DEVELOPMENT OF THE NEXT-GENERATION OF DEWATERING TECHNOLOGIES FOR MATURE FINE TAILINGS (MFTs) FROM OIL SANDS PROCESSING

DEVELOPMENT OF THE NEXT-GENERATION OF DEWATERING TECHNOLOGIES FOR MATURE FINE TAILINGS (MFTs) FROM OIL SANDS PROCESSING

By

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TITLE: Development of the next-generation of dewatering technologies for mature fine tailings (MFTs) from oil sands processing

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LAY ABSTRACT

The oil sands industry has been challenged by regulators to develop dewatering technologies that can stop any further growth in the massive size of existing tailings ponds and also reclaim the contents of those ponds. The current dewatering technologies have different challenges that were tried to address in this study. At the first part of the research, it was tried to develop a method for rapid investigation of the effects of salt addition followed by a mechanical method (centrifugation) on dewaterability of MFTs. In the second part it was tried to investigate freeze-thaw as a natural dewatering technique and also to investigate the possibility of mechanizing this process. In the last part, an alternative dewatering technology (rotary filtration), that is predicted to be cheaper than centrifugation, was used to dewater MFTs (amended by polymer). Therefore, a lab-scale version was made and used for polymer amended MFTs dewatering. By using this technology the solids content of MFT had around 20 wt% increase (compare to the untreated MFTs).

ABSTRACT

The oil sands industry is currently facing a challenge by regulators to develop dewatering technologies that can halt any further growth in the massive size of existing tailings ponds and also reclaim the contents of those ponds. The most recent technology involves in-tank and/or in-line addition of flocculants followed by a dewatering step (e.g. centrifugation, thin-lift dewatering). This work has focused on three different dewatering technologies. Firstly, a high-throughput method was developed to investigate the effects of ionic composition adjustment on MFTs dewatering through a centrifugation process. As a result, it was found that samples with different concentrations and valency of cations had different settling kinetic and higher concentrations and valency of cations caused faster settling. Also, changes in the ionic composition of samples suggest that there is a strong interaction (ion exchanging) between MFTs and added solution. Secondly, the effects of different factors (e.g. freezing time and temperature) on freeze-thaw dewatering of MFTs were studied using a temperature monitoring setup. It was found that partial freezing causes less dewatering compared to complete freezing after thawing. Finally, a lab-scale unit of low-speed rotary filtration was built and it was implemented to dewater polymer amended MFTs. By using this unit, effects of different factors were investigated on the dewatering efficiency of the rotary filtration unit through a DOE study. The DOE results showed that the flocculation conditions have a big impact on performance of the rotary filtration and for some of the DOE conditions, cakes were formed with more than 47 wt% which couldn't be reached by just gravity settling of polymer amended MFTs. Also, freeze-thaw of the cakes after rotary filtration could increase the solids content.

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LIST OF ABBREVIATIONS

- DOE: Design Of Experiment
- FFT: Fluid Fine Tailings
- FSC: Final Solids Content
- ICP-OES: Inductively Coupled Plasma-Optical Emission Spectrometry
- MFTs: Mature Fine Tailings
- NIR: Near Infrared
- RF: Rotary Filtration
- RFP: Rotary Fan Press
- SC: Solids content

Chapter 1: Background

1.1 Oil sands review

Oil sands constitute one of the world's largest sources of petroleum. Canada has the largest deposit of this type in Northern Alberta and Saskatchewan. Figure 1.1 shows the areas of oil sands in Western Canada. These deposits cover approximately 14,000 km². Usually, a layer of overburden (an almost bitumen-free layer consisting of sand, silt, clay and shale) lies on the top of the bitumen deposit. For the Athabasca oil sand deposit, the bitumen content (crude bitumen) ranges from 8% to 14%, the water content ranges from approximately 3% to 6% by total mass, and the mineral content (predominantly quartz, sand, silts and clay) varies approximately from 84% to 86% by total mass [1]. Currently, the total amount of recoverable bitumen is estimated to be at 300 billion barrels [1]. The first commercial oil sands operation began in 1967 with Great Canadian Oil Sands, now Suncor Energy. Different methods are currently used for bitumen extraction. Figure 1.2 shows these methods with their current proportion in bitumen production from oil sands.



Figure 1.1The areas of oil sands in Western Canada (taken from: en.wikipedia.org/wiki/ Athabasca_oil_sands)



* Typically upgrader is a facility that upgrades bitumen to synthetic crude oil (from extra heavy. Upgrader facilities are usually located by oil sands production.

Figure 1.2 The proportion of oil sands operating capacity (bitumen production 1000 bpd) with different methods (obtained from : navigator.oilsandsreview.com/listing updated Jan 2016)

1.2 Extraction processes

1.2.1 In-situ

If the thickness of overburden is more than 75-100 meters, in-situ recovery techniques are used to extract bitumen [2]. Some of these methods are: Steam Assisted Gravity Drainage (SAGD) and Cyclic Steam Stimulation (CSS) [2]. These techniques follow almost similar concepts. They usually involve injecting of steam into the deposit area to decrease the viscosity of the bitumen and facilitating the bitumen movement.

1.2.1.1 Cyclic Stream Stimulation (CSS)

In this method, hot steam (at 300°C- 340°C) is injected into the oil sands formation for an extended period of time [2]. Then it is allowed soaking for a couple of days or weeks. Afterward, the heated bitumen and water are pumped to the surface. Once the pumping rate falls off, another cycle of injection and soaking will be applied. This process will be going on till it's no longer economical. Typically, cycles times are between 6 to 8 months and the expected recovery is around 25 % [2].

1.2.1.2 Steam-Assisted Gravity Drainage (SAGD)

In this process, there are two parallel wells going through oil sands seam (one at the bottom of the formation and the other one 5 meters above it). The wells are usually in group central pads, so, they can extend for several kilometers in different directions. The steam injected through the upper well, heats the oil sands and condensed steam and bitumen drains by gravity to the other well and subsequently are pumped to the surface. SAGD has proven to be cheaper than CSS and allows a high rate of bitumen production and can recover 50% of the bitumen in place [2].

1.2.2 Surface Mining

If the overburden thickness is less than 60 meters, surface mining is an economically feasible extraction process [2]. In surface mining, oil sands ores are mined and transported to a crusher unit where the ore is crushed and mixed with warm to hot water, steam, and process aids such as caustic or sodium citrate for hydro-transportation via pipeline. Inside the pipeline, the bitumen is separated from sands due to heating and mechanical shearing. By aeration (which causes bubble attachment to bitumen droplets), the separated bitumen creates a froth. Further aeration happens in floatation cells to separate the remaining bitumen in the slurry. As the next step, solids and water are removed from bitumen froth by froth treatment. The aforementioned separation process is known as Clark Hot Water Extraction (CHWE) process. Table 1.1 shows the major operators with their operating capacity of surface mining (bitumen production bpd).

Table 1.1 Surface mining operating capacity (barrel of bitumen per day) of major operators (obtained from http://navigator.oilsandsreview.com/listing updated Jan 2016)

Operator	Capacity (bpd)	
CANADIAN NATURAL RESOURCES LIMITED	17000	
IMPERIAL OIL LIMITED	220000	
SHELL ALBIAN SANDS	255000	
SUNCOR ENERGY INC.	207000	
SYNCRUDE CANADA LTD.	407000	

Other extraction processes are Cold Heavy Oil Production with Sand (CHOPS), Vapor Extraction (VAPEX), Toe to Heel Air Injection (THAI), Combustion Overhead Gravity Drainage (COGD) and oil sands solvent extraction.

1.3 Oil sands tailings management strategies

The by-product of the surface mining extraction process is a fluid tailings stream containing sand, fines (silts and clays), water and small amounts of unrecovered bitumen. This slurry is discharged to the containment area and sands are settled quickly. Then, the rest of slurry (mostly a balance of water and fines) run off the sand deposit. The settled sands form beaches and the runoff fines and water, known as Fluid Fine Tailings (FFT), makes a pond. FFT has between 15wt% - 30 wt% solids. As the fine solids settle, a layer of clarified water is formed on top of the pond which is reused in the extraction process. With time, additional settling makes tailings with a higher solids content (around 30 wt%) known as Mature Fine Tailings (MFTs). Further settling has an extremely low rate (may take more than a century) [3]. Oil sands companies are following the zero-

discharge policy (issued by the Alberta Environmental Protection and Enhancement Act 1993) [4]. Therefore, all oil sands process water (including tailings) must be kept on site. This regulation has resulted in around 1000 million cubic meters tailings which is about 580 times bigger than the volume of Rogers Centre in Toronto.

An alliance of oil sands producers, Canada's Oil Sands Innovation Alliance (COSIA), was launched on March 2012 focusing on facilitating the improvement of environmental issues related to Canada's oil sands through collaborative action and innovation. The four Environmental Priority Areas (EPAs) for this alliance are: tailings, water, land and greenhouse gases [5]. Based on the agreements, tailings management should focus on using achieved outcomes, assessment based on evidences, collaboration of industries on solutions, and integration of environmental, economic and social aspects [3]. Also, the objectives of tailings management should be:

- 1- Before or at mine closure (as a long term objective), make a closure landscape to protect the ground water and surface water to get contaminated by tailings stream area.
- 2- At a limited time frame after completing deposition (as a short term objective), reclaim the area by placing a cover to have access and plant growth.
- 3- Investigate on reliable solutions that fit operating realities.

Therefore, the oil sands operators should focus on developing methods which are technically sound, environmentally responsible and cost-effective to meet the tailings management objectives. In addition, they should submit the plans that include measurable performance goals and also, measure performance and report performance and take required action if the performance does not meet the desirable outcomes [3].

These objectives should be balanced with a high value placed on progressive reclamation so that excessive liability and closure costs are not deferred and results are demonstrated early in the developments. The tailings management methods and resulting deposits must support the reclamation outcomes for mine closure. Interim measures and requirements should focus on those outcomes, avoiding criteria that could impede innovation and development or prevent the use of optimum methods. A performance-based approach to tailings management will ensure tailings deposits meet requirements for reclamation outcomes [3].

Also, Alberta Energy Regulator (AER) is a regulatory body which has to provide regulations to make sure that development of Alberta's energy resources is efficient, safe, orderly, and environmentally responsible. One of the regulations is Directive 074 (now suspended) which describes the tailings performance criteria and requirements. Below are the objectives defined by this directive for tailings management: [6]

• To minimize and eventually eliminate long-term storage of fluid tailings in the reclamation landscape;

• To create a trafficable landscape at the earliest opportunity to facilitate progressive reclamation;

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• To eliminate or reduce containment of fluid tailings in an external tailings disposal area during operations;

• To reduce stored process-affected waste water volumes on site;

• To maximize intermediate process water recycling to increase energy efficiency and reduce fresh water import;

• To minimize resource sterilization associated with tailings ponds; and

• To ensure that the liability for tailings is managed through reclamation of tailings ponds.

1.4Tailings stability

1.4.1 Microstructure of MFTs

As mentioned above, MFTs can hold water in its structure for a long period of time. It was suggested that MFTs has a card-house microstructure with large pore spaces which can keep process water, also, the tortuous drainage patterns cause a low hydraulic conductivity at a high void ratio [7]. Yong and Sethi [8] suggested that the high water holding capacity is due to the presence of swelling clays such as smectite (causing the house-card structure) and amorphous solids like iron oxide. Also, a study by Kotlyar characterized the properties of different particle fractions present in the MFTs and was shown that the ultrafine solids (<0.3 μ m) in MFTs form gels that give structure to the MFTs and impede consolidation [9].

1.4.2 Effect of bitumen

Another reason of stability of MFTs might be the presence of bitumen. The bitumen-free tailings have faster settling compared to clay-bitumen-water system of MFTs [10]. The Scanning Electron Microscope (SEM) images acquired by Mikula et al [11] show the presence of bitumen in MFTs as free droplets (1 to 10 µm in size) and contaminating the edges of clays. In addition, it has been found that the presence of residual bitumen causes a decrease in the hydraulic conductivity (hydraulic conductivity describes how easy a fluid can move through pore spaces or fractures) of MFTs, as free bitumen blocks the pore spaces between particles, preventing water release and hindering consolidation, as shown in Figure 1.3 [10]. A study by Majid et al. [12] found that MFTs treatment with sodium silicate followed by an agglomeration technique can cause bitumen removal from MFTs. The bitumen removal is followed by further dewatering of remaining solids (compared to samples where bitumen was not removed). It should be noted that these tests were done without adding any other additives such as coagulant or flocculants. The majority of solids settled into a phase containing 60 wt% solids, while the finest solids fraction remained suspended. These results suggest that bitumen plays a role in MFTs stability. However, it is difficult to correlate the change in settling to the removal of bitumen because the tailings used in that study were dispersed with sodium silicate.



Figure 1.3 Effect of bitumen on particle settlement and permeability [10]

1.5 Dewatering technologies for oil sands tailings

Previously, oil sands industries used ponds for tailings storage and this has ended up having an area of about 170 km² of tailings ponds. Therefore, a strong contrast to the policies, set out by the regulators to decrease and finally eliminate the long-term storage of tailings and reclaim the mining areas, made them investigate more on developing new dewatering technologies. Solutions such as an enhanced capture of fines in beaches, nonsegregating tailings and thickened tailings all were tried to reduce the volume of tailings. Also, other technologies such as in-line thickening, thin lift dewatering, centrifugation or freeze-thaw have been developed to address this problem. Some of these technologies are mentioned below:

1.5.1 Centrifugation

The dewatering of tailings streams can be accelerated with a mechanical process known as centrifugation. In this process, the centrifugal force, known as 'g force', causes the separation of solids from water. Studies have been done on centrifugation of tailings and amended tailings. This technology is now commercially feasible for tailings dewatering and Syncrude has built a full-scale centrifugation plant with 18 decanter centrifuges for tailings dewatering. In this method tailings are supplied from ponds and diluted (to 20 wt% solid) and then flocculated with polyacrylamide flocculants and introduced to the decanter centrifuges to get a cake with 55wt% to 60 wt% solids. As it can be seen in Figure 1.4, the feed is introduced from one side (through rotating screw conveyor) into the rotating bowl. Centrifugal forces accelerate the settling of heavy solids, where they settle on the bowl wall and the solids are then conveyed along the bowl wall by the conveyor to the solids discharge. On the other side, the liquid flows around the conveyor and exits over liquid discharge.



Figure 1.4 A schematic diagram of a Horizontal Decanter Centrifuge (Taken from: hutch-hayes.com)

1.5.2 In-Line Flocculation /Thin Lift dewatering

Flocculants (usually organic polymers) are added to tailings streams. Consequently, flocs with higher hydraulic conductivity are formed. Afterward, the flocculated tailings are spread into thin layers for densification through initial drainage, atmospheric drying, and freeze-thaw dewatering (known as thin-lift dewatering). In 2010, Syncrude has started a field scale test of in-line flocculation and thin lift drying as a fines management technology.

1.5.3 Freeze-thaw

This technology includes depositing of layers of MFTs during cold seasons for freezing and thawing during the following summer. Freeze-thaw cycles cause dewatering (the mechanism will be described in chapter 3). The effectiveness of this natural process depends on different factors such as the thickness of the frozen layers [14].

BGC Engineering Inc. [15] has provided a review on different technologies for oil sands tailings treatment. There are many proposed short-term and long-term solutions to reduce or eliminate the accumulation of fine mineral tailings via enhanced solids sedimentation as well as sludge desaturation. Unfortunately over time, most of the developed technologies have not been considered commercially robust or reliable. As discussed previously, this issue can be a consequence of the complex nature of tailings. Therefore, the current theories on the fundamental properties and behaviours of fine mineral tailings mostly follow empirical or semi-empirical approaches performed with ideal (single solid component) slurries and less commonly, real tailings. Thus, it's difficult to predict the best industrial equipment selection, design, and operation based on the conclusions out of the existing studies. Thus, most of the industries dealing with fine tailings need expertise coupled with extensive performance data as evaluations from lab and pilot-scale tests are mandatory before their full-scale implementation [16]. On the other hand, the conventional methods for studying tailings treatments are mostly laborious and time-consuming which confine fast and reliable results required for developing the current technologies as well as expanding the fundamental theoretical knowledge.

1.6 Research objectives

The main objective of this work was to develop a robust, reliable, and integrated process for the treatment of the tailings streams that are produced during the processing of Alberta oil sands deposits. The specific objectives were as follows:

- To drive a high-throughput method to investigate the effects of adding different concentrations of cations (K^+ , Na^+ , Ca^{2+} , Mg^{2+}) from different commercially available salts on the kinetics of MFTs dewatering and the quality of the process affected water in a polymer-free centrifugation process.

- To investigate the freeze-thaw mechanism and the influence of the process conditions such as freezing/thawing rates, water chemistry, and chemical amendments.

- To Dewater MFTs via an alternative mechanical dewatering technology that is predicted to be cheaper than centrifuge-based technologies.

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1.7 Organization of the thesis

This thesis is organized into five chapters. A brief description of the contents of each chapter is presented in the following section. Each chapter has a self-contained review of the pertinent literature to guide the reader.

The main focus of chapter 2 is on developing a high-throughput method for investigating the effect of ionic composition adjustment on dewatering behaviour of MFTs through a centrifugation process. In chapter 3, the effects of different variables (such as freezing temperature, freezing time and ionic composition) were studied on dewatering of MFTs through the freeze-thaw process. In this section, the changes of temperature were monitored during different freezing conditions of different samples. Chapter 4 presents the work on the feasibility of using a Rotary Filtration (RF) for dewatering of MFTs. Also, the developed bench-scale setup was used to study the process variables such as water chemistry, polymer flocculant addition and RF screen slot size to maximize dewatering performance. The conclusions and also recommendations for future works have been mentioned in chapter 5.

Chapter 2: The effect of ionic adjustment on centrifugation of MFTs

This chapter focuses on the effects of inorganic salts on dewatering behaviour of MFTs. A high-throughput method was established and used to study the dewaterability of salt-amended tailing through a centrifugation process.

2.1 Background

In this section, the previous studies are reviewed. Also, the colloid-electrolyte interactions as well as colloid electrolyte-polymer interactions are discussed and coagulation, flocculation, and dispersion behaviour are tried to understand in light of double layer theory concepts. In addition, the rheological aspects of clay suspension and the effects of electrolytes are discussed. Next, the concept of centrifugation process and its challenges are expressed through reviewing the previous works. Finally, a comparison is drawn between the conventional tests in tailings treatment and high-throughput methods which are used widely in many research areas.

2.1.1 Suspensions and particles dynamic

Colloids are dispersions of small particles that range in size from 1 nanometer to 10 micrometers. The motions of these particles are strongly influenced by Brownian motion and they form a homogeneously dispersed mixture in aqueous fluids [17], [18]. As discussed in chapter 1, the tailings from bitumen extraction process settle into layers of stable suspensions in the ponds.

2.1.2 Clays and their behaviour in suspension

Clay particles are mostly composed of silicon-oxygen tetrahedrons (T) and aluminum or magnesium-oxygen octahedrons (O) sheets [19]. Figure 2.1 shows the structure of clay particles. However, different types of clays have different patterns of these sheets as their unit layer. As an example, Illite has a tightly bound three-layer structure, composed of an aluminum-oxygen-hydroxyl octahedron layer which is between two silicon oxide tetrahedron layers. Kaolinite, as an example of a two-layered clay particle, has a unit layer of one tetrahedral silicon-oxygen sheet attached to one octahedral aluminum-oxygen-hydroxyl sheet [19].



Figure 2.1 Three-dimensional structure of the clay layers making up kaolinite [19]

Studies have shown that kaolinite particles have a plate-like shape and consist of two distinct basal planes (or faces) [19]–[21]. The most common structure of clay particles is composed of hexagonal sheets with length to thickness ratio of 10:1. Isomorphic substitution is a process that causes charge imbalances within clay particles, where high valence cations in the layers of the clay are substituted by cations of lower valency. For instance, when a tetravalent silicon ion is exchanged by a trivalent aluminum ion (as they have a similar morphology) a negative charge is created on the final structure [22], [23]. The charges on the T-basal plane are assumed to be permanent and independent of pH. The primary alumina and silica bonds are broken on the edge of the plate and become protonated in water, leading to a pH dependent charge [24]. In acidic environments, the edge of the kaolinite is positively charged and in alkaline conditions, they are negatively charged. Thus, according to the ionic species and their strength in water, these particles can stay dispersed or associate with each other in different ways. For an acidic suspension, the negatively charged basal plane may interact with the positively charged edges. As two interactions between particles, Figure 2.2 shows the edge-to-face and edge-to-edge modes of association. Figure 2.2 (a) shows a perfect clay crystal built by piling unit layers on top of another and Figure 2.2 (b) shows the "house of cards" structure that can entrap large amounts of water within the associations and lead to the long-lasting structure of the MFTs slurry discussed earlier [19].

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Figure 2.2 Different structures of clay particles. (a) perfect crystal, (b) house of cards[19]

Michaels and Bolger [25] studied the interactions of kaolinite's fine particles. As they stated, two major forces exist against each other: attractive van der Waals forces and repulsive electrostatic double layer force. As the fine particles have high surface area, these two forces outweigh any influence of other forces like hydrodynamic and gravitational forces. These two forces strongly influence the rheology of the suspension. Also, the dominant colloidal force depends on factors such as the surface charge of the particle, pH, ionic strength and ionic species in water [25]. To understand the effective treatment and flocculation or coagulation of these systems, it is crucial to understand how the interaction between clay particles and additives (like coagulants or polymer flocculants) works. The following section represents the theory describing the forces of attraction and repulsion in a colloid suspension.

2.1.3 Electrical Double Layer

As colloidal particles have small size, the stability of a colloidal system depends on surface properties and interparticle interactions. In colloidal systems, fine particles tend to have charged surface [25]. As the particles in the vicinity of a particle have the same situation, they repel each other which makes them stable in the suspension (as observed in MFTs). Gouy-Chapman and Stern double layer models explain the electrostatic interaction between charged particles and ions in an electrolyte solution [26].

In colloidal systems, a charged surface attracts counter-ions in solution (oppositely charged ions), while the ions of similar charge to the surface (co-ions) are pushed away. When an excess amount of counter-ions surround the charged surface of particle the electric double layer will be formed. Stern models show the profile of electrical potential distribution near the charged surface. Figure 2.3(a) shows the distribution of counter-ions and co-ions around the charged surface and Figure 2.3(b) represents the corresponding electric profile [26], [27]. The Stern layer is the region between the particle surface and the location in solution which moves with the particle. The Stern layer potential is at its maximum level on the surface and decreases linearly from this point to the Stern layer due to the presence of immobilized counter-ions [26], [27]. The potential at the Stern plane is called the Stern potential. After this plane, the potential decreases exponentially. The Shear plane is considered to be the no-slip boundary around the surface. The potential at the point between this no-slip layer and the ion diffuse layer is known as zeta potential (ζ). The zeta potential is the measurable potential difference between the charged surface and the surrounding bulk phase. The
zeta potential is measured experimentally and used to anticipate the fine particle stability in suspensions. The potential within the double layer region, like the zeta potential, is dependent upon the type of electrolytes and their concentrations. Thus, the manipulation of these factors affects the attractive and repulsive forces between particles as well as the stability of the suspension.



Figure 2.3 Electrical double layer according to Stern model and corresponding electrical potential profile. (a) Distribution of counter-ions and co-ions around the charged surface and (b) the corresponding potential profile [26]

2.1.4 DLVO Theory

The DLVO theory (named for the research of Derjaguin and Landau in 1941 and Verwey and Overbeek in 1948) explains the forces between particles in a suspension and is used to predict colloidal stability. This theory considers attractive van der Waals and the repulsive electrostatic double layer forces as two balancing forces and it ignores other forces like hydrodynamic forces. In this theory, the net interaction, resulting from the attraction and repulsion forces between particles, determine the stability of the particles [26]. If the repulsive electrostatic double layer forces overweigh the attractive van der Waals forces, the net interaction between the particles is repulsive and particles cannot aggregate. Therefore, there is an energy barrier in a suspension that prevents the aggregation of particles. Also, the aggregates size relies on the balance between repulsive and attractive forces. An aggregate can thus be viewed as a basic unit which is formed due to strong attraction among its constituent particles [28], [29].

2.1.5 Mechanisms of coagulation and flocculation

To accomplish the aggregation of colloidal particles in a stable suspension the system must reach the required activation energy. This can be gained by physical forces like centrifugation, or by increasing the kinetic energy of a particle with increasing the temperature. Also, the destabilization of a suspension can happen through some methods that involve in changing the magnitude of the energy barriers. The energy barrier for particle aggregation can be decreased or removed to make the net interaction attractive. Different mechanisms, which can be classified as either coagulation or flocculation, can change the energy barrier. Coagulation is defined as particle aggregation brought by the

addition of inorganic salts to reduce electrostatic double layer repulsive force [30]. Therefore, coagulation generally refers to the process of changing the forces that are acting to keep the particles apart from each other. This is accomplished by the addition of inorganic chemicals, known as coagulants that reduce the particle's repulsive forces. The most important mechanism for flocculation is bridging, which is considered to be a consequence of adsorption of the segments of flocculants macromolecules (which mostly are polymers) onto the surfaces of more than one particle leading to the formation of larger size aggregates, known as flocs. The large flocs settle quickly under gravity [31]. The applications and aspects of using polymers as flocculants will be reviewed with more details in chapter 4. This chapter mainly focuses on the effects of inorganic salts on MFTs properties, especially dewatering behaviour.

2.1.6 Double layer compression

Double layer compression caused by an increase in electrolyte concentration in the suspensions. The higher ionic strength (defined as below) of the electrolyte in the solution pushes the counter-ions of the Stern plane closer to the particle surface.

Ionic strength
$$=\frac{1}{2}\sum c_i z_i^2$$
 Eq 2.1

where c_i is the molar concentration of ion i (mol/L), z_i is the charge number of that ion. Basically, more ions of opposite charge diffuse to the layers around the particle and compress the electric double layer. Increasing the ionic strength of electrolyte decreases the thickness of the layer that the colloidal particles are influenced by the repulsive electrostatic double layer [31]. Therefore, two particles can get closer to each other and aggregate as they are able to fall into the range where the van der Waals attractive forces dominate.

2.1.7 Surface charge neutralization

When the charged counter-ions have a specific affinity for the surface of the colloid the charge neutralization of a particle's surface happens. This affinity goes beyond the electrostatic attraction for double layer compression. As the concentrations of counter-ions increases in the solution, they will have a stronger tendency to adsorb onto the particle surface and reduce the surface charge of particles and this leads to the point where the zeta-potential is neutralized or reversed. Multivalent ions such as Al^{3+} and Ca^{2+} are more effective than monovalents for this purpose. Therefore, additives such as lime, alumina, and gypsum are widely used in water treatment industries [32]. Oil sands producers add these types of salts, as a part of composite tailings process (CT process), for tailings treatment. In this technology, a mixture of gypsum and coarse sands are mixed into the MFTs [15]. Calcium ions from gypsum cause double layer compression of the fine particles, which improves the aggregation [33]. In CT operations, hydro-cyclones use centripetal force produced to compress solid sediments. After a month, a consolidated sediment of 80-85% solids is produced [33]. A similar method was also tried to produce non-segregated tailings using sulfuric acid [34].

2.1.8 Rheology of clay suspension and the effects of electrolytes

Rheology is defined as the study of the flow of matter, generally in a liquid or soft solid state. Rheology gives information which is essential to engineering applications like

designing and creating dewatering systems. Numbers of different models have been developed to describe the rheological properties and behaviours of different fluids and liquids. The most basic model is Newton's law of viscosity. Newtonian fluids have a linear relation between shear stress and shear rate, and the proportionality constant, known as viscosity, is shear-independent. To characterize the rheological behaviour of a Newtonian fluid only one parameter, viscosity, is required. However, the rheological behaviour of many fluids and mixtures do not obey this law. Thus, defining the rheological properties of non-Newtonian fluids requires considering more than one parameter. Generally for MFTs, the slurry viscosity decreases with increasing shear, as more loose aggregates are fractured than formed per unit time (shear thinning behaviour); when at rest, a shear yield stress is developed as the aggregates obtain structural integrity; and under constant shear, the competing processes of shear fracturing and weak aggregation reaches steady state, thus, the slurry viscosity decays to an equilibrium value. As a result, most fine solids suspensions become pseudoplastic and exhibit thixotropic behaviour upon agitation [30].

As mentioned above, clay particles are surrounded by counter-ions in the Stern layer. Clay particles can adsorb a certain amount of exchangeable cations in a suspension. For instance, Montmorillonite adsorbs 126 millimole cations per 100 gram particles, illite 20-40 millimole cations per 100 gram particles, kaolinite 8 millimole cations per 100 gram particles and feldspar only 2.5 millimole cations per 100 gram particles [35]. Clay suspensions with different cations have different rheological properties. Non-clay particles adsorb few cations; therefore, the properties of coarse

sediment suspension are not affected by the cations [30], [35]–[38]. Wang et al. [39] observed that at low clay concentrations, clay suspension with Na⁺ exhibited higher yield stress than those with Ca^{2+} and Mg^{2+} . At high clay concentrations, however, clay suspensions with divalent cations had much larger yield stress than those with monovalent cations. At low concentrations, clay particles were in dispersive state, and volume concentration of particles played the most important role in rheology of the sediment suspension. Swelling of particles in the suspension with Na⁺ increased the effective volume concentration; therefore, the suspension exhibited larger viscosity and yield stress. However, at high concentration, clay particles built a flocculant net structure. Therefore, rheological properties of the suspension highly depend on the strength of the net structure, and swelling of particles is of only secondary importance [39]. In general, multivalent cations have a greater tendency to tie clay-mineral flakes together than univalent cations. In the case of common monovalent cations, there would probably be little tendency for the ions to tie the particles together, and under some conditions, it might enhance the repulsive force between the particles (depends on its counter-ion) [39].

Figure 2.4 shows the pictures of clay particles in suspensions with different cations (Ca^{2+} and K^+). The clay particles with Ca^{2+} joined together and built a net structure like a house of cards (a); the clay particles with K^+ nevertheless, piled in a jumble (b) [39]



Figure 2.4 Structures of suspensions of clay amended with (a) Ca^{2+} and (b) K^{+} [39]

Boger and Leong [40] studied the effects of pH, clay concentration, ionic strength (surface charge density) and they found that by varying these variables there is a transition point (transition from attractive to repulsive particle-interaction which causes floc formation) that the rheological behaviour of clay suspension is converted from Newtonian to non-Newtonian (pseudoplastic). Also, Keren [41] studied the influence of pH-value on the viscosity of clay suspensions and found that clay suspensions had larger yield stress at lower pH-value and lower viscosity and no yield stress at higher pH-value. According to the effect of electrolytes on the electrical double layer, it would be expected that the addition of sodium chloride enhances the association of clay particles and increases the viscosity of the suspension. Nash [42] showed that this holds only at high concentrations of sodium chloride. In fact, addition of sodium chloride at low concentrations caused a decrease in viscosity. This effect may be due to the adsorption of chloride on the clay particles. Nash [42] also studied the effect of aluminium and calcium addition and observed that both showed the same behaviour as sodium addition except that there was not a minimum in viscosity for aluminium addition. It was

suggested (as shown in Figure2.5) a reaction between aluminium and clay which causes the flocculation of clay particles as well as increasing in viscosity [42]:



Figure 2.5 Reaction between aluminium and clay particles [42]

Penner and Lagaly [43] demonstrated that the flow behaviour of sodium montmorillonite dispersions and kaolin slurries can have different responses to different anions [43]. They also observed that with increasing salt or acid concentration the viscosity of sodium montmorillonite dispersions decreased to a minimum, then increased sharply. The concentration at this point was identified as the critical coagulation concentration (c_k). Salts with multivalent anions such as sulfates and phosphates increased the critical coagulation concentration. The critical coagulation concentration for sodium montmorillonite was a function of the montmorillonite concentration and the type of ions. For instance, in 2% sodium montmorillonite dispersions, for sodium chloride and sulfate was higher than c_k in dilute dispersions (0.025%). For the strongly liquefying agents like Na₂HPO₄, NaH₂PO₄, and H₃PO₄, the opposite was true [43]. Also, coagulation with sodium diphosphate Na₄P₂O₇ was not observed [43]. Also, the viscosity of concentrated kaolin slurries decreased when salts were added. Phosphates strongly

reduced the viscosity. Also, pseudoplastic flow changed into Newtonian behaviour and the slurry became liquid like water [43]. Studies suggested that added anions can be adsorbed at positive edge sites by electrostatic interactions or exchanged for structural OH groups at the edges [43], [44]. When multivalent anions replace one OH group or are attached to one positive edge site, the negative charge density at the edges increases. This reaction generally decreases the viscosity and increases the stability of the colloidal dispersion against salts [43], [45], [46]. Generally, for the diluted suspension of clays the coagulation is initiated by edge (-)/face (-) contacts as salt addition makes the force between the edges and faces attractive (DLVO theory). The increased negative edge charge density, in the presence of phosphate, causes the mechanical instability of the edge/face contacts, therefore, coagulation occurs when the salt concentration reaches the c_k value for the face(-)/face(-) coagulation [45]. At high concentrations of clay mineral, the strong repulsion between the faces forces the particles into a parallel orientation which promotes the edge(-)/edge(-) coagulation [43], [44]. Also, it is assumed that coagulation begins to operate when the interaction between the negative edges becomes attractive. It is evident that this process requires distinctly smaller phosphate concentrations than the face/face coagulation in the dilute dispersions.

2.1.9 Centrifugation as a dewatering technique

Based on the literature review given in this chapter, this section describes the expected dewatering behaviour of MFTs. Centrifugation is one of the mechanical methods used to accelerate the dewatering of tailings. By using this method, a quite large volume of tailings can be dewatered to desirable solids content and transported to the

final disposal area. This mechanical method has been considered commercial for oil sands tailings dewatering. Syncrude has built a full-scale centrifuge plant (containing 18 decanter centrifuges) estimated to cost \$1.9 billion. The centrifugal force (known as 'g force') is the motive force in centrifugation. The efficiency of a centrifuge or greater removal of water is determined by the ratio of centrifugal force to gravity [47]. While being rotated in a centrifuge, particles assemblages are formed by the collision among the particles. In addition, unequal particle size distribution causes settlement of particles with different sizes at different time. The preferential settling of coarser particles and particle assemblages with respect to fines results in flow channels and allows releasing part of the pore water from the particle assemblages [48]. The collision efficiency is one of the important parameters for centrifuge dewatering that is influenced by the physicochemical behaviour of the system. Therefore, in this chapter, the effects of ionic composition on centrifugation behaviour of MFTs is studied and correlated to the changes in water chemistry.

In current practice, the centrifugation of oil sands tailing has two steps. The first step is MFTs amending by flocculating aids and followed by centrifugation of amended MFTs. This step results in 2 streams: a relatively solid-free water of about 0.5-1wt% solids called the centrate and a solid soft-soil material of 55-60 wt% solids called the cake [49], [50]. The second step includes further dewatering by natural processes, (consolidation, desiccation and freeze-thaw). Although using polymers in conjunction with centrifugation has shown an effective role for MFTs dewatering, there are some limitations for centrifugation of polymer amended tailings. Rima [51] developed a

research methodology to study the dewatering properties of MFTs using a bench scale centrifuge in conjunction with polymer modification. Rima tried different test conditions such as centrifugation time and force, type and concentration of polymers. Rima found that beyond a gravitational force in centrifugation the dewatering declines owing to floc breakage due to excess centrifugation force and surface saturation. Also, studies mentioned another issue of using polymers which is the floc breakage during transportation or mixing step [51]–[53].

2.1.10 High-throughput vs conventional methods

As mentioned above, there are lots of different facts and options that may require being considered for an integrated treatment process. However, the conventional settlement tests need a lot of materials and, mostly, are time-consuming and laborious which confine investigation of different factors in a short period of time or not able to monitor settling kinetic during a process. Also, in case of failure in experiment a remarkable amount of materials and time will be wasted. While high-throughput studies have scaled down (i.e. micro-scale) the conventional processes and are widely used in process analytical technologies in many studies like optimizing the performance of flocculation [54], [55], adsorption [56], chromatography [57], and liquid-liquid extraction [58]. For instance, Mohler et al. developed a high-throughput workflow using a sophisticated robotic equipment and automated digital image analysis to accelerate the development of improved flocculants for remediating oil sands tailings [59]. In this chapter, a stability analyzer was used, to study the settling behaviour of MFTs. This analyzer, LUMiFuge, has been used in many studies as a high-throughput technique to investigate the stability and separation kinetics of suspensions [60], [61]. By using LUMiFuge, separation kinetics can be studied under accelerated conditions while eight samples running in parallel using volumes less than 2 mL. Implementation of this technique enabled us to study different factors in different conditions in a short period of time by consumption of a little amount of materials. In addition, it delivers more reliable results as the dynamic behaviour of the tailings under centrifugal acceleration is also investigated [62].

2.1.11 Objectives

The objectives of this chapter are to use a high-throughput method to investigate the effects of adding different concentrations of cations (K⁺, Na⁺, Ca²⁺, Mg²⁺) from different commercially available salts on the kinetic of MFTs dewatering and the quality of process affected water in a polymer-free centrifugation process. This method was implemented to rapidly compare different salt types with different conditions and find out the optimum concentration of ions from the proper salts and operating conditions which may result in optimization of the treatment's costs and efficiency. In addition, the quality of process affected water can be predicted and used in designing of a post-treatment process. Table 2.1 Properties of MFTs

2.2 Experimental

2.2.1 Materials

A 5-gallon bucket of MFTs was purchased from Alberta Innovates Technology Futures® on August 2014. To analyze the properties of MFTs pore water, 1000 mL of MFTs was centrifuged at 3270g for 2 hours (using Allegra X-12) and the supernatant was separated and sent to AGAT Laboratories for analysis. Table 2.1 shows the properties of MFTs.

$\begin{array}{c|c} Parameter & Value \\ \hline pH^{*} & 8.30 \\ \hline Solids \ content \ (wt\%) & 31.7 \ wt\% \\ \hline Density \ (g/mL) & 1.19 \ g/mL \\ \hline Ionic \ composition \ of \ MFTs \\ pore \ water \ (ppm)^{*} & \hline Cations: \ Ca^{2+}(11.3), \ Mg^{2+}(10.3), \ Na^{+}(590), \ K^{+}(13.8) \\ \hline Anions: \ HCO_{3}^{-}(899), \ CO_{3}^{2-}(6), \ OH^{-}(<5), \ Cl^{-}(411), \\ NO_{3}^{-}(<0.5), \ SO_{4}^{2-}(2.8) \\ \hline \end{array}$

*Measured by AGAT Laboratories (Ltd)

Potassium chloride (EMD chemicals), sodium chloride (VWR), calcium chloride dehydrate (Fisher Scientific), gypsum (Drierite Co.), magnesium chloride hexahydrate (Fisher Scientific) and magnesium sulfate monohydrate (Sigma-Aldrich) and deionized water (DI water) were used to make the solutions.

2.2.2 Solution preparation

To investigate the sedimentation of solid particles as a function of cations at different concentrations, twenty four sets of different concentrations of sodium,

potassium, magnesium and calcium were chosen and corresponding solutions were made (Figure 2.6 shows the design spaces) using DI water and the required amounts of the aforementioned salts (two solutions were made for each set). To have more confidence in results, all the tests were done for each two solutions with the same target concentration except the settling test for solutions with different concentration of potassium and sodium (which was done for one set).



Figure 2.6 The design spaces, (a) solutions with 10 ppm Ca^{2+} and Mg^{2+} and different concentrations (ppm) of K^+ and Na^+ with chloride as the counter-ion, (b) solutions with no K^+ and Na^+ and different concentrations (ppm) of Mg^{2+} and Ca^{2+} (with chloride as the counter-ion for one set and with sulfate as the counter-ions for the other set of solutions)

As the first part of the experiment, the effect of monovalent cations (K⁺and Na⁺) was studied by fixing the concentration of Ca^{2+} and Mg^{2+} , using magnesium and calcium chloride, and changing the concentration of potassium and sodium, from sodium and

potassium chloride, between 0 and 900 ppm. 10 ppm was selected for Ca^{2+} and Mg^{2+} as it was very close to the concentrations of those ions in the MFTs pore water (see Table 2.1). From twelve sets of solutions with different concentrations of sodium and potassium, nine sets have been discussed in detail and the results for the rest have been presented in appendices (see section 2.5).

The next part of the study involved fixing the concentrations of K⁺ and Na⁺ at 0 ppm (in the solutions) while the concentrations of Ca^{2+} and Mg²⁺varying between 0 and 500 ppm. In this part, two kinds of salts were used. Initially, the calcium and magnesium sulfate were used to make six sets of different concentrations of divalent cations and afterward, the calcium and magnesium chloride were implemented (see section 2.5 for more details).

2.2.3 Settling test

The settling of solid particles in the mixture of MFTs-solution was studied using a temperature controlled bench-top/stability analyzer (LUMiFuge Model LF111 LUM Ltd., Berlin, Germany). Prior to taking samples from the MFTs bucket, a rotary mixer was used to mix the MFTs. Then, samples were extracted at random positions from the central region of the bulk. Afterward, 5 ml of MFTs was combined with 5 ml of each solution and then mixed using a vortex mixer for approximately a minute (the initial solids content of the mixtures was approximately 17.2 wt%). For the settling test, 1.6 ml of each MFTs-solution mixtures was transferred to the LUMiFuge tubes using Gilson's MICROMAN pipettes. As it is shown in Figure 2.7, the tubes were placed horizontally in the LUMiFuge instrument. The selected centrifugal analysis parameters were: rotational speed of 2000 rpm (which is equal to a centrifugal force of 581.2g) for a period of 45 minutes at ambient temperature. In addition, to compare the effect of salt addition and centrifugal force, different speeds (500 rpm= 36.2g, 1000 rpm= 145.3g, 2000 rpm= 581.2g and 4000 rpm= 2325.1g) were tried for samples containing 50 vol% 900K/900Na (the solution with target concentrations of 900 ppm for K⁺ and Na⁺) for 45 minutes. LUMiFuge measures near-infrared (NIR) transmission profiles continuously during centrifugation and for the selected conditions it resulted in 15 profiles (one profile per 3 minutes). LUMiFuge software, SEPView 6, calculated the integral of every transmission curve over a chosen length (the sample length).



Figure 2.7 (a) Inside the LUMiFuge 111 with the test tube (b) its measuring scheme (Taken from applied colloids surfactants.blogspot.ca)

A graphical representation of transmission (%) as a function of position presents the transmission profile. The bottom part of the tubes with concentrated solid particles will scatter and absorb the light; hence, transmission will be lower. In contrast, clear water on the top of the samples will raise the transmission levels. The location of each profile shows the settling rate and estimation of solid content in the bottom phase. To find an estimation of the solids content of each sample, a linear equation was fitted between the location of profiles and the volumes of the samples in the LUMiFuge tubes. To do so, the LUMiFuge was run for the tubes with 0.30, 0.90, 1.20, and 1.60 ml of DI water twice (Figure 2.8 shows the LUMiFuge profiles and regression line). NIR has different absorption at the border of two environments (water and air). The fitted equation is shown below (Figure 2.8(b) also shows an example of the LUMiFuge profiles):

$$V = -0.0725(X) + 9.387$$
 Eq2.2

where V is the volume of sample (mL) in LUMiFuge tube and X is the position in LUMiFuge profiles (mm). Knowing the volume inside the tube as a function of profile's position, the solids content of settling phase can be estimated by equation below:

$$SC (\%) = \frac{V_0/2 \times \rho_{MFTs} \times SC_{MFTs}}{V_0/2 \times (\rho_{MFTs} + \rho_{solution}) - (V_0 - V_b) \times \rho_{supernatant}} Eq2.3$$

where SC is the solids content of the bottom phase in the LUMiFuge tubes (wt%), V_0 is the initial volume of sample in tubes (mL), ρ_{MFTs} is the density of MFTs (g/mL), SC_{MFTs} is the solids content of MFTs without dilution (wt%), $\rho_{solution}$ and $\rho_{supernatant}$ are densities of solution and supernatant respectively which both are assumed to be 1g/mL and V_b is the volume (mL) of the bottom phase.



Figure 2.8 (a) Volumes in the LUMiFuge tubes versus the positions in LUMiFuge profiles (b) example of the positions that are used in Eq2.2 and Eq2.3.

2.2.4 Characterization of water chemistry

15 mL of each solution was mixed with 15 mL of the MFTs in 50 mL centrifuge tubes (as the separated water from the LUMiFuge test was not enough for ICP-OES analysis). Then, the mixture was centrifuged at 3750 rpm (centrifugal force of 3270 g) for 2 hours using Allegra X-12 series to accelerate the separation of pore water from solid particles and get a clear supernatant for all of the samples. After centrifugation, the top phase was separated for ionic composition analysis.

The Jarrell-Ash 9000 Inductively Coupled Plasma/Optical Emission Spectrometer (ICP-OES) at McMaster Steel Research Centre was used to study the effects of solutions on the changes of ionic composition in the pore water of the MFTs and MFTs-solution mixtures and also to measure the concentrations of cations in prepared solutions. In this method, the excited atoms, produced by inductively coupled plasma, emit electromagnetic radiation at wavelengths characteristic of a particular element. The intensity of this emission is indicative of the concentration of the element within the sample [63]. The wavelengths: 766.49 nm and 769.89 nm for potassium, 588.99 nm and 589.59 nm for sodium, 393.36 nm, 396.84 nm and 422.67 nm for calcium and 279.55nm, 280.27 nm and 285.21 nm for magnesium were monitored. To see whether different centrifugation conditions affect the ionic composition of the separated water or not, one of the solutions was selected (0Mg/500Ca) and in four tubes (15 mL tubes), 7 mL of MFTs was mixed with 7 mL of the solution and then AllegraX-12 centrifugal force of 3270 g) for each of them. Then, the supernatants were analyzed with ICP-OES. All the results were almost the same for the 4 tubes suggesting that centrifugation condition has almost no effect on the ionic composition of pore water of MFTs-solution mixtures.

2.3 Results and discussion

2.3.1 Ionic strength effect on dewatering

Different concentrations of cations vary the settling behaviour of MFTs. Also, valency has an effect and it is known that divalent cations are more effective than monovalent. Figure 2.9 shows the NIR transmission versus position in the test tube during centrifugation (LUMiFuge profiles). The selected condition (581.2g for 45 minutes and one profile per three minutes) could clarify the differences between different

solutions and compare the settling kinetic as well as solids contents. As it can be seen in Figure 2.9(a), low concentration of sodium and potassium (100K/100Na) is not effective in dewatering of MFTs and the profile just has 3 mm change after 45 minutes (compared to the point relates to initial position). However, for 900K/900Na just after 9 minutes, the position of the profile had 10 mm (Figure 2.9(b)) change and for 500Mg/500Ca, it just happened after 3 minutes (Figure 2.9(c)). The closeness of the last profiles suggests that they are showing the maximum final position corresponds to maximum separation with this centrifugal force. These results show that ionic composition has an effect on settling behaviour of MFTs during centrifugation. As mentioned, to aggregate particles in a stable suspension the system must reach the required activation energy [30]. This can be gained by physical forces like centrifugation. However, the magnitude of the energy required for aggregation can be increased by destabilization of a suspension by making the net interaction attractive [30]. The addition of cations such as K^+ , Na^+ , Mg^{2+} , and Ca^{2+} can reduce the repulsive forces between particles (through double layer compression or surface charge neutralization), so, they reduce the energy barriers required for aggregation. Therefore, by applying centrifugation force samples with higher concentrations of cations and with higher valency need less energy for aggregation (followed by settling), thus, they settle faster.



Figure 2.9 The NIR transmission versus position in tubes (LUMiFuge profiles) and the test tubes after centrifugation for 50 vol% MFTs+ 50 vol% (a) 100K/100Na, (b) 900K/900Na with chloride as the counter-ion and (c) 500Mg/500Ca with chloride as the counter-ion.

Regarding the scale of tailings, centrifugation is a fairly expensive process; therefore, optimizing the process conditions is of an extreme importance. Rima [51] tried different forces between 160g and 2550g, different centrifugation time (5, 10, 15 and 20 minutes) and also two different dosages of an anionic polymer (10 ppm and 20 ppm). Rima [51] started with 29 wt% solids and at the best condition, after 5 minutes centrifugation at 630g with the higher concentration of polymer, reached to around 47wt%. By increasing centrifugation time almost the same result was observed, however, increasing the gravity force reduced the separation which shows the limitation of centrifugation of polymer amended MFTs due to flocs breakage [51]. As it can be seen in Figure 2.10 these limitation doesn't exist for salt addition (higher gravity force and longer centrifugation cause more separation inside the studied ranges). In addition, there is a

synergic effect of centrifugation force and salt amendment on dewatering process. Figure 2.10 shows the SC for 50 vol% MFTs + 50 vol% 900K/900Na at different centrifugal forces. As it's expected, by increasing the centrifugal force, the dewatering gets faster and reaches higher SC in a shorter period of time. However, this improvement can be satisfied by ionic adjustment at lower centrifugal forces which will cut the expenses of centrifugation process. The SC results for MFTs + 900K/900Na at 2325.1g (Figure 2.10) is comparable to SC results for 500Mg/500Ca at 581.2g (Figure 2.12) which had 4 times lower centrifugal force.



Figure 2.10 SC of 50 vol% MFTs+ 50 vol% of 900K/900Na with 10 ppm Mg^{2+} and Ca^{2+} with chloride as the counter ion at different centrifugal forces.

Figure 2.11 shows the SC (from Eq2.3) for the samples with different concentrations of potassium and sodium during centrifugation. The results for 500K/500Na, 900K/100Na, 500K/900Na, and 900K/500Na have not been mentioned in Figure 2.11 but they are located between 100K/900Na and 900K/900Na and the SC increases based on their order mentioned above. Figure 2.11 generally shows that samples with higher concentrations of cations had faster settling and higher solids content. The SC for 100K/100Na increased almost linear with a mild slope during centrifugation and reached 19.5 wt% after 45 minutes. However, 100K/500Na had different behaviour and SC increases nonlinearly as the time passed and reached 31.6 wt%. The SC results for 500K/100Na, 100K/900Na show a 'S' shape trend but for 900K/900Na, a steep increase was observed during the first moments of centrifugation.



Figure 2.11 SC of 50 vol% MFTs+ 50 vol% of the solutions containing different concentrations (ppm) of K⁺ and Na⁺ and approximately 10 ppm Mg²⁺ and Ca²⁺ with chloride as the counter-ion during centrifugation in LUMiFuge (2000 rpm = 581.2g for 45 minutes).

The molecular weight of potassium is almost double of sodium; therefore, for the same weight of each cation, there are more units of sodium rather than potassium. However, as it can be seen in Figure 2.11, samples with higher concentrations (ppm) of potassium had better settling results compared to samples with higher concentrations of sodium (e.g. 500K/100Na compared to 100K/500Na). The high concentration of sodium

in MFTs which is attributed to NaOH addition during the extraction process which decreases the tendency of exchanging sodium in added solution with cations around clay particles. However, potassium is less available in MFTs, probably by adding solutions with higher concentrations of potassium more exchange happens and higher settling will observe.

The card-house structure for non-treated MFTs is caused by equilibrium of repulsive forces between clays and long range attractive forces (van der Waals forces) which has a great ability to keep water [35]. By increasing the ionic strength of the medium (increasing ionic concentration and valency) in which the clay particles are dispersed, and by lowering the surface potential of the clays, the above-mentioned repulsive force is reduced. Consequently, the clays particles are getting close enough and decrease the thickness of Stern layer so that van der Waals attraction allows aggregation of the clays [64]. As the centrifugation starts, the repulsive forces for samples with higher concentrations and more valency are not strong enough to keep the particles apart and particles have less tendency to retain water in their structure, therefore, they release water faster. In addition, for samples with S shape trend of increasing the SC, major dewatering happened in the middle of centrifugation test suggesting that destruction of the structure needs more time depending on ionic strength and availability of pore water around clay particles. Therefore, during centrifugation of sample containing 100K/100Na the particles repulsive interactions are strong enough to preserve the structure although centrifugal force is applying. However, for mixtures of MFTs with 500K/100Na, more cations are available and the repulsive forces are weaker. As the test begins the structure

of clay particle starts to lose water and at a certain point they cannot tolerate the applying force and will collapse. Finally, for 900K/900Na, the high concentration of cations weakened the particles structures enough to destruct as the force is applied.

Figure 2.12 shows the SC for the samples containing the solutions with different concentrations of magnesium and calcium (with sulfate as the counter-ion). The addition of 0Mg/100Ca showed almost the same behaviour as 100K/100Na suggesting that the reduction of repulsive forces was not enough for the destruction of the existing structure of MFTs particles and aggregation of the particles.



Figure 2.12 SC (average of two tests) of 50 vol% MFTs+ 50 vol% of the solutions containing different concentrations of Mg^{2+} and Ca^{2+} (ppm) and approximately 0 ppm Na⁺ and K⁺ with sulfate as the counter-ion during centrifugation in LUMiFuge (2000 rpm = 581.2g for 45 minutes).

The 'S' shape trend is observed again for 100Mg/0Ca which shows 100 ppm Mg^{2+} works better than 100 ppm Ca^{2+} . 100 ppm Mg^{2+} is equal to $4.16 \times 10^{-3} (mol/L)$ Mg^{2+} , so, the solution with the same molar concentration of calcium (4.16 × $10^{-3} (mol/L)$) has 166.6 ppm Ca^{2+} . The SC results for these solutions (0Mg/166.6Ca and 100Mg/0Ca) were almost the same during the centrifugation. The key point here is that for the same numbers of cation units (with the same counter-ion), magnesium and

calcium work almost the same. Also, Table 2.1 shows that the concertation of magnesium and calcium are almost the same in MFTs pore water (11.3 ppm Ca²⁺, 10.3 ppm Mg²⁺) which suggests that they both have almost the same concentrations around clay particles, so, they almost have the same tendency to exchange. However, there might be a little bit loss of calcium as calcite [64]. The sharp increase in SC at the first moments of centrifugation for the mixture of MFTs with 100Mg/100Ca and more concentrated solutions shows that the repulsive forces between clay particles are weakened enough to collapse very fast and release water by applying centrifugal force. However, it seems that there is a minimum concentration to get the fastest kinetic. As it is observed, mixtures of MFTs with 500Mg/0Ca and 500Mg/500Ca have almost the same settling kinetic and also they have a small difference with settling behaviour of 0Mg/500Ca. As mentioned above, Wang et al. [39] stated that clay particles adsorb a certain amount of exchangeable cations in a clay suspension. It seems that mixtures of MFTs with 500Mg/0Ca and 500Mg/500Ca passed those saturation points.

A comparison between Figure 2.11 and Figure 2.12 demonstrates the effect of valency on settling behaviour of MFTs. The SC results for 100Mg/100Ca and 900K/900Na are comparable which solution with 100 ppm magnesium and calcium has almost 9 times less concentration of cations (compared to 900K/900Na) but shows almost the same settling behaviour. The same comparison can be drawn between 100Mg/0Ca and 500K/100Na.

2.3.2 Ionic composition changes

The settling results show ionic composition adjustment affects the settling of solid particles. It suggests that there are some interactions between ions in added solution and particles in MFTs. The ionic composition of process affected water of the mixtures was studied to find out how MFTs–solution interactions work. When solution A and B with known concentrations of a component (M) are mixed together, the concentration of M in the final solution is the arithmetic mean of concentrations in solution A and B. In '50 vol% MFTs+50 vol% solution' these two solutions are the solution and MFTs pore water. If there is no interaction between the solution and MFTs, the final concentration (C_{predicted}) of each cation is as below:

MFTs water content (vol%) =
$$68.3 \left(\frac{\text{g water}}{100 \text{ g MFTs}}\right) \times \frac{\rho_{\text{MFTs}}(\frac{\text{g MFTs}}{\text{mL MFTs}})}{\rho_{\text{pore water}}(\frac{\text{g pore water}}{\text{mL pore water}})}$$
 Eq 2.4

$$C_{\text{predicted}} = \frac{0.5 \times C_{\text{s}} + 0.5 \times \text{MFTs water content} \times C_{\text{p}}}{0.5 + 0.5 \times \text{MFTs water content}}$$
Eq 2.5

where $C_{predicted}$ is the final concentration in the MFTs-solution mixture (without considering any reaction), ρ_{MFTs} is density of MFTs (g/mL) and $\rho_{pore water}$ is density of MFTs pore water (which assumed to be 1 g/mL) C_s is the concentration in the solution and C_p is the concentration in the MFTs pore water. The actual concentration represents the concentration of cations (measured by ICP-OES) in the supernatants of 50 vol% MFTs + 50 vol% of each solution after centrifugation. Figures 2.13(a) and Figure 2.13(b) show the actual concentrations over predicted ones for all the samples. The order of xaxis is based on increasing the ionic strength of the solutions. As it is shown, the actual concentrations of sodium have the least deviation from predicted ones. In Figure 2.13(b), 'Actual/Predicted concentration' for potassium and sodium show higher values by increasing the ionic strength of solutions which the dewatering behaviour also follows this trend (Figure 2.11). However, Figure 2.13(a) shows that potassium has a more effective role in exchanging ions with magnesium and calcium which is resulted in better dewatering (Figure 2.11). 100K/900Na, 500K/500Na have higher ionic strength than 900K/100Na but less deviation of actual concentrations from predicted ones for magnesium and calcium and also poorer dewatering behaviour. The same phenomenon is observed for 500K/900Na compared to 900K/500Na. Generally, for the samples, the actual concentrations of cations which exist in the solutions at high concentrations are less than predicted concentrations and the other ones are higher which is hypothesized to be the results of ion exchanging, precipitation and other reactions inside the MFTssolution mixtures [64]. For 0Mg/500Ca, the actual concentration of magnesium and for 500Mg/0Ca the actual concentrations of calcium are 6 and 9.8 times higher than the predicted ones respectively. Firstly, this shows a very strong interaction of those solutions and clay particles in MFTs (which the settling results also confirm that), secondly, it can be concluded that MFTs has more calcium and magnesium than exist in MFTs pore water and in case of adding proper solution with specific ionic strength they can be exchanged and dissolve in pore water.



Figure 2.13 Actual/Predicted concentration of supernatants of 50 vol% MFTs+ 50 vol% solution and ionic strength of the solutions with different concentrations of (a) sodium and potassium chloride and (b) magnesium and calcium sulfate (each point shows the average value of the two runs + error bar which is \pm the difference between each run and the average)

For solutions with different concentrations of sodium and potassium, an increase in actual concentrations of sodium is observed compared to the predicted. Even though, by adding 100K/100Na , which has 100 ppm sodium, the actual concentration of sodium showed a positive deviation from predicted one and calcium and magnesium which had low concentrations in solution (10 ppm) showed negative deviation. It means that clay particles absorbed the magnesium and calcium from pore water and released sodium. For solutions with different concentrations of calcium and magnesium, sodium just had small positive deviations from predicted concentration for different samples and it shows an increase in the concentration of sodium in pore water by increasing the concentration of divalents in the added solution. However, potassium got more positive deviation (actual concentration > predicted concentration) and this deviation has an increasing trend by adding solutions with the higher concentrations of magnesium and calcium. These observations show that the clay structures have a very low tendency to absorb more sodium in their network as they might be saturated by addition of NaOH during the extraction process. MacKinnon et al. [64] also studied the effect of coagulants on water chemistry. By using mass balances, MacKinnon et al. assessed the fate of the added calcium and suggested three main sinks for the added calcium from the gypsum. Approximately one-third exchanges on the clays (subsequent release of Na^+), one-third is lost as the calcite precipitate (results in reduction in alkalinity), and about one third remains in solution as Ca^{2+} ion which was 70-120 ppm Ca^{2+} in CT released water [64]. The results from Figure 2.11, 2.12 and Figure 2.13 draw a comparison between settling behaviour and changes in pore water chemistry (caused by interaction between MFTs and solutions). For solutions with different concentrations of sodium and potassium, the better settling results were accompanied by increasing the concentration of magnesium and calcium. However, when solutions with different concentrations of magnesium and calcium were added, the higher release of sodium and potassium and the divalent (calcium or magnesium) with less concentration in added solution were followed by better settling results. As mentioned, one of the parameters in the optimization of a dewatering process is choosing the proper materials. For ionic adjustment, the proper salt has to be selected which might differ according to availability around the dewatering site location. The effects of cations on centrifugation of MFTs were discussed above. However, all these cations could come with different counter-ion (chloride, nitrite, sulfate, phosphate) and these counter-ions might affect the settling behaviour and change the water chemistry. Therefore, for choosing the best salt, the effects of anions which come with cations should be studied.

Figure 2.14 and Figure 2.15 compare the final solids content (FSC) which is the solids content after 45 minutes of centrifugation and changes in water chemistry for solutions with different concentrations of calcium and magnesium with chloride and sulfate as the counter-ions. As it can be seen, samples with chloride and sulfate (as their counter ions) show almost same settling results and also resulted in almost same changes in concentrations of potassium, sodium, magnesium and calcium after centrifugation (Figure 2.14). However, different anions like phosphates might have a different effect which should be studied in future works.



Figure 2.14 The comparison between FSC of 50 vol% MFTs + 50 vol% of solutions with sulfate and chloride as the counter-ions (Each point shows the values relate to the solutions with the same concentrations of magnesium and calcium but with different counter-ions). The values represent the average of the first and second tests (centrifuged at 581g for 45 minutes). Each point shows the average value of the two runs + error bar which is \pm the difference between each run and the average.



Figure 2.15 Comparison between the Actual /Predicted concentration in supernatants from the mixtures of 50 vol% MFTs with 50 vol% of different solutions with sulfate and chloride as the counter-ion for(a) potassium, (b) sodium, (c) magnesium, (d) calcium. The values represent the average values of the first and second tests (each point shows the average value of the two runs + error bar which is \pm the difference between each run and the average).

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2.4 Conclusion

The implemented high-throughput method used in this work has been shown to be an effective technique to speed-up the investigation of different factors and different additives in a MFTs dewatering process. The key findings of this works are summarized below:

• Samples with different concentrations of cations showed different settling kinetic, during centrifugation. Solids content of the settling part for 100K/100Na increases almost linear with centrifugation time but it has an S shape trend for 500K/100Na and a logarithmic one for 900K/900Na. For divalents cations, 0Mg/100Ca has almost a linear trend which turns to nonlinear trends for other solutions.

• The solutions with high concentrations of potassium caused faster settling compared to the solutions with high concentrations of potassium which may be a result of high concentration of sodium in MFTs pore water.

• The LUMiFuge results enabled us to draw a correlation between the effect of cations (concentration and valency) and centrifugation parameters (force and residence time). This ability will speed up the optimization processes. The settling results of 900K/900Na at 2325.1g is comparative to the settling results of 500Mg/0Ca at 581.2g which has less salt and almost 4 times less centrifugal force.

• The changes in ionic composition show the interactions between added salt and MFTs (which might be because of ion exchanging, precipitation or reactions). Also, the

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correlation between these changes and settling results shows that the higher interaction comes with the better settling results.

• Both ionic composition changes and settling results show that sulfate and chloride behave the same as the counter ions of magnesium and calcium.

2.5 Appendix

Table 2.A.1 Concentrations of solutions measured by ICP-OES.

			K (ppm))	Na (pp	m)	Ca (pp	m)	Mg (pj	om)
Counter-ion	Solution	Target concentration (ppm)	First test	Second test	First test	Second test	First test	Second test	First test	Second test
Chloride	0K/0Na	0 K; 0 Na; 10 Ca;10 Mg	0.0	0.0	0.0	0.0	10.9	7.1	14.2	8.4
Chloride	0K/900Na	0 K ;900 Na; 10 Ca;10 Mg	0.1	0.1	855.4	876.1	9.8	7.5	12.7	8.1
Chloride	100K/100Na	100 K ;100 Na; 10 Ca;10 Mg	88.2	91.8	103.3	90.9	10.5	7.1	13.5	8.4
Chloride	100K/500Na	100K ;500 Na; 10 Ca;10 Mg	88.2	82.6	522.0	442.8	9.9	6.8	12.9	8.2
Chloride	100K/900Na	100K ;900 Na; 10 Ca;10 Mg	84.4	67.0	933.3	856.7	9.8	7.2	12.7	8.4
Chloride	500K/100Na	500 K ;100 Na; 10 Ca;10 Mg	462.4	446.3	100.1	89.8	10.2	6.8	13.1	8.2
Chloride	500K/500Na	500 K ;500 Na; 10 Ca;10 Mg	479.2	475.3	480.5	500.4	9.8	6.8	12.7	8.3
Chloride	500K/900Na	500 K ;900 Na; 10 Ca;10 Mg	470.7	486.7	918.6	883.3	9.6	7.1	12.5	8.7
Chloride	900K/0Na	900 K; 0 Na; 10 Ca;10 Mg	854.0	846.8	1.8	4.6	9.8	7.2	12.8	8.3
Chloride	900K/100Na	900 K ;100 Na; 10 Ca;10 Mg	883.7	828.3	103.3	88.6	10.0	6.9	12.8	8.7
Chloride	900K/500Na	900 K ;500 Na; 10 Ca;10 Mg	853.5	835.9	918.7	880.9	9.5	6.9	12.4	8.7
Chloride	900K/900Na	900 K ;900 Na; 10 Ca;10 Mg	853.5	835.9	918.7	880.9	9.5	6.9	12.4	8.7
Sulfate	0Mg/100Ca	0 K; 0 Na; 100 Ca; 0 Mg	0.0	0.0	1.0	1.0	123.5	102.0	0.1	0.1

Real concentration

Sulfate	100Mg/0Ca	0 K; 0 Na; 0 Ca;100 Mg	0.0	0.0	0.9	0.9	0.6	0.6	111.7	105.2
Sulfate	100Mg/100Ca	0 K; 0 Na; 100 Ca;100 Mg	0.0	0	1.1	1.06	112.7	99.6	131.8	102.7
Sulfate	0Mg/500Ca	0 K; 0 Na; 500 Ca; 0 Mg	0.0	0.0	1.0	1.0	504.5	541.0	2.3	0.2
Sulfate	500Mg/0Ca	0 K; 0 Na; 0 Ca;500 Mg	0.0	0.0	0.0	0.0	0.2	0.1	571.3	505.0
Sulfate	500Mg/500Ca	0 K; 0 Na; 500 Ca;500 Mg	0.7	0.0	1.6	2.1	521.4	498.9	527.5	526.9
Chloride	0Mg/100Ca	0 K; 0 Na; 100 Ca; 0 Mg	0.1	0.0	1.1	2.1	100.0	94.3	0.1	0.1
Chloride	100Mg/0Ca	0 K; 0 Na; 0 Ca;100 Mg	0.1	0.4	1.1	1.1	0.4	0.8	106.4	101.8
Chloride	100Mg/100Ca	0 K; 0 Na; 100 Ca;100 Mg	0.1	0.1	1.1	1.1	110.9	106.8	109.1	101.6
Chloride	0Mg/500Ca	0 K; 0 Na; 500 Ca; 0 Mg	0.2	0.1	7.2	2.0	498.0	470.0	0.1	0.1
Chloride	500Mg/0Ca	0 K; 0 Na; 0 Ca;500 Mg	0.6	0.1	1.5	1.2	1.1	0.0	531.2	491.5
Chloride	500Mg/500Ca	0 K; 0 Na; 500 Ca;500 Mg	0.7	0.0	1.6	2.1	521.4	498.9	527.5	526.9

Table 2.A.2 Final solids content (FSC) of samples containing 50 vol% solutions and 50 vol% MFTs after centrifugation with LUMiFuge at 2000 rpm ($581 \times g$) for 45 minutes.

		FSC wt%	
Counter-ion	Solution	First test	
Chloride	0K/0Na	18.9	
Chloride	0K/900Na	35.9	
Chloride	100K/100Na	19.5	
Chloride	100K/500Na	31.6	
Chloride	100K/900Na	36.5	
Chloride	500K/100Na	34.9	
Chloride	500K/500Na	37.2	
Chloride	500K/900Na	38.4	
Chloride	900K/0Na	37.3	
Chloride	900K/100Na	38.0	
Chloride	900K/500Na	39.6	
Chloride	900K/900Na	39.9	

FSC wt%

Counter-ion Solution		First test	Second test		
Sulfate	0Mg/100Ca	21.7	20.8		
Sulfate	100Mg/0Ca	34.0	32.1		
Sulfate	100Mg/100Ca	37.7	38.4		
Sulfate	0Mg/500Ca	49.1	44.4		
Sulfate	500Mg/0Ca	48.7	52.0		
Sulfate	500Mg/500Ca	49.2	49.1		
Chloride	0Mg/100Ca	21.0	20.9		
Chloride	100Mg/0Ca	33.4	34.7		
Chloride	100Mg/100Ca	39.1	39.4		
Chloride	0Mg/500Ca	46.7	48.1		
Chloride	500Mg/0Ca	47.1	47.2		
Chloride	500Mg/500Ca	49.5	47.6		

Table 2.A.3 Concentration of the cations in the supernatants from mixtures of 50 vol% solutions and 50 vol% MFTs after centrifugation

	Solution	K (ppm	K (ppm)		Na (ppm)		Ca (ppm)		Mg (ppm)	
Counter -ion		First test	Second test	First test	Second test	First test	Second test	First test	Second test	
Chloride	0K/0Na	7.9	8.7	332.7	286.8	5.3	4.3	6.0	6.9	
Chloride	0K/900Na	14.8	14.2	778.1	655.6	14.4	12.0	14.6	11.1	
Chloride	100K/100Na	26.5	27.5	395.4	384.1	7.5	6.4	7.1	8.5	
Chloride	100K/500Na	31.3	27.0	575.0	557.4	12.3	9.8	12.1	9.2	
Chloride	100K/900Na	32.5	27.5	805.8	774.1	16.6	14.2	16.7	13.1	
Chloride	500K/100Na	127.5	94.4	433.3	425.6	15.0	12.0	14.7	11.2	
Chloride	500K/500Na	118.0	103.7	604.0	579.9	19.9	16.5	19.3	15.3	
Chloride	500K/900Na	123.9	116.5	846.4	769.1	25.2	21.4	24.1	19.9	
Chloride	900K/0Na	236.5	204.7	379.9	388.2	21.3	17.8	21.0	16.5	
Chloride	900K/100Na	267.0	206.2	470.8	428.7	22.6	18.7	21.9	17.5	
Chloride	900K/500Na	248.0	205.4	644.0	607.5	27.9	22.3	26.6	20.6	
Chloride	900K/900Na	259.0	238.9	846.0	823.2	32.5	26.6	30.9	25.1	
Sulfate	0Mg/100Ca	13.2	12.1	343.3	345.7	9.4	10.9	7.4	7.6	
Sulfate	100Mg/0Ca	12.3	12.5	359.5	354.6	10.2	12.8	14.3	15.8	

Sulfate	100Mg/100Ca	14.8	12.6	390.2	393.8	25.1	20.7	24.2	22.5
Sulfate	0Mg/500Ca	17.9	16.1	412.3	416.6	122.5	90.9	28.9	28.4
Sulfate	500Mg/0Ca	18.4	18.4	443.7	443.7	48.2	48.2	137.4	137.4
Sulfate	500Mg/500Ca	23.7	21.5	438.4	457.9	246.7	194.5	241.7	211.7
Chloride	0Mg/100Ca	16.0	11.2	369.0	337.0	9.3	9.6	9.2	8.0
Chloride	100Mg/0Ca	15.0	13.6	378.0	355.3	11.2	10.4	16.8	15.6
Chloride	100Mg/100Ca	15.1	16.6	375.0	382.9	25.1	23.1	22.4	23.3
Chloride	0Mg/500Ca	18.9	17.2	421.7	412.9	110.3	121.8	20.6	28.1
Chloride	500Mg/0Ca	21.0	21.4	404.7	416.3	59.3	50.0	172.0	172.6
Chloride	500Mg/500Ca	24.0	24.6	456.8	440.2	232.7	215.0	232.0	220.2

Chapter 3: Freeze-thaw

3.1 Background

As mentioned in chapter 1, freeze-thaw is a natural process for MFTs dewatering. Generally, freezing pore water, physically, rejects impurities including ions and also interstitial mineral from the forming ice crystal network towards spaces already occupied by mineral solids, which causes their aggregation [65]. Thus, during subsequent thawing, the entrained water experiences increased permeability (the ability to transmit water and air) and also seepage can occur leading to release water from MFTs [66].

3.1.1 Effect of freeze-thaw on MFTs

Observing the structure of MFTs and its changes during freezing will help understanding the freeze-thaw mechanism. Proskin [35] used Scanning Electron Microscopy (SEM) to investigate the effect of freezing on the microfabric of MFTs. The taken photos showed that the card-house fabric was altered to a compacted, face to face aggregated after freezing and thawing. The compaction of the voids is related to the decant water upon thawing. Proskin [35] stated that ice network provides channels for the released water to flow towards the surface during thawing, as the soil peds settle down. During freezing, pore water is partially frozen at sub-zero temperatures so, there is a surface tension difference between the ice crystals and the pore water which generates a suction force. The suction gradient drives adjacent pore water flow to the freezing front and forces clay particles to consolidate even without adding overburden stress. In addition, the non-planar freezing front absorbs water in different directions. Once the stresses, created by the ice formation, go beyond the tensile strength of the MFTs, ice veins and lens will be formed [35], [67].

Freezing also affects pore water chemistry. The crystal lattice of ice is very selective because of its great regularity. At low freezing rate and along with the formation of ice crystals, ions are rejected and concentrated at grain boundaries [67]. The diffuse double layer theory states that the increase in concentration of ions around clay particles decreases the repulsive force between the negatively charged clay particles. However, the van der Waals attractive force is not dependent upon fluid chemistry. Subsequently, the particles are more likely to flocculate and re-orient themselves to accommodate the changes in repulsive forces [23], [35].

In order to identify the factors affecting dewatering, many factors such as the initial solids content, layer thickness, freezing rate, freeze-thaw cycles and chemical additives have been studied. Johnson et al. [68] conducted small-scale laboratory freeze-thaw tests on Syncrude MFTs and observed up to half of the pore water was released after one cycle of freeze-thaw and additional cycles caused further dewatering but with less efficiency. Generally, the lower initial solids content experienced more significant dewatering. Thus, compared to the first cycle, additional cycles of freeze-thaw became less efficient. Moreover, Johnson et al. [68] found that by increasing the initial solids content the changes in solids content after freeze-thaw decreases exponentially. Large scale multi-layer freeze-thaw tests were also implemented to compare with the large scale single layer tests. The results showed that multi-thin layer freeze-thaw could improve

dewatering by 40% compared to the single layer freeze-thaw. Sego and Dawson [14] studied both small scale single layer and large scale multi-layer freeze-thaw tests on Syncrude MFTs. The results indicated that higher post-thaw solids content of samples was resulted by larger sample height and lower freezing rate. Also, it was concluded a lower freezing rate yields higher thaw strain. Sego and Dawson [14] and Proskin [35] also tried freeze-thaw tests in conjunction with chemical amendment. Proskin found that reducing pH and increasing the concentration of multi-valence cations before freezing could generate higher post-thaw solids content after thawing. The released water after freeze-thaw also looked clear and had small patches of bitumen floating on the surface [35]. Proskin [35] claimed that freeze-thaw (without chemical amendment) affected concentrations of some ions while the pH and electrical conductivity were almost unchanged. However, the released water of chemical amended MFTs had lower pH and two times the electrical conductivity compared with pond water[35].

3.1.2 Applicability of thermal models for freeze-thaw behaviour of MFTs

An appropriate thermal model is required to study the freeze-thaw dewatering of tailings, especially MFTs. Johnson et al. [68] studied the freeze-thaw behaviour of Syncrude MFTs by conducting a large-scale, one-dimensional, laboratory test and they checked the Stefan solution (Stefan solution is a kind of boundary value solution for a partial differential equation to the case in which a phase boundary can move with time). - 24°C was selected as the freezing temperature and the proportionality coefficient was determined in the thick single layer freezing tests. It was then applied for predicting the freezing time for multi-layer MFTs. All the layers had the same thickness. According to

the Stefan solution, it was predicted that the time required to freeze a layer in multi-layer freezing was much shorter (compared to single-layer), while the results showed the freezing time was almost the same. Therefore, the Stefan solution was proved to be imprecise in thermal analysis of MFTs. However, the rationality of the selected freezing temperature is questionable. As the temperature profiles showed the freezing temperature was between -1 and -3°C. The heat from the newly deposited layer of MFTs was released to both air and the underlying MFTs. Therefore, the temperature of older MFTs changed to around -4°C and was still below freezing. Thus, the time to cool the MFTs to -24°C should be removed from freezing time and more work was required to examine the applicability of Stefan solution.

Proskin [35] stated that the Stefan solution only considered the heat transferred to air and didn't consider the heat conduction downwards. Proskin used the Stefan solution to deal with the downward heat flow during freeze-thaw. In addition, other factors such as changes in thermal properties and the thaw strain were considered in the prediction of the thawing front. Proskin found that the predicted freezing time was two to four times longer than the measured freezing time. Then, it was claimed that the test facility deficiencies (lack of perfect insulation and low frequency of temperature recording) shortened the freezing time. However, there was a consistency between predicted thawing time and the measured thawing time. By drawing a comparison, Proskin [35] concluded the Stefan solution is appropriate and precise in a thermal analysis of MFTs. In the field tests freezing rates were obtained from field freezing data and afterward, freezing temperatures were back-calculated. Finally, the frozen/thawed depths were predicted by changing the freezing temperature, the correlation between surface and air temperature, and thin layer thickness.

3.1.3 Consolidation behaviours of MFTs and the effects of freeze-thaw

Unlike ordinary normally consolidated clay, the compressibility of as-received MFTs (never frozen) at lower stress level depends on the initial solids content. Suthaker [69] stated that the aging process yields various micro-structures and it accounts for the variation in compressibility of as-received MFTs. For the effects of freeze-thaw, the increase in solids content is obvious. The void ratio is decreased; the thawed MFTs have less compressibility compared to as-received MFTs at lower stress level. Compared to asreceived MFTs, thawed MFTs have higher void ratio at higher effective stress and has lower void ratio at lower effective stress. In other words, the compressibility of thawed MFTs is more sensitive (than as-received MFTs) to void ratio [35]. Suthaker [69] and Proskin [35] found that there is a power law relationship between permeability and void ratio of as-received MFTs. Proskin [35] investigated the effect of freeze-thaw on the permeability of MFTs. As mentioned above, cracks formed during freezing provided flow channels during thawing and post-thaw consolidation, which facilitate the dewatering. At lower stress level, the thawed MFTs were demonstrated to have a permeability almost two orders that of as-received MFTs with the same void ratio. As the overburden stress increases, the structure of thawed MFTs collapses and cracks are closed. However, at higher stress level, the permeability of thawed MFTs gets closer to that of as-received MFTs and it is, therefore, more sensitive to void ratio. Suthaker [69] stated that, compressibility and permeability aside, consolidation behaviour is also

affected by thixotropic strength and creep properties of the materials. Creep is the timedependent volumetric strains/shear strains at a rate controlled by the viscous resistance of the soil structure [23]. Suthaker [69] found that the creep rate of MFTs linearly increases with void ratio. Suthaker [69] also stated that other factors may affect the creep rate: the over consolidation ratio (OCR) and the size of load increment. Higher OCR and smaller load increment decrease the magnitude of creep. As a rheological property of MFTs, the structure becomes weaker during remolding and gains back strength with time at a constant void ratio and water content. This rheological phenomenon is thixotropy and it commonly happens for a water-clay system. The inter-particle bonding gets stronger during time; therefore, the consolidation behaviour may be influenced. Suthaker [69] investigated the thixotropic behaviour of MFTs by performing cavity expansion tests. Suthaker [69] found that the MFTs with higher water content had lower thixotropic strength. Also, Suthaker found that thixotropic strength increased quadratically with age.

3.1.4 Objectives

Freeze-thaw is known as a natural dewatering process and industries can take an advantage of this process for a cheap yet effective dewatering of MFTs. However, the natural freeze-thaw process is limited by weather changes and both freezing and thawing can occur in a specific period of year. To address this problem, an objective of this study was to study and optimize the factors dealing with freeze-thaw process (e.g. freezing time and temperature) and to investigate the possibility of mechanizing of this process (to develop a continuous freeze-thaw process). In addition, this process should be considered along with the other processes like centrifugation to get an effective dewatering of MFTs.

The current study compared the effect of different sequences of freeze-thaw and centrifugation on dewatering of MFTs.

3.2 Experimental

3.2.1 Materials

As the MFTs from the first bucket (the one that was used for the experiments in chapter 2) was not enough for the tests related to freeze-thaw, another 5-gallon bucket of MFTs was purchased from Alberta Innovates Technology Futures® in April 2015. Table 3.1 shows the properties of MFTs from these two buckets. As it is seen, they have almost the same properties. The pore water chemistry was analyzed by AGAT Laboratories (Ltd).

Parameter	Value (April 2015)	Value (August 2014)
рН	8.41	8.30
Solids content (wt%)	31.2 wt%	31.7 wt%
Density (g/mL)	1.14 g/mL	1.19 g/mL
Ionic composition of MFTs pore water (ppm)	Cations: Ca ²⁺ (13.7), Mg ²⁺ (12.8), Na ⁺ (669), K ⁺ (14.9)	, Cations: Ca ²⁺ (11.3), Mg ²⁺ (10.3), Na ⁺ (590), K ⁺ (13.8)
	Anions: HCO ₃ (915), CO ₃ ²⁻ (20), OH ⁻ (<5), Cl ⁻ (451), NO ₃ ⁻ (<1.0), SO ₄ ²⁻ (3.6)	Anions: HCO ₃ ⁻ (899), CO ₃ ²⁻ (6). OH ⁻ (<5), Cl ⁻ (411), NO ₃ ⁻ (<0.5), SO ₄ ²⁻ (2.8)

Table 3.1 Properties of MFTs from different buckets

3.2.2 Freezers

To investigate the effect of freezing temperature, different freezer at, -21°C (VWR SCBMF-1420), -12 °C (VWR SCBMR-2030) and -8.5 °C (Allegra X-12 series) were selected. The freezers temperatures were measured by thermocouples and data loggers. The extracted data from data loggers showed that the temperature was fluctuating round a constant temperature for each freezer (caused by the regulator inside the freezer that controls the temperature by turning the motor on and off) and the average of those temperatures are reported as the temperature of a freezer.

3.2.3 Solution preparation

To investigate the effect of water chemistry on freeze-thaw behaviour of MFTs, different solutions were made and mixed with MFTs prior to the freeze-thaw test. Gypsum (Drierite Co.), magnesium sulfate monohydrate (Sigma-Aldrich) and DI water were used to make the solutions. Table 3.2 shows the concentrations of ions in solutions.

Table 3.2 Cation concentrations of solutions

Solution	Ionic concentrations (ppm) (measured by ICP-OES)					
	Potassium	Sodium	Magnesium	Calcium		
1000Mg	0.0	0.6	982.3	0.1		
500Ca	1.2	0.5	0.0	476.0		
900Ca	0.0	0.0	0.0	890.0		

3.2.4 Temperature monitoring

The changes in temperature were monitored during freeze-thaw by using OMEGA data loggers (OM-CP-TC101A) and OMEGA thermocouples (type T) with the accuracy of ± 0.5 °C. The thermocouples were fixed at the middle of the 50 mL or 15 mL conical centrifuge tubes (with MFTs samples). Figure 3.1 shows the data loggers and thermocouples placed within the test tubes. Also, OM-CP data logger software was used to program and extract the data from the data loggers. For all the freezing tests, the data loggers were set to measure at 30 sec interval and they started to read the temperature before freezing till the end of thawing.



Figure 3.1 Data loggers and thermocouples used for monitoring the temperature changes

3.2.5 Comparison between freeze-thaw and centrifugation

3.2.5.1 Water chemistry changes

To compare the effect of freeze-thaw and centrifugation on pore water chemistry, 32 mL MFTs was mixed with 8 mL of pore water (pore water was obtained by centrifuging the MFTs and separating the supernatant), DI water, 500Ca and 900Ca in 50 mL Falcon tubes to obtain a sample with 80 vol% MFTs and 20 vol% solution (each test was done in duplicate). Then, one of the samples with the same mixture were placed in -21°C freezer (overnight) and then thawed at ambient temperature for a couple of hours and the other one were centrifuged for 1 hour at 3270g. Afterward, the supernatants of all the samples were characterized using ICP-OES and the concentrations of sodium, potassium, magnesium and calcium were measured.

3.2.5.2 Settling behaviour

To study the effect of centrifugation, freeze-thaw and combination of them with different sequences on dewatering of MFTs, the following scenarios were designed. Scenario 1 (FTh) was to freeze the samples at -21°C freezer (overnight) and then thaw them at ambient temperature and measure the solids content of the settled part. Scenario 2 (C) was to centrifuge sample at 3270g for 2 hours (using AllegraX-12 centrifuge). Scenario 3 (FTh-C) was to do scenario 1 followed by scenario 2 (on the same sample) and scenario 4 (C-FTh) was to do scenario 2 followed by scenario1. Each scenario was done with 8 mL undiluted MFTs, and also was done with the mixture of 8 mL MFTs with 2 mL of pore water or 1000Mg (each test in duplicate). The temperature changes were

monitored during freeze-thaw steps. After thawing, the supernatants were pipetted out and some samples were collected from the settled part and weighed before and after drying to calculate the solids content.

3.2.6 Effect of freezing time and freezing temperature on settling of MFTs

Each sample had 8 mL undiluted MFTs or MFTs with 2 mL of 1000Mg. First, samples were frozen overnight in the -8.5 °C, -12 °C, -21°C freezers (undiluted MFTs was frozen just at -21°C) and then thawed at ambient temperature. All the temperature profiles showed plateaus during freezing (see Figure 3.4) correspond to the phase changing (from liquid to solid) at freezing point. Then, based on the length of the freezing plateaus for each freezing temperature, different freezing times were determined. Afterward, freeze-thaw was done for all the freezing times and freezing temperatures and the solids content of the settled part was calculated.

3.3 Results and discussion

3.3.1 Comparison between freeze-thaw and centrifugation

3.3.1.1 Water chemistry

The ionic compositions of the supernatants of the samples after freeze-thaw (with freeze-thaw conditions mentioned in section 3.2.5.1) were analyzed and compared with the supernatants of the samples after centrifugation. Figure 3.2 shows the $\frac{\text{Actual}}{\text{predicted}}$ concentrations (explained in section 2.3.2) for the mixture of MFTs with different solutions after freeze-thaw or centrifugation. The changes in water chemistry

were discussed in chapter 2 for the 50/50vol% mixtures of MFTs and different solutions and here it will be used for 80/20 vol% of MFTs and solutions (Eq 3.1).

Cpredicted

$$= \frac{0.2 \times C_{s} + 0.8 \times MFTs \text{ water content} \times C_{p}}{0.2 + 0.8 \times MFTs \text{ water content}}$$
Eq 3.1

The deviations of " $\frac{\text{Actual}}{\text{predicted}}$ concentration" values from 1 show that there is an interaction (e.g. ion-exchanging) in all the samples (for both centrifugation and freeze-thaw). Also, this ratio is almost the same for centrifugation and freeze-thaw of samples containing 500Ca and 900Ca. It was suggested that the ion-exchanging happens prior to centrifugation and causes coagulation of particles. However, there are differences in $\frac{\text{Actual}}{\text{predicted}}$ concentrations for potassium, magnesium in samples diluted with DI water and pore water. The reason might be the concentrations of calcium as DI water and pore water had less than 20 ppm Ca²⁺.



Figure 3.2 Actual/Predicted concentration of supernatants of 80 vol% MFTs+ 20 vol% of (a) DI water (b) pore water, (c) 500Ca and (d) 900Ca (freezing was done in -21°C for overnight and thawing happened at ambient temperature). Each bar shows the average value of the two runs + error bar which is \pm the difference between each run and the average.

3.3.1.2 Settling behaviour

Figure 3.3 shows the solids content of the bottom phase after four scenarios of dewatering. According to Figure 3.3, freeze-thaw didn't cause further dewatering for centrifuged samples (the results related to C and C-FTh show almost same solids content). Also, it shows that the solids contents of all the samples are almost the same for

FTh test. However, adding 1000Mg solution improved the solids content in the other scenarios. Based on Figure 3.3 the best sequence of centrifugation and freeze-thaw, in terms of higher solids content, is scenario 3 (FTh-C) which can get a cake with about 63 wt%. The current practice for MFTs treatment includes a centrifugation process followed by depositing the cake in the dedicated disposal area (DDA) for future reclamation and further dewatering by natural freeze-thaw process. Although there are limitations for freeze-thaw process (e.g. weather changes) but the results on Figure 3.3 suggest that this process in more effective if is used prior to centrifugation.



Figure 3.3 Solids content of the settled part, after different scenarios of dewatering (FTh: freeze-thaw, C: centrifugation, FTh-C: freeze-thaw followed by centrifugation, C-FTh: centrifugation followed by freeze-thaw). Each point shows the average value of the two runs + error bar which is \pm the difference between each run and the average

3.3.2 Effect of freezing time

Freezing time is one of the factors dealing with the freeze-thaw behaviour of MFTs [35]. Optimizing freezing time and the temperature required for freezing can increase the efficiency of multilayer (natural) freeze-thaw and can be used in designing a mechanized freeze-thaw process. Figure 3.4 shows temperature profile of freezing (at - 21°C) and thawing (at ambient temperature) of 8 mL MFTs. The first plateau on the left side is related to the time needed for MFTs to freeze (changing from liquid phase to solid phase). The length of the freezing plateau shows the time which is required for complete freezing (freezing time is the time between putting samples inside the freezers and taking them out). Therefore, freezing times shorter than that might result in partial freezing. To study the effect of partial freezing on dewatering of MFTs, different freezing time shorter or longer than complete freezing time were considered and tested for MFTs and mixture of MFTs with 1000Mg.



Figure 3.4 The temperature profile of freezing (in -21°C freezer) and thawing (at ambient temperature) of 8 mL undiluted MFTs

Figure 3.5 shows the length of freezing plateau for 8 mL of undiluted MFTs samples with different freezing time in -21 °C freezer. As it is shown, samples with the freezing time less than 75 minutes have different length of freezing plateau but for freezing time longer than 75 minutes the temperature profiles have almost the same length of freezing plateau. Also it shows the solids content of the settled part of the samples with different freezing time after freeze-thaw. For samples with freezing time longer than 75 minutes, the solids contents of the settled parts (after thawing) are almost the same. It suggests that partial freezing (samples with shorter length of freezing plateau), compared to complete freezing, caused less dewatering but once the samples passed the freezing plateau, more freezing time had no effect on dewatering (since all the ice crystals are formed and will not change). Figure 3.6 visually shows that freezing times shorter than complete freezing time result in less separation of solids.



Figure 3.5 Length of freezing plateau and the solids content (wt%) after thawing of 8 mL undiluted MFTs samples with different freezing time (frozen in -21°C freezer) with 31.2 wt% initial solids content



Figure 3.6 Test tubes after freeze-thaw with 8 mL undiluted MFTs (frozen in -21°C freezer) with different freezing time

Also, the effect of freezing time for the mixture of 8 mL MFTs with 2 mL of 1000Mg solution was studied while samples were frozen in -8.5°C, -12°C and -21°C freezers. Figure 3.7 shows the solids content of the bottom phase after freeze-thaw. According to Figure 3.5 and Figure 3.7, the solids contents of the samples of 2 mL 1000Mg solution and MFTs (kept in -21°C freezer for 90 minutes or 120 mins) have a slight difference with the solids contents of the 8 mL undiluted MFTs with the same freezing conditions. Results show that freezing time has an effect on dewatering behaviour of MFTs. During freezing, the ice forming crystals reject the impurities including particles and dissolved ions from their structures. This phenomenon forces the ions to surround the particles and coagulate them. Consequently, the more formation of ice crystal, the more rejection of impurities and the more coagulation. Therefore, there is less dewatering for partial freezing as the ice crystals are not formed completely.

As it can be seen in Figure 3.7 the samples in -21°C freezers are frozen faster than the other freezers. The solids contents of samples with more than around 75 minutes freezing time are almost the same suggesting that 75 minutes is almost the complete freezing time for the mixture of 8 mL MFTs+2 mL of 1000Mg in 15 mL Falcon tubes in the -21°C freezer. However, samples in -12°C and -8.5°C have slower freezing and longer freezing time. Although the differences between the solids content of samples (frozen at different freezers) are not huge but generally, higher freezer temperature (between the aforementioned freezers) causes better separation of solids from water and higher solids content of the settled part. The reason might be the fact that the freezer with higher temperature provides slower freezing rate so, the freezing water has enough time to create purer ice crystals and reject more impurities thus, particles have more time to rearrange and coagulate



Figure 3.7 Solids content of 8 mL MFTs+2 mL of 1000Mg after freeze-thaw for samples with different freezing time and freezer temperatures with 25.6 wt% initial solids content

3.4 Conclusion

The effect of centrifugation, freeze-thaw and combination of them were investigated on water chemistry changes and dewatering behaviour of MFTs-salt solution mixture. It was found out that freeze-thaw and centrifugation have almost the same impact on water chemistry due to the interaction between added solution and clay particles in MFTs. Also, freeze-thaw of MFTs followed by centrifugation can get a cake with more than 60 wt% solids. Freezing time and freezing temperature are also found to be effective factors in freeze-thaw dewatering. Partial freezing, compared to complete freezing, causes less dewatering but once the sample passed the freezing plateau, more freezing time has no effect on dewatering since all the ice crystals are formed and will not change. Also higher freezing temperature (among the studied freezing temperatures) causes better dewatering as the freezing rate is slower and freezing water has more time to create purer crystals and reject impurities including clay particles and ions and on the other hand, clay particles and rejected ions have more time to create aggregates.

Chapter 4: Rotary filtration of polymer amended MFTs

4.1 Introduction

This chapter is focusing on the dewaterability of polymer amended MFTs through a rotary filtration process. Flocculation is widely used in treatment of different wastewater streams like municipal and industrial wastewater [70]. There are wide ranges of polymeric flocculants and choosing the right polymer for a specific application requires detailed knowledge about flocculation mechanism and correlation between polymers properties and flocculation mechanism.

4.1.1 Flocculation mechanisms

Charge neutralization is one of the destabilization mechanisms of colloidal suspensions by polymers. When a polymer has a charge with the opposite sign of the charge on the surface of particles, the polymer will adsorb on the surface through electrostatic interactions. The mechanism is known as the "electrostatic patch" [71]. In this mechanism, the polymer chain is adsorbed onto the surface of a charged particle, and then is subjected to conformational changes so, most or all of the charged sites on the polymer are in contact with the particle surface. Then, the charged patches on adjacent particles attract to close proximity and flocculate. This mechanism generally corresponds flocculants with lower molecular weight [71]. Ruehrwein and Ward [72] suggested bridging as a flocculation mechanism for the first time. Polymers have usually long chain and, during flocculation, they come into contact with particles, and some of their functional groups will interact with the particles and attach to their surfaces. The other

segments of the polymer molecular will potentially adsorb onto several other particles, Therefore, the polymer molecule acts as a "bridge" to create a larger aggregate [72]. Long chain polymers should be added to a suspension in an optimal concentration, beyond which addition of more polymer has an adverse effect on flocculation [73]. By overdosing a flocculant, the available surface of a particle will be limited for bridging and leads to a restablization of the suspension, known as steric stabilization (see Figure 4.1) [74]. On the other hand, low-level dosing causes insufficient bridging leading to the formation of small flocs.



Figure 4.1 (a) Adsorption of polymer on a particle surface and formation of loops available for binding. (b) Polymer bridging between particles (aggregation). (c) Restabilization of colloid particles [74]

For an effective bridging, the molecule of polymer must span the gap between the particles. For polymers with higher molecular weight, the chain extends further away from the particle surface and can interact with more particles, therefore, reach equilibrium slower. Therefore, polymers with higher molecular weight usually make larger flocs [75]. The lower molecular weight polymers usually form small tight flocs with small amounts of entrapped water. However, the larger flocs, made by high molecular weight polymers, are less shear-stable and might be broken up when subjected to the shear stress in a pump or pipeline. Moss and Dymond [76] stated that the average polymer molecular weight is not the only important factor in flocculation; several other factors including polymer dosage, particle size, effects of shear and agitation, particle concentration, and the polymer molecular weight distribution affect the flocculation efficacy. High shear agitation might break the flocs in flocculating suspension. Floc breakage leads to the formation of smaller flocs with a lower settling rate. Also, breakage of flocs is usually followed by exposure of particle surfaces to polymer adsorption, as a result, the adsorption capacity of the flocculant will increase but flocs cannot reform efficiently as the excess adsorbed polymer causes repulsion. The optimal agitation condition should provide a balance between sufficient turbulence for the efficient mixing of the polymer and particle collision (for floc formation) against floc breakage. Finding the optimum dosage for a polymer depends on satisfying optimal agitation [77], [78]. The investigations carried out by McFarlane et al. [79] and Hogg [80] explained that the adsorption of polymers onto fines is extremely rapid, lasting for only a few seconds when there is sufficient agitation. This phenomenon might result in local overdoses when the polymer prefers to adsorb onto larger particles [79], [80]. MacFarlane et al. [79] found that the adsorption rate of different polymers has an inverse correlation with the settling rate. Hogg also observed that the slowest adsorbing polymer results in the highest settling rates and largest flocs [80].

4.1.2 Previous Studies on Flocculation of Oil Sands Fine Tailings

The process of flocculation has been reported in the literature as an effective method for increasing the efficiency of the fine tails consolidation process [15], [30]. The flocculation of fine tailings with many different inorganic electrolytes and organic polymers have been studied [77], [81]. These studies have shown that flocculants are less efficient at the normal pH of the tailings slurry (~ 8.5). Therefore, adjusting pH to either below 7.5 or above 9.5 will cause better flocculation. Cymerman and Xu [82] showed that high molecular weight, medium charge anionic copolymers of acrylamide and acrylates, such as Magnafloc 1011(also known as Percol 727), induced flocculation of the fine tailings at the normal pH of the tailings slurry with relatively low dosages. They showed that flocculation of MFTs with Magnafloc 1011 led to fast settling flocs and a turbid supernatant water layer containing about 1.5 % solids by weight. Afterward, Sworska et al [31] studied the effect of Magnafloc 1011 dosage, divalent cation concentration and pH on settling rate and clarity of Syncrude fine tailings. Different dosages of the flocculant led to different optimal pH ranges (probably due to contamination of the mineral surface with polar organic matter). Further studies conducted by Sworska et al. [83] on Syncrude fine tailings depicted that mixing conditions strongly impacts the flocculation performance. Their investigation showed that turbulent hydrodynamic condition is an ideal condition to improve the polymer distribution in the suspension and results in a smaller polymer dosage required to achieve good flocculation [83]. A flocculant screening investigation was done by Xu et al. [84] on Syncrude extraction tailings produced similar results. They stated that anionic polymers

with a narrow range of charge densities can flocculate the fine tailing efficiently at a process water pH of 8.5 [84]. Xu et al. [84] showed that the large anionic polymers (Percol LT27A and Percol 727) caused fast settling of tailings at optimal dosages, however, they were vulnerable to overdosing and restabilizing the suspension. However, the mentioned polymers were unable to obtain a clear supernatant even at optimal dosage

It might sound counter-intuitive that an anionic polymer (e.g. Magnafloc 1011) is the most effective at flocculating the negatively-charged particles of MFTs (cause both have negative charges). It was proposed that there is polymer molecule expansion because of repulsion force between the mineral surface and polymer [74][85]. This phenomenon facilitates the flocculation of Magnafloc 1011 and increases bridging of hydrogen-bonding functional groups by increasing the polymer length and long adsorption time [85]. Alagha et al. [85] used Quartz Crystal Microbalance with Dissipation (QCM-D) monitoring to track the adsorption conformation and proposed that Magnafloc polymer chains preferably adsorb onto the surface of alumina ('O' basal plane) on kaolinite particles through hydrogen bonding and weak electrostatic attraction force. On the other hand, the existing repulsive forces on this high-molecular weight polymer cause less compaction of the polymer on the surface, which facilitates the bridging between particles [85].

4.1.3 Rotary Filtration

The issue with polymer treatments is that the flocculation of MFTs by polymers (such as Magnafloc 1011) does not significantly increase the consolidation (compressibility) of the settled suspension. As a requirement of tailings managements, disposal areas should be trafficable and have a high shear yield stress. Therefore, flocculation must be accompanied by a mechanical process such as filtration or centrifugation for further consolidation [5], [86], [87].

Centrifuges are effective in dewatering of tailings. Syncrude has built a centrifugation plant with 18 one-metre-diameter decanter centrifuges that spin between 1,200 and 1,700 revolutions per minute. The capital cost of this plant is around \$1.9 billion and estimated to have a capacity to generate 7.3 million tonnes of cake per year which by a rough calculation (assuming that the solids content of the cake is 55 wt% and solids content of MFT is 30 wt%) it equals to 14.6 million tonnes of MFTs [30]. However, centrifuges consume large amounts of electricity. Rotary filtration is a technology for sludge dewatering. Basically, sludges (usually flocculated with polymers) are pumped into a gap between two rotating screens with parallel slots (with rotation speed of less than 5 rpm) and they move with rotating screens and the filtrate passes through the screens slots. The pressure inside the gap is usually less than 10 psi and is provided by the feed (back pressure). Although there are limited resources to compare the rotary filtration and centrifugation such as the final solids content and inlet flow rate, but Fournier Inc. has listed some of the advantages of their rotary press over decanter centrifugation that some of them are presented in Table 4.1 [88].

Rotary press	Decanter centrifugation				
Low rotational speed: 0.5 to 2.5 RPM. No (or very low) live floor loads.	High rotational speed: 1500 to 3500 RPM. High live floor loads. Building needs to be designed especially to handle these loads				
Reduced noise: Acoustic protection is not					
required.	High noise: Noise attenuation is required				
	as part of the building construction.				
Low Power Consumption:	High Power Consumption:				
Estimated to be 10 kW-hr/dry ton.	Estimated to be: 171 kW-hr/dry ton				
Simple and short start-up and shut down					
procedures.	More complex and lengthy start-up and shut down procedures.				
	*				

Table 4.1 The advantages of rotary press over decanter centrifugation [88].

The first patent related to rotary screens was filed by G. Matthias [89]. Briefly, Matthias's system had a horizontal cylindrical shape with one rotating screen at the middle (perpendicular to the cylindrical surface of the machine). The inlet of fluid flow (sewage) was on one side of the screen and the filtrate was collected on the other side of the screen. There have been different patent stating different configurations of this technique for dewatering [89]–[93]. Currently, Prime Solution Inc and Industries Fournier Inc are two companies that commercially producing dewatering systems based on rotating screens in North America. Generally, their systems comprise a liquid extraction assembly for extraction of liquid from a humid mass in housing with inlet and outlet. The housing is designed to have mass forced by back pressure provided by inlet flow. The housing systems include at least one rotating screen neighboring the path (between inlet and outlet) with a plurality of parallel elongated slots. The pressure, provided by input, pushes the mass toward the screens slots and the liquid drains through

the screens slots. Prior to introducing the humid mass into the mentioned housing system, polymers or other conditioning agents are added to fresh sludge and the amended sludge is introduced to the housing at low pressure [94]–[97]. Figure 4.2 is a schematic of a process taken from the website of Prime Solutions, a company located in Michigan (USA) that manufactures totally enclosed continuous system for dewatering of municipal and industrial sludge. The size of the rotating screens (diameter) depends on the application and varies between 18 to 48 inches for Rotary Fan Press (RFP) [98]. The screen size of Fournier Rotary Press has almost the same range as RFP [99]. The average feed of Rotary Press machines is dependent to the type of sludge and some other factors such as initial solids content of the sludge and the rotation speed of screens (usually between 0.2 and 5 rpm) are obtained. The inlet feed of RFP can vary between 1 to 15 gallon/minute. These rotary presses have application in treatment of municipal sludge, pulp & paper sludge, industrial sludge and manure.



Figure 4.2 Dewatering through rotating screens [100]

4.1.4 Objectives

The objective of this chapter was to determine the feasibility of using a Rotary Filtration (RF) for dewatering of MFTs. To the best of my knowledge, RFs have never been applied to oil sands tailings. Thus, this work initially focused on a proof-of-concept demonstration using custom-made test cells. Afterward, the bench-scale setup was used to study the process variables such as water chemistry, polymer flocculant addition, and RF screen slot size to maximize dewatering performance.
4.2 Materials and methods:

4.2.1 MFTs and diluents

As the residual amount of MFTs from the experiments described in chapter 2 and 3 was not sufficient for the experiments described in this chapter, two 5-gallon buckets of MFTs were purchased from Alberta Innovates Technology Futures® in June 2015 and combined in a 10-gallon vessel. The resulting mixture had a solids content of 29.5 wt% and density of $1.22 \frac{g}{mL}$; the details on the pore water chemistry (as determined by AGAT Laboratories) are given in Table 4.2. The gel-like structure of MFTs prevents proper addition and mixing of polymers with particles suspensions [87]. Alamgir et al. [87] observed that addition of flocculants to undiluted MFTs (31 wt% solids) didn't enhance the settling and filtration of the MFTs. Therefore, for the work presented in this chapter, MFTs was diluted to ~ 11 wt%. The initial tests were done using DI water as a diluent. However, as the water chemistry plays an important role in MFTs consolidation [31], [87], two diluents were considered in the Design Of Experiment (DOE) plan: the actual 'pore water' that is obtained by batch centrifugation of MFTs and a 'pore water surrogate'. The latter was prepared by adding 10.77 g NaHCO₃, 6.13 g NaCl, 0.40 g Na₂CO₃, 0.267 g KCl, 1.015 g MgCl₂ and 0.51 g CaCl₂ to 8 liter DI water. Table 4.2 shows the properties of these two diluents as determined by the analysis done by AGAT Laboratories.

	рН	HCO ₃ ¹⁻	CO_3^{2-}	OH-	Cl-	SO ₄ ²⁻	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺
Pore water	8.40	978	25	<5	381	2.1	17.6	15.0	689	17.5
Surrogate	8.73	710	91	<5	560	<2.0	6.68	10.2	669	21.6

Table 4.2 Properties of the diluents (concentrations in ppm)

4.2.2 Flocculants

In this study, six different polymer flocculants were generously provided by BASF[®]. They are part of the Magnafloc series of polymers and thus are anionic polyacrylamide. The molecular weight and charge density properties are listed in Table 4.3; as per previous studies [101], [102], we rely on the qualitative information that is supplied by the manufacturer to compare the flocculants.

Table 4.3	Characteristics	of Magnafloc	polymeric	flocculants
		U	1 2	

Polymer Name	Molecular Weight (Da)	Charge Density
Magnafloc 155	High	Low/medium
Magnafloc 1011	17.5×10 ⁶	27%
Magnafloc 336	High	30%
Magnafloc 919	2×10 ⁶	Medium
Magnafloc 156	High	Medium
Magnafloc 5250	High	30%

4.2.3 Lab-scale Rotary Filtration (RF) unit

4.2.3.1 Early versions of the lab-scale RF unit

The initial work on RF processing of polymer-amended MFTs was done with stainless steel screens provided by Prime Solutions. These screens were made of Stainless Steel 314 and had longitudinal parallel slots (the slot size was approximately 0.355 mm).

The first version of the lab-scale RF unit was built as shown in section 4.5 (Appendix). It had a rotating screen at 45 rpm at the bottom of the reservoir and after pouring the flocculated MFTs inside the reservoir air pressure was applied from the top (less than 5 psi). This unit was used for some preliminary screening studies using all the polymers listed in Table 4.3 at 300 and 600 g/t. Encouraging results were motivation for next design described below.

The second version of the lab-scale RF unit was built as shown in Figure 4.3, had a 100 mm diameter stainless steel screen (from Prime Solutions) rotated at 5 rpm by a motor and another 50 mm diameter stainless steel screen connected to a shaft and rotated by hand at 5 rpm (the 50 mm screen was cut from another 100 mm screen by water jet). The catch basin under the 100 mm screen had two sections – an inner section was used to collect the material went through the screen while the outer section was used to collect any material that leaked through the edges.



(a)

(e)



Figure 4.3 Second version of lab-scale RF unit, (a) in the vertical position of RF reservoir, (b) in a horizontal position of RF reservoir (c) catch basin with the 100 mm screen, (d) the 50 mm screen, (e) the threaded rod for rotating the 50 mm screen

4.2.3.2 The final version of the lab-scale RF unit

In order to solve the leakage problems associated with the earlier versions of the RF unit, a custom-made 3D-printed screen was made. A ProJet[®] 3510 SD printer was

implemented to print 3 sets of screens (made of polyamide) with slot sizes of 0.355 mm, 0.262 mm and 0.165 mm and with the slot profiles similar to the stainless steel one provided by Prime Solution Inc[®]. A key feature of this design was a groove to accommodate a Teflon o-ring to seal the gap between the rotating screen and the RF reservoir. Also, vacuum grease was applied to the surfaces between 100 mm screen and RF reservoir to make sure the sealing was as leak-free as possible. Figure 4.4 shows the 3D printed screens with their designing and Figure 4.5 shows the third version of the RF unit.



Figure 4.4 The 3D printed screens with their drawing. (a)100 mm screen and (b) 50 mm screen. S is the slot size of the screen and (Y) shows the shape of the slots profiles



Figure 4.5 Third version of RF unit,(A) is the threaded rod that is connected to the 50 mm screen and was rotated by hand to move the 50 mm screen toward 100 mm screen, (B) is the catch basin, (C) is the inlet, (D) RF reservoir, (E) is the motor.

4.2.4 Preparation of polymer-amended MFTs

Stock solutions of 2000 ppm of each polymer were prepared and then diluted as required. To fully dissolve the polymers in DI water (to make the solutions), the stock solutions were agitated for an hour and for each set of tests freshly prepared stock solutions were used. For the first and second version of our lab-scale RF unit, 100 mL MFTs (122.2 g) were mixed with 200 mL (200 g) DI water in a 500 mL beaker using a 2 inches magnet bar for 1 minute at 600 rpm. Afterward, the speed of stirrer was increased to 800 rpm for 10 sec and 10.8 mL of 1000 ppm or 2000 ppm polymer solution was added to the mixture for dosing 300 or 600 (g/tonne of dry solids) flocculant respectively (this dosage range was recommended by BASF). Then, the stirrer was turned down to 200 rpm for 10 sec

and turned off afterward. Then, the samples had 15 minutes rest time. As we didn't have enough MFTs, 50 mL MFTs (61.1 g) were mixed with 100 mL (100 g) diluent (surrogate, pore water, DI water) in a 500 mL beaker using a 2 inches magnet bar for 1 minute at 600 rpm for the tests with the third version of our lab-scale RF unit. Afterward, the speed of stirrer was increased to 800 rpm for 10 sec and 10.8 mL of 500 ppm or 1000 ppm polymer solution was added to the mixture for dosing 300 or 600 (g/ tonne of dry solids) flocculant respectively. Then, the stirrer was turned down to 200 rpm for 10 sec and turned off afterward. The majority of the tests were done with a rest time of 15 minutes, however, a select number of tests were done at shorter rest times.

4.2.5 RF processing of polymer-amended MFTs

This setup was used for DOE test in the horizontal configuration. After 15 mins rest time of flocculated MFTs (after flocculation), all the samples had a supernatant on top and flocculated MFTs on the bottom which was poured into the RF reservoir together. Then, the two rotating screens at 5 rpm pushed the materials toward each other and the filtrate went through the slots of the screens (the unit was perfectly sealed). The filtrate area of each screen was about 19 cm². Mass balance and solids content analysis of all the parts including the formed cake between the screens, solid and liquid phases of filtrate were done.

To evaluate the effect of slot size of the screens (0.165 mm, 0.262, 0.355mm), three sets of RF tests with three different screens (each in duplicate) were done using DI

water as the diluent and 300 (g/t) of Magnafloc 155. The main reason for using DI water rather than pore water was the limited access to pore water.

In this work, the DOE approach was used to investigate the effect of factors represented in Table 4.4 on the performance of the RF unit. DOE is the design of any task or experiment to study or explain the effect of variation in different factors on an outcome. DOE involves in providing a plan for experiments by considering statistically optimal conditions and the constraints of available resources and minimize the effect of disturbances (uncontrolled and unmeasured variables). The establishment of validity, reliability, and replicability are the main concerns of DOE. DOE has been implemented in many studies for optimization of different processes [103]–[105]. It was decided to do fractional factorial in 8 sets; each set in duplicate. All the test variables rather than factors mentioned in Table 4.4 were kept constant.

Factor	Low level (-1)	High level (+1)
Polymer type	Magnafloc 1011	Magnafloc 155
Polymer dosage	300 g/t	600 g/t
Screen slot size	0.165 mm	0.355 mm
Diluent	Surrogate	Pore water

Table 4.4 DOE factors with high and low levels

As in industrial scale 15 minutes rest time might be too long, the best condition in DOE plan with the highest solids content of the formed cake was selected and done again

with 30 sec, 100 sec, 5 minutes and 15 minutes rest time in flocculation step. Afterward, the resulted cakes were frozen at -21 °C (overnight) and then thawed at ambient temperature. After freeze-thaw, the changes in solids contents were analyzed.

4.2.6 Gravity settling

The last part of this work was comparing the solids content of the cake after RF test and gravity settling test. To do so, the conditions in DOE plan which resulted in a cake with around 40 wt% solids content or higher (tests with Magnafloc 155 as the flocculant) were chosen. However, after flocculation, samples were poured into graduated cylinders (rather than into RF reservoir) and the changes of mudlines were monitored for 2 weeks under gravity settling. After 2 weeks the solids content of supernatants and settled parts were measured and compared to the results of RF tests.

4.3 Results and discussion

To modify the first version of RF unit we should picked one polymer (among the polymers we had) that can flocculate MFTs and get the best result after RF test. The criterion for choosing the best polymer was the highest solids content of the cake after RF test. Magnafloc 155 at 300 g/t and 600 g/t had a cake with around 40 wt% solids content after the tests with the first version of RF unit. Therefore, Magnafloc 155 (at 300 g/t) was chosen to use in modification of RF unit. The results of the tests with the first version of RF unit. The results of the tests with the first version of RF unit. The results of the tests with the first version of RF are presented in section 4.5 (Appendix). After choosing Magnafloc 155 as the best polymer, two more tests were done with the first version of RF by considering mass

balance. Table 4.5 shows the results. These results enabled us to draw a better comparison between the first and second version of RF unit.

Table 4.5 Solids content and mass balance of tests with the first version of RF unit (using Magnafloc 155 at 300 g/t)

	Mass/Total mass (%)	Solids content (wt%)
Cake	16.1±1.1	41.3± 1.7
Total filtrate	24.2±1.0	17.4 ± 4.0
Filtrate solid phase	11.2±1.6	34 ± 0.9
Filtrate liquid phase	13.0.5±1.1	3.0 ± 0.4
Lost*	6.7 <u>+</u> 1.1	-
Supernatant	9.3±2.3	4.2 ± 0.4

*Lost includes the trapped in screens (~2%) and leakage

4.3.1The second version of RF unit

As mentioned above, Magnafloc 155 was chosen for flocculation of MFTs. After flocculation different scenarios were followed for different samples. First, the supernatant was separated and the flocculated MFTs was poured in the RF reservoir for both horizontally and vertically configurations. The 50 mm screen was rotated and moved toward the 100 mm screen and always tests were stopped when the distance between two screens was around 1cm. Also, for the horizontal configuration, filtrates were collected from both sides of the RF reservoir. Table 4.6 shows the solids contents and mass balance of each part. Also, Figure 4.6 shows the cake and 2 phases of filtrates (a liquid phase which is mostly separated water and a solid phase which is mostly the flocculated MFTs that went through the screens). Another test was done with the vertical configuration and MFTs was flocculated by 300g/t of Magnafloc 155 and then, poured into the RF reservoir (second version) without separating the supernatant after 15 minutes rest time (Figure 4.7 shows the cake after RF test)

without separation (WOS)										
	Verti	cal (WS)	Horizor	ntal (WS)	Vertical (W	VOS)				
				Solids		Solids				
Components*	Mass/total	Solids content	Mass/total	content	Mass/total mass	content				
I I I I	mass (%)	(wt%)	mass (%)	(wt%)	(%)	(wt%)				
Cake	16.1±1.1	41.3 ± 1.7	16.4±2.0	43.5 ± 0.2	14.3	43.6				
Total filtrate	17.9 ± 3.5	7.1±0.9	18.1±0.2	7.2 ± 0.1	81.1	5.1				
Filtrate solid										
phase	3.3±0.2	34.8 ± 2.2	2.6 ± 0.5	$41.5{\pm}~6.2$	2.4	45.6				
Filtrate liquid										
phase	14.6±1.5	1.6 ± 0.1	15.5 ± 1.5	1.5 ± 0.1	79.0	3.9				
Lost**	5.4±1.3	_	3.9±1.2	-	2.1	-				
Supernatant	57.5±0.4	3.5 ± 0.0	58.0±2.0	2.4 ± 0.4	-	-				
1										

Table 4.6 Solids content and mass balance of tests with the second version of RF unit with separation of supernatant (WS) and without separation (WOS)

*Solids content of the flocculated MFTs for all the tests ~21 wt%

**Lost includes the trapped in screens(~2%) and leakage



Figure 4.6 (a) Second version of RF during the test in vertical configuration(b) cake after RF test, (c) filtrate with 2 phases (DI water and Magnafloc 155 at 300 g/t were used and supernatant was separated after flocculation)

As in industrial scale of RF process, sludges (usually after flocculation with polymers) go directly into the gap between the rotating screens. Therefore, for the rest of the tests with the second or the third version of RF setup, the supernatants weren't separated prior to RP test. Thus, MFTs, after flocculation and 15 minutes rest time, was poured into RF reservoir (in the vertical position) without separating the supernatant. Then after the test the solids content and mass balance analysis were done.



Figure 4.7Cake and filtrate after RF test with the second unit without separation of supernatant (using DI water and Magnafloc 155 at 300 g/t).

Generally, the main differences between the first and the second version of RF units were the speed of rotation and the pushing mechanism. All the tests with the second version had a better quality of filtrate. The overall solids content of the filtrate for the tests with the first version (with 300g/t Magnafloc155) was around 17 wt% (Table 4.5) but for the second version the overall solids contents were less than 8 wt%. The first version had a rotating screen at 45 rpm which applied more shear stress to the cake and that might cause the breakage of flocs. In addition, applying air pressure might push the flocs through the screen before cake formation. Also, in both versions, the flocs penetrated into the gap between 100 mm screen and the plate on the bottom of the RP reservoir (due to lack of proper sealing) and the high shear stress between them would break the flocs and push them through the screen (Figure 4.8).



Figure 4.8 Penetration of flocs into the gap between the 100 mm screen and the plate on the bottom of the RF reservoir for the second version of RF(DI water and Magnafloc 155 at 300 g/t were used)

4.3.2 The third version of RF unit

4.3.2.1 The effect of screens slot size

The third version of RF unit didn't have the leakage problem. Therefore, it was used for the rest of the tests. First, the effect of screen size was evaluated. 50 mL MFTs was diluted with 100 mL DI water and 300 g/t of Magnafloc 155 was added to flocculate MFTs. After 15 minutes rest time the samples (without separating the supernatant) were poured in the RF reservoir with different screens with 0.165 mm, 0.262 mm, 0.355 mm

slot sizes. Figure 4.9 and 4.10 show the solids content and mass balance of the cakes and the filtrates after the RF tests respectively. For all the tests with different screens, the solid phase of the filtrate was less than 1% of total mass suggested that all the flocculated MFTs was packed in the cakes between the screens. Although, there is a slight difference in solids contents results of the tests (cake and filtrate), all three screens showed almost the same results. As mentioned, water chemistry has an effect on polymer flocculation of MFTs [83], [87]. Therefore, changing the diluent from DI water to pore water or the surrogate might affect the floc formation and flocs size which then, the slot size of screens might have an impact.



Figure 4.9 Solids content of cake and filtrate (overall solids content) for RF tests with screens with different slot size (using DI water and Magnafloc 155 at 300 g/t). Each bar shows the average value of the two runs + error bar which is \pm the difference between each run and the average



Figure 4.10 Mass (%) of cake and filtrate for RF tests with screens with different slot size (using DI water and Magnafloc 155 at 300 g/t). Each bar shows the average value of the two runs + error bar which is \pm the difference between each run and the average.

4.3.2.2 DOE experiments

Rotary filtration has different process variables, this section tried to study some of them. Table 4.3 shows the variables investigated in this part with their low and high levels. -1 was assigned to the low levels and +1 was assigned to the high levels and they were used in modeling of the results. Magnafloc 155 was the best polymer based on the tests with the first version of RF and Magnafloc 1011 was recommended by BASF and has been used in different studies [83], [87]. Based on Table 4.4 there were 4 factors. However, the required MFTs don't let us doing a full factorial study. Therefore, we did fractional factorial and the tests were done in duplicate and with a random sequence to

minimize the disturbance. Therefore, the number of the tests was $2 \times 2^{4-1} = 16$. Table 4.7 shows the value of each variable in each test.

Order of		А	В	С	D=ABC
doing test	Test#	Type of polymer	Dosage	Screen size	Diluent
6	T#1	-1	-1	-1	-1
5	T#2	1	-1	-1	1
3	T#3	-1	1	-1	1
11	T#4	1	1	-1	-1
13	T#5	-1	-1	1	1
12	T#6	1	-1	1	-1
14	T#7	-1	1	1	-1
1	T#8	1	1	1	1
16	T#9	-1	-1	-1	-1
4	T#10	1	-1	-1	1
15	T#11	-1	1	-1	1
8	T#12	1	1	-1	-1
10	T#13	-1	-1	1	1
9	T#14	1	-1	1	-1
7	T#15	-1	1	1	-1
2	T#16	1	1	1	1

Table 4.7 The value of each variable in each test and the test sequence

After each test solids content and mass of cake and filtrate (both liquid and solid phase) were measured. Figure 4.11 shows the solids content of the cakes and filtrates after the RF tests. As it is shown, all the samples flocculated with Magnafloc 1011 had the cakes with a solid content less than 35 wt% and samples flocculated with Magnafloc 155 resulted in the cakes with solids content between 40 wt% and 48 wt%. Also, the quality of filtrates was better (lower solids content) for the samples flocculated with Magnafloc 155.



Figure 4.11 Solids content of (a) cake and (b) filtrate after RF test. (DOE results) (c) the legend of the figures (each bar shows the average value of the two runs + error bar which is \pm the difference between each run and the average)

The data were collected and modeled with RStudio®. Figure 4.12 shows the significant regression coefficients (Pareto plot) dealing with solids content of the cakes. As Figure 4.12 shows, polymer type had the most significant positive effect on solids

content of the cakes. It means that using Magnafloc 155 (+1 was assigned to Magnafloc 155) in conjunction with RF can form a cake with higher solids content. The second most significant coefficient was for the interaction between polymer type and dosage. Therefore, Magnafloc 155 at higher dosage worked better than the lower one and Magnafloc 1011 worked better at the lower dosage than the higher one. The interaction between polymer type and screen size had negative regression coefficients which means that by using Magnafloc 155 the smaller slot size caused higher solids content of the cake but by using Magnafloc 1011, the screen with bigger slot size resulted in higher solids content. Other factors are not significant as the 95% confidence intervals span zero for them (see Table 4.8). It seems that using Magnafloc 1011 in junction with RF didn't cause an effective dewatering.





Figure 4.13 shows the regression coefficients for tests with only Magnafloc 155. As it depicts, dosage had the most significant effect and suggests higher dosage caused higher solids content in the cake. Also, as the second most significant factor, using the pore water caused higher solids content. Finally, larger slot size had a negative effect on cake solids content. Based on Figure 4.12 diluent had the least significant effect compared to other factors but in Figure 4.13 it is the second significant factor but can vary the solids content by less than ± 2 wt% and the range for confidence interval spans zero which suggests that the effect of diluent was statistically insignificant. Therefore, it can be concluded that the most determinative effect of diluent is the presence of ions (which the concentrations of ions in the surrogate were almost similar to pore water). Also, most of the significant factors dealt with polymer flocculation (type of polymer, dosage). This suggests that the performance of the RF unit strongly relies on the flocculation process. Based on the results and observations, an effective flocculant should form stable flocs. Also, in the structure of flocculated MFTs, there should be a weak interaction between entrapped water and flocs which facilitates the dewatering and formation of cake during RF test.



Figure 4.13 The regression coefficients (Pareto plot) of the results related to DOE plan dealing with the solids content of the cake just for the samples flocculated with Magnafloc 155.

Figure 4.14 shows the regression coefficients for overall filtrate solids content (including the solid and the liquid phase of filtrate). The most important factor is the polymer type and Magnafloc 155 caused better quality (less solid content) of filtrate. According to Figure 4.14, type of polymer is the most significant factor affecting the mass of solid in the filtrate. Using Magnafloc 1011 caused a significant increase in amount of the solid phase in the filtrate (Figure 4.15 confirms it). As it is seen, other factors are not as effective as the type of polymer and the confidence intervals also span zero for them. However, using Magnafloc 1011 resulted in better quality of liquid phase of filtrate. The liquid phase of filtrate mostly consists of the supernatant after filtration.



Figure 4.14 The regression coefficients (Pareto plot) of the results related to the DOE plan dealing with the overall filtrate solids content (wt%)



Figure 4.15 The regression coefficients of mass (%) of solid phase of filtrate

Figure 4.16 suggests that flocculation with Magnafloc 1011 compared to Magnafloc 155, caused lower solids content in the supernatant. As an explanation, it can be said that molecules of Magnafloc 1011 catch more particles (including finer particles) to form flocs which cause less turbid supernatant. As the finer particles are also involved in the floc formation and probably provide a larger surface area to interact with polymer chains and occupied their active sites (e.g. functional groups than can make hydrogen binding), there will be less active sites on polymer molecules to bridge between bigger particles or flocs to create larger aggregates. Therefore, RF cannot create a solid cake out of those flocs.



Figure 4.16 The regression coefficients of solids content (wt%) of liquid phase of filtrate of DOE plan

Figure 4.17 shows the cakes, the filtrates and the screens after RF test for test #11 and #8 which got the lowest and highest solid content of the cakes respectively. It can be seen that for test # 8 (flocculate MFTs with 600 g/t Magnafloc 155) the filtrate has almost no solid phase and the screen is clean (no flocculated MFTs) and also the cake is pretty solid. However, for test #11 (flocculate MFTs with 600 g/t Magnafloc 1011) the solid phase is obvious in the filtrate and the flocculated MFTs are stuck to the back side of the screen and also cake is fairly loose.





Figure 4.17 (a) cake, (b) filtrate and (c) screen after test for test#8 (600 g/t Magnafloc 155, diluent: pore water, slot size: 0.355mm) and (d) cake, (e) filtrate and (f) screen after test for test#11 (600 g/t Magnafloc 1011, diluent: pore water, slot size: 0.165mm)

	Cake ***SC (wt%)					Filtrate						
	Considering both polymers		Just Magnafloc155		Overall SC		Mass of solid		SC of liquid			
Coefficient					(w	(wt%)		phase (g)		(wt%)		
	*LB	**UB	LB	UB	LB	UB	LB	UB	LB	UB		
(Intercept)	34.1	36.9	43.7	46.4	6.2	7.3	21.9	28.1	2.9	3.5		
Polymer type	8.1	11.0	NA	NA	-1.9	-0.8	-24.4	-18.3	1.4	2.0		
Dosage	-1.2	1.6	0.9	3.5	-0.9	0.2	-3.6	2.6	-0.6	0.0		
Screen size	-0.3	2.6	-2.0	0.6	-0.5	0.6	-2.6	3.6	-0.4	0.2		
Diluent	-1.6	1.2	-0.3	2.4	-0.7	0.4	-0.8	5.3	-0.2	0.3		
Polymer type:Dosage	0.6	3.4	NA	NA	-0.9	0.2	-3.8	2.3	-0.5	0.1		
Polymer type:Screen size	-3.3	-0.4	NA	NA	-0.4	0.7	-2.8	3.3	-0.2	0.4		
Dosage:Screen size	-0.2	2.7	NA	NA	-0.5	0.6	-6.4	-0.2	-0.2	0.4		

Table 4.8 Confidence interval for the coefficients of modeling the data from the DOE plan

*Lower bound of 95% confidence interval

Upper bound of 95% confidence interval *SC: solids content

As mentioned, 15 minutes it's not a feasible rest time in industrial scale of RF. Therefore, to study the effect of rest time on performance of RF test (third version), the conditions of test#8 were selected (diluent: pore water, polymer: 600g/t Magnafloc 155, screen slot size: 0.355 mm) and 30 sec, 100 sec, 5 minutes and 15 minutes of rest time MFTs were given to MFTs after flocculation and prior to the RF test. It has to be mentioned that it took around 5 minutes for 2 screens to get close to each other (1 cm gap between them). Therefore, this time can be considered as an additional rest time for flocculated MFTs. Figure 4.18 compares the solids content of the cake after RF test and freeze-thaw (frozen at -21°C overnight and thawed at ambient temperature) for samples with different rest times. Except 30 sec, all the other rest times resulted in a cake with almost the same solids content. In addition, freeze-thaw added to the solids content of the cake by around 7wt%.



Figure 4.18 Solids content of cakes after RF (Magnafloc 155 at 600 g/t, diluent: pore water, slot size: 0.355 mm) with different rest times and the solids content of the cakes after freeze-thaw (frozen at -21 °C overnight and thawed at ambient temperature). T#8 and T#16 are the solids content of the cakes resulted from T#8 and T#16 of DOE plan which had 15 mins rest time.

4.3.3 Comparing the results of DOE with gravity settling

The purpose of this section is to compare the results of the RF tests and long-term gravity settling of flocculated MFTs (For all the samples that got a cake with around 40 wt% solids or more). The MFTs was diluted with pore water or the surrogate and flocculated with low and high dosages of Magnafloc 155 (300 g/t and 600g/t). The flocculated MFTs was poured into the graduate cylinder and the changes in mullines were monitored. The mulline between the bottom phase (flocculated MFTs) and the phase on top of that didn't change after day 3 of the gravity settling. After 2 weeks of settling the solids content of the cake were measured and compared to the solids contents

of the cakes from RF test. Figure 4.19 shows that for each condition the solid content of the cake for RF test was 10- 17 wt% higher than gravity settling. This graph shows that the cake that RF forms in less than 10 minutes can't be formed by long-term gravity settling (2 weeks). Also, it suggests that formation of a cake with around 48 wt% in related to the rotation and pressing which are done by the screens.



Figure 4.19 Comparison between solids content of cakes after flocculation followed by RF test (DOE) and cake after flocculation followed by gravity settling (each point shows the average value of the two runs + error bar which is \pm the difference between each run and the average)

4.4 Conclusion

A lab-scale unit of rotary filtration system was developed and it was tested for dewatering of polymer amended MFTs. This lab-scale unit enabled us to run more than 50 tests with less than 2 gallons of MFTs. However, the commercial pilot plants or lab scale units might need more than 1 gallon for just one test. The DOE results showed that the flocculation conditions have a big impact on performance of the rotary filtration. Magnafloc 155 is a negatively charged polymer with high molecular weight (low/medium charge) and Flocculated MFTs with this polymer at 600 g/t could form a solid cake (more than 47 wt%) after rotary filtration test. Although, Magnafloc 1011 has been used in many studies and it is known as an effective flocculant for MFTs flocculation, the MFTs flocculated with Magnafloc 1011 didn't work effectively in conjunction with rotary filtration. This might be due to structural differences between Magnafloc 1011 and Magnafoc155. Another reason might be the flocculation condition such as concentration of polymer solution the speed or shape of mixer or rest time. The rotary filtration for flocculated MFTs with different rest time showed that giving rest time to flocculated MFTs is important in terms of formation of flocs and interacting with each other. However, it has to be optimized.

4.5 Appendix

The first version of RF unit had a stainless steel screen (100 mm diameter provided by Prime Solution Inc) with the slot size of 0.355mm rotating at 45 rpm using a motor. The inner diameter of the reservoir was 50 mm (providing filtrate area of approximately 19 cm²). A 5 psi pressure was applied from the top by air flow. Also, the filtrate was collected on the bottom of the screen in a basin. (see Figure 4.A.1). Different polymers were tested with this setup according to the following steps: After flocculation of MFTs supernatant was separated and the solids content of supernatant and flocculated MFTs were measured. Then, the flocculated MFTs were poured into the reservoir while the

screen was rotating at 45 rpm. Afterward, the air pressure was applies at 5 psi. Then, after a couple of minutes, the motor was turned off (to stop rotating the screen) and solids contents of the filtrate and the cake on the top of the screen were measured. Depending on the test conditions, filtrate had a liquid phase which was visually same as the supernatant and a solid phase which assumed to be the flocculated MFTs that went through the screen (see Figure 4.A.2). As the first version had lots of leakage, it was hard to get a reliable mass balance. Based on solids content results of the cakes, the best polymer was selected for evaluation of the second version of lab-scale RF unit. Table 4.A.1 shows the solids content of different parts after RF tests with the first version.



Figure 4.A.1 First version of RF unit (a) before assembling (b) after assembling. (1) 45 rpm motor, (2) catch basin, (3)100 mm stainless screen with 0.355 mm slot size (4) the pressure gauge, (5) reservoir's cap with a valve for pressurized air (6) reservoir.

Table 4.A.1 The solids contents (wt%) of components before and after RF test with different Magnafloc polymers at different dosages using the first version of RF unit

	Magna	afloc	Magnafloc		Magnafloc		Magnafloc		Magnafloc		Magnafloc	
	155		5250		336		156		919		1011	
	Dosage	e (g/t)	Dosag	e (g/t)	Dosag	e (g/t)	Dosag	ge (g/t)	Dosage	e (g/t)	Dosage	e (g/t)
Component	300	600	300	600	300	600	300	600	300	600	300	600
Supernatant	3.6	1.6	2.5	2.2	1.8	2.1	2.1	1.4	0.8	0.9	4.4	4.7
Flocculated MFTs	27.3	24.6	23.4	13.4	12.6	20.4	20.5	15.6	14.9	13.2	24.7	18.6
Cake	40.8	40.9	36.9	27.3	27.3	21.2	30.4	29.6	24.9	24.7	36.8	29.6
Filtrate												
liquid phase	34.1	27.4	2.5	6.5	1.9	0.3	3.4	1.3	0.5	1.3	4.4	4.4
Filtrate												
solid phase	24.2	24.3	15.9	17.5	18.1	14.9	18.1	17.2	15.8	17.2	30.4	26.3



Figure 4.A.2 (a) MFTs flocculated with 300g/t Magnafloc 155 (after 15 minutes rest time) and (b) formed cake after RF test with the first version of the RF unit.

Chapter 5: Conclusion and Recommendations for future works

5.1Conclusion

In this research different methods of MFTs dewatering were investigated. In chapter 2, a high-throughput method was developed and used to investigate the effects of ionic composition on dewatering behaviour (through a centrifugation process). The results showed that samples with different concentrations of ions have different settling kinetic, during centrifugation. The LUMiFuge results enabled us to draw a correlation between the effect of cations (concentration and valency) and centrifugation parameters (force and residence time). This ability will speed up the optimization processes. As an example, the settling results of 900K/900Na at 2325.1g is comparative to the settling results of 500Mg/0Ca at 581.2g with has less salt and almost 4 times less centrifugal force. The changes in ionic composition show that the interactions between added salt and MFTs (which might be because of ion exchanging, precipitation or reactions). Also, the correlation between these changes and settling results show that the higher interaction comes with the better settling results.

Chapter 3 investigated the effect of different factors (such as freezing time and freezing temperature) dealing with freeze-thaw dewatering of MFTs and MFTs-salt solutions. It was found that partial freezing causes less dewatering compared to complete freezing (Complete freezing refers to any point in cooling temperature profile after the freezing plateau). Also, different consequences of using freeze-thaw and centrifugation processes were tested for undiluted MFTs and diluted MFTs with different solutions and
found out that by using centrifugation followed by freeze-thaw a cake with more than 60 wt% solids content can be achieved.

In chapter 4 a lab-scale unit of rotary filtration system was developed and tested for dewatering of polymer amended MFTs. This system enabled us to dewater polymer amended MFTs up to a cake with around 48 wt% solids content. This cake was the best condition of the DOE tests (DOE was used to investigate the effect of polymer type, dosage, water chemistry, and slot size of the rotating screens). Also, DOE results showed that the flocculation conditions have a big impact on results of the rotary filtration

5.2 Recommendation for future works

The developed high-throughput method (used in chapter 2) can be used more in optimization of ionic composition adjustment by using different salt with different cations and anions. As an example LUMiFuge can be used to investigate the effects of cations with higher valencies such as Al^{3+} or Fe^{3+} . Also, the effects of salts with larger anions with higher valencies (such as $Na_4P_2O_4$) should be studied. In addition, it would be an efficient method to investigate the polymer flocculation (with different polymers) of MFTs and draw a comparison between settling behaviour of polymer amended MFTs and ionic composition adjusted MFTs. This can be done by studying the settling results (solids content) as a function of polymer dosage or added salt and centrifugation conditions such centrifugation time and force. Also, these results could help to compare the cost of centrifugation of polymer amended MFTs and ionic adjusted MFTs.

About the freeze-thaw, when the ice crystals are formed, they almost reject all the solid particles. However, a part of pore water is released and another part is reabsorbed to the clay particles after thawing. Thus, it might be a chance to increase the released water after thawing by changing the size or the shape of the frozen MFTs. For instance, making different droplets of MFTs with different volumes (e.g. 1µl to 1mL) and then monitoring the dewatering through freeze-thaw. In this process, adding salts (like gypsum) can be considered. If smaller droplets caused higher dewatering then, the next step can be working on a continuous process of making and freezing (or freezing and thawing) droplets of MFTs. This process can take an advantage of cold weather condition in the oil sands areas in Canada.

As mentioned in chapter 4, the developed rotary filtration system can be used for dewatering of MFTs. However, the unit has not been optimized completely. One of the factors that should be considered in the future modification of this unit is the speed of the screens. It is suggested to use slower speed with a faster pushing mechanism to give the flocculated MFTs less rest time. As the results show the flocculation conditions have a big impact on the performance of RF, and we observed that the RF unit didn't work well with one of the studied polymers. Therefore, it suggests that the structure, properties and architecture of polymer play an important role so, they have to be studied. For example, the charge density of polymers can be measured by charge titration or polymer branching structure can be analyzed by using multi-angle light scattering methods. As another suggestion to improve the dewatering efficiency of RF, changing the water chemistry of MFTs by adding salts like gypsum to improve the quality of filtrate should be considered in future works. Also, the current unit can be modified to a continuous process with an input with constant pressure and flow rate and that pressure can be used as the back pressure to force the liquid to go through the screens slots. At last but not least different experiments should be designed for better understanding of dewatering mechanism through rotary filtration. As an example the screens can rotate in opposite directions or tests can be done without rotation of screens and the screens can be used to push the flocculated MFTs towards each other by just moving and not rotating.

6. References

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