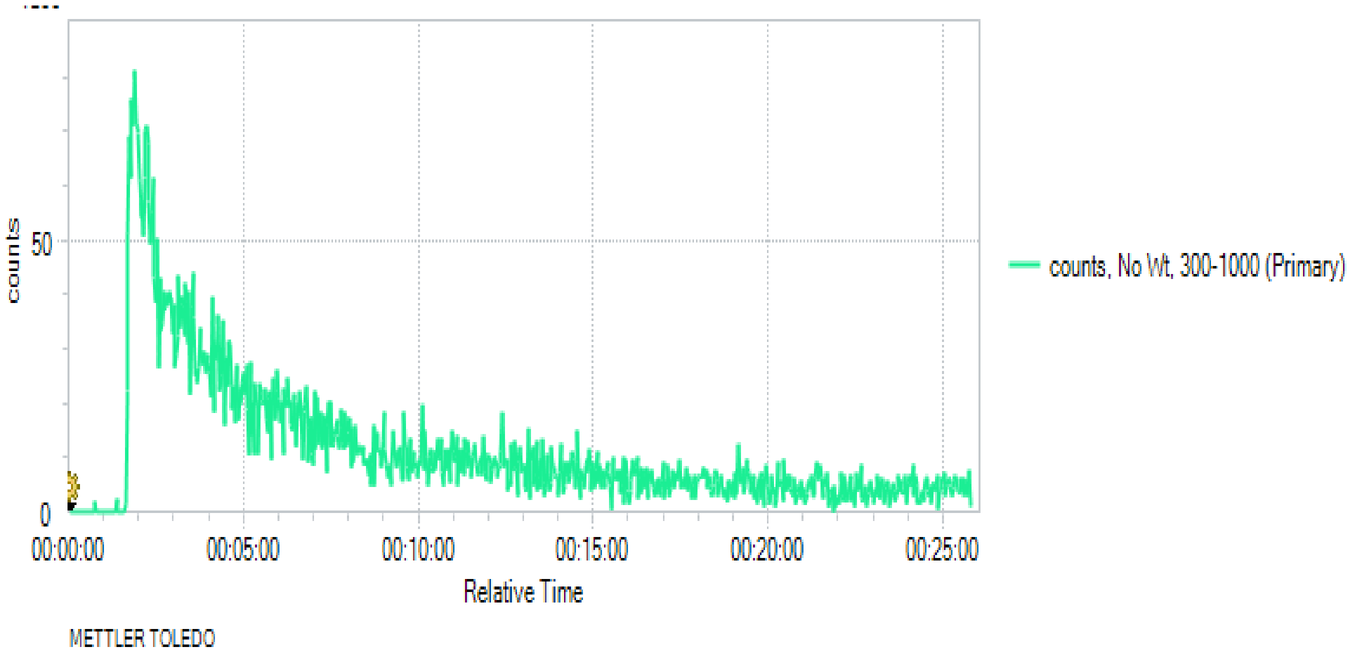


Figure A.3(d): Counts of particles of size 300-1000 µm against time for kaolinite flocculation at 400 rpm. A3335 added at 01:40.

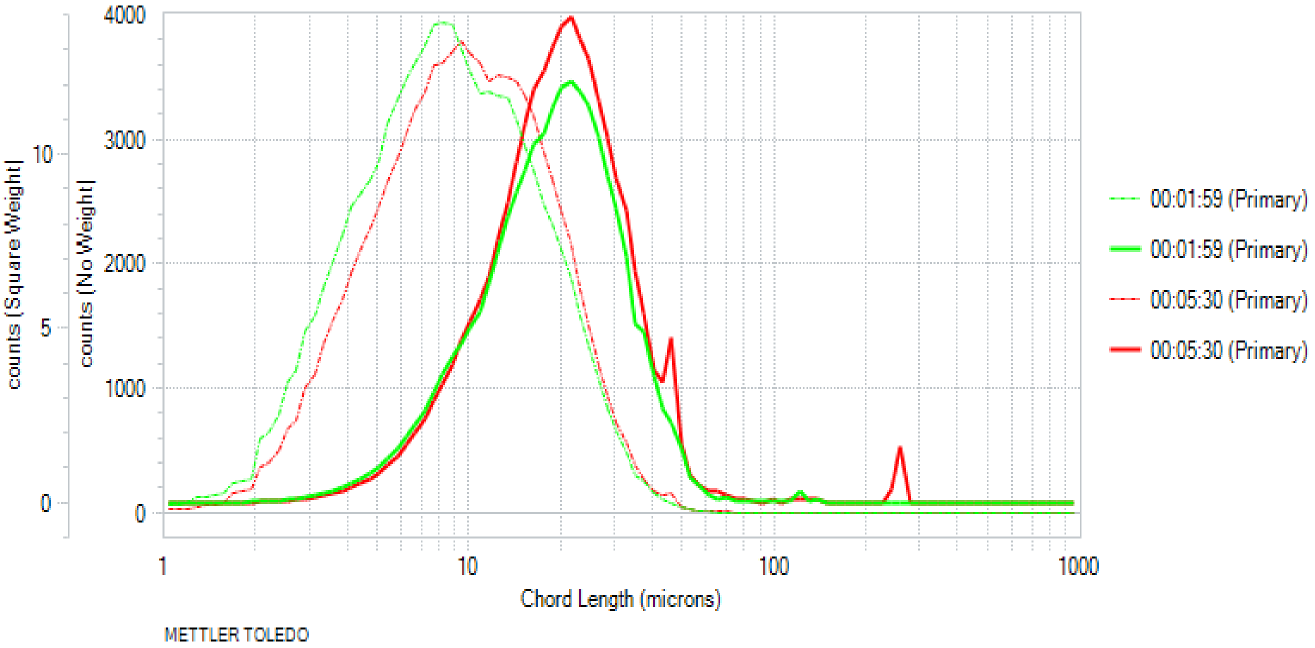
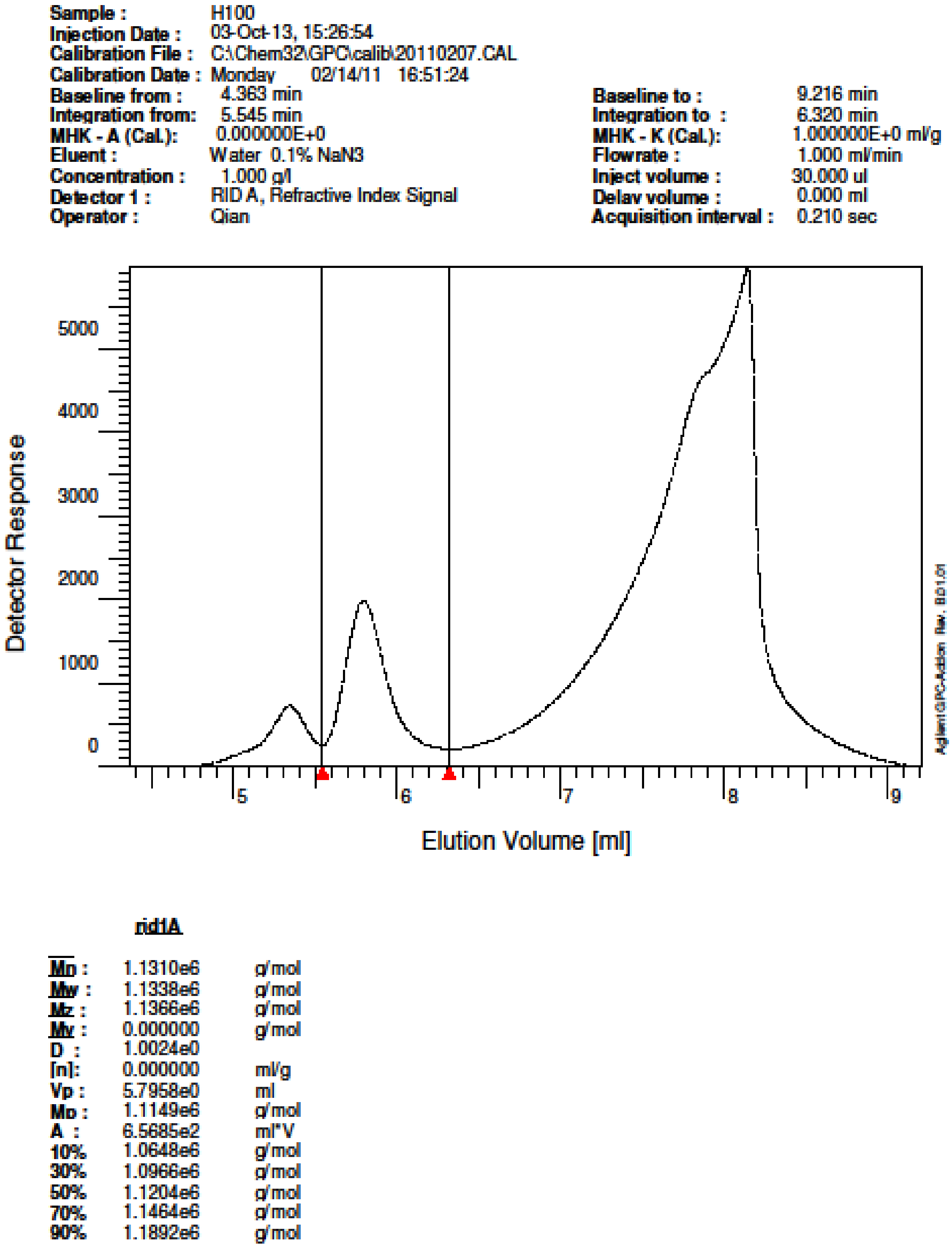


Figure A.4 - Counts vs chord length for MFT flocculation at 400 rpm stirring



Sample : H100
Injection Date : 03-Oct-13, 15:26:54
Calibration File : C:\Chem32\GPC\calib\20110207.CAL
Calibration Date : Monday 02/14/11 16:51:24
Baseline from : 4.363 min
Integration from: 5.545 min
MHK - A (Cal.): 0.000000E+0
Eluent : Water 0.1% NaN3
Concentration : 1.000 g/l
Detector 1 : RID A, Refractive Index Signal
Operator : Qian

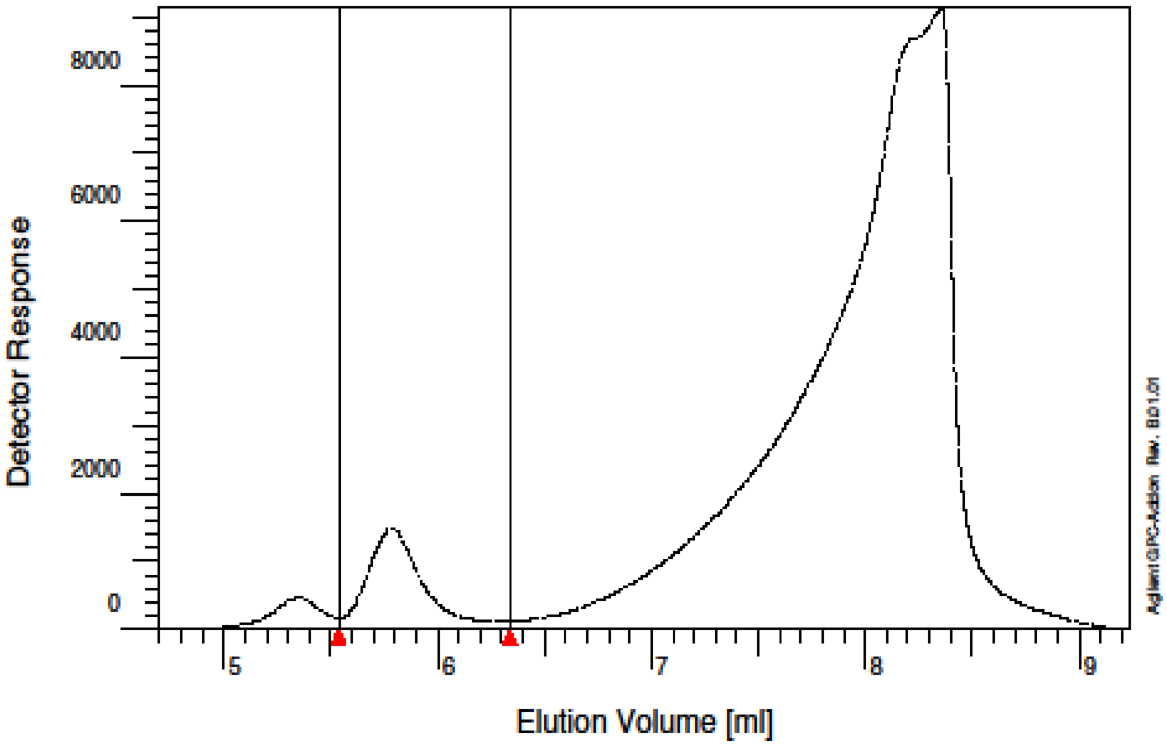
Baseline to : 9.216 min
Integration to : 6.320 min
MHK - K (Cal.): 1.000000E+0 ml/g
Flowrate : 1.000 ml/min
Inject volume : 30.000 ul
Delay volume : 0.000 ml
Acquisition interval : 0.210 sec

rid1A

Mn :	1.1310e6	g/mol
Mw :	1.1338e6	g/mol
Mz :	1.1366e6	g/mol
Mv :	0.000000	g/mol
D :	1.0024e0	
[n]:	0.000000	ml/g
Vp :	5.7958e0	ml
Mp :	1.1149e6	g/mol
A :	6.5685e2	ml*V
10%	1.0648e6	g/mol
30%	1.0966e6	g/mol
50%	1.1204e6	g/mol
70%	1.1464e6	g/mol
90%	1.1892e6	g/mol

Figure A.5 – Gel Permeation Chromatogram for Celquat H100

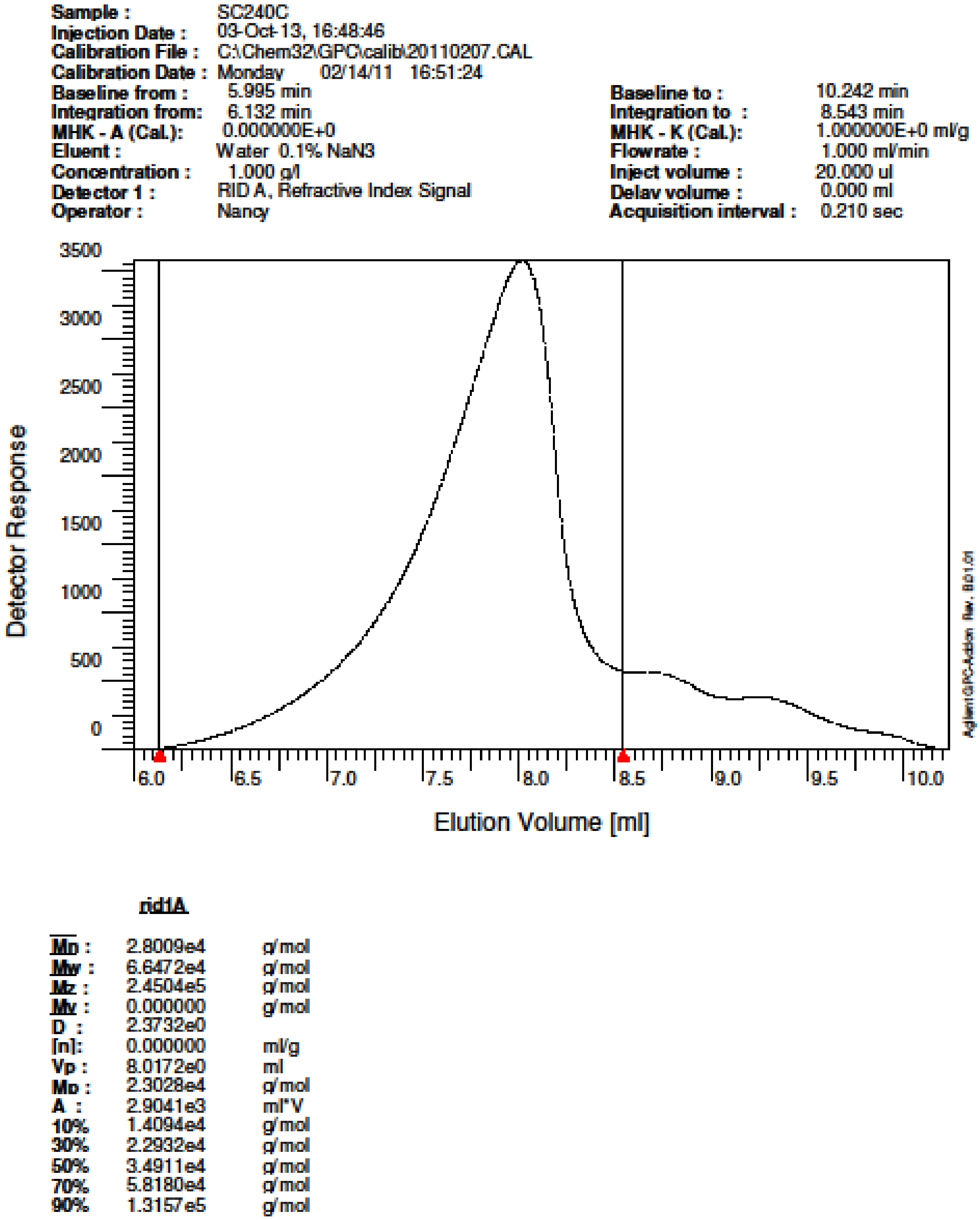
```
Sample :            L200
Injection Date :    03-Oct-13, 16:07:21
Calibration File :  C:\Chem32\GPC\calib\20110207.CAL
Calibration Date :  Monday      02/14/11    16:51:24
Baseline from :      4.694 min                                  Baseline to :             9.242 min
Integration from:    5.537 min                                  Integration to  :         6.337 min
MHK - A (Cal.):     0.000000E+0                                 MHK - K (Cal.):          1.000000E+0 ml/g
Eluent :            Water  0.1% NaN3                            Flowrate :                1.000 ml/min
Concentration :      1.000 g/l                                  Inject volume :          30.000 ul
Detector 1 :        RID A, Refractive Index Signal              Delay volume :            0.000 ml
Operator :          Qian                                        Acquisition interval :    0.210 sec
```



```
              ridlA

Mn :     1.1250e6        g/mol
Mw :     1.1275e6        g/mol
Mz :     1.1301e6        g/mol
Mv :     0.000000        g/mol
D  :     1.0022e0
[n]:     0.000000        ml/g
Vp :     5.7852e0        ml
Mp :     1.1107e6        g/mol
A  :     4.5246e2        ml*V
10%      1.0639e6        g/mol
30%      1.0936e6        g/mol
50%      1.1157e6        g/mol
70%      1.1400e6        g/mol
90%      1.1815e6        g/mol
```

Figure A.6 – Gel Permeation Chromatogram for Celquat L200



Sample : SC240C
Injection Date : 03-Oct-13, 16:48:46
Calibration File : C:\Chem32\GPC\calib\20110207.CAL
Calibration Date : Monday 02/14/11 16:51:24
Baseline from : 5.995 min
Integration from: 6.132 min
MHK - A (Cal.): 0.000000E+0
Eluent : Water 0.1% NaN3
Concentration : 1.000 g/l
Detector 1 : RID A, Refractive Index Signal
Operator : Nancy

Baseline to : 10.242 min
Integration to : 8.543 min
MHK - K (Cal.): 1.000000E+0 ml/g
Flowrate : 1.000 ml/min
Inject volume : 20.000 ul
Delay volume : 0.000 ml
Acquisition interval : 0.210 sec

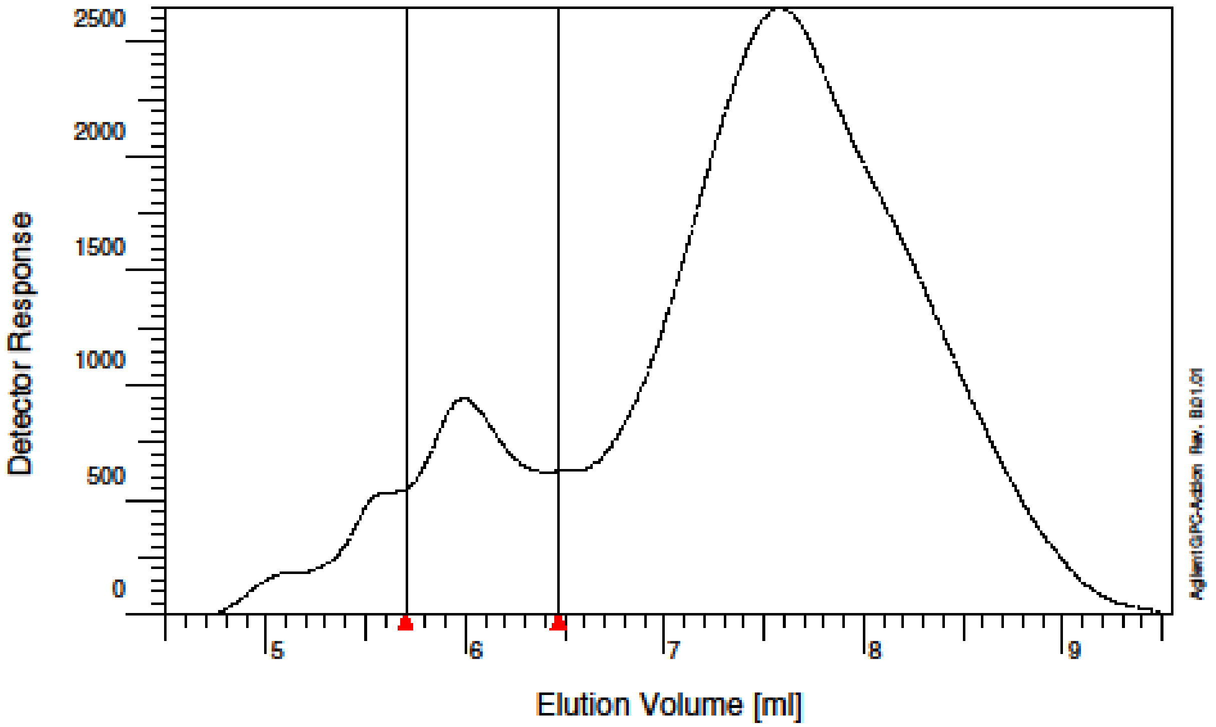
rid1A

$\overline{\mathrm{Mn}}$:	2.8009e4	g/mol
$\overline{\mathrm{Mw}}$:	6.6472e4	g/mol
$\overline{\mathrm{Mz}}$:	2.4504e5	g/mol
$\overline{\mathrm{Mv}}$:	0.000000	g/mol
D :	2.3732e0	
[n]:	0.000000	ml/g
Vp :	8.0172e0	ml
Mp :	2.3028e4	g/mol
A :	2.9041e3	ml*V
10%	1.4094e4	g/mol
30%	2.2932e4	g/mol
50%	3.4911e4	g/mol
70%	5.8180e4	g/mol
90%	1.3157e5	g/mol

Figure A.7 – Gel Permeation Chromatogram for Celquat SC240c

Sample : LS50
Injection Date : 03-Oct-13, 17:29:42
Calibration File : C:\Chem32\GPC\calib\20110207.CAL
Calibration Date : Monday 02/14/11 16:51:24
Baseline from : 4.491 min
Integration from: 5.700 min
MHK - A (Cal.): 0.000000E+0
Eluent : Water 0.1% NaN3
Concentration : 1.000 g/l
Detector 1 : RID A, Refractive Index Signal
Operator : Nancy

Baseline to : 9.555 min
Integration to : 6.468 min
MHK - K (Cal.): 1.000000E+0 ml/g
Flowrate : 1.000 ml/min
Inject volume : 50.000 ul
Delay volume : 0.000 ml
Acquisition interval : 0.210 sec



rid1A

$\overline{Mn}$: 1.1306e6 g/mol
$\overline{Mw}$: 1.1450e6 g/mol
$\overline{Mz}$: 1.1568e6 g/mol
$\overline{Mv}$: 0.000000 g/mol
D : 1.0127e0
[n]: 0.000000 ml/g
Vp : 5.9903e0 ml
Mp : 1.1929e6 g/mol
A : 5.7010e2 ml*V
10% 1.1798e6 g/mol
30% 1.1611e6 g/mol
50% 1.1411e6 g/mol
70% 1.1184e6 g/mol
90% 1.0923e6 g/mol

Figure A.8 - Gel Permeation Chromatogram for Celquat LS50

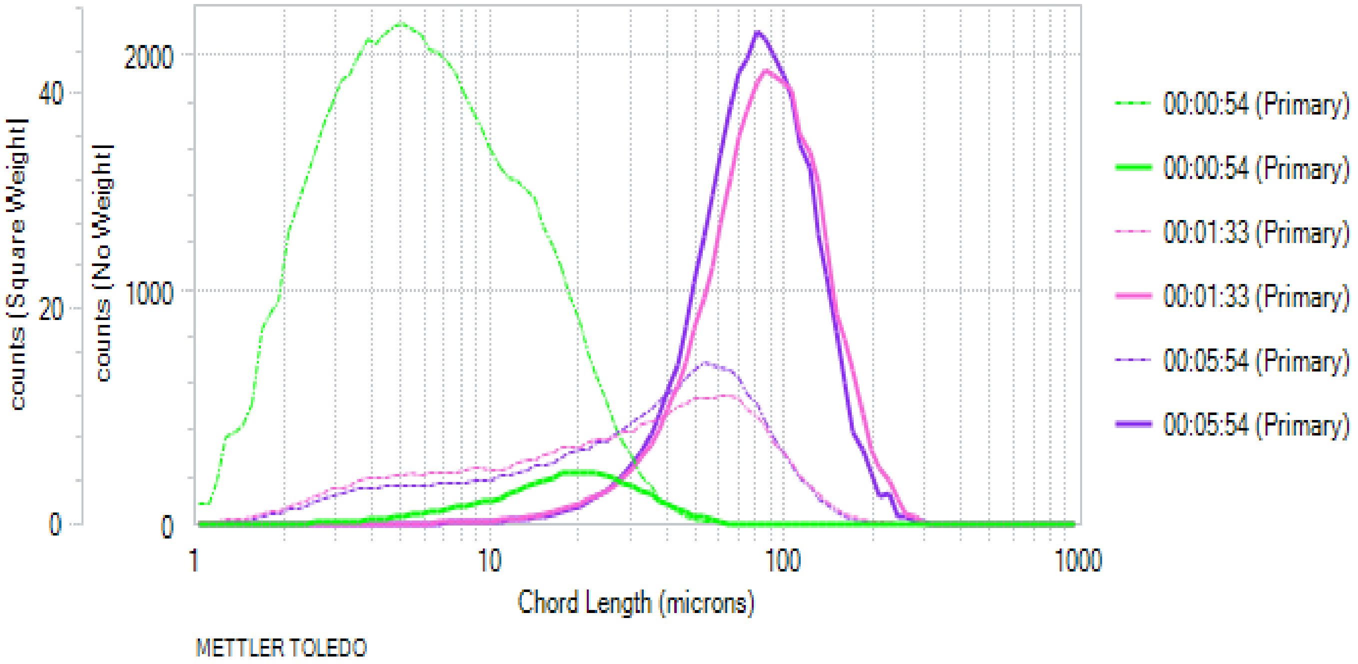


Figure A.9 – Counts vs Chord length (square weighted) for kaolinite suspension with B2 added at 01:30.

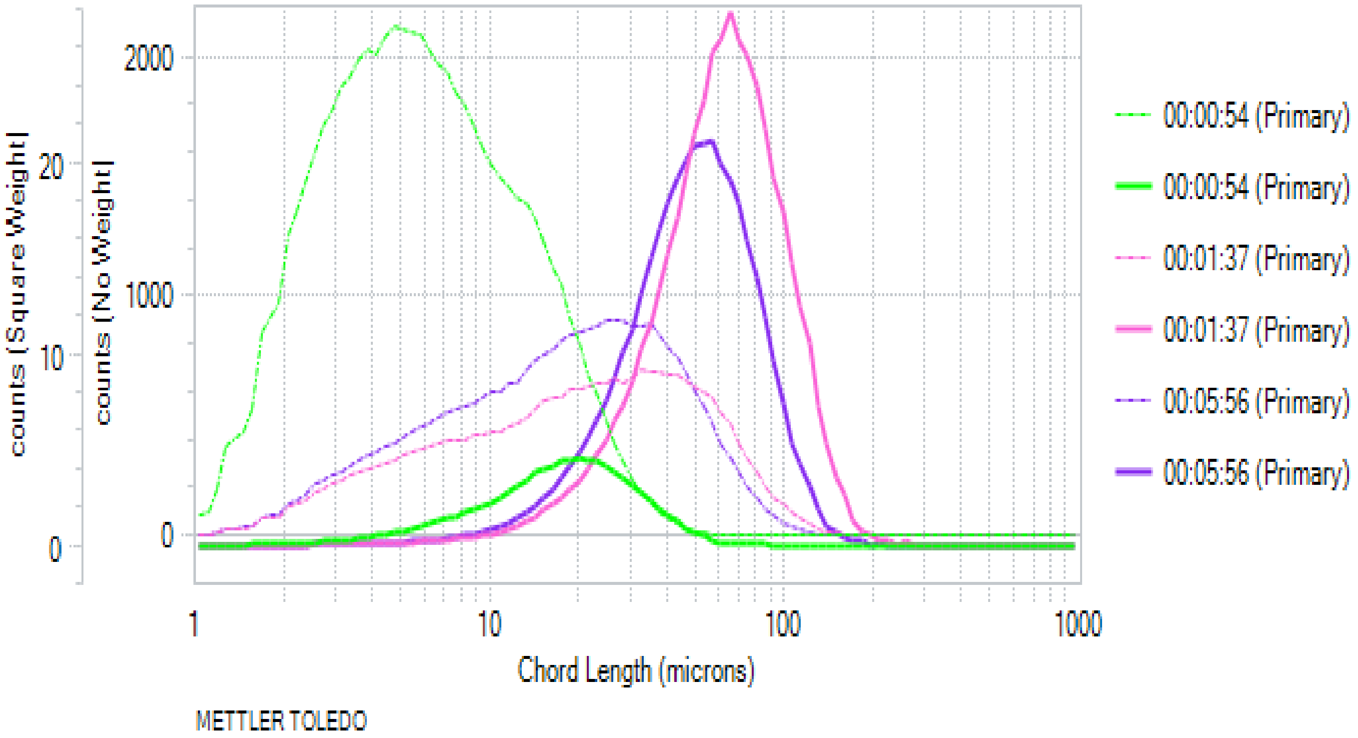


Figure A.10 – Counts vs Chord length (square weighted) for kaolinite suspension with B3 added at 01:30.

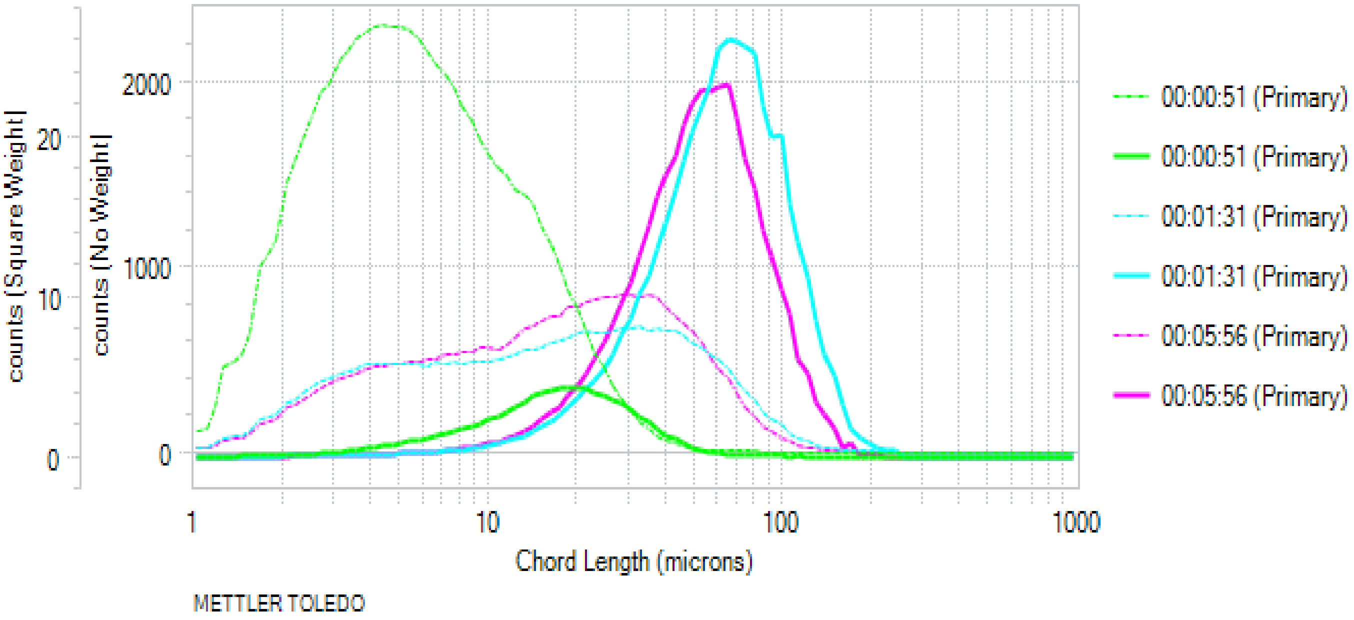


Figure A.11 – Counts vs Chord length (square weighted) for kaolinite suspension with B4 added at 01:30.

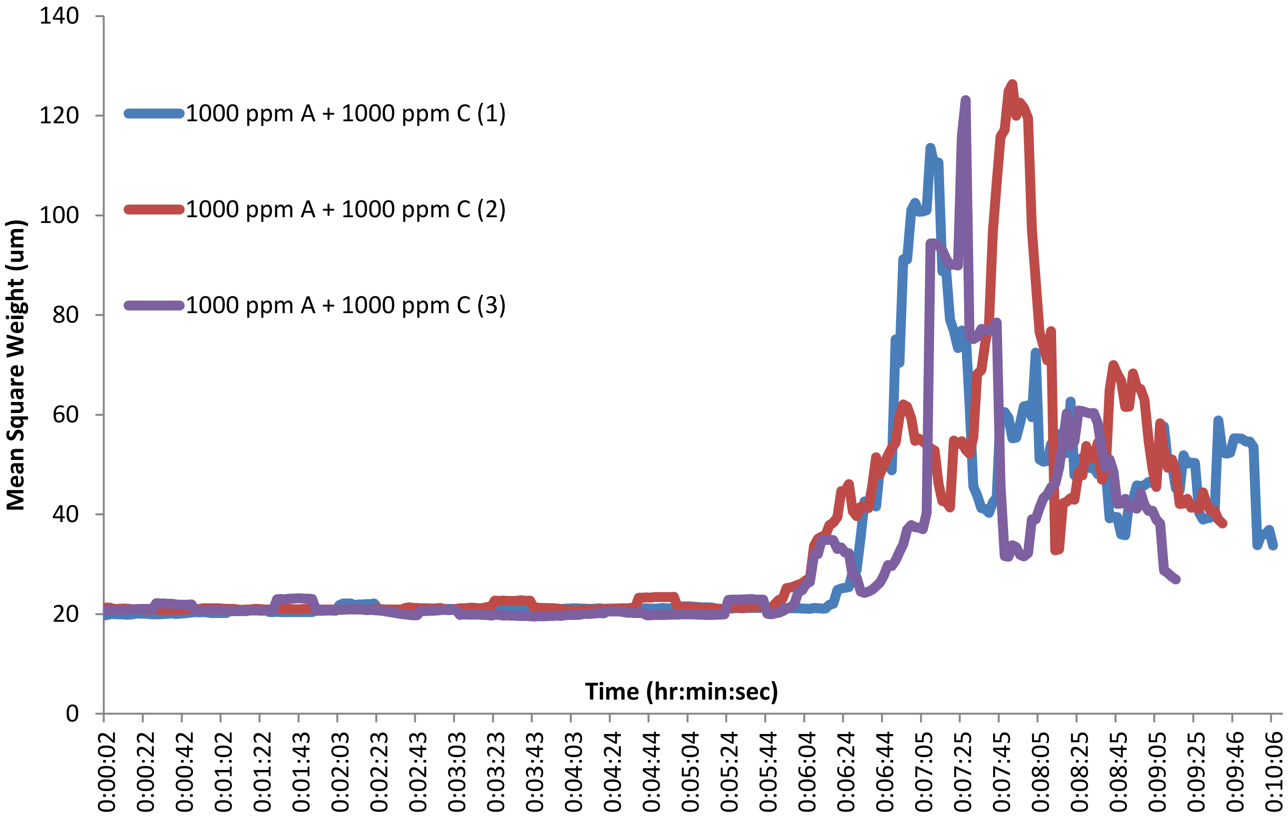


Figure A.12 – Reproducibility of flocculation performance using 1000 ppm lignosulfonate (A) followed by 1000 ppm A3335 (C)

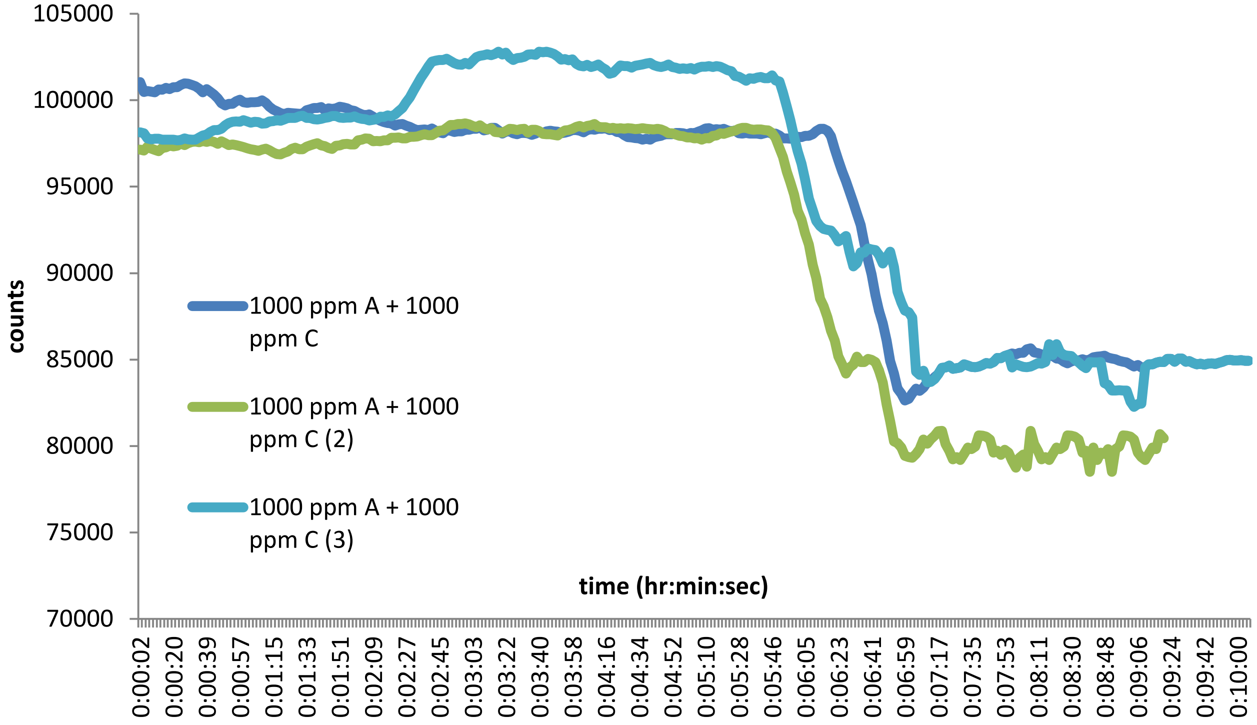


Figure A.13 – Reproducibility of fines capture performance using 1000 ppm lignosulfonate (A) followed by 1000 ppm A3335 (C)