University of Alberta

Effect of Residual Bitumen on Polymer-assisted Flocculation of Fluid Fine Tailings

by

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Abstract

In bitumen recovery from oil sands, a percentage of the bitumen is lost to tailings. The effect of fugitive bitumen on fines settling and consolidation in tailings ponds remains controversial. In the current study, the settling performance of mature fine tailings (MFT) in response to flocculant addition was considered by studying MFT of varying bitumen content. Bitumen content in the MFT was adjusted by controlled removal of bitumen using a Denver flotation cell. The initial settling rate of flocculated MFT was observed to increase with decreasing bitumen content from 0.45 to 0.18 wt%. A further reduction in bitumen content was found to dramatically decrease the settling rate of flocculated MFT. Such behaviour seems counterintuitive since the polymer flocculant was found to have a low affinity for bitumen contaminated surfaces, as measured by quartz crystal microbalance with dissipation (QCM-D), which would predict a further increase in settling rate of flocculated MFT with decreasing bitumen content. Reasons for this behavior were investigated and it was observed that the decrease in settling rate coincided with long periods of intense mixing in the Denver cell. The underlying reason for this behavior is the subject of ongoing investigation. The current study confirms the use of flotation as a viable option to control MFT bitumen content and improve the settling rate of flocculated MFT.

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Chapter 1: Introduction

1.1 Oil sands overview

Oil sands constitute one of the world's largest unconventional oil reserves. The largest deposit of this type is found in Northern Alberta, Canada. These deposits cover approximately 14,000 km^2. Current estimates put the total amount of recoverable oil at 300 billion barrels [1], with 25 billion barrels being currently under development. [2] The first commercial oil sands operation began in 1967 with Great Canadian Oil Sands, now Suncor Energy Inc. In 1978 Syncrude began its oil sands production and is currently the largest oil sands operator. More recently, a number of other companies have also begun oil sands operations and production is forecasted to be 3.7 million barrels per day by 2020. [2]

These oil sands ores are comprised of around 85 wt% solids, including sand and fine clays (fines are defined as particles less than 44μm), with 8-14 wt% bitumen and a small amount of water. Unlike conventional oil, bitumen is highly viscous and cannot be extracted by conventional means. Currently, a large portion of this bitumen is produced by mining the oil sand ore and extracting the bitumen using the hot/warm water extraction method. [2]

The generalized flow diagram for this process is shown in Figure 1-1. The oil sand ore is crushed and mixed with hot water and chemical additives to liberate bitumen from the sand grains. The oil sand-water slurry is conditioned in large pipelines or tumblers where it separates from the sand grains and then attaches to air that is introduced or entrained to the system. The aerated bitumen forms a froth that separates from the solids and water. Water chemistry has been shown to have a significant impact on bitumen recovery. Typically, sodium hydroxide is added to the water to raise pH, which has been shown to significantly improve bitumen recovery from the ore [1]. Typically, optimum recovery is achieved in the pH range between 8.5 and 9.0.

Additional flotation stages are used to recover residual bitumen which is not recovered in the primary froth. The bitumen froth is then treated with solvents to separate the bitumen in the froth from water and solids present. The water and solids remaining after bitumen recovery are referred to as tailings and are discharged from the extraction plant to large containment areas referred to as tailings ponds. In addition to water, sand and fine clays, these tailings contain a small amount of unrecovered or fugitive bitumen.

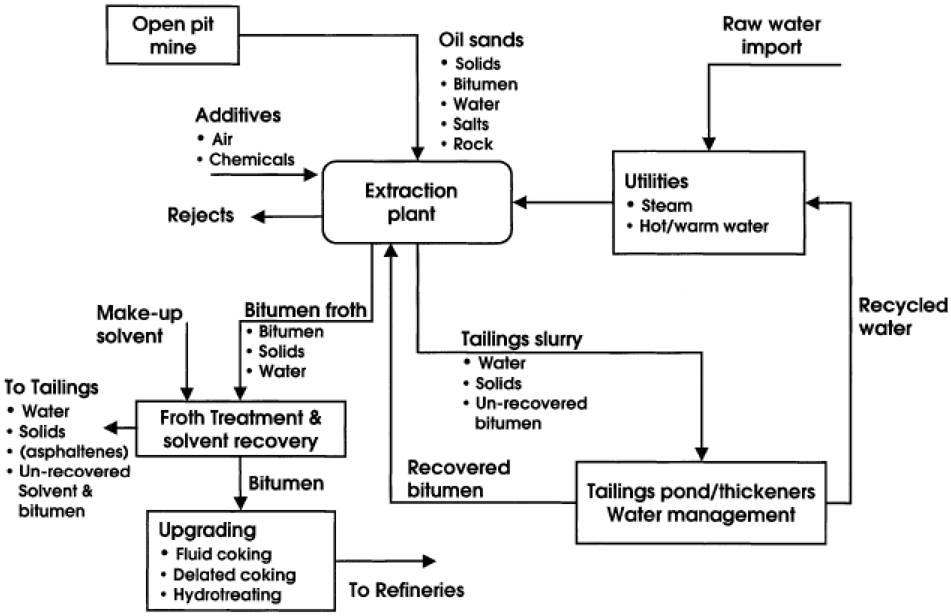

Figure 1-1: Generalized scheme of oil sands processing using water based processes [1]

The typical tailings pond is shown in Figure 1-2. For every cubic meter of bitumen produced, approximately 7.5 m^3 of tailings materials are produced leading to an estimated 954,000 m^3 of tailings produced annually. [3] Coarse sands in the tailings pond deposit rapidly and are used in construction of the dykes and beaches of tailings ponds. The fines and clays separate from the sand and flow into the pond as a relatively dilute slurry of approximately 8 wt% solids. [4] These fine particles gradually settle until the suspension reaches approximately 30 wt% solids after which little to no further consolidation occurs. Once the tailings have reached this state they are referred to as mature fine tailings (MFT). Such tailings have been found to remain stable for several decades. [5]

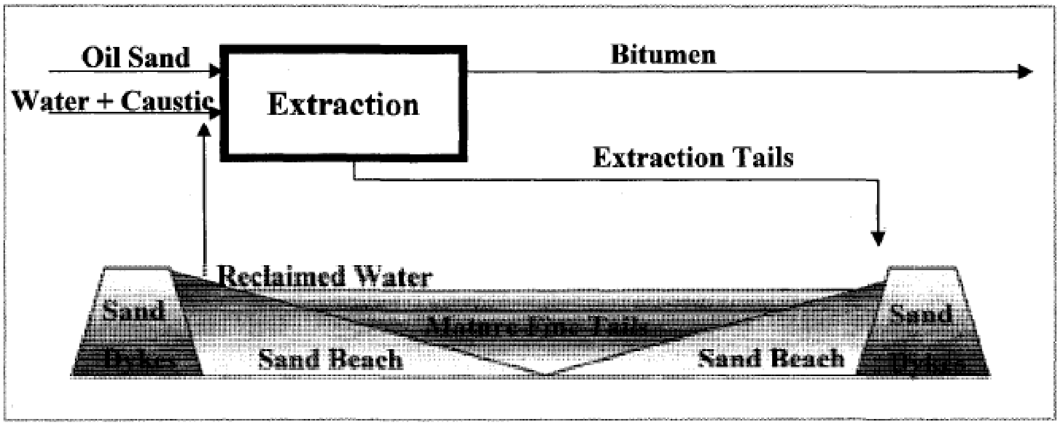

Figure 1-2: Typical oil sands tailings pond [6]

As shown in Figure 1-2, the clear water in the upper layer of tailings ponds can be recycled for use in the extraction plant, but a significant portion of water is trapped in the MFT, requiring more fresh water being used to make up the losses. With increasing oil sands operations there is increasing demand for additional fresh water. Furthermore, the slow consolidating properties of the MFT causes the accumulation of substantial volumes of fluid tailings. As of 2011, tailings ponds covered an area of 170 km^2. [7]

The tailings pond water contains a number of pollutants which are acutely toxic to aquatic life.[8] These include naphthenic acids, polycyclic aromatic hydrocarbons, benzene and toluene as well as inorganic compounds such as lead and arsenic. [8] Naphthenic acids have been found to be the primary source of toxicity in the tailings water. Furthermore, as the impoundment structures that contain the tailings are made of permeable sand, some process water containing toxic substances is able to seep from the tailings ponds to the surrounding groundwater and Athabasca River. [3] Because of these issues remediating these tailings deposits has become necessary. In 2009 the Government of Alberta, Energy Resource Conservation Board (now Alberta Energy Regulator), issued Directive 74, requiring oil sands operators to reduce their accumulated tailings and convert the fluid tailings into trafficable deposits suitable for reclamation of the landscape. This has led to the active development and implementation of new tailings treatment technologies.

1.2 References:

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Chapter 2: Literature Review

2.1 MFT formation

The slow consolidation of MFT has been attributed to a number of factors. Yong and Sethi [1] attributed the high water holding capacity to the presence of swelling clays such as smectite and amorphous solids including iron oxide. However such minerals are not present in significant quantities in all tailings samples. [2] Mikula et al. [3], observed tailings particles in cryo-vitrified samples of MFT using SEM. For certain samples, the particles were arranged in a regular repeating structure that spanned the entire sample. This type of structuring was only observed in tailings samples where significant amounts of bicarbonate was present, indicating that bicarbonate ions may play a role in the structure forming properties of MFT. In addition, a number of studies have been conducted to characterize the properties of different particle fractions present in the MFT. These studies have shown that the ultrafine solids (<0.3 µm) in MFT form gels that give structure to the MFT and impede consolidation. [4] The SEM images obtained by Mikula et al. [3] also show bitumen in MFT present as free droplets of 1 to 10 µm in size as well as contaminating the edges of clays, possibly contributing to the tailings structure. Furthermore, it has been found that residual bitumen decreases the hydraulic conductivity of MFT, [5][6] with free bitumen blocking the pore spaces between particles, impeding water release and hindering consolidation, as shown in Figure 2-1. A study by Majid et al. [7] found that bitumen could be removed from MFT by treating it with sodium silicate to disperse the fines and bitumen, followed by an agglomeration technique to collect the free bitumen. After bitumen removal it was observed that the remaining solids dewatered further than samples where bitumen was not removed. It should be noted that these tests were conducted without any additional settling aids, such as coagulant or flocculant. The majority of solids formed a sediment of up to 60 wt% solids, while the finest solids fraction remained suspended even after 90 days of settling. These results would suggest that bitumen plays a role in MFT stability. However it must be noted that these tailings were dispersed with sodium silicate, therefore it is difficult to correlate the change in settling to the removal of bitumen. These findings would suggest that the stability and high water retention of MFT is due to a combination of fine solids contamination and the presence of residual bitumen, though it is unclear which contributes more significantly.

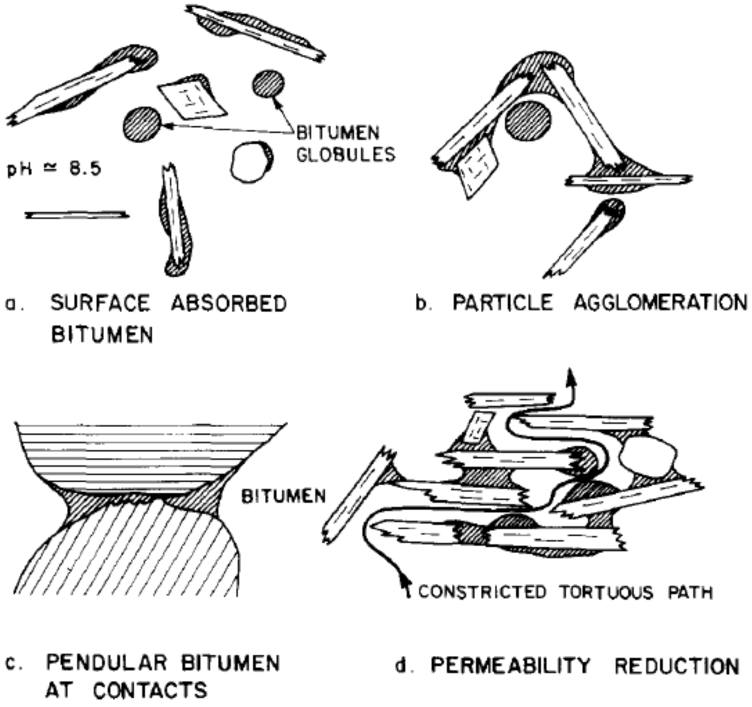

Figure 2-1: Effect of bitumen on particle settlement and permeability [5]

2.2 Tailings remediation methods

A number of methods have been developed to treat MFT. Some of them will be discussed in the following section.

2.2.1 CT process:

In the CT process, a coagulant, typically lime or gypsum, is added to a mixture of coarse sand and fine tailings to form a non-segregating mixture which rapidly dewaters to form a dense deposit. Factors which affect the formation of non-segregating deposits include: fines content, particle size gradation, mineralogy and water chemistry. [8] Previous research into the CT process has found that non-segregating mixtures can be formed over a range of sand to fines ratios (SFR) with the optimum ratio being typically 4:1. This process has been effective in reducing MFT inventory but has a negative impact on the quality of water released from the tailings as the added gypsum increases the calcium ion content of the recycled water which is detrimental to bitumen recovery. [9]

2.2.2 CO_2 enhanced CT process:

A possible modification to the existing CT process is to add CO_2 along with typical coagulants such as gypsum to further enhance the consolidation of the tailings as well as sequester CO_2 emissions. The enhancement of consolidation by CO_2 is primarily due to the decrease in pH caused by the dissolution of CO_2, resulting in a reduction of zeta potential of the fine clays. [10] This change in water chemistry also results in the dissolution of calcium and magnesium from solid carbonates present in the tailings resulting in increased compression of the particles electric double layer and enhancing coagulation. [11] The CO_2 process was found to be as effective as gypsum addition at consolidating the tailings with the added benefits of not adding calcium directly, leading to lower scaling potential and less calcium present in the recycle water in addition to the sequestration of CO_2 emissions. [11]

2.2.3 Freeze thaw dewatering:

Due to the variable climate of Northern Alberta, tailings deposits are subject to cycles of freezing and thawing as seasons change. Freeze-thaw cycles have been shown to assist in the dewatering of MFT. [12] This occurs by the compaction of the solids within the ice network formed as water expands during freezing. Furthermore, as the bulk water surrounding the solids freezes, salts are displaced into the pore spaces between solids [12] causing a reduction in the electrical double layer repulsion between tailings particles. In addition, the formation of ice layers within the sediment causes the pore water to migrate to the ice layer due to differences in surface tension between the ice and unfrozen pore water. [13] The freeze-thaw process has been shown to increase the solids content of Suncor MFT from 30 wt% to approximately 50 wt%. [14] However, this increase is still insufficient to meet the requirements for stackable tailings.

2.2.4 Flocculation-assisted thin lift/drying:

Another commonly used technology for tailings treatment is the flocculation of fine tailings with polymeric flocculants. These flocculants attach to particles, forming links which bind the particles together into faster settling aggregates called flocs. The details of the flocculation process will be discussed further in Section 2.5.

Many studies have been conducted on treatment of oil sands tailings with polymer flocculants. After testing many different polymers of varying molecular weight and charge density it was discovered that for a single flocculant system at a given dosage, high molecular weight, anionic polyacrylamide based flocculants are most effective in improving settling rate, supernatant clarity and consolidation of oil sands tailings. [15] However, flocculation alone is not sufficient to produce tailings deposits with the necessary geotechnical strength. To further enhance the consolidation of flocculated fine tailings, the thin lift method was developed. In this method, flocculated tailings are deposited in thin layers, or “lifts” on a gentle slope to allow further dewatering by drainage, evaporation or freeze-thaw. [16]

2.2.5 Flocculation-assisted centrifugation:

Centrifugation is a process whereby a centrifugal force is applied to a mixture causing the materials to separate based on their respective densities. For the treatment of MFT, centrifuging the flocculated tailings has been shown to significantly increase the final solids content from what would be possible from flocculation alone. Final solid contents of 50-60 wt% were obtained by centrifuging flocculated tailings at a speed of 1250 rpm. [17] These values are significantly higher than those observed without centrifugation; typically 30-35 wt%. [15] However, the higher operational cost of centrifugation makes it less attractive as a tailings treatment option. [18]

2.2.6 ATA process:

As an alternative to the conventional flocculation process, the ATA process (Activator-Tether-Anchor process) uses a polymer to "activate" fine tailings by flocculating them and a "tether" polymer to form a monolayer on coarse sand which acts as "anchor" particles. The two streams are then mixed and the flocculated fines attach to the coarse sand via the tether polymer, resulting in an overall larger floc with enhanced settling and consolidation properties due to the presence of coarse sand. [19]

2.3 Clay mineral description

Clay minerals account for a large portion of the solid material found in MFT. As such the properties of clay minerals will be discussed in the following section. Clay minerals are comprised of repeating sheets of silicon bonded to oxygen in a tetrahedral arrangement and aluminum bonded to oxygen and hydroxyl groups in an octahedral arrangement. Some types of clays may contain magnesium or iron instead of aluminum. [20] The clay type depends not only on the chemical composition of its layers but also on the ratio of octahedral to tetrahedral layers. For example, kaolinite clays have a 1:1 ratio of tetrahedral to octahedral layers, while illite and smectite clays have a 2:1 ratio as shown in Figure 2-2. Clays with 2:1 ratios such as illite and smectite also have a layer of cations between each of the clay layers. The layered structure of clays results in clay particles having a relatively flat, plate-like structure with distinct edges and faces (basal planes) which have differing surface properties. [21]

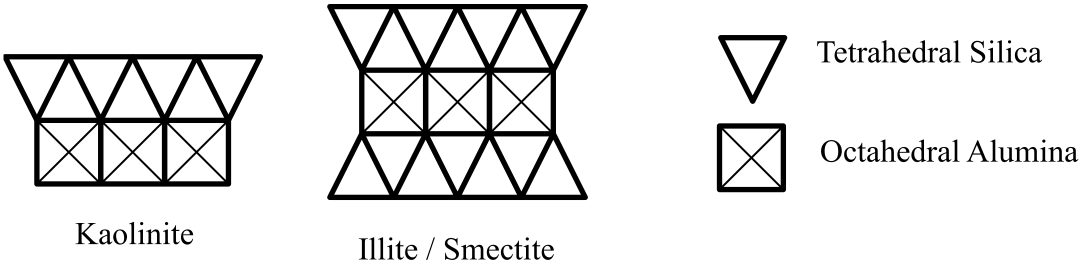

Figure 2-2: Typical structure of kaolinite, illite and smectite clays

On the basal plane of clays, imperfections in the crystal lattice can result in silicon or aluminum atoms being replaced by cations with a lower valence. For example silicon can be replaced by aluminum or aluminum can be replaced by magnesium. This process is referred to as isomorphic substitution. The lower valence results in a deficit of positive charge, leading to a permanent negative charge on the clay basal plane. [22] However, on the edges of clay particles lattice bonds are broken resulting in the formation of silanol and aluminol sites which react with water, creating a pH dependent charge characteristics. [20] As a result, clay particles in water can have a different charge on their edges from that on their faces depending on suspension pH. Therefore, under the right conditions it is possible for the edges of clays to have a charge opposite to that of the clay faces. Under these conditions it can be expected that clay edges and faces will attach to one another, forming a porous “house of cards” structure which can result in the gelation of the suspension. [21] The situation can also be complicated somewhat by the fact the edges and faces of clay particles may not be evenly cleaved, resulting in jagged, stair-case like structures on the faces of clay particles leading to “edge-like” behavior on the faces of such clay particles [23] as shown in Figure 2-3.

However, more recent investigations into the surface properties of clays have found evidence of pH dependent charge on clay basal planes. [24][25] By depositing kaolinite nanoparticles on substrates having a positive or negative charge they were able to preferentially orient the nanoparticles to expose either the silica or alumina basal planes for analysis with atomic force microscopy (AFM). Results of their AFM studies indicated that silica basal plane maintained a negative charge, though the magnitude of the charge varied depending on pH. Alumina basal plane however, showed complete charge reversal at a pH of 4, [23] or 6. [24] These results may indicate that the surface properties of clays are more complex than originally thought.

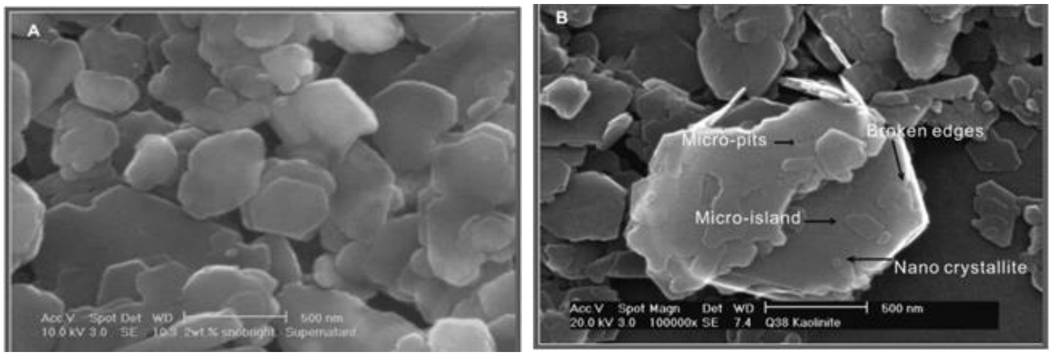

Figure 2-3: High resolution SEM images of (A) highly crystalline and (B) poorly crystalline kaolinite clays [23]

Another important aspect of clays is the cation exchange capacity (CEC). This is a measure of a clays tendency to adsorb ions from solution. Ions can be adsorbed to edge sites to some extent but they are primarily adsorbed to charged sites between layers. For example, in clay minerals such as kaolinite, there is a lower degree of isomorphic substitution than other types of clays, leading to a low degree of ion adsorption and therefore a low CEC. For illite, there is a high degree of substitution in the tetrahedral layers, resulting in the need for interlayer cations (typically potassium) to balance the charge. Since the highly charged layers exist directly adjacent to the interlayer spaces these cations are tightly bound to the charged sites and therefore not easily exchanged. [21] However, for smectite clays there is a greater degree of substitution in the octahedral layers which cannot bind directly to ions in the interlayer spaces, allowing these ions to be readily exchanged. Since cations are often hydrated by a layer of water molecules, the high CEC of smectite clays causes significant amounts of water to enter into the interlayer spaces causing the clays to swell. [20] In addition, the increased ion concentration in the interlayer spaces causes substantial swelling due to osmotic pressure. Swelling of these types of clays can as much as double the volume of the clays [21] and consequently such clays are known to have poor settling rates and poor sediment consolidation, thus hindering remediation of tailings containing these types of clays. [26]

Studies on the types of minerals found in oil sands tailings have shown that they contain largely quartz with kaolinite and illite comprising the majority of the clays.[27][28] Some authors reported small amounts of chlorite and montmorrillonite. Other minerals such as pyrite, siderite and anatase have also been reported. Omotoso et al. [27] found that a portion of the kaolinite and illite contained layers of interstratified smectite, contributing to a higher measurable surface area due to clay swelling.

2.4 Settling theory

The terminal settling velocity (v) of a solid sphere in a fluid medium can be determined by the Stokes' equation:

$$v = \frac{g(\rho_s - \rho_f)d^2}{18\mu} \tag{2-1}$$

where d is the particle diameter, ρ is the density of the particle (s) and fluid (f), μ is the fluid viscosity and g is the gravitational constant. From this equation it can be inferred that the greater the particle diameter the higher the settling rate will be. For a concentrated suspension of particles, the particles hinder the fluid motion around them, thus increasing friction and lowering the overall settling rate. This regime is referred to as hindered or zone settling. Settling in this regime can be described by the Richardson-Zaki correlation:

$$v = v_\infty(1 - \alpha)^n \tag{2-2}$$

where v is the hindered settling velocity, v_∞ is the velocity for a single particle predicted by the Stokes' equation, α is the volume fraction of fluid and n is referred to as the Richardson-Zaki coefficient. This coefficient typically has a value of 4.65 for settling of a fixed volume of suspension in a closed container. It can be seen that increasing the volume fraction of solids (i.e. solids content) will decrease the overall settling rate for a given particle-fluid system.

2.5 Theory and practice of flocculation and coagulation

In industrial processes it is often necessary to separate solid particles from a liquid medium. This is often accomplished by sedimentation or filtration. These processes can be enhanced by bringing small particles together to form larger aggregates. This can be achieved by reducing electrical double layer forces, allowing attractive van der Waals forces to dominate. This process is referred to as coagulation. Flocculation is the process where particles are brought together to form large aggregates. This can involve bringing together small aggregates formed by coagulation, binding particles together using high molecular weight polymers or a combination thereof. Flocculation using polymers does not require charge neutralization. [29] This type of flocculation is used in the thin-lift techniques for oil sands tailings treatment described above. As polymer flocculation is the focus of the current work, it will be discussed in detail in this section.

Polymer flocculants can be made of a variety of chemical compounds and their properties, including molecular weight, charge (neutral, cationic or anionic) and charge density can be tailored to the needs of the process. Common industrial flocculants include polyacrylamides (PAM), polyethylene oxide (PEO) and polydiallyldimethylammonium chloride (PDADMAC).[29]

There are two primary methods by which polymers flocculate particles: i) bridging and ii) electrostatic patch. In bridging flocculation, the polymer adsorbs onto two or more particles bridging them together, [15] as shown in Figure 2-4. The polymer must have a high molecular weight so that segments of the polymer can extend past the electrostatic barrier of the particles. For electrostatic patch, the polymer must be highly charged and the charge must be opposite to that of the particles. This method is similar to coagulation as the surface charge of particles is altered, but instead of neutralizing the charge of the entire particle, the polymer adsorbs on the surface creating a region of opposite charge allowing other particles to attach to that site. This is shown in Figure 2-4. In this work, the flocculants used had high molecular weight and low charge density. Therefore of these two mechanisms, bridging flocculation is more relevant.

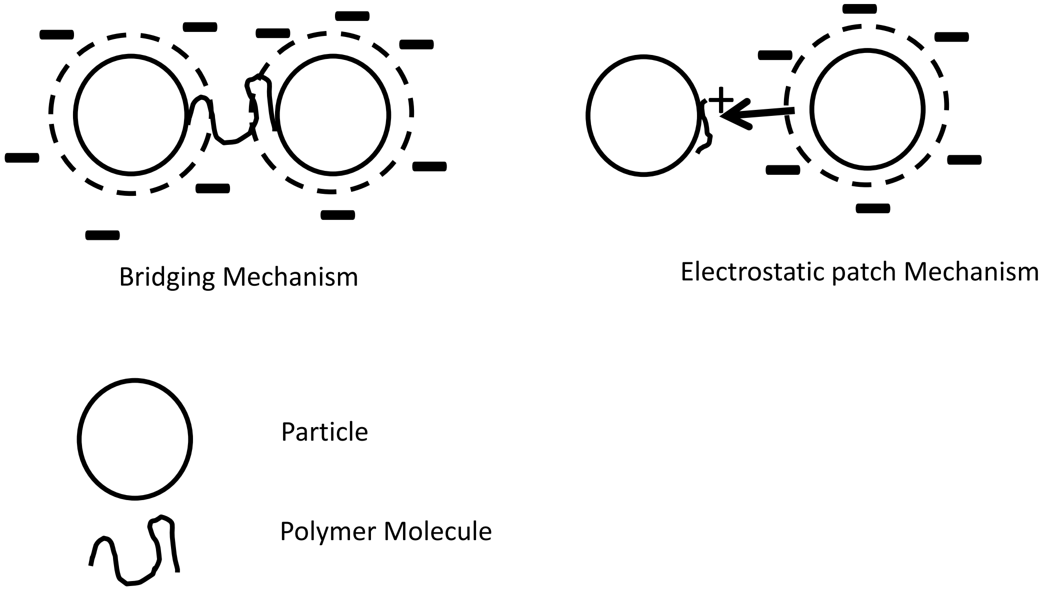

Figure 2-4: Schematic of flocculation mechanisms

2.5.1 Flocculation stages:

In the process of polymer flocculation there are 5 general steps: [30]

1) mixing of polymer and suspended particles
2) adsorption of polymer molecules on particle surfaces
3) re-conformation of polymer molecules
4) flocculation of particles having adsorbed polymer
5) floc breakage

In practice these steps are known to occur simultaneously and compete with each other to some extent. Factors relating to each of these steps will be discussed in the following sections.

2.5.2 Effect of mixing:

Mixing is required to distribute the added polymer solution evenly throughout the suspension, as well as to induce particle-polymer and particle-particle collisions. If mixing is insufficient, local overdosing of polymer may occur, causing the surfaces of the affected particles to become saturated with polymer, leading to steric repulsion of polymer strands and preventing the formation of inter-particle bridges. [30] However, if mixing is too intense the excess shear can cause breakage of flocs, leading to a reduced floc size and lower settling rate. [26] Some degree of floc breakage can be beneficial as it exposes new surface area for additional polymer adsorption and floc growth. [29] Therefore an optimum mixing intensity exists for flocculating systems. This has been observed in practice by a number of studies. [31][32][33]

2.5.3 Adsorption:

Polymer adsorption on a particle surface depends on the polymer type and can occur through a number of mechanisms, including electrostatic attraction, hydrogen bonding, hydrophobic interactions, specific chemical bonds or a combination of these. [34]

According to Hogg, [35] the polymer adsorption process can be considered as a collision process where the polymer molecules act as particles of a given size dependent upon their molecular weight. The rate of adsorption is related to the collision frequency which can be calculated using equation 2-3:

$$K = \frac{2K_BT}{3\mu}\left(2 + \frac{x_i}{x_p} + \frac{x_p}{x_i}\right) + \frac{\bar{G}}{6}\left(x_i + x_p\right)^3 \qquad (2\text{-}3)$$

where x_i and x_p represent the effective diameters of particles and polymer molecules, respectively, K_B is the Boltzmann constant, T is absolute temperature, μ is viscosity, and $\overline{G}$ represents the mean shear rate in the system. The first term represents the contribution of Brownian motion, while the second term accounts for the effect of mixing. Generally, the effect of mixing is much more significant than Brownian motion so that the first term can often be ignored. This equation indicates that the rate of polymer adsorption is dependent on the mixing parameters of the system as well as the effective hydrodynamic radii of the polymer molecules and solid particles. It also shows that the rates of collision will be greater for larger particles and polymer molecules. The rate of polymer adsorption is also dependent on collision efficiency, which is proportional to the expression θ(1-θ). θ is the fractional surface coverage of the adsorbed polymer. [30] From this expression it can be inferred that maximum flocculation efficiency occurs when surface coverage is 50%. However, the model described above does not take into account factors such as electrostatic charge. These factors will be discussed in subsequent sections.

2.5.4 Adsorption of polyacrylamide:

As mentioned previously, one of the most common industrial flocculants is polyacrylamide. Anionic forms of these polymers, such as polyacrylamide-polyacrylate copolymers are also widely used. The polymer used in this study was an anionic polyacrylamide, so this type of polymer will be described in this section. The functional unit of this polymer is shown in Figure 2-5.

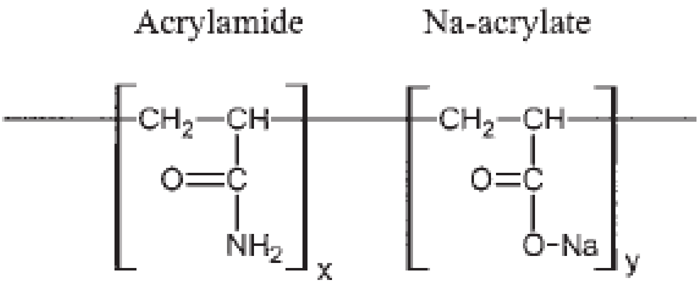

Figure 2-5: Functional unit of hydrolyzed polyacrylamide [36]

These polymers have been found to adsorb onto particle surfaces through the formation of hydrogen bonds between amide groups and hydroxyl groups found on the particle surfaces. [37] In the case of clays, these polymers have been found to attach primarily to sites on the edges of clays, with little attachment on the clay basal planes. [38] However, Alagha et al. [25] showed that anionic polyacrylamide exhibits limited, reversible adsorption on the silica basal plane of clays likely through hydrogen bonding. The low adsorption was attributed to electrostatic repulsion between the negatively charged surface and polymer. The same polymer showed substantially greater adsorption on alumina basal plane resulting from electrostatic attraction due to the opposite charge of the alumina surface at the pH used in the study.

2.5.5 Conformation:

Once adsorbed, the polymer can re-conform on the particle surface, depending on the nature of polymer-particle interactions. If the polymer adopts a flat conformation it may not extend far enough from the particle surface to form bridges with other particles, as well as blocking further polymer adsorption and hindering overall flocculation. [39] A study on the conformation of polyacrylamide adsorbed onto mica, conducted using AFM, found that the adsorbed polymer forms a series of loops and tails of varying lengths, with small loops being the most common, indicating that the majority of the polymer extends away from the surface. [40] Alagha et al. [25] studied the adsorption of anionic polyacrylamide on the alumina and silica layers of kaolinite particles. It was observed that on alumina surfaces the polymer initially adsorbed with a relatively flat conformation but over time, as more polymer adsorbed the conformation became more extended due to repulsion between polymer molecules. As mentioned previously, the adsorption of polyacrylamide on the silica layer was low and reversible, but while the polymer was adsorbed it showed a more extended conformation than on the alumina surfaces. This was most likely due to the electrostatic repulsion between the polymer and the surface at the experimental conditions used. In practice, Nasser et al., [41] found that for kaolinite suspensions, the polymers which adopt a more extended conformation on the particle surface produced larger, faster settling flocs than those with a more compact conformation.

2.5.6 Floc formation:

Once polymer strands have been adsorbed onto particle surfaces, additional polymer-particle collisions lead to formation of aggregates or flocs. The collision rate between different sized particles (denoted i and j) can also be described by equation 2-3 above, with the polymer size x_p replaced with x_j, the diameter of a particle of size i and j.

As flocs form and grow they adopt a fractal configuration. The mass of a fractal aggregate can be related to its size by the expression:

$$m \propto L^{d_f} \tag{2-4}$$

where m is the mass of the aggregate, L is the primary dimension, typically diameter, and d_f is a parameter called “fractal dimension” which accounts for the empty space within the aggregate. For a solid particle the value of d_f is 3, but for porous flocs the value is typically between 1.5 and 2.5. [42] The porous nature of flocs has two primary implications on floc settling. The first is that, depending on porosity, the density of an aggregate can be significantly lower than that of the primary particles that comprise it. The density of an aggregate, $\rho_{a,}$ can be related to its void fraction, ε, by the expression:

$$\rho_a = \rho_l + (\rho_p - \rho_l)(1 - \varepsilon) \tag{2-5}$$

where ρ_p and ρ_l are the particle and liquid densities, respectively. When the value of the void fraction is large (close to 1) the aggregate density will be very close to that of the fluid, resulting in lower settling rate. However, the porous nature of flocs allows the suspending fluid to pass through them, increasing their settling velocity. This affect is typically accounted for by applying a correction factor, Ω, a function of primary particle size and void fraction, to the expression for settling rate. [43]

In the case of clays, their flat, plate-like structure also has a significant impact on the flocculated structures that they form. As mentioned previously, polyacrylamide polymers have a significant preference for the edge sites of clays. This causes clays to flocculate in an edge-edge configuration, leading to large but porous aggregates that despite high settling rate still retain a large amount of water. Additional compaction is generally needed to increase consolidation by forcing the clays into a more compact face-face orientation. [23] The surface structure of clays can also have a significant impact on aggregate structure. Clays with a low degree of crystallinity have irregular “stair-case” like structures on their basal planes, which have properties similar to the edge sites of clays. This results in a greater degree of edge-face attachments during flocculation, which results in flocs with lower density and poorer settling and consolidating properties. [23]

2.5.7 Floc breakage:

The break-up of flocs results from hydrodynamic shear and can occur either by erosion of primary particles from the surface of the floc, or by fracturing of the entire flocculated structure. According to Yeung et al., [44] breakage of the floc will occur at the weakest point within its structure. For a dense floc, with a high fractal dimension, surface erosion is more likely as the particles on the surface have fewer attachments than those in the interior. For flocs that are more porous, fracturing of the entire structure is more likely. The capacity of particles to re-flocculate after breakage depends strongly on the type of flocculant used. After breakage, high molecular weight flocculants show limited capacity to re-flocculate due either to scission of the polymer chains or to re-conformation of the polymer strands into a less extended orientation which limits attachment to other particles. However, low molecular weight, high charge density polymers show a significantly greater capacity to re-aggregate as these types of polymers cause particle attachment by electrostatic attraction rather than by bridging. [45]

2.5.8 Effect of charge:

As mentioned above, the type of charge and charge density of the polymer can have a significant effect on its interaction with particles. Firstly, the charge of a polymer effects its conformation while in solution. For a cationic or anionic polymer, electrostatic repulsion between charged segments causes it to adopt a more extended conformation than a neutral polymer. [39] An extended conformation is beneficial for flocculation as it increases the hydrodynamic radius of the polymer. Such property allows the polymer to better extend past the electrostatic barriers of particles, leading to more effective bridging. Furthermore, electrostatic interactions between particles and polymer strands can have a significant effect on adsorption. For oppositely charged polymer-particle systems, the adsorption rate is enhanced due to electrostatic attraction. For polymer-particle systems with the same charge, adsorption is inhibited, [46] especially for low molecular weight, high charge density polymers. [35] However, for high molecular weight, low charge density polymers the interactions between uncharged polymer segments and particle surfaces may be strong enough that the electrostatic effects are less important. According to Nasser et al. [47] polymer charge also has a significant effect on the conformation of the adsorbed polymer. For a negatively charged surface, such as kaolinite, adsorbed anionic polymers will adopt an extended conformation due to electrostatic repulsion and will therefore form larger, faster settling flocs than cationic polymers. However, this study also found that if the anionic charge density was too great a reduction in floc size was observed. Furthermore, the study found that cationic polymers form stronger, more compact flocs due to a greater number of polymer-particle attachments, which is preferable for some applications.

2.5.9 Effect of molecular weight:

In general high molecular weight is necessary for bridging flocculation, as the molecule must be large enough to span the gap between particles and extend beyond the range of electrostatic repulsion.[29] [39] The adsorbed polymer also increases the effective hydrodynamic radius of the particle allowing collisions to occur more readily; therefore a greater molecular weight is beneficial.[39] Furthermore, according to Hogg, [35] high molecular weight flocculants can form more links with the particle surface than can low molecular weight flocculants, leading to stronger flocs. However, the author also states that the collision efficiency for high molecular weight polymers is greater for large particles (>1 μm) than for smaller particles, as such particles have less surface area available for adsorption. Also, equation 2-3 shows that the collision frequency will be greater for larger particles, resulting in the preferential flocculation of large particles leaving smaller particles relatively un-flocculated. The preferential flocculation of larger particles leads the formation of large flocs which have high settling rate, but because smaller particles remain relatively unflocculated, the resulting supernatant will have high turbidity. This effect has been observed in practice by Yuan et al. [48] The authors found that a sequential addition of high and low molecular weight polymers provided the best results for settling rate and supernatant clarity.

2.5.10 Effect of solution chemistry:

The chemistry of the suspending water can have a dramatic effect on adsorption and settling performance. Firstly, the pH of the suspension determines the charge of the suspended particles and can also affect the conformation of polymer flocculant in solution. Sworska et al. [49] found that settling of oil sands tailings with anionic polyacrylamide, improved at low pH due to decreased electrostatic repulsion between suspended particles. However, higher polymer dosages were needed to obtain reasonable settling rates, as the polymer used adopted a less extended conformation at low pH. The presence of divalent cations, such as Ca^{2+} and Mg^{2+} has also been found to have a profound effect on flocculation. Sworska et al., [49] found that the presence of these ions significantly enhanced settling and supernatant clarity for tailings suspensions with alkaline pH. Using Atomic Force Microscopy (AFM), Long et al. [36] found a significant enhancement of the adhesive force between silica particles with anionic polyacrylamide in the presence of Ca^{2+} and Mg^{2+}. It was proposed that the adsorption of divalent cations on the negatively charged particle surfaces, in addition to compressing the electric double layer, provides sites for the adsorption of anionic polyacrylamide molecules, enhancing adsorption and flocculation.

2.5.11Effect of bitumen:

As mentioned previously MFT contains approximately 1-3 wt% bitumen. While some studies have been conducted on the effect of bitumen on MFT stability, very little research currently exists on the effect of bitumen on the flocculation of oil sands tailings using polymer flocculants.

Long et al. [50] investigated the interaction of polyacrylamide and oil sands surfaces using an AFM technique called single molecule force spectroscopy to determine the attachment force between polyacrylamide molecules and model oil sand surfaces, including silica, mica (representing clays) and bitumen. It was found that both the attachment energy of the polyacrylamide and the probability of attachment were lower for bitumen than the other surfaces. This observation might imply that the presence of bitumen would hinder the flocculation of MFT by polyacrylamide. Further investigation of this area is needed, which is the goal of this thesis.

2.6 Thesis objective

The objective of this thesis is to investigate the effect of bitumen removal from mature fine tailings (MFT) on interactions of remaining fine solids with polymer flocculants. Adsorption characteristics of polymers in the absence and presence of hydrocarbons on solid surfaces will be determined and correlated to settling behaviors of fine solids under the corresponding environment.

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Chapter 3: The Impact of Fugitive Bitumen on Polymer-based Flocculation of Mature Fine Tailings*

The following paper was published previously. The objective of this paper was to investigate the role of residual bitumen on the flocculation of oil sands tailings using polymer flocculants. This paper constitutes a significant portion of the work done on this project and is reprinted here in its entirety.

3.1 Introduction

The oil sands deposits in Northern Alberta, Canada constitute one of the world's largest oil reserves. [1] For several decades bitumen has been recovered from the oil sands via a hot/warm water extraction process. During extraction the oil sands ore is mixed with hot water and agitated to promote bitumen liberation/detachment from the sand grains. Often, to maximize bitumen recovery, caustic (typically sodium hydroxide) is added to the slurry water as a process aid to raise pH. Increasing pH modifies the slurry chemistry by: i) releasing natural surfactants from bitumen ,[2] ii) modifying electrical surface potentials of bitumen and solids, [1] iii) reducing the divalent ion concentration and, iv) decreasing solids hydrophobicity.[3] Beyond critical caustic loading, processing conditions become unfavorable, reducing overall bitumen recovery. Typically, optimum recovery is achieved in the pH range 8.5 – 9.0.

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Flotation of bitumen forms a bitumen froth containing approximately 60% bitumen, 30% water and 10% solids by weight. Typically, the froth accounts for around 90% or greater bitumen recovered from the oil sands ore.

Unrecovered bitumen is lost with the coarse solids removed through the bottom of the primary separation vessel and the fine middlings which are subsequently reprocessed by flotation to recover residual bitumen. Eventually the two streams are combined and discharged to tailings ponds. Coarse sands deposit rapidly, while the fines and clays settle slowly. Over an extended period of time, fine tails form a viscous, gel-like suspension that resists consolidation. Such material is referred to as mature fine tailings (MFT) which contains approximately 30% solids by weight and remains stable for several decades.[4]

Methods for treatment of MFT to improve settling and consolidation have received significant attention in recent years. Several patents and publications describing techniques to enhance tailings consolidation are available in the open literature. The proposed approaches can be summarized as: i) composite/consolidate tailings (CT) process, ii) CO_2 enhanced CT process, iii) flocculation-assisted centrifugation, iv) freeze thaw dewatering, and v) flocculation-assisted thin lift/drying.[5][6] The use of polymer flocculants has been considered in detail. While improving the settling of fines/clays at an optimum dosage, the addition of polymer does not significantly improve consolidation without additional mechanical forces.[7] Novel approaches using stimuli-sensitive polymer,[8] and hybrid-polymers[9] have been considered, but remain somewhat inadequate to address the ongoing requirements for tailings management. Alamgir et al.[7] considered a two-step flocculation-assisted filtration process to produce trafficable filter cake/deposits from MFT. Through appropriate dilution of MFT and the addition of Al-PAM (cationic organic-inorganic hybrid polymer), MFT was transformed into a stackable cake by flocculation-assisted thickening and the subsequent filtration of the sediment. While such studies represent a significant advancement in tailings treatment, little consideration has been given to the role of fugitive bitumen.

Several studies have shown that the ultrafine solids in MFT have a high propensity towards gel formation. These solids in the presence of multi-valent cations promote the formation of large, porous aggregates that rapidly settle to form sediment beds. However, the large aggregates retain substantial amounts of water and resist consolidation.[10] Structuring of such aggregates and gelation are more pronounced for solids contaminated by organic matter such as humic matter.[11] It is believed that hydrophobic interactions between bitumen-contaminated particles help to bridge neighboring particles, contributing to network strength and gelation.[12][13] The associated and free bitumen in MFT has been shown to decrease hydraulic conductivity,[14][15] blocking the fluid pores, impeding water release and hindering consolidation. While research shows improved settling by removal of bitumen,[16] there remains conflicting discussion with the presence of fugitive bitumen being identified as a binding agent to flocculate fines and increase the settling rate.[14]

The role of fugitive bitumen on flocculation performance of MFT has not been considered. Indirectly, Long et al.[17] using single-molecule force microscopy studied the adsorption of a partially hydrolyzed, high molecular weight, anionic polyacrylamide (HPAM) on sand, clay and bitumen surfaces. The probability of picking up HPAM strands by AFM tip was significantly lower on the bitumen surface, indicating fewer HPAM molecules being adsorbed on bitumen, as compared with both clay and sand. The measured desorption force was considerably lower on a bitumen surface than on a clay surface. Such selectivity of HPAM for different surfaces would suggest polymer performance to deteriorate with increasing bitumen loading in MFT. The objective of the current study is to understand the role of fugitive bitumen on the flocculation and settling performance of MFT. Bitumen content in MFT is varied by controlled removal of bitumen using flotation or solvent washing.

3.2 Materials and methods

Samples of raw MFT and process water were obtained from Syncrude Canada Ltd. The composition of the raw MFT was determined by Dean-Stark analysis to contain 1.4 wt.% bitumen, 31.7 wt.% solids and 66.2 wt.% water. MFT samples were blended vigorously and diluted to 10 wt.% with process water prior to their use. The polymer flocculant used throughout the study was AF246 (Hychem Inc., USA), an anionic, high molecular weight hydrolyzed polyacrylamide polymer. In advance of flocculation experiments 1000 ppm (1 g/L) polymer stock solution was prepared in deionized water and agitated for 12 h. All stock solutions were used within 24 h.

3.2.1 Control of bitumen content:

Protocol 1 by Denver cell flotation of MFT: 800 g of diluted MFT was preconditioned at 1200 rpm for 5 min. Flotation air was then introduced at a rate of 150 mL/min. The flotation time was varied to yield samples with varying bitumen content. The composition of the resultant samples was determined by Dean-Stark analysis. It should be noted that after flotation the solid content of the diluted MFT could be considered unchanged due to a limited amount of fine solids along with the slurry water being carried into the froth. Figure 3-1 shows the final bitumen content of the diluted MFT as a function of flotation time.

Protocol 2 by MFT blending: Low bitumen content samples obtained by protocol 1 were blended with diluted raw MFT (bitumen content ~ 0.45 wt.%). The reason for blending is to achieve a desired bitumen content to differentiate the effect of selective removal of solids by flotation on MFT flocculation and settling. To ensure effective blending the combined MFT sample was mixed at 500 rpm for 1 h using an overhead mechanical stirrer with a 4-blade, 2-inch width impeller. The solids content in the mixed sample remained at 10 wt.%.

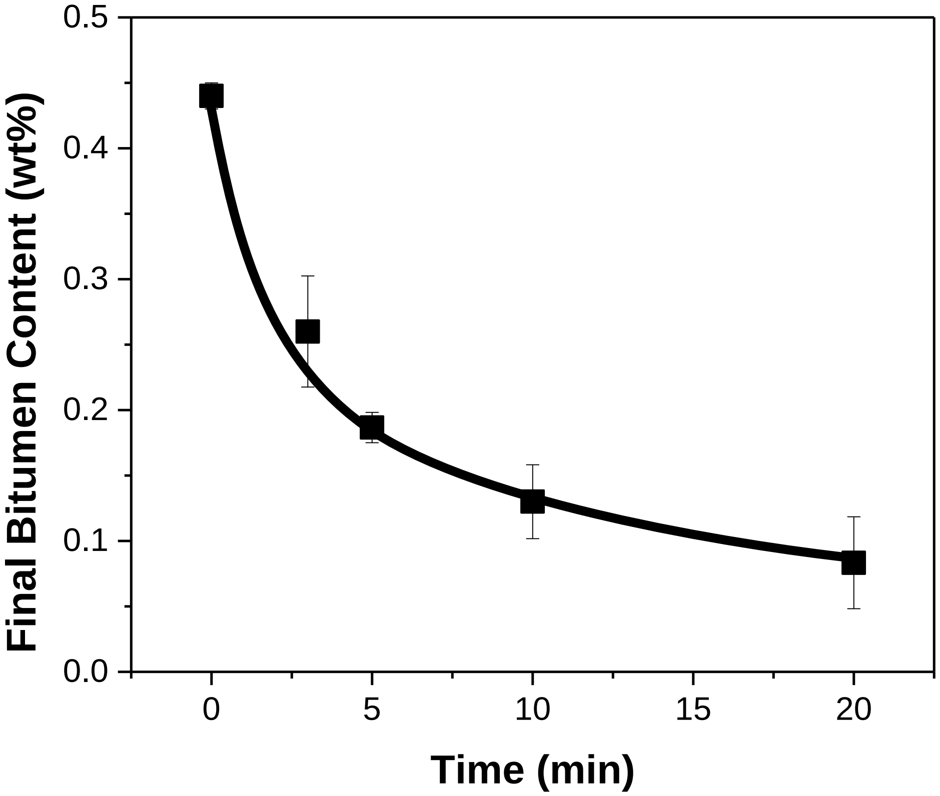

Figure 3-1: Bitumen content in MFT as a function of flotation time

Protocol 3 by solvent washing of MFT: Diluted MFT was washed in excess toluene to remove all toluene-soluble organics. A schematic of the cleaning procedure is shown in Figure 3-2. MFT was mixed with equal volumes of toluene [A] and agitated overnight [B]. The mixture was centrifuged at 3000 rpm for 5 min [C]. The supernatant containing dissolved bitumen was decanted and replaced with fresh toluene. The process was repeated until the supernatant appeared clear [D]. A portion of the solids was observed to partition between the organic and aqueous phases. These solids are believed to be bi-wettable as described by Kotlyar et al.. [10] To ensure complete removal of toluene these solids were separated, dried and re-dispersed in a small amount of process water to maintain the solids content of diluted MFT. The suspension was then thoroughly blended following the procedure described in protocol 2 [E].

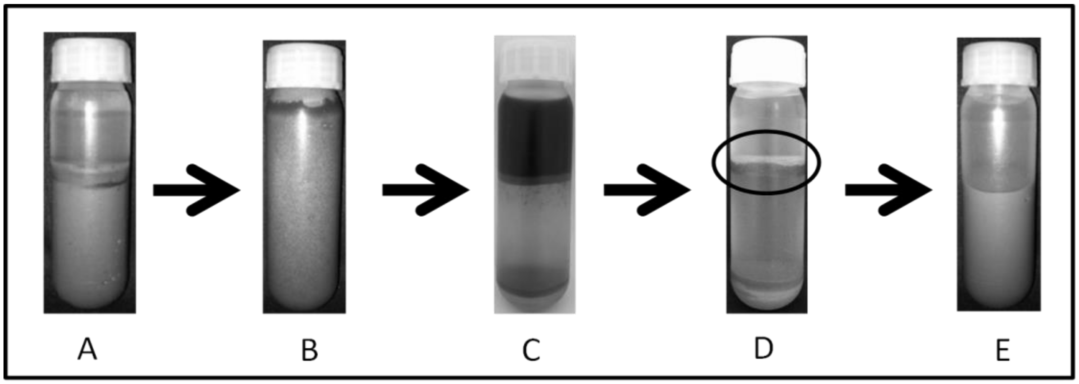

Figure 3-2: Solvent washing procedure to remove all soluble organic species

3.2.2 Batch settling:

Samples obtained using the above protocols were mixed thoroughly for 1 h prior to use. In a 250-mL beaker fitted with four baffles, 100 g of tailings were placed and mixed at 500 rpm for 5 min with an overhead mechanical stirrer of a 4-blade, 1-inch width impeller, to ensure complete sample homogeneity. The impeller speed was reduced to 350 rpm while 5 g of polymer stock solution was added over a period of 1 min (overall dosage: 50 ppm based on the mass of slurry). Upon completion of polymer addition agitation was stopped and the suspension was transferred to a 100-mL graduated cylinder. The cylinder was sealed and inverted 5 times to evenly distribute the suspension within the cylinder. The “mud-line” height was recorded as a function of time, with the initial linear settling regime of the settling curve being used to calculate the settling rate.

3.2.3 Floc size:

A model S400A Focused Beam Reflectance Measurement (FBRM®) probe (Mettler Toledo, USA) was used to measure floc growth after polymer addition. This technique uses a focused laser light (laser wavelength 780 nm) to generate a focal spot that is rotated around a circular path. Intersection of the laser beam at the focal spot by particles generates distinct pulses of the reflected light. The pulse width multiplied by the scan speed (laser rotation speed) is translated into a particle chord length. The probe counts thousands of particles per second and creates a chord length histogram/distribution. [18] A chord length distribution is similar, though not identical to a particle size distribution. A chord length can be the distance between any two points on the edge of a particle and would therefore always be less than or equal to the particle's diameter. However, it has been reported that the mean square weighted chord length is similar to the mean particle diameter obtained using other methods, such as laser diffraction. [19] For the flocculation study, samples were prepared following the protocol described previously in batch settling (mixing maintained at 350 rpm) with the FBRM® probe being positioned at 80^o to the horizontal in the 250-mL beaker at the start of each run. The FBRM ® laser scan speed was fixed at 2 m/s and the "coarse" detection mode was used for all experiments.

3.2.4 Total organic carbon (TOC) analysis:

To study polymer flocculation performance, the TOC concentration in the supernatant after batch settling was measured using a Shimadzu TOC-V

CHS/CSN Model Total Organic Carbon Analyzer (Shimadzu Corporation, Japan). This method measures TOC by acidifying a sample of water and then sparging to remove purgeable organic and inorganic carbon. The sample undergoes a reaction with a catalyst to produce CO_2 which is then detected by a non-dispersive infrared (NDIR) detector. First, approximately 30 mL of sample obtained using protocol 1 was centrifuged at 14000 rpm for 20 min. The supernatant was then decanted and the TOC of the supernatant measured to establish a baseline for each sample. After flocculant addition and batch settling, approximately 30 mL of the supernatant was extracted and centrifuged at 14000 rpm for 20 min to remove the remaining solids. The TOC was measured to determine the polymer excess (free polymer) relative to the TOC from the baseline measurement.

3.2.5 Quartz crystal microbalance with dissipation monitoring (QCM-D):

Polymer adsorption onto model clay surfaces (silica, alumina and bitumen coated on silica QCM-D sensors) was determined by QCM-D (Q-Sense E4, Sweden). QCM-D is an ultra-sensitive balance in which the resonance frequency of a piezoelectric quartz crystal (5 MHz) is damped through the addition of a mass, at nanogram scale, to the crystal surface. In addition to resonant frequency, crystal dissipation monitored in the absence of a drive voltage provides structural information of the adsorbed polymer layer and its viscoelastic response.[20] Depending upon the nature of the adsorbed layer the added mass can be calculated using appropriate modeling. Sauerbrey equation is commonly used for a rigid adsorbed layer that is distributed evenly and with the mass change smaller than 2%.[21] For a “soft” (viscoelastic) layer, the adsorbed mass generates friction which increases dissipation.[21] For such a system, the Sauerbrey equation is not valid and the Voigt Model for viscoelastic layers should be used.[22] Prior to each measurement or bitumen coating, all sensors were sonicated in Milli-Q water and cleaned using UV irradiation (~9 mWcm^{-2} at 254 nm) for at least 10 min, rinsed thoroughly with Milli-Q water and finally blow-dried with ultra-pure nitrogen. To coat a thin layer of bitumen on a QCM-D silica sensor, the silica sensor surface was first hydrophobized using dichlorodimethylsilane (DDMS, Fisher Scientific, USA) by placing a clean silica sensor in a 250-mL beaker with a small, open vial containing approximately 2 mL of DDMS for 2 min. The beaker was covered with aluminum foil to allow DDMS vapors to deposit on the sensor. The sensor was then heated to 80 ^{o}C under vacuum for 24 h, causing the DDMS to bind chemically to the silica substrate. Using a spin coater (WS-400A-^NPP/Lite, Laurell Technology Corporation, USA) rotating at 2500 rpm, 8 drops of diluted bitumen (5 wt.% bitumen in toluene) were added dropwise onto the sensor surface. The sensor was allowed to rotate at this speed for 50 s, followed by rotation at 4000 rpm for 40 s to ensure an even layer and evaporate any excess solvent.

With the crystal mounted, the resonant frequency of the crystal was monitored to assess its cleanliness. The background solution (0.1 μm filtered process water, pH 8.2) was pumped through the measurement chamber at 0.15 mL/min until a stable baseline was attained. Once stable, the baseline was recorded for approximately 10 min, after which a 500 ppm polymer solution prepared in the same filtered process water was continuously pumped through the measurement chamber. The shift in resonant frequency and dissipation were monitored until steady state readings were obtained. Typically the experiment ran for 30 min.

3.2.6 X-ray diffraction (XRD):

A Rigaku rotating anode XRD (Rigaku Corporation, Japan) equipped with a copper radiation source and a scan speed of 2^o/s over a range of 10^o to 110^o was used to obtain diffraction patterns of the minerals. MFT solids of varying bitumen content prepared by protocol 1 were separated using Dean Stark extraction and ground to a powder using a mortar and pestle. Quantification of the mineral phases (Rietveld refinement) was obtained with Siroquant^{TM} software (Sietronics, Australia).

3.3 Results and discussion

3.3.1 Settling performance:

Figure 3-3 shows the initial settling rates of diluted MFT containing a varying amount of bitumen (protocol 1) in the presence of 50 ppm flocculant. For the highest bitumen content (0.45 wt.%) the settling rate was measured to be ~2.5 m/h. This value is similar to that previously reported by Alamgir et al.[7] for a similar polymer (Magnafloc 1011) at equivalent polymer dosage and solids content. With a reduction in the bitumen content to 0.18 wt.% , the settling rate increased to ~7 m/h, indicating an increase in polymer performance. With the bitumen content in the range 0.11 to 0.23 wt.%, the settling rates of MFT in the presence of 50 ppm flocculant are essentially the same in the range of ~ 6 – 7 m/h.

The measured variability associated with these experiments most likely results from the inconsistent break-up of large flocs under shear during transfer and inversion of the settling column (sample conditioning). Also with high settling velocities, accurate visual determination of the mud-line becomes increasingly more difficult, thus contributing to an increase in the experimental error. Interestingly, with further bitumen removal to 0.08 wt.%, the settling rate of the resultant MFT after 50 ppm flocculant addition was observed to decrease to ~1.3 m/h, a value lower than the MFT without bitumen removal (0.45 wt.% bitumen) at same flocculant dosage. The substantial reduction in settling rate does not follow the perceived trend of improved settling performance with reduced bitumen content. Further discussion on the reduction in settling rate at low bitumen content will be provided later in this paper.

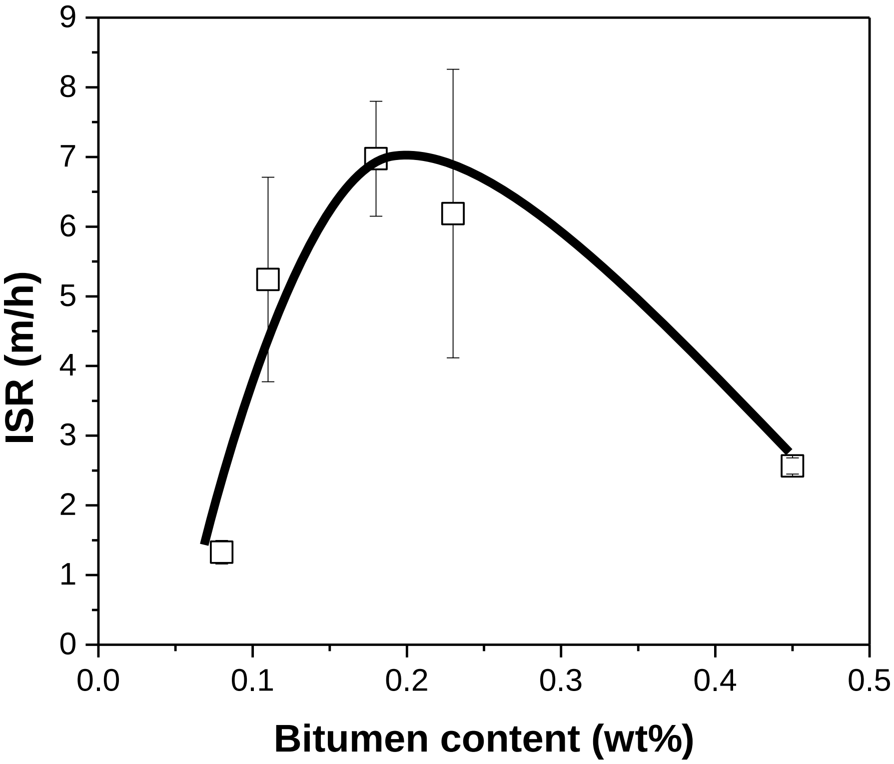

Figure 3-3: Effect of bitumen content on the initial settling rate of diluted MFT with 50 ppm flocculant addition, bitumen content controlled by protocol 1

To better understand the flocculation performance at different bitumen contents, FBRM® was used to measure in real time the floc size (mean square weighted chord length) under constant shear. Figure 3-4 shows the growth of flocs (ultimate floc size dependent on floc strength and dynamic shear) formed through the addition of 50 ppm flocculant. These experiments were conducted for three different bitumen contents of 0.08, 0.18 and 0.45 wt.%, which is inclusive of the lowest and highest settling rates shown in Figure 3-3. Immediately after polymer addition flocs form rapidly, reaching a maximum size within ~50 seconds. The floc size is then observed to decrease, resulting from either restructuring or fragmentation, and eventually reaching a steady-state size within 1 hr. For the MFT of the highest and lowest bitumen content, 0.45 and 0.08 wt.%, the maximum square weighted chord lengths were ~280 and ~300 μm, respectively. A square weighted chord length of ~350 μm was measured for the diluted MFT containing 0.18 wt.% bitumen, in agreement with the higher settling rate shown in Figure 3-3.

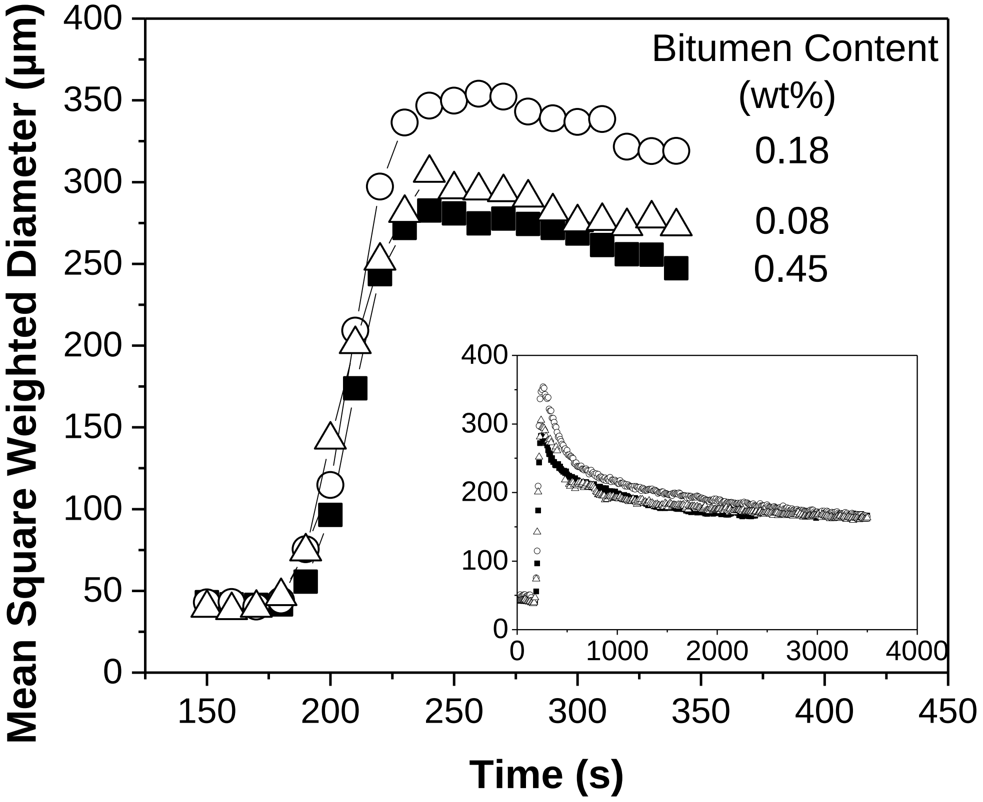

Figure 3-4: Flocculation kinetics as a function of bitumen content in MFT (protocol 1) with corresponding initial settling rates of ○ : 6.98m/h, △ : 1.33 m/h, and ■ : 2.57 m/h

A decrease in settling rate and floc size at low bitumen content would indicate that a small amount of bitumen retained in the diluted MFT is detrimental to flocculation of MFT fines. This is contrary to the findings of Majid et al.[16] who showed that any amount of bitumen removal resulted in a significant increase in both settling and consolidation of solids. However, it should be noted that the study of Majid et al.[16] was for MFT without flocculant addition, with settling and consolidation performance monitored over weeks to months.

For the hydrolyzed polyacrylamide polymer, approximately 50% of the total mass is organic carbon. With 50 ppm polymer addition, based on total slurry mass, the total organic carbon added to the system is 0.025 g. If no polymer were to adsorb on the fine clays that would correspond to a maximum change in TOC concentration of approximately 25 mg/L. Figure 3-5 shows the measured TOC after polymer addition, relative to the baseline. Clearly, there is a dependency on the bitumen content, with the optimum bitumen content resulting in the lowest increase in the measured TOC concentration (~ 2.5 mg/L). As the settling performance reduces the increase in the measured TOC concentration is shown to increase. For the lowest bitumen content (0.08 wt.%) where the initial settling rate remains extremely low, the increase in the TOC concentration is high, in the region of ~13 mg/L, confirming poor interaction of the polymer with the remaining fines after extended bitumen extraction from the MFT.

A further study to measure polymer adsorption on representative particle surfaces (silica, alumina and bitumen) was conducted using QCM-D. Figure 3-6 shows the frequency and dissipation shifts of the 3rd overtone with continual pumping of 500 ppm polymer solution over the sensor surface. Preferential adsorption of the polymer was measured on alumina, with little adsorption on silica and bitumen coated surfaces. Such adsorption characteristics would indicate that the anionic polyacrylamide interacts with the fines through electrostatic attraction between negatively charged anionic polymers and positive alumina sites on clay edge surfaces. For alumina, the resonance frequency (F3/3) of the crystal rapidly decreased to an equilibrium value of –15 Hz and the dissipation simultaneously increased to $\sim 5 \times 10^{-6}$, indicating the formation of a viscoelastic film. Using the Voigt model with frequency and dissipation data of the 3rd and 5th overtones, a corrected equilibrium mass uptake of ~9 mg/m^2 was measured on the alumina surface. These polymer adsorption results on both silica and alumina are consistent with Alagha et al.[23] who reported a mass uptake on silica and alumina equal to 0 and ~10 mg/m^2, respectively, for a similar anionic polymer (Magnafloc1011). The QCM-D data confirms hindrance to flocculation by bitumen-contaminated fine solids, which is consistent with the observed lower initial settling rate of MFT containing higher content (0.45 wt.%) of bitumen.

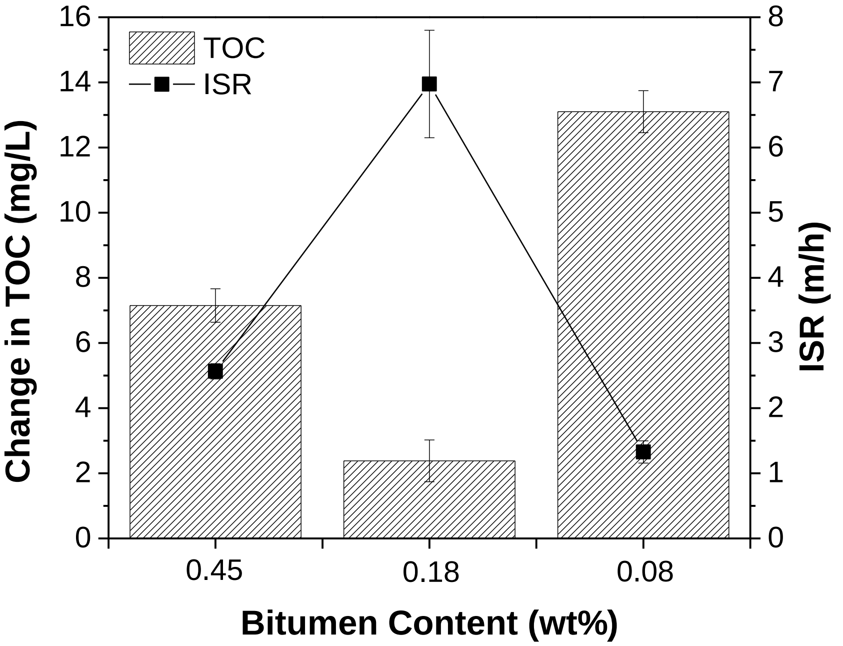

Figure 3-5: TOC increase from baseline and the corresponding initial settling rate after addition of 50 ppm polymer to MFT at pH 8.5, with bitumen content controlled by protocol 1

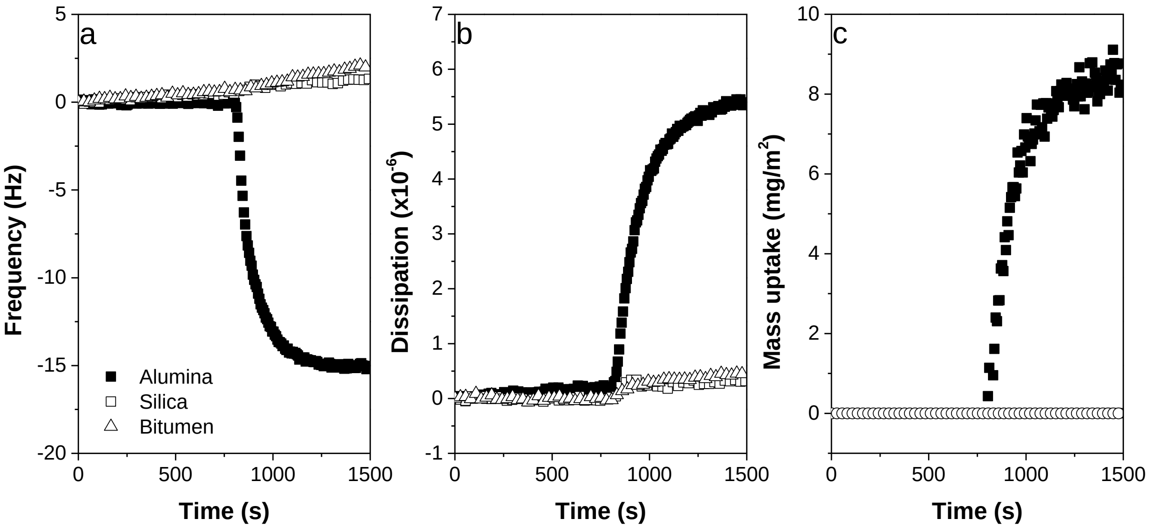

Figure 3-6: Adsorption of polymer flocculant (AF246) from 500 ppm solutions of pH 8.5 on model particle surfaces: frequency (a), dissipation (b) and mass uptake (c) as a function of time.

However, contrary to conventional thinking and the QCM-D results, extensive removal of bitumen from MFT by flotation is shown to correspond with decreased settling rates, smaller sized flocs, and lower polymer adsorption, as shown in Figures 3-3, 3-4 and 3-5, respectively. To further understand the role of bitumen content on the flocculation of fine solids in MFT, two additional protocols to control bitumen content were considered. Protocol 2 includes blending of MFT after extraction of bitumen (0.08 wt.%, extended flotation) with diluted raw MFT (0.45 wt.%, untreated) to produce an overall bitumen content of 0.18 wt.% [blend composition: 73% of MFT containing 0.08 wt.% bitumen with 27% diluted MFT of 0.45 wt.% bitumen]. Protocol 3 includes solvent washing of diluted MFT (0.45 wt.% bitumen, no flotation) and MFT after bitumen extraction by extended flotation to 0.08 wt.% bitumen to remove any remaining toluene soluble organics. Figure 3-7 compares the results obtained with samples prepared using protocols 1 and 2 at an equivalent bitumen content of 0.18 wt.%. Clearly there is a substantial difference in the settling rate of MFT, albeit equivalent bitumen contents. The settling rate after 50 ppm polymer addition to the sample prepared using protocol 2 remains low ~1.2 m/h, even though the bitumen content is at the optimum level as determined by protocol 1. Since protocol 2 includes the blending of two poorly settling suspensions, the result may not be unexpected. The result does however confirm that the bitumen content is not a universal criterion for controlling solids-flocculant interactions and hence flocculation. The state of the bitumen in MFT and/or composition of fine solids need to be considered carefully to understand the role of bitumen content in flocculation of MFT.

For samples prepared using protocol 3, one would expect similar settling characteristics as the bitumen is completely removed from the MFT solids. However, a substantial difference in settling performance was observed between the two solvent-washed samples as shown in Figure 7 (triangle symbols). For the solids obtained by directly washing the dilute raw MFT (0.45 wt.% bitumen), the initial settling rate of the MFT with 50 ppm flocculant addition is very high, in the range of ~9 m/h. However, for the solids obtained by solvent washing of MFT after bitumen removal by extended flotation (0.08 wt.% bitumen before washing), the settling rate was much lower at ~1.8 m/h. Conflicting settling rates between the two solvent washed samples suggest that the extended flotation of diluted raw MFT to obtain the samples of 0.08 wt.% bitumen content using protocol 1 has modified the solids composition of the resultant MFT in such a way that either the remaining particles are less responsive to the added flocculant or particles which could enhance fine particle flocculation, mostly hydrophobic particles have been preferentially removed by the flotation as anticipated.

Even though there is preferential flotation of the hydrophobic species, measurement of particle concentration by gravimetric method, particle size distribution by light scattering, fines mineralogy by XRD (Figure 3-8) and methylene blue index of fines (< 44 µm) suggest that these two tailings samples are similar.

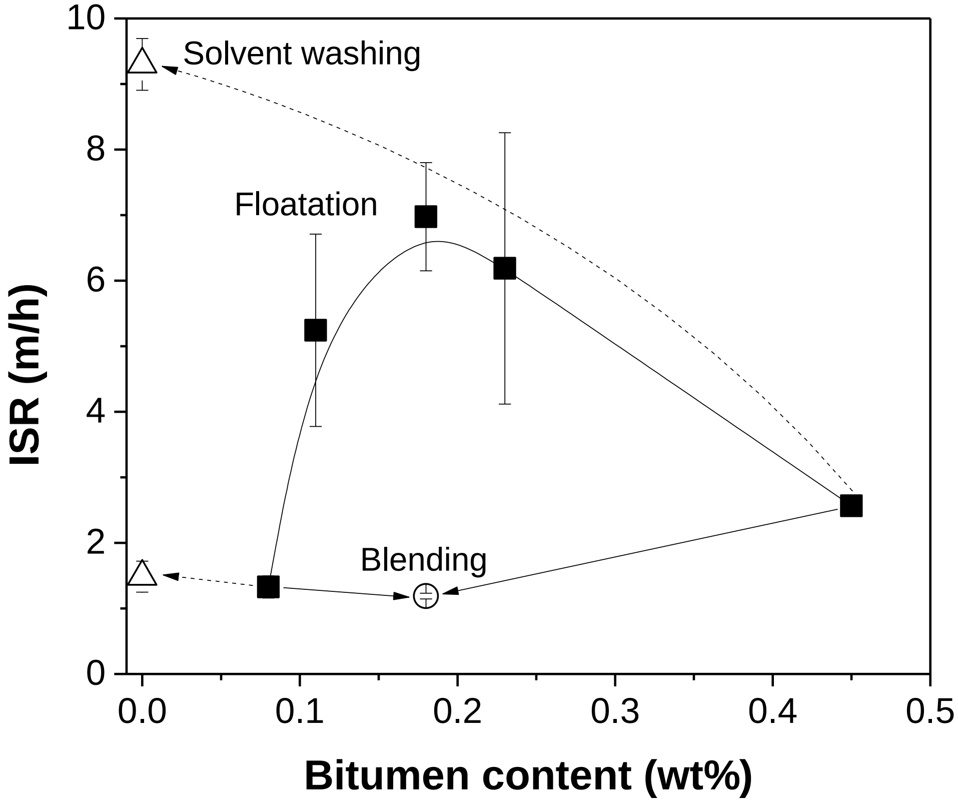

Figure 3-7: Impact of bitumen removal protocols on the initial settling rate of diluted MFT;
protocol 1 : ■; protocol 2: ○; protocol 3: △

However, the initial settling rate data highlight contrasting behavior which would suggest that the properties of particles removed by flotation and the associated bitumen are the difference in controlling flocculation behavior of solids at very low bitumen content. Research to fully characterize clays and organic matter contamination of these solids and their interactions with flocculant is ongoing.

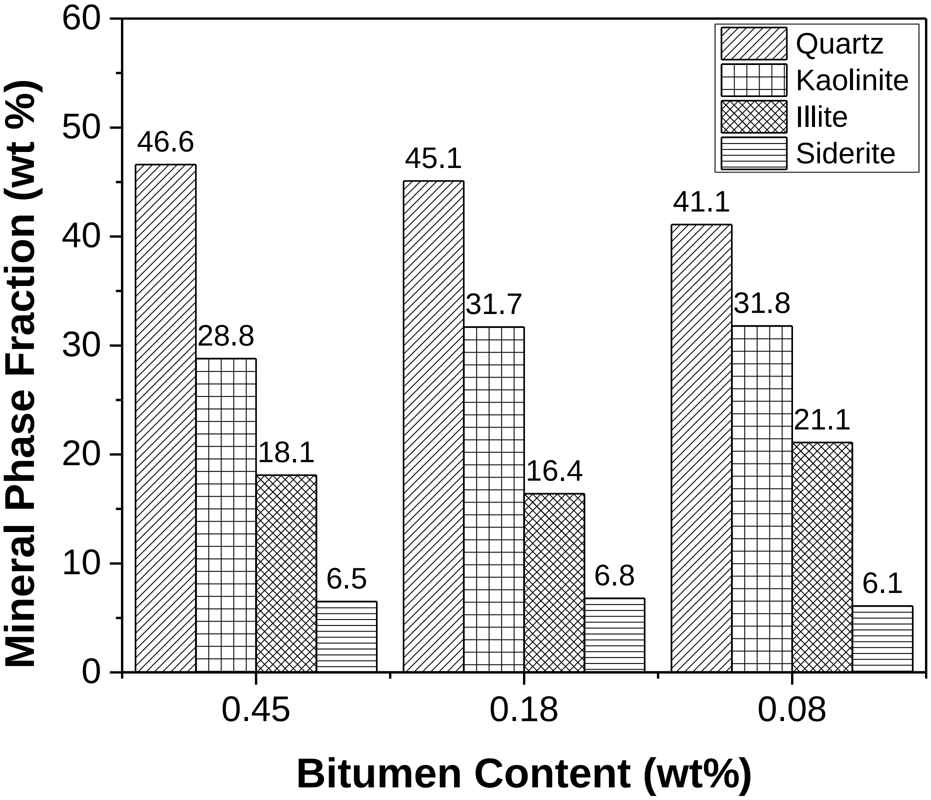

Figure 3-8: Mineral phases of solids from MFT samples of varying bitumen content controlled by protocol 1. Lower bitumen content by longer MFT flotation

3.4 Conclusions

The major conclusions from this work are summarized as follows:

- The removal of bitumen from MFT by Denver cell flotation was found to improve flocculation and settling performance within the bitumen content range 0.45 – 0.18 wt.%. Any further removal of bitumen by flotation was shown to be detrimental to flocculation of remaining fine solids.
- The anionic polymer used throughout the study was shown to preferentially adsorb on alumina, with little adsorption on silica and

bitumen substrates. The polymer interaction with fines is mainly through electrostatic attraction.

- Solvent washing of diluted MFT was shown to increase the settling rate from ~2.5 m/h to greater than 9 m/h. Solvent washing of the MFT after bitumen removal by extended flotation was shown to have a marginal improvement in settling performance, with the settling rate remaining low in the region ~ 1.5 m/h.
- Although removal of bitumen from MFT by toluene washing could significantly improve flocculation and settling of diluted MFT, complete removal of bitumen from MFT by flotation is not recommended as it leads to poor flocculation and slow settling of the resultant MFT.

3.5 References:

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Chapter 4: Additional Analysis of MFT Settling Behavior

4.1 Introduction

To better understand the role of bitumen in polymer based flocculation, additional tests following the work described in the previous chapter were conducted. The primary goal was to understand the difference in settling rate between the samples where bitumen was removed using the toluene wash procedure (protocol 3) and those that utilized the Denver cell flotation procedure (protocol 1). It was inferred that in addition to bitumen removal, the difference in settling characteristics may be due to the effect of the Denver cell mixing or flotation due to the selective removal of hydrophobic, organic contaminated particles during the flotation process. Experiments to test these hypotheses were conducted and the results are described in this section. Also included are data supplemental to the work described previously that could not be included in the publication due to constraints of the length. Furthermore, to determine if the results obtained for Syncrude MFT are representative for MFT from other sources, additional tests were performed on MFT samples obtained from Albian Oil Sands. The results for those experiments are detailed in the second half of this section.

4.2 Materials and methods

Samples of process water used for sample dilution were obtained from Syncrude Canada Ltd. Concentrations of selected ions are shown in Table 4-1 as determined by atomic adsorption spectroscopy (AAS).

Table 4-1: Concentration of selected ions in process water determined by AAS

	Ion concentration (ppm)			
pH	Na^+	Mg^{2+}	Ca^{2+}	Fe^{3+}
8.5	284.5	15.1	33.2	<0.1

4.2.1 Particle size analysis:

Particle size distributions of selected MFT samples were measured using the Mastersizer 3000 (Malvern Instruments, UK). This apparatus determines light scattering patterns which are used to model particle size, based on the principle that small particles scatter light at wider angles than larger particles. The transmission of light through particles is accounted for by the particles' refractive index. For these experiments an average of the refractive indices of silica, kaolinite and illite was used as these are the most abundant components of MFT. [1]

4.2.2 Thin film flotation:

To determine if a substantial portion of hydrophobic solids are removed from the tailings during Denver cell extraction, the thin film flotation method was used, following the procedure of Liu and Xu. [2] Tailings samples of varying bitumen content were prepared using Denver cell extraction as described in the previous chapter. Solids were separated from water and residual bitumen by Dean-Stark extraction. The collected solids were crushed with a mortar and pestle to break up any lumps. A small amount of tailings particles were spread gently on the surface of a water-methanol solution and left for approximately 10 min. The hydrophobic particles remained floating on the surface and the hydrophilic particles sank to the bottom. Therefore these particle fractions were referred to as floats and sinks, respectively. The floats were carefully skimmed off of the surface and then both fractions were dried. After drying, the two fractions were weighed and the fraction of hydrophobic particles was calculated. The surface tension of the solution was adjusted by varying the ratio of water to methanol.

4.2.3 Thermogravimetric analysis (TGA):

To assess the relative amounts of organic material present with the tailings solids, thermogravimetric analysis (TGA) was conducted. The apparatus used was a TGA Q500 manufactured by TA instruments (New Castle, DE, USA). A small amount (~10 mg) of tailings solids, obtained using the procedure described in the previous section, was placed in a platinum sample pan. The pan was loaded into the furnace chamber and heated up to 1000^{o}C at a rate of 10^{o}C/min under nitrogen atmosphere. The mass loss due to thermal decomposition of the sample was recorded. It should be noted that clays, such as kaolinite, decompose under high temperatures, between 450-700^{o}C. [3] Therefore not all of the mass loss is due to the breakdown of organics. To establish a baseline for the mass loss due to thermal breakdown of mineral solids, organic matter was removed from one sample of solids by low temperature ashing (LTA). The sample was ashed using a K1050X Plasma Asher (Quorum Emitech, Kent, England) following the procedure of Adegoroye et al. [4] After organic matter was removed by ashing, the sample was analyzed by TGA as described above.

4.2.4 Effect of froth solids on settling:

To determine the effect of hydrophobic solids removed during flotation (referred to as froth solids) on settling, the following procedure was employed. Bitumen was extracted from tailings samples using a Denver cell, following protocol 1, described in Chapter 3. After a 20 min flotation period the collected froth and remaining tailings were washed with toluene to remove bitumen (protocol 3), as described previously. The washed tailings were divided into two equal portions and half of the washed froth (solids and water which partitioned to the froth phase during extraction) were added to one portion of tailings so that the fraction of hydrophobic solids present in the sample would be the same as it was prior to flotation. Settling tests were performed on each of these samples to determine if the fraction of hydrophobic froth solids present improves flocculation, as was speculated based on previous settling test results.

4.2.5 Mixing tests:

To assess the impact of Denver cell mixing, without flotation, on the flocculation and settling of tailings, settling tests were performed on tailings samples that underwent mixing in the Denver cell for varying lengths of time. To conduct these tests modified versions of protocols 1 and 3 (referred to as protocols 1b and 3b, respectively) were devised. For protocol 1b, 800 g of diluted MFT was placed in the Denver cell. Samples were mixed at 1200 rpm for varying lengths of time, corresponding to those used for protocol 1, but no air was introduced during this process. At the end of the mixing period any froth that had formed due to entrained air was scooped off. The composition of these tailings was determined by Dean Stark analysis. Settling tests were then conducted on the tailings as described previously. Furthermore, to assess the effect of mixing on samples without bitumen, the same tests were conducted on samples of toluene washed tailings (protocol 3b). Portions of MFT were toluene washed, as described previously. 800 g portions of the toluene washed tailings was placed in the Denver cell and mixed at 1200 rpm for varying lengths of time without the introduction of air, as with protocol 1b. After the mixing was complete, settling tests were also performed on these mixed tailings samples.

4.2.6 Albian tailings:

A number of the tests conducted on Syncrude MFT were also conducted on Albian tailings. Samples of raw MFT were obtained from Albian Sands Energy Inc. The composition of the raw Albian MFT sample was determined to be 3.2 wt% bitumen, 41 wt% solid and 54.6 wt% water by Dean-Stark analysis. The procedure used to prepare samples of differing bitumen content was the same as described in Chapter 3, referred to as protocol 1. Settling tests, FBRM analysis and particle size distributions were all conducted using the same procedures as described previously.

4.2.7 Zeta potential measurements:

Zeta potential measurements were made for both Albian and Syncrude tailings using a ZetaPALS (Brook Haven Instruments, US). This instrument utilizes light scattering to measure the electrophoretic mobility of particles. For each measurement, a few drops of the tailings sample were diluted to approximately 20 mL with process water. Approximately 2 mL of diluted tailings was loaded into the measurement cell. Ten measurements were made with each sample and the average of these measurements was taken as the final result.

4.3 Results and discussion

Particle size distributions for selected Syncrude tailings samples obtained following protocols 1 and 3 are shown in Figure 4-1. It can be seen that the size distributions for all samples follows essentially the same pattern. There is a bimodal distribution with peaks centered approximately at 8 µm and 0.15 µm. It can also be seen that the size distribution remains essentially unchanged after Denver cell extraction using protocol 1 as well as toluene washing in protocol 3. This is fortunate as preferential removal of a certain particle size fraction during either of these protocols would bias the settling data.

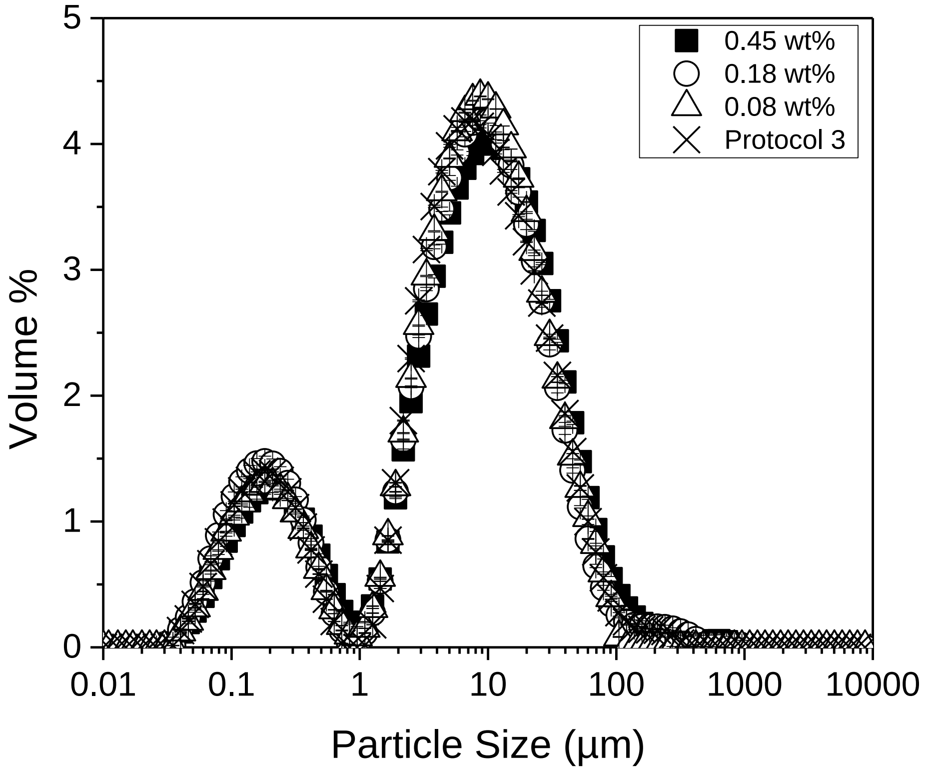

Figure 4-1: Particle size distribution of Syncrude MFT following protocols 1 and 3

4.3.1 Effect of hydrophobic solids:

Thin film flotation: If hydrophobic particles have an effect on tailings flocculation it is necessary to determine the fraction of such particles present before and after bitumen extraction. The results of the thin film flotation experiments are shown in Figure 4-2. It can be seen that samples that underwent longer periods of Denver cell extraction, have lower fractions of hydrophobic solids. Without Denver cell extraction, approximately 50% of the solids present are hydrophobic, while after bitumen removal the hydrophobic fraction decreases to around 35% and then to

15% with the longest flotation time (20 min). This is expected as hydrophobic solids are more likely to partition to the froth during flotation.

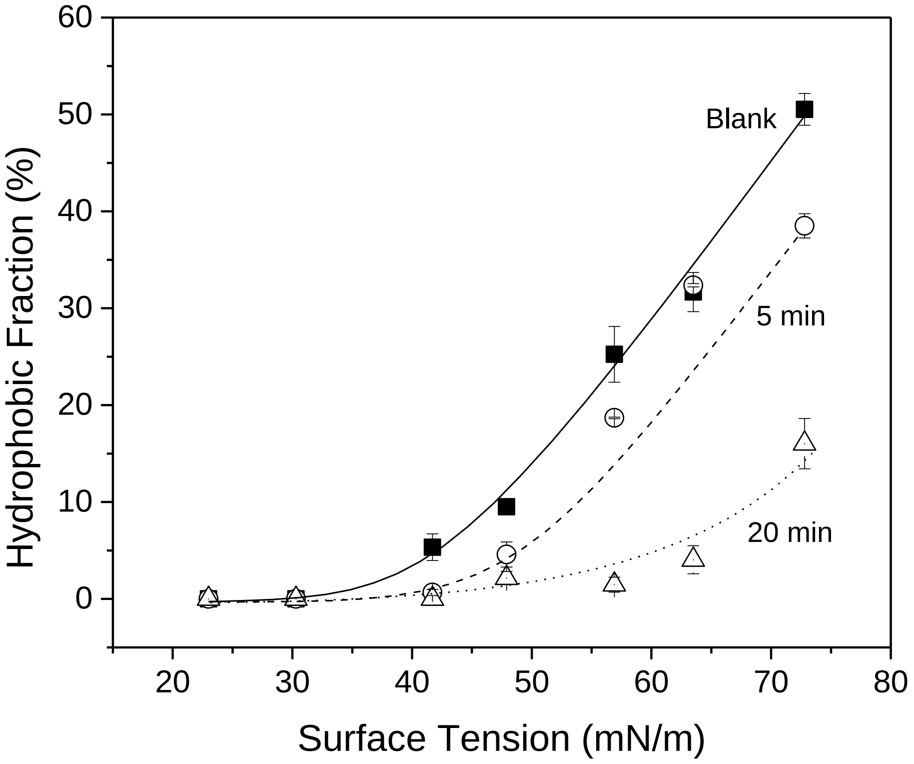

Figure 4-2: Fraction of hydrophobic particles vs. surface tension for extraction tailings

Thermogravimetric analysis of tailings solids: Previous studies [5] have indicated that the hydrophobicity of tailings solids is due to the presence of toluene insoluble organic matter. To determine the amount of organic matter present on the extraction tailings TGA was performed. Figure 4-3 shows the TGA profiles for extraction tailings as well as tailings solids treated by LTA. It should be reiterated that these tailings solids were separated by Dean Stark extraction, therefore most if not all of the bitumen has been removed prior to the TGA experiments. Therefore, all organics present are insoluble in toluene.

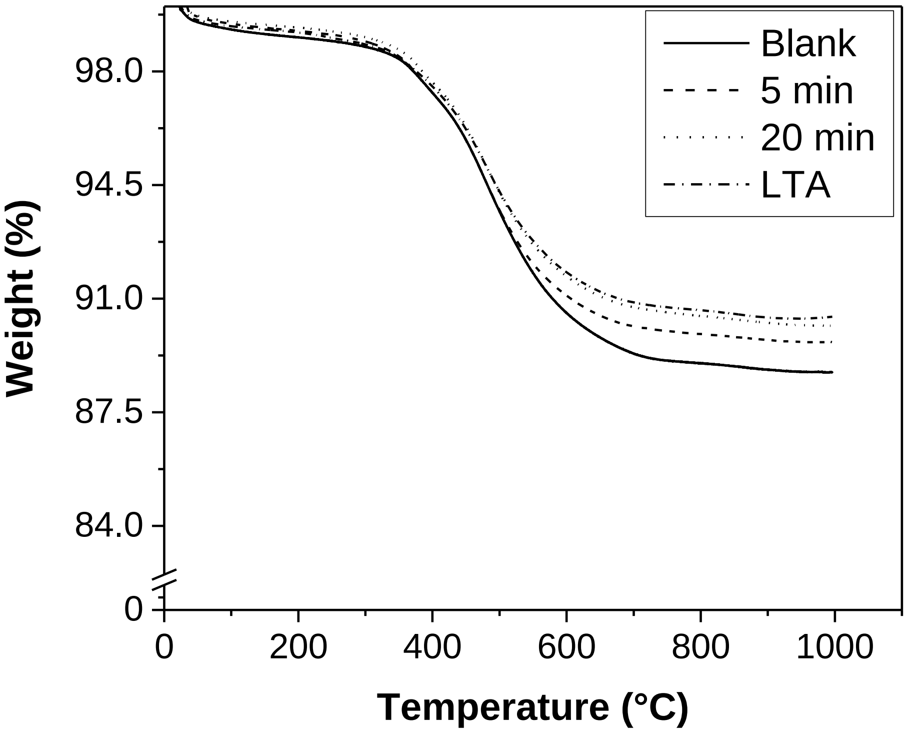

Figure 4-3: TGA profile for extraction tailings and tailings solids treated by LTA

The total mass loss for each of the extraction tailings samples decreases with increasing extraction time, in good agreement with the wettability data in Figure 4-2, i.e. less hydrophobic solids should have less organic matter. Using the mass loss of the LTA solids as a baseline for the mass loss due to decomposition of mineral components, the fraction of organic matter present on the three samples can be determined. The fractions of organic matter for the three samples are 1.7 wt%, 0.8 wt% and 0.3 wt% for extraction times of 0 min (blank), 5 min and 20 min respectively. These results correspond to the thin film flotation results, showing that increasing amounts of adsorbed organic matter on solids causes increasing hydrophobicity. It is also noteworthy to mention that the hydrophobic fraction of the LTA solids was negligible; indicating that solids hydrophobicity in oil sands tailings is due to the presence of organic matter on the solids. Furthermore, these results show that the sample with the longest extraction time (lowest bitumen content) is largely depleted in hydrophobic solids. This corresponds to the drop-off in settling rate observed previously (Figure [3-3]). It is possible that the drop-off in settling rate is due to the depletion in hydrophobic solids because hydrophobic interactions between particles contribute to flocculation by providing an additional force (hydrophobic force) which binds particles together. [6] This would account for the difference in settling rate observed for toluene washed tailings versus tailings that underwent toluene wash following long periods of Denver cell extraction as shown in Figure 3-7. Denver cell extraction depleted hydrophobic solids, which may have aided flocculation, leading to an overall reduction in settling rate. However, as the hydrophobic interactions between these particles are not well understood, one cannot be sure that this is the case. Additional settling tests were conducted to investigate this hypothesis. The results of those experiments are described in the next section.

Effect of froth solids on settling results: Figure 4-4 shows the settling rate of tailings that are depleted in hydrophobic solids compared to tailings that are not. It can be seen that with froth solids added the settling rate is approximately the same as samples without froth solids. This is unexpected as samples with froth solids added should be identical to samples that underwent solvent washed only (protocol 3), which showed significantly higher settling rates. This result implies that the presence or absence of the hydrophobic solids that are removed with the froth during extraction does not have a significant impact on flocculation. The decrease in settling rate must therefore be caused by some other factor related to the Denver cell extraction process. It was observed that the decrease in settling rate at low bitumen content corresponded to the longest period of Denver cell extraction. It was hypothesized that the long period of mixing in the Denver cell may have an effect on flocculation. Therefore, tests involving Denver cell mixing, without air addition, were conducted.

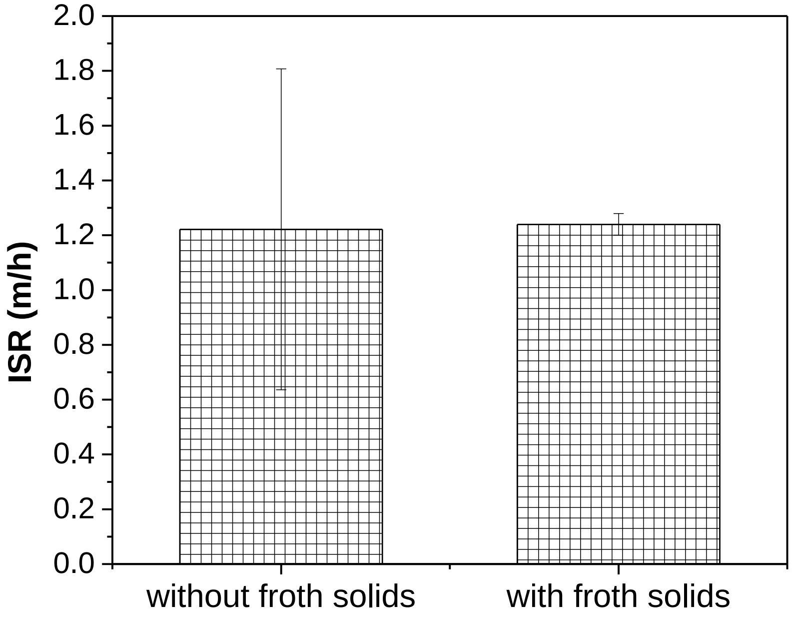

Figure 4-4: Impact of froth solids on the initial settling rate of diluted MFT (50 ppm AF246)

4.3.2 Effect of Denver cell mixing prior to settling tests:

The results of the mixing tests (protocols 1b and 3b) are shown in Figure 4-5. Also shown for comparison purposes are the results for settling tests for samples with bitumen content varied by Denver cell extraction (protocol 1). Bitumen content of these samples is listed near the respective data points.

Protocol 3b: It can be seen that for mixing time of 0 to 10 min the settling rate of protocol 3b samples does not change significantly, remaining at ~7 m/h. However, after a period of 20 min mixing the settling rate decreases significantly to ~2 m/h. As shown previously for protocol 1 samples, with no bitumen removal (0.45 wt% bitumen), the settling rate is low at ~2.5 m/h, indicating that bitumen is detrimental to flocculation. With increasing bitumen removal the settling rate peaks at around 7 m/h, comparable to what was observed for the solvent washed tailings. This indicates that when the majority of bitumen is removed flocculation and settling are largely unhindered by the remaining bitumen. It can also be observed that after 20 min of Denver cell extraction the settling rate decreases significantly, similar to what was observed for the solvent washed sample that underwent the same mixing time.

Protocol 1b: Figure 4-5 also shows the results for protocol 1b. The final bitumen content after mixing is approximately the same for all mixing times, with longer mixing time resulting in slightly lower bitumen content as would be expected. Furthermore, the bitumen content is higher overall than what was observed when air was introduced in the extraction process, but still near 0.2 wt% of bitumen, where the settling rate was the highest for protocol 1. It can be seen that for the mixing times of 5 and 10 min the settling rate of these samples does not change significantly, remaining at ~6.5 m/h, which is similar to what was observed previously for protocol 1 and protocol 3b samples that underwent the same mixing time. However, after a period of 20 min the settling rate decreases significantly to ~1.5 m/h, similar to what was observed previously for both protocol 1 and protocol 3b after the same mixing time. These results imply that Denver cell extraction has two competing effects on the settling rate of tailings. Removal of bitumen by flotation causes an increase in settling rate, while excessive mixing causes settling rate to decrease thus leading to the observed peak in settling rate for protocol 1 samples. The underlying reason for the detrimental effect of mixing has yet to be determined and is the subject of ongoing investigation.

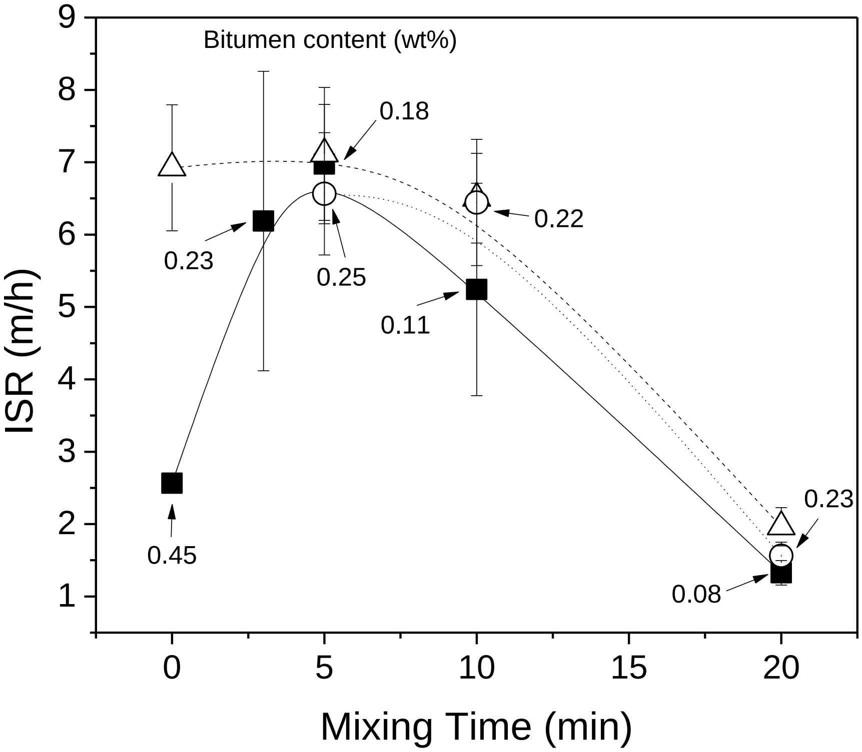

Figure 4-5: Impact of Denver cell mixing on the initial settling rate of diluted MFT; protocol 1: ■; protocol 1b: ○; protocol 3b: Δ (Numbers in the figure refer to bitumen content of corresponding samples)

An alternative explanation for the drop-off in performance at low bitumen content was proposed in a recent study by Carreras et al. [7] In their study similar methods to the ones used in Chapter 3 were employed. They found a maximum settling rate occurred at a bitumen to solids ratio of approximately 0.01 and that the settling rate decreased when bitumen content was decreased further. This was the case for both real tailings, obtained from batch extraction, as well as model tailings containing kaolinite and bitumen that was dispersed by sonication. However, the mechanism that these authors propose is that free bitumen, present as distinct droplets, has a detrimental effect on settling due to hydrodynamic effects, while a small amount of bitumen attached to fine particles helps to bind the particles together, enhancing flocculation. Thus, these authors contend that the decrease in settling rate observed at low bitumen content is due to excess bitumen removal. Additional work will need to be conducted to better understand how bitumen interacts with tailings particles and the extent to which it can bind particles together to determine which of the possible explanations for the decrease in settling rate at low bitumen content is correct.

3.3.3 Comparison of Syncrude and Albian MFT:

As with Syncrude tailings, the bitumen content of Albian MFT was controlled by Denver cell extraction (protocol 1). The final bitumen contents following protocol 1 are shown in Figure 4-6.

Flocculation and settling results: Figure 4-7 shows the settling test results for Albian MFT (protocol 1), with the same experimental parameters as for the Syncrude MFT. It can be seen that with no bitumen removal, i.e. the highest bitumen content of 0.79 wt%, the settling rate was 0.35 m/h. Similar to what was seen with the Syncrude MFT, the settling rate increased to 0.47 m/h at an intermediate bitumen content of 0.28 wt% and then decreased to 0.25 m/h at a lower bitumen content of 0.17 wt%. Overall, the settling rates were substantially lower for Albian MFT than for Syncrude MFT, despite having the same experimental conditions with similar bitumen content and similar particle size distributions. Reasons for these observations will be discussed later in this section.

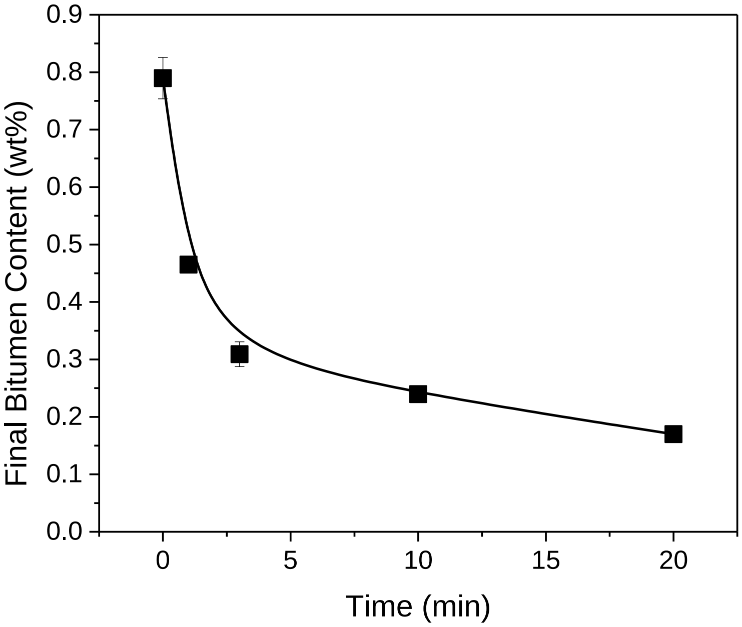

Figure 4-6: Final bitumen content of Albian MFT with extraction time

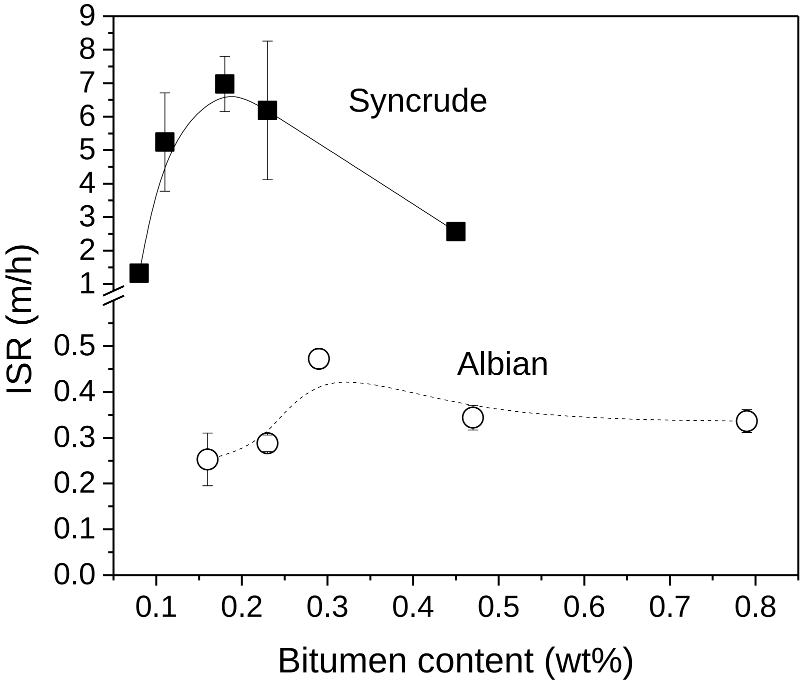

Figure 4-7: Effect of bitumen content on the initial settling rate of diluted Syncrude and Albian MFT flocculated with 50 ppm AF246 (protocol 1)

As with Syncrude MFT, FBRM® was used to measure in real time the floc size (mean square weighted chord length) under constant shear for Albian MFT. These experiments were also conducted for three different bitumen contents of 0.17, 0.28 and 0.79 wt%, inclusive of the lowest and highest settling rates observed for Albian tailings. The results are shown in Figure 4-8. The overall trend in flocculation behavior was similar to that observed for Syncrude tailings, with a maximum size reached within ~50 seconds. The floc size was then observed to decrease, as seen previously, reaching a steady-state size within 1 hr. As expected the maximum floc size of these samples is overall much smaller than for Syncrude MFT, corresponding to the lower settling rate. The maximum floc size observed for the sample with the highest settling rate (0.28 wt% bitumen) was approximately 200 µm. For the samples with the highest and lowest bitumen content, 0.79 and 0.17 wt.%, the maximum square weighted chord lengths were ~140 and ~150 µm, respectively.

Overall, Syncrude and Albian tailings show similar trends in terms of the effect of bitumen on flocculation and settling with a maximum settling rate occurring in the range of 0.2-0.3 wt% bitumen. These results are similar to those obtained by Carreras et al. [7] who found a maximum settling rate at approximately the same ratio of bitumen to solids for both model tailings samples as well as suspensions of fines obtained from batch extraction tests using ore samples.

Comparison of Syncrude and Albian tailings properties: To determine the reason for the significantly lower settling rates between Syncrude and Albian MFT, a number of properties for each of these two samples were characterized. As shown previously, the bitumen content was higher overall for Albian tailings than for Syncrude tailings, but after extraction the bitumen contents were similar. Even for samples with similar bitumen content the settling rate differs significantly. Therefore the bitumen content is not the cause. The particle size distributions of Albian and Syncrude MFT are shown in Figure 4-9. It can be seen that Albian and Syncrude MFT have approximately the same particle size distributions, with Albian MFT having a slightly smaller average size. As well, the Albian MFT shows a small peak centered around 400 µm, which is likely a small amount of coarse material (likely sand) that was trapped in the MFT. As with the Syncrude MFT, the particle size distributions of Albian samples also show no difference after bitumen removal by Denver cell extraction, confirming that there is no preferential distribution of particles based on size during the flotation process. As the particle size distributions are very similar between the two types of tailings, the differences in settling rate is not due to a difference in particle size.

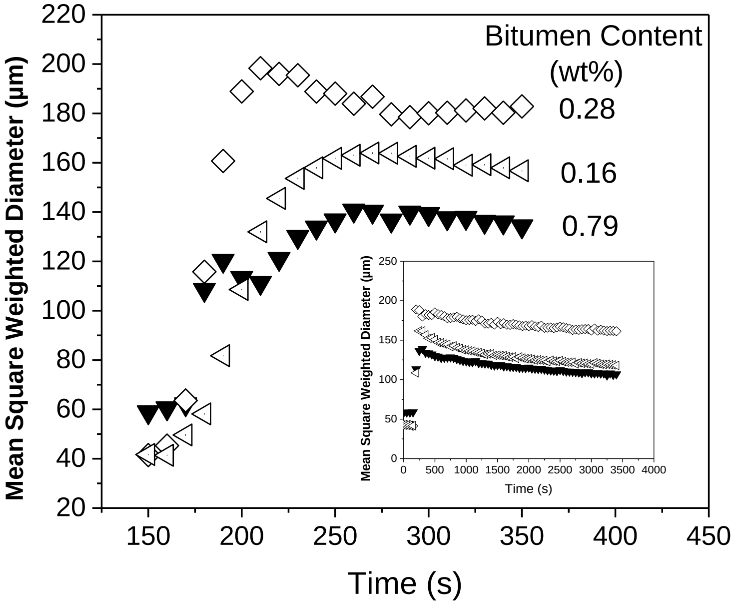

Figure 4-8: Flocculation kinetics as a function of bitumen content of Albian MFT (protocol 1) with corresponding initial settling rates of ◇ : 0.47m/h, ◁ : 0.25 m/h, and ▼ : 0.33 m/h.

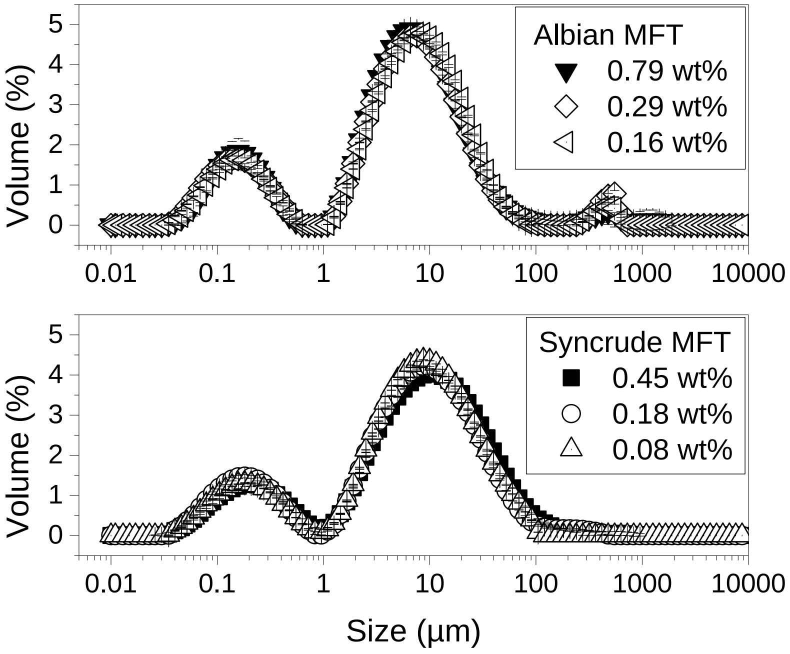

Figure 4-9: Particle size distribution of Syncrude and Albian MFT following protocol 1

Differences in mineralogy may play a role in flocculation. Therefore, X-ray diffraction was performed on solids isolated from Albian tailings following the same procedure as for Syncrude tailings, described in Chapter 3. The results are shown in Figure 4-10. These results show that the mineral composition of the Albian tailings is very similar to that of the Syncrude samples. Therefore, a difference in mineralogy can be ruled out as a factor which caused the difference in settling performance.

To determine if there was a significant difference in the ionic concentration of the tailings water, atomic adsorption spectroscopy analysis was performed on water separated from each tailings sample by centrifugation. The results are shown in Table 4-2.

Table 4-2: Concentration of selected cations in tailings water

	Ion concentration (ppm)			
	Na^+	Mg^{2+}	Ca^{2+}	Fe^{3+}
Syncrude	565.2	10.6	22.8	<0.1
Albian	201.0	12.4	17.8	<0.1

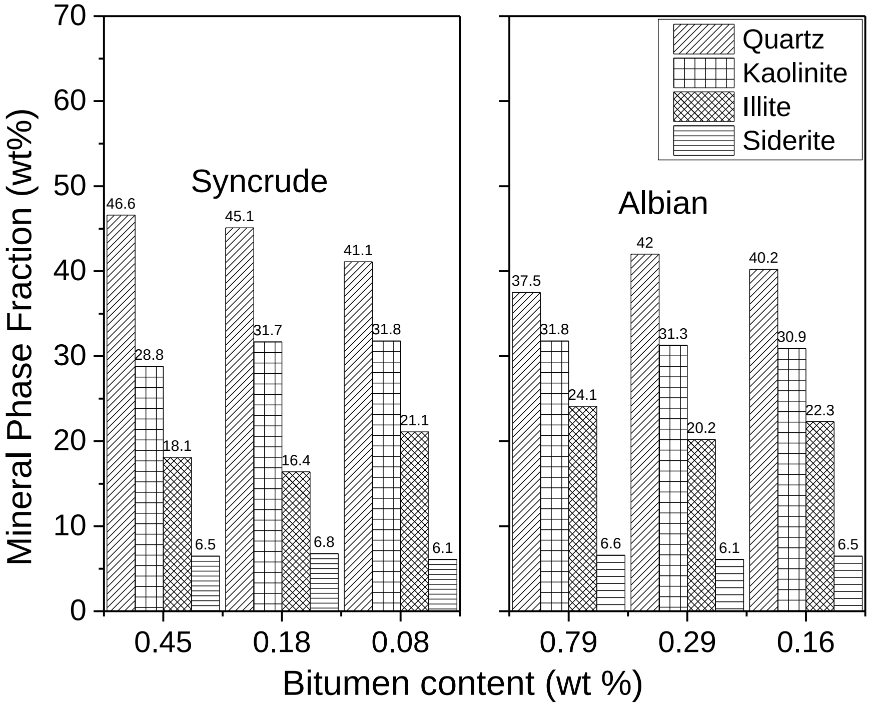

Figure 4-10: Mineral phases of solids from Syncrude and Albian MFT samples of varying bitumen content controlled by protocol 1. Lower bitumen content by longer MFT flotation.

It can be seen that the concentration of sodium is significantly higher in the Syncrude tailings than in Albian tailings. In addition, the calcium concentration is also slightly higher in the Syncrude tailings while magnesium is approximately the same. The higher ionic strength of the Syncrude tailings water may at least partially explain the difference in settling rate. With higher ionic strength the repulsion between tailings particles is reduced leading to improved flocculation. However, both samples were significantly diluted with the same process water (ion concentrations are listed in Table 4-1). After determining the overall ion concentrations from a weighted average of the concentrations in the tailings and process water, the difference in calcium content is negligible and the sodium concentration is approximately 80 ppm greater for Syncrude tailings. Though the difference in sodium ion concentration for diluted tailings is less significant than in the un-diluted case, the greater ionic strength of the Syncrude tailings may still partially contribute to a higher settling rate.

Figure 4-11 shows the zeta potential of Syncrude and Albian tailings samples with different bitumen contents. It can be seen that the zeta potential of both tailings is relatively constant with bitumen content and that the Albian tailings have a slightly more negative zeta potential overall. Though this may be a contributing factor, the small difference in zeta potential is not likely to be responsible for the large differences in settling rates.

Another possible contributing factor is the presence of contaminating organic matter on the particle surfaces. To determine if there are significant differences in the amount of organic matter present on the solids of these two tailings samples, thermogravimetric analysis was conducted. The results are shown in Figure 4-12. It can be seen that the mass loss of the blank Albian tailings sample is overall greater than the blank Syncrude sample, indicating greater organic contamination. However, with greater extraction time the overall mass loss is very similar to that observed for Syncrude tailings, implying that after flotation the amount of organic contaminated solids is relatively similar between Syncrude and Albian samples.

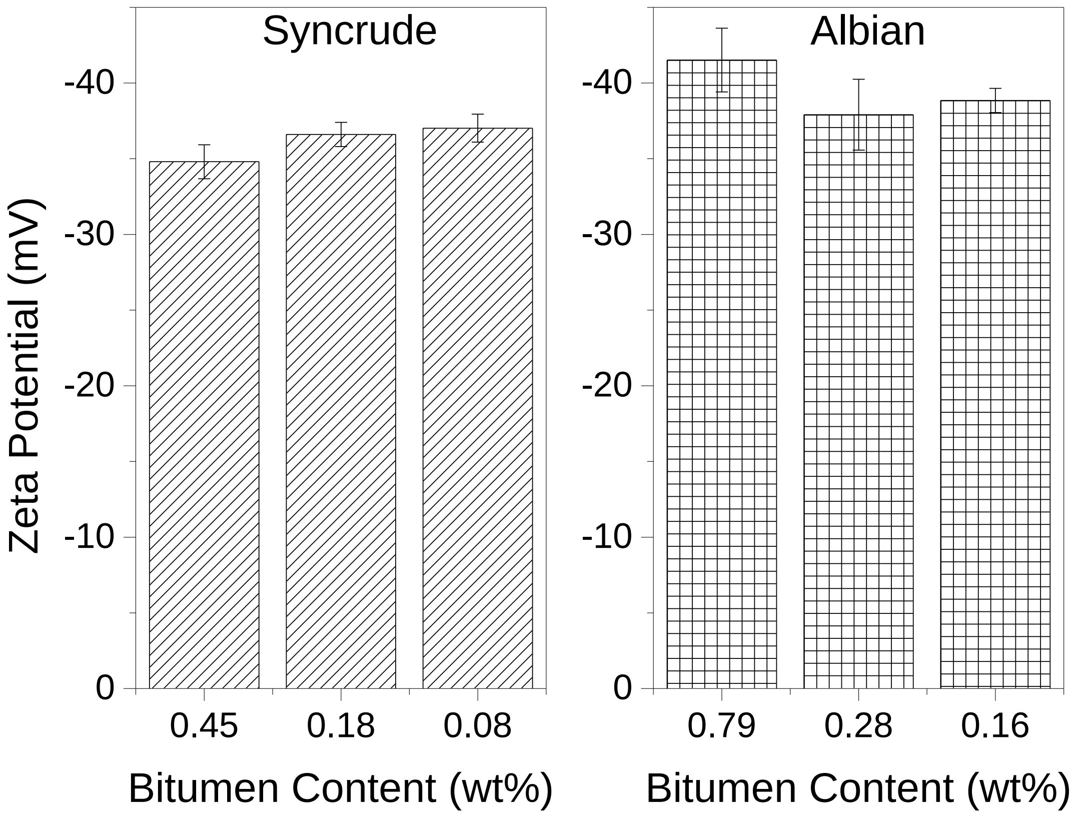

Figure 4-11: Zeta potential of Syncrude and Albian tailings vs. bitumen content

When compared to the baseline measurement made with LTA solids it can be inferred that the insoluble organic content of Albian tailings samples is 3.88 wt%, 2.15 wt% and 0.23 wt% for extraction time of 0 min (blank), 3 min and 20 min, respectively. It must be noted that the LTA solids used as a baseline are from Syncrude tailings and may not represent an accurate baseline for Albian samples. However the mineralogy of Syncrude and Albian tailings is very similar, hence, the mass loss due to mineral decomposition should be very similar for both tailings samples. Overall, the Albian tailings have a greater organic content than that of Syncrude tailings prior to flotation, but following flotation the organic content of both samples is very similar. Therefore, the amount of insoluble organic matter present with the tailings is most likely not responsible for the overall lower settling rate of the Albian MFT.

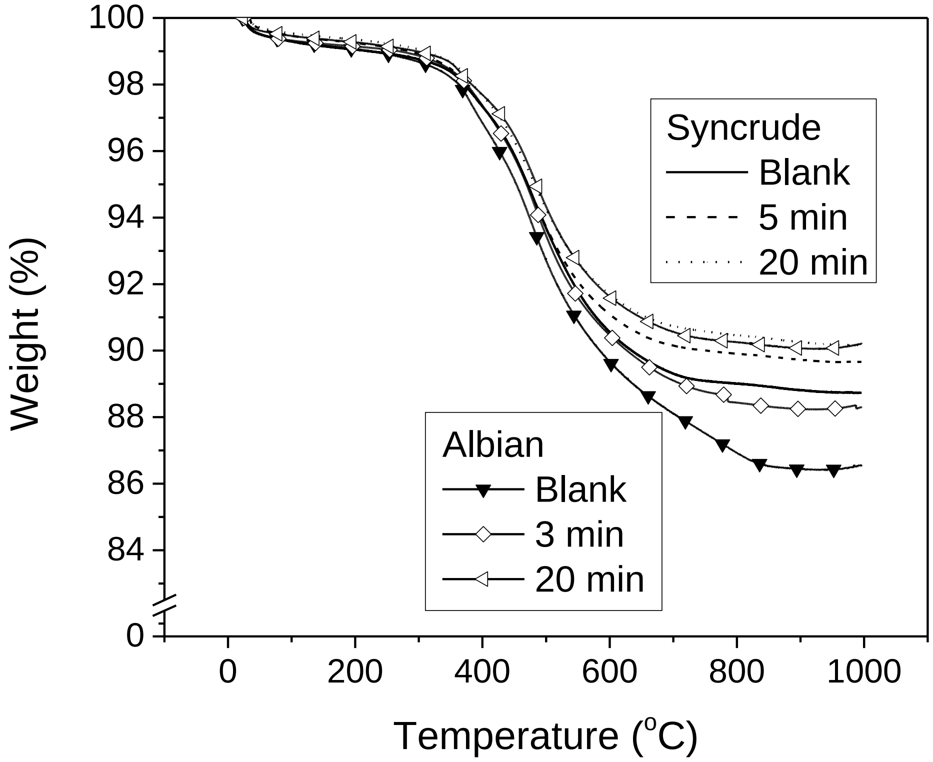

Figure 4-12: TGA profiles for Syncrude and Albian extraction tailings

It remains unclear what other factors may be responsible for the observed differences in settling between the two tailings samples. Other possibilities include differences in the structure of clays (i.e., the clays found in Albian tailings have a lower degree of crystallinity and a greater degree of “stair-case” like structures present) or differences in the type of organic matter present. More research will be needed to identify and characterize all of the factors relating to tailings flocculation.

4.4 Conclusions

The major conclusions from this work are summarized as follows:

- Denver cell flotation was found to remove a substantial portion of hydrophobic solids from the tailings.
- The hydrophobicity of tailings can be attributed to a small amount of toluene insoluble organic matter present on the tailings solids which can be removed by low temperature ashing.
- The presence or absence of hydrophobic solids which partitioned to the froth during flotation was not found to have a substantial effect on flocculation and settling of tailings.
- Denver cell mixing was identified as a possible cause for the observed reduction in settling rate after long extraction times. The underlying reason for this is the subject of ongoing investigation
- The settling behavior following bitumen removal shows similar trends for tailings samples of different origins, implying that the results obtained for Syncrude tailings are relevant to other tailings samples as well. However, the overall settling rate was substantially lower for Albian tailings than for Syncrude tailings.
- A number of tailings properties were characterized for both samples. Though some differences exist, none of the factors investigated stands out as the

definitive factor accounting for the observed differences in tailings settling rate with flocculant addition.

4.5 Suggestions for future work

Additional work should be conducted to identify how bitumen interacts with fines in real MFT to determine the relative amounts of free bitumen and bitumen attached to fines in typical MFT samples. Methods to precisely control the fraction of bitumen present in these two states will need to be developed either by selective removal of bitumen from real tailings or by addition of bitumen to model tailings. Some preliminary work with the addition of bitumen to model tailings has been conducted and the results are shown in Appendix B. Once that has been accomplished, the effect of both free and attached bitumen on polymer adsorption and the resulting flocculation and settling should be determined.

A detailed rheological study on oil sands tailings in high shear environments, such as those found during Denver cell flotation, should be conducted to determine if tailings rheology is a function of shear and agitation time. As well, bitumen removal by Denver cell flotation should be conducted at lower mixing speeds to determine if the same decrease in settling rate occurs with less intense agitation.

The interactions between polymer flocculants and the insoluble organic matter present on oil sands tailings should also be investigated to better understand the effect of organic matter on polymer adsorption and the resulting flocculation of the fine tailings.

As well, the adsorption of polymer and resulting flocculation of MFT following low temperature ashing should be studied and the results correlated to the mineralogical composition of the tailings. Furthermore, the effect of bitumen content on tailings flocculation with different types of flocculants, such as cationic or neutral, should be investigated to determine if the results obtained with the anionic polymer used in this study also apply.

4.6 References:

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Appendix A: Creating Non-segregating Tailings by Activated Sand Particles

A.1 Introduction

In addition to the study on the effect of fugitive bitumen in polymer based flocculation of MFT, an additional study was conducted to develop a novel treatment method to form non-segregated tailings (NST). The concept originated outside the scope of the original thesis objective. However, extensive research has been conducted and as such the data and discussion forms a supplementary chapter of the current thesis.

As mentioned previously, NST is typically formed by the CT process that utilizes sand present in the oil sands ore and the coagulation of fine tailings to form a non-segregating mixture. However, with continual chemical addition, such as calcium, the water chemistry and salinity of the recycled process water can have a detrimental impact on bitumen extraction.[1] Similarly, the ATA process described previously [Section 2.2.6] uses a combination of cationic and anionic polymer to bind fine clays to coarse sand particles forming a fast settling mixture with superior consolidating properties.[2] However, the additional cost of more than one chemical flocculant is undesirable. The newly proposed concept of utilizing one polymer to activate sand particles and subsequent flocculation with the tailings fines to form NST offers many desirable processing features such as: i) removes the concern of polymer overdosing, ii) mitigates the buildup of polymer (chemicals) in recycle water, iii) a more robust process in comparison with the CT process, and iv) single polymer provides ease of processing. A schematic of the process is shown in Figure A-1.

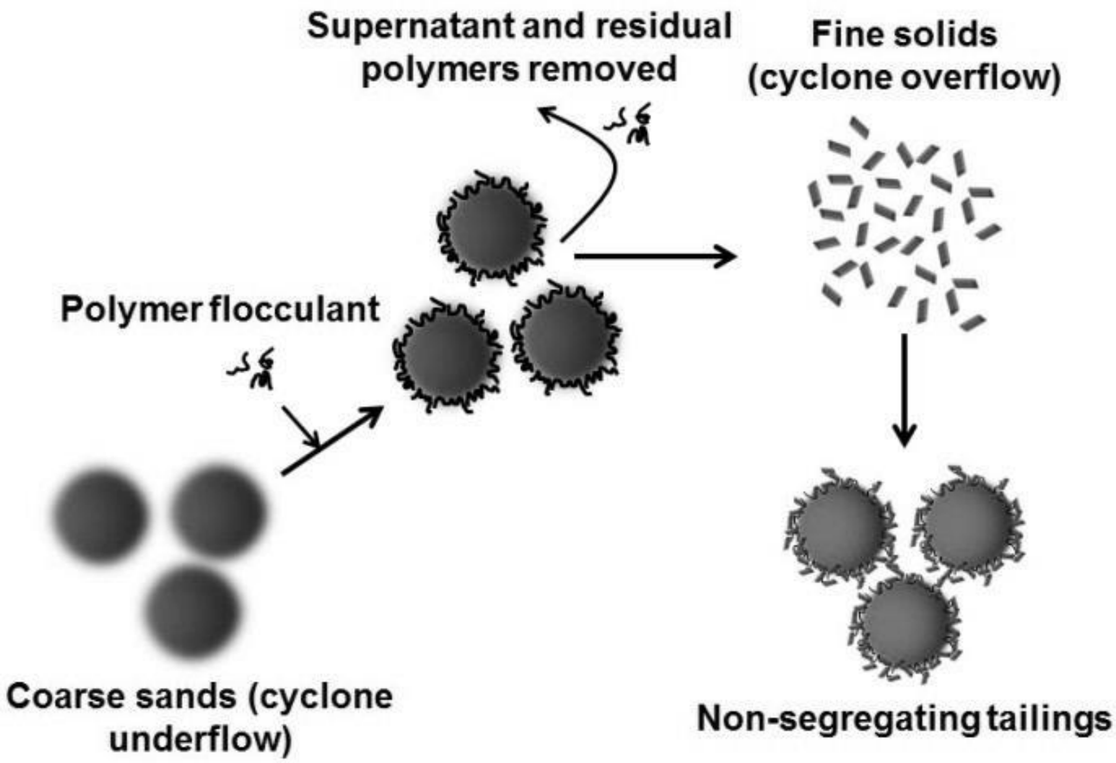

Figure A-1: Schematic of proposed NST mechanism

A.2 Materials and methods

A.2.1 Materials:

Ottawa Sand obtained from Sil Industrial Minerals (Edmonton, AB) was used throughout the study. The tailings were cyclone overflow tailings (referred to as fluid fine tailings or FFT) and were obtained from Syncrude Research (Edmonton, AB). The composition of these tailings was determined to be 15.8 wt% solids, 0.47 wt% bitumen and 83.1 wt% water by Dean-Stark analysis. The polymer used in this study was polydiallyldimethylammonium chloride (PDADMAC) obtained from Sigma Aldrich (Oakville, Ont.) as a 20 wt% solution. This polymer was chosen for its cationic charge and high charge density characteristics, which are perceived to be of desirable properties to reverse the charge of sand such that the negatively charged fines will interact through electrostatic attraction with anticipated bridging.

A.2.2 Settling tests:

Direct polymer addition: The method can be considered a traditional approach to flocculate solids, with polymer added directly to the particle suspension. These tests were used to form a baseline for the novel NST process, as well as highlighting some of the drawbacks associated with a direct flocculation approach.

In advance of flocculation experiments 10000 ppm polymer stock solution was prepared in process water and agitated for 12 h, before dilution to attain the desired polymer concentration. The concentrations used were 10000, 6000, 4000 and 2000 ppm. These concentrations were selected so that the desired polymer dosage could be added to the slurry with a constant volume of polymer solution (5 mL). All stock solutions were used within 24h.

Approximately 1 L of FFT was mixed thoroughly for 1 h with a 3 inch pitched blade impeller at 500 rpm prior to its use. The desired amount of sand was placed in a 250-mL beaker fitted with four baffles, then the corresponding amount of FFT and process water were added to achieve the desired sand to fines ratio (SFR

1, 2 and 4) while maintaining a total solids content of 16 wt%. The total mass of each slurry batch was 100 g. The mixture was homogenized at 500 rpm for 5 min with an overhead mechanical stirrer of a 4-blade, 1-inch width impeller. The impeller speed was reduced to 350 rpm while 5 mL of polymer stock solution, prepared at the appropriate concentration for the desired dosage, was added over a period of 1 min. Upon completion of polymer addition agitation was stopped and the suspension was transferred to a 100-mL graduated cylinder. The cylinder was sealed and inverted 5 times to evenly distribute the suspension within the cylinder. The “mud-line” height was recorded as a function of time, with the linear settling regime of the settling curve being used to calculate the initial settling rate. After 5 min approximately 30 mL of supernatant was decanted for turbidity measurements using a HF Micro 100 Turbidity meter (HF Scientific, Fort Myers FL). For some samples there was an insufficient volume of supernatant formed, so turbidity measurements could not be taken. After 24 h the final sediment height was observed and the final solids content of the sediment was calculated from the volume of sediment and the known mass of solids present in the sediment.

Treated Sand: The method describes the novel form of NST. As previously mentioned, the approach does not rely on the direct addition of polymer to the coarse / fines mixture, but the initial treatment of sand with a cationic polymer and addition of treated sand to the diluted FFT.

The desired amount of sand (same as described above) was mixed with 100 g of 10000 ppm stock solution and agitated for 1 h. The sand was settled for approximately 5 min and the supernatant decanted. In an attempt to further remove any remaining polymer solution, the sand was filtered under vacuum with a Buchner funnel and Whatman P4 filter paper and then rinsed with approximately 300 mL of deionized water while still under vacuum. In some cases the rinsing step was omitted and the sand was only filtered until the mass of polymer solution remaining was approximately 15% of the sand mass.

The desired amount of FFT was diluted with the appropriate amount of process water to maintain the total solids content (sands + fines) and achieve sand to fines ratio as described above. The mixture was homogenized at 500 rpm with a 1 inch impeller in a 250-mL beaker fitted with 4 baffles for 2 min. The mixing speed was reduced to 350 rpm and the filtered sand was added gradually over 30 s. Upon completion of treated sand addition, agitation was stopped and the suspension was transferred to a 100-mL graduated cylinder. The remainder of the test was conducted using the settling procedure described above.

A.2.3 Drainage and Yield Stress:

To evaluate the dewatering and strength characteristics of the formed sediments drainage and shear yield stress experiments were conducted by Mr. Ian Osborn who is greatly acknowledged for his contribution to this research. For those tests, custom made settling columns were used that incorporated detachable sections enabling yield stress measurement to be conducted on the formed sediment eliminating any handling issues. For drainage tests, the bottom plate of the column could be removed to allow water to drain, with the water mass recorded periodically. This setup is shown in Figure A-2. The sediment was supported by a wire mesh covered by a Whatman P4 filter paper. Yield stress measurements were made using a Haake VT550 (Thermo Scientific, Canada) with vane geometry. Yield stress is determined from the maximum torque that could be applied to the sediment before it began to flow. Yield stress measurements required a large sediment volume, hence the mass of the tailings suspensions was increased to 300 g. To mix this larger volume the impeller size was increased to a 2 inch pitched blade impeller. All other parameters were held constant.

A.2.4 Streaming potential measurements:

To measure the surface charge of the sand before and after polymer adsorption, the streaming potential was measured using a SurPASS electro-kinetic analyzer (Anton Paar, Ashland VA). This apparatus measures the electric potential of large particles or surfaces for which electrophoretic mobility measurements are difficult to attain.

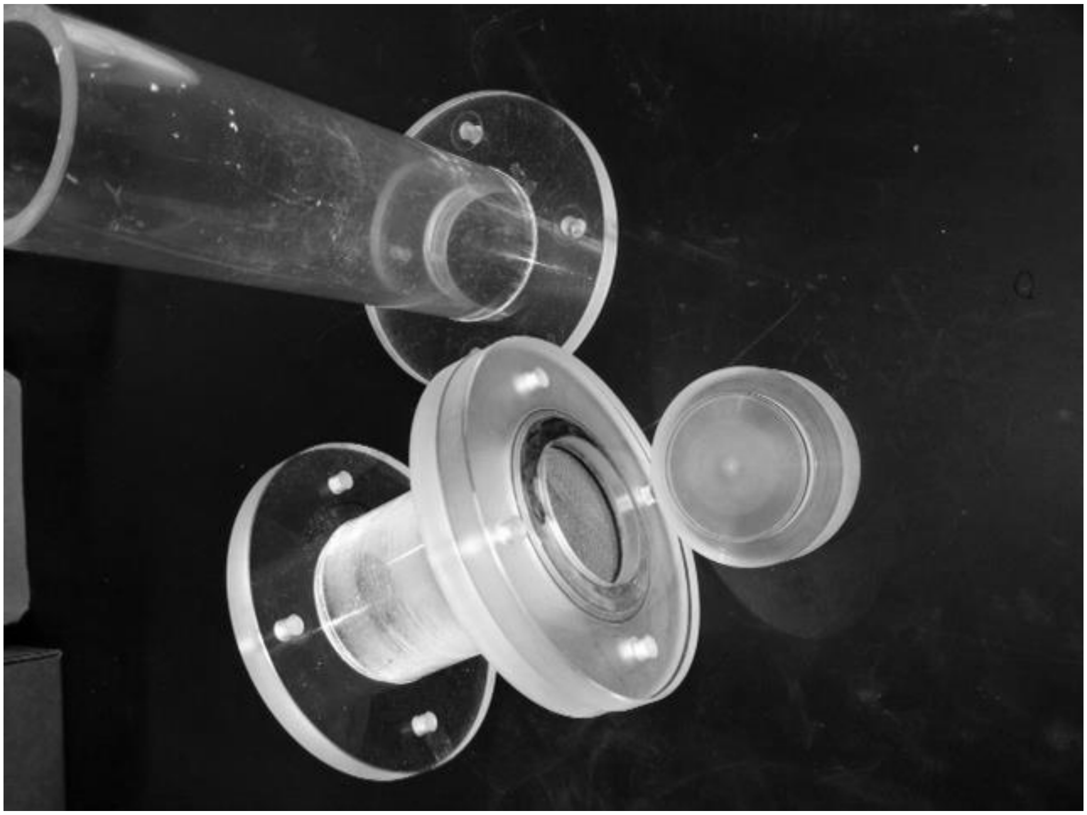

Figure A-2: Drainage column setup

The sample is loaded into a cylindrical cell and held in place by porous plugs placed on either side of the sample. The background electrolyte is pumped through the sample bed where a separation of charge occurs due to counter-ions being more concentrated within the immobile Stern layer surrounding the solid particles. The potential difference or streaming potential, generated by the separation of charge is measured by electrodes mounted at either side of the cell. Sand was treated with polymer solution and separated by filtration as described above. Approximately 4 g of sand (treated or untreated) was loaded into the apparatus' cylindrical cell and held in place by the porous plugs mounted on both sides of the sand bed. The background solution used was 1 mM KCl with pH adjusted to 8.5. To determine the stability of the polymer interaction with the sand particles, treated sand sample was rinsed between successive measurements with approximately 100 mL of background solution using the Surpass instruments "rinse" function, for a period of 300 s at a pressure of 400 mbar. The solution used for rinsing was discarded after each cycle.

A.2.5 Total Organic Carbon:

Total organic carbon (TOC) measurements were made using a Shimadzu TOC-V CHS/CSN Model Total Organic Carbon Analyzer (ShimadzuQ4 Corporation, Japan). This method measures TOC by acidifying a sample of water and then sparging to remove purgeable organic and inorganic carbon. The sample undergoes a reaction with a catalyst to produce CO_2 which is then detected by a non-dispersive infrared (NDIR) detector. Firstly, a portion of diluted FFT was centrifuged at 14000 rpm for 20 min and TOC of the supernatant was measured to establish a baseline for samples containing tailings water. After polymer or treated sand addition and batch settling, approximately 30 mL of the supernatant was extracted and centrifuged at 14000 rpm for 20 min to remove the remaining solids. The TOC was measured to determine the polymer excess (free polymer) relative to the TOC from the baseline measurement. To determine the amount of polymer adsorbed onto sand when the sand is treated with 10000 ppm stock solution, TOC measurements were performed on the stock solution as well as the supernatant of the stock solution after treating sand. The amount of polymer adsorbed was calculated based on the difference in TOC of the 2 samples.

A.3 Results and discussion

A.3.1 Direct Addition:

The results for the settling tests conducted with direct polymer addition are shown in Figures A-3 to A-6. Figure A-3 shows the initial settling rates obtained for the different sand to fines ratios at varying polymer dosages.

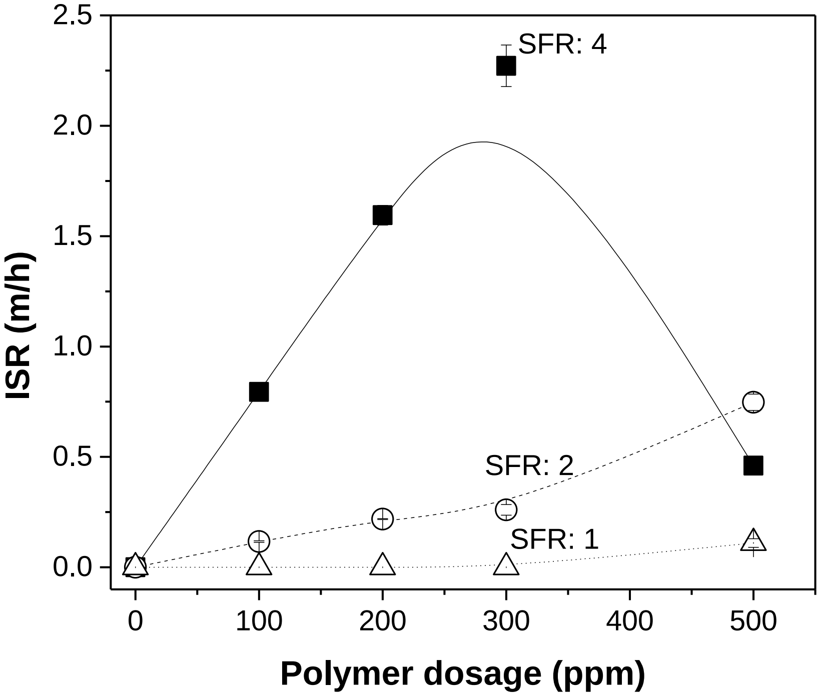

Figure A-3: Settling rate of sand-fines mixtures vs. pDADMAC dosage (Total solids content: 16 wt%)

As expected, higher SFR showed higher settling rates due to the greater fraction of coarse particles present. SFR 4 showed the highest overall settling rates of over 2 m/h at the optimum dosage of 300 ppm. Figure A-4a shows the consolidated sediment at this optimum polymer dosage after 24 hr. It can be seen that there is no apparent segregation of fines and sand, indicating the formation of non-segregating tailings sediment. In contrast, Figure A-4b shows the sediment at the same SFR with 100 ppm polymer addition. The majority of sand has not attached to fines and has settled to the bottom independently of the fines, indicating that the system was under-dosed. At high polymer dosages the settling rate decreased significantly due to polymer overdosing resulting in re-stabilization of the fines. This is shown in Figure A-4c where it can be seen that, similar to the under-dosing case, the sand has settled independently of the fines due to the excess polymer causing repulsion between sand and fines.

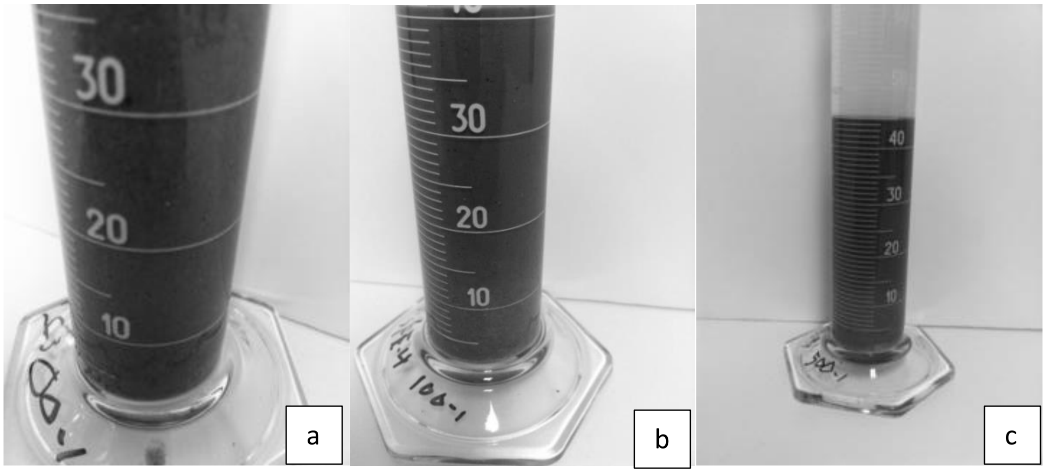

Figure A-4: Sediment formed using: a) 300 ppm, b) 100 ppm and c) 500 ppm pDADMAC with SFR4 after 24 hr.

Lower SFR showed substantially slower settling rates. With SFR 2, the initial settling rate did not exceed 0.75 m/h even at the highest polymer dosage used. Furthermore, SFR 1 showed almost no settling at any of the polymer dosages used. Figure A-5 shows the turbidity results for SFR 4. For the other samples the settling rate was too low to produce a sufficient volume of supernatant within the

5 min period before the supernatant sample was withdrawn. Therefore, only the data for SFR 4 was included. It can be seen that the turbidity of the supernatant was relatively low, at approximately 20 NTU until the system was overdosed at 500 ppm resulting in a substantial increase in turbidity to 400 NTU. This also indicates that the system was overdosed at this dosage as a significantly greater portion of fines remained suspended due to re-stabilization by the excess polymer. Figure A-6 shows the final solids content of the sediment after 24 hr. As expected, the overall solids content increases with SFR as coarse sand tends to form more compact sediment than fine particles.

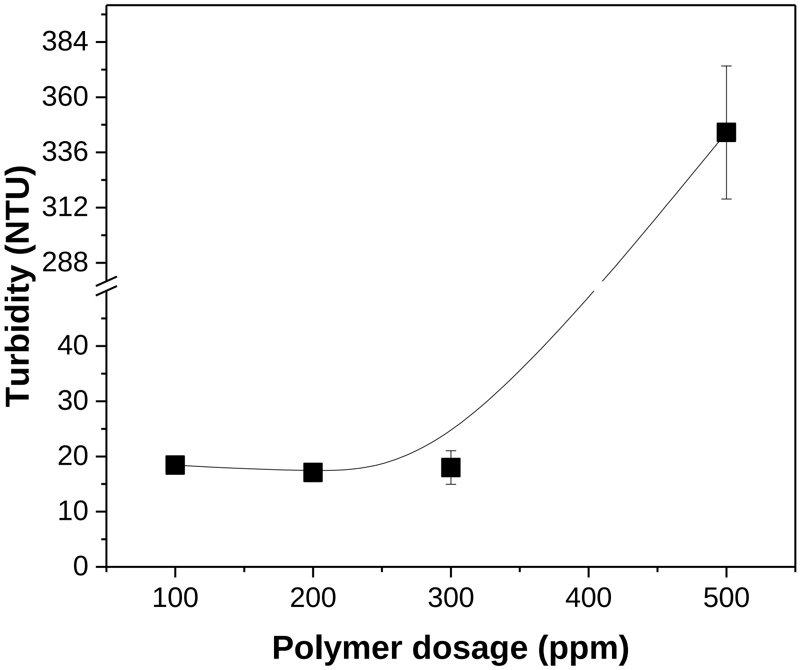

Figure A-5: Supernatant turbidity of SFR4 vs. pDADMAC dosage

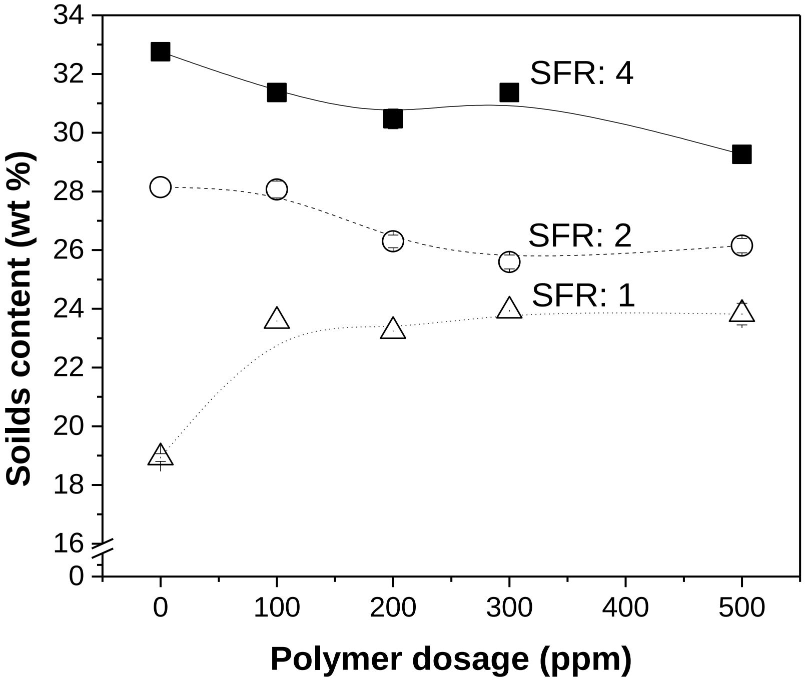

Figure A-6: Final solids content after 24 hr. settling of sand-fines mixtures vs. pDADMAC dosage

When the polymer is added directly to a mixing suspension of sand and fines, the polymer will cause the flocculation of fines - fines and fines - sand particles. Fines attached to sand particles will settle rapidly due to the large size of sand grains. However fines flocculated with other fines would be expected to settle slower due to the porosity of the flocs and smaller overall floc size, but faster than the dispersed fines. To determine if the fines were being flocculated and settling independently of the sand, settling tests were performed on suspensions of fines alone. The FFT was diluted to ratios equivalent to the SFR's used in the previous tests so that the fines contents were equivalent but no sand was present. Figure A-7 shows the results of the settling tests for the diluted tailings. It can be seen that the settling rates obtained for diluted tailings are generally lower than for samples where sand was present, in spite of the lower total solids contents. The highest settling rate obtained at a dilution ratio of 4:1 was approximately 0.55 m/h, significantly lower than the maximum settling rate of 2.3 m/h obtained with SFR 4. This observation indicates that the presence of sand helps to improve the settling of fines either by the flocculation of fines with sand, slipstreaming, where fine particles are pulled in the wake of fast settling sand grains or a combination thereof. The settling results for a dilution ratio of 2:1 are generally similar to what was observed with SFR 2 with settling rates of approximately 0.25 m/h at polymer dosages of 200 to 300 ppm. However, unlike the case where sand was added the settling rate peaks at 300 ppm and decreases at 500 ppm, indicating overdosing. This result is most likely due the lower solids content when sand is not added. Similar to what was observed with SFR 1, a dilution ration of 1:1 showed almost no settling except at the highest polymer dosage.

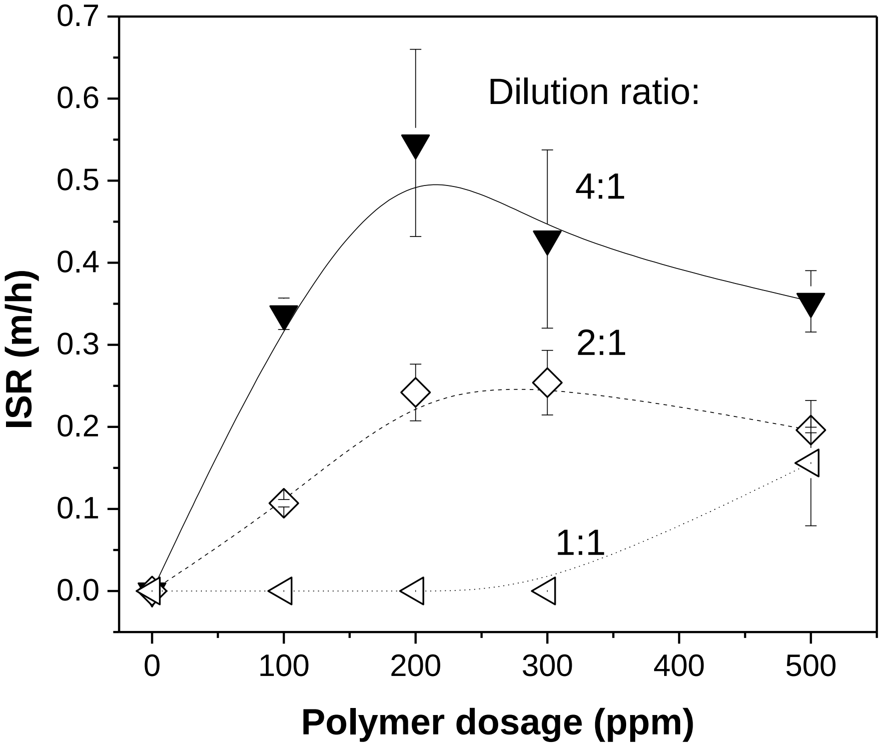

Figure A-7: Settling rate of fines only vs. pDADMAC dosage. (Original solids content 16 wt%)

A.3.2 Treated Sand:

For the treated sand method, it must be established that the adsorbed layer of polymer will not desorb to any significant extent after the sand has been transferred to the fines suspension. To determine irreversibility of polymer adsorption on coarse sand particle, the streaming potential of sand was measured before and after polymer treatment and then after several rinsing cycles using the SurPASS surface potential analyzer. Figure A-8 shows the results obtained using the SurPASS.

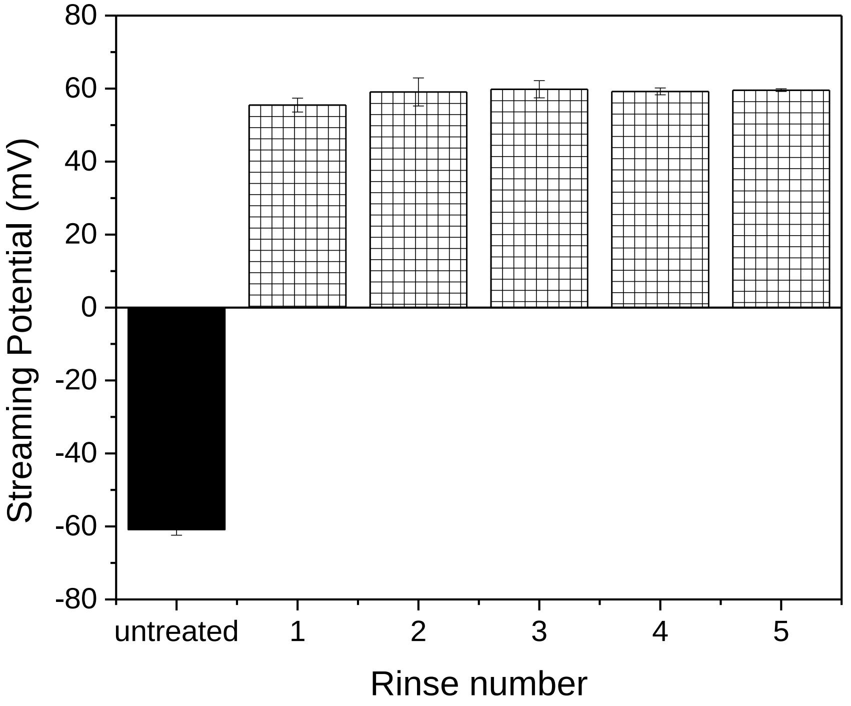

Figure A-8: Streaming potential results for untreated sand and sand treated with 10000 ppm pDADMAC solution

Before treating sand with polymer, the measured streaming potential was highly negative, having a value of approximately -60 mV. After treating the sand and subsequent rinsing the measured surface potential was reversed, having a value of approximately 55 mV showing that the positively charged polymer has adsorbed strongly and is present in sufficient quantity on the surface to completely reverse the surface charge. The streaming potential remains constant even after several rinsing cycles, indicating that the adsorbed polymer layer is very stable and does not desorb to any significant extent.

However, when settling tests were conducted with treated sand, unexpected results were obtained. When the sand was rinsed and then added to the fines mixture, no significant attachment of fines to sand was observed as shown in Figure A-9.

Figure A-9: SFR 4, pDADMAC treated sand after 10 min

The reason for the lack of interaction between positively charged sand and negatively charged fines (zeta potential = -36 mV) is subject of ongoing research. It is possible that the molecular weight of the polymer is too low to provide sufficient bridging between the sand and fine particles. However, the dominant flocculation mechanism in this case should be the electrostatic patch mechanism which promotes flocculation by electrostatic attraction and does not require the polymer to extend outwards from the particle surfaces to bridge particles. Another possibility is that the amount of sand used was insufficient to capture all of the fines present. More work will be required to determine the underlying issue. However, when the sand was not rinsed and a small amount of polymer solution (15 wt% of total sand mass) remained with the treated sand, flocculation to form NST was observed.

Figures A-11 to A-13 show the settling results obtained for treated sand at SFR 4 compared with the direct addition data at the same SFR. It can be seen that the settling rate with treated sand is approximately 2.6 m/h, very similar to the direct addition method at the optimum dosage. The supernatant turbidity obtained for the treated sand was low ~17 NTU, as well the final sediment solid content ~32 wt%, also similar to what was observed for the direct addition method. An image of the sediment obtained using this method is shown in Figure A-14. It can be seen that the sand and fines do not segregate for this method as with the direct addition method at optimum dosage. However, if the fines were directly adsorbed onto the treated sand, as was the intention of this method, it is expected that the resulting settling rate would be higher as the sand-laden flocs would settle at a rate similar to sand (> 20 m/h). Instead, the settling rate is approximately the same as for the direct addition method, which would imply that some of the fines are flocculating separately from the sand as was inferred for that method. The similarity with the direct addition method most likely results from excess polymer solution (approximately 2 g of 10000 ppm stock solution) that remained after sand filtration.

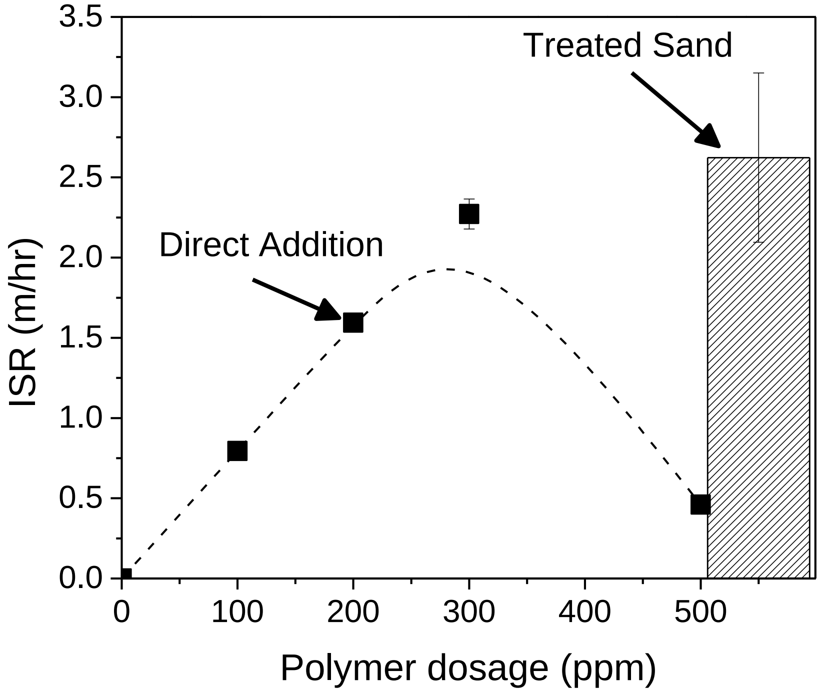

Figure A-11: Settling rate of SFR 4 vs. pDADMAC dosage

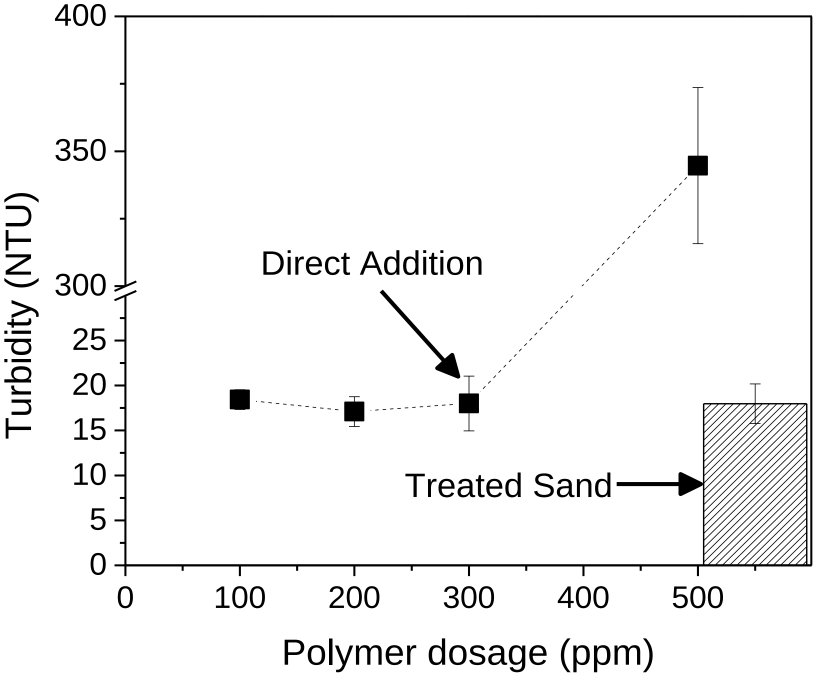

Figure A-12: Supernatant turbidity of SFR 4 vs. pDADMAC dosage

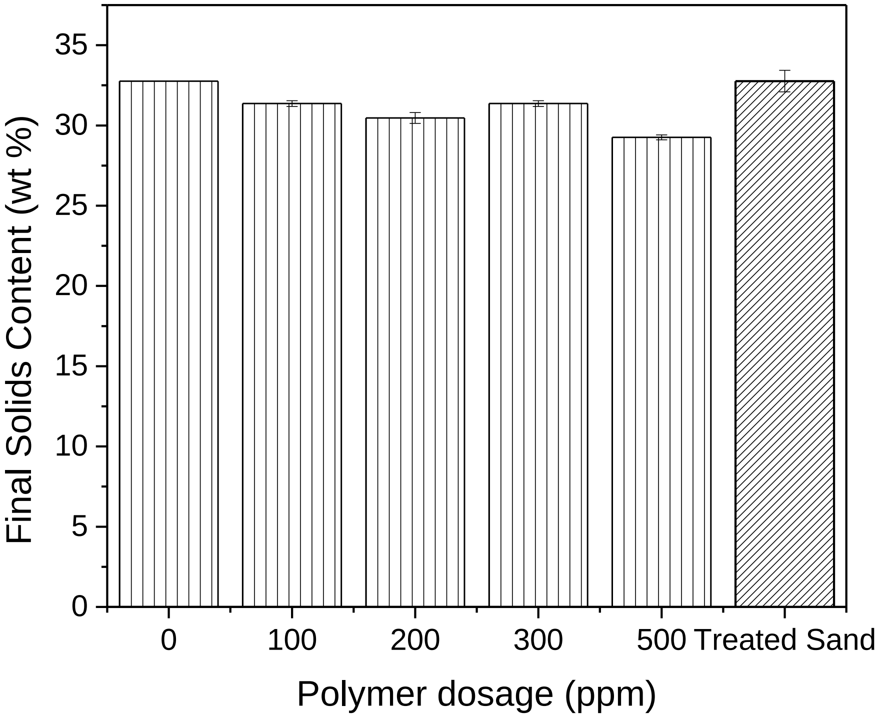

Figure A-13: Final solids content after 24 hr. of SFR 4 vs. pDADMAC dosage

Figure A-14: SFR 4 treated sand after 1 hr

This inference is supported by the TOC results shown in Figure 5-15. The increase in TOC shows that a small amount of polymer is not adsorbed onto the particles and remains in the supernatant. The change in TOC is comparable between the treated sand and direct addition methods, indicating that there is free polymer remaining in both systems. From TOC analysis of the polymer solution used to treat the sand, it was determined that the polymer adsorption onto sand was approximately 0.98 mg/g of sand. This amount of polymer would be the equivalent of a 125 ppm dosage. With the residual polymer solution left in the system (~2 g of 10000 ppm solution) the total dosage of adsorbed and un-adsorbed polymer would be approximately 325 ppm, indicating that the overall polymer dosage is essentially the same as for the optimum dosage determined from the direct addition method which helps to explain why the settling and TOC results are so similar.

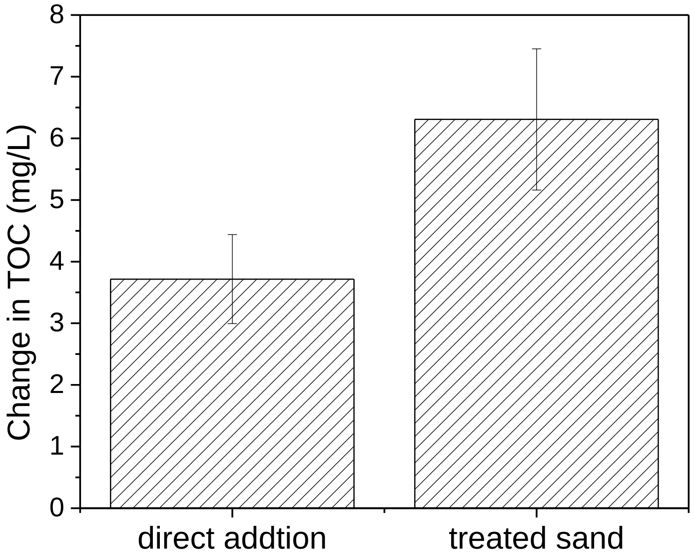

Figure A-15: Change in TOC of supernatant water after settling tests using direct polymer addition or by addition of treated sand

However, despite the similar settling characteristics observed for the two methods, there are differences in the characteristics of the sediment formed as shown in Figure A-16. Approximately 40 wt% of sediment water drained in 30 min for the treated sand sediment; significantly higher than the direct addition sediment that only drained 25 wt% in the same time period. This indicates that the treated sand method forms flocs with higher permeability, allowing water to drain more easily.

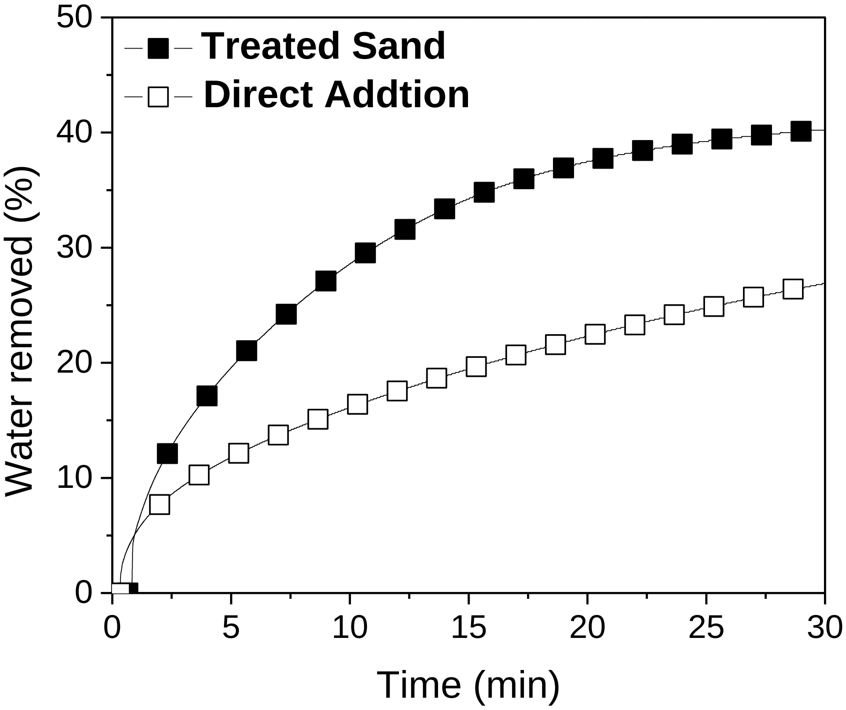

Figure A-16: Drainage of sediment water after settling tests using direct polymer addition or by treated sand method (Experiments conducted by Mr. Ian Osborn)

Figure A-17 shows the change in solids content as well as the resulting yield stress of the sediment before and after the drainage process. The solids content increases by approximately 10 wt% after 30 min of drainage with an additional 5 wt% after 24 h, which shows that the majority of free water in the sediment drains very quickly. It can also be seen that the yield stress of the sediment increases substantially from less than 100 Pa to 350 Pa after 30 min of dewatering and a marginal improvement over 24 h, reaching a yield stress of 400 Pa.

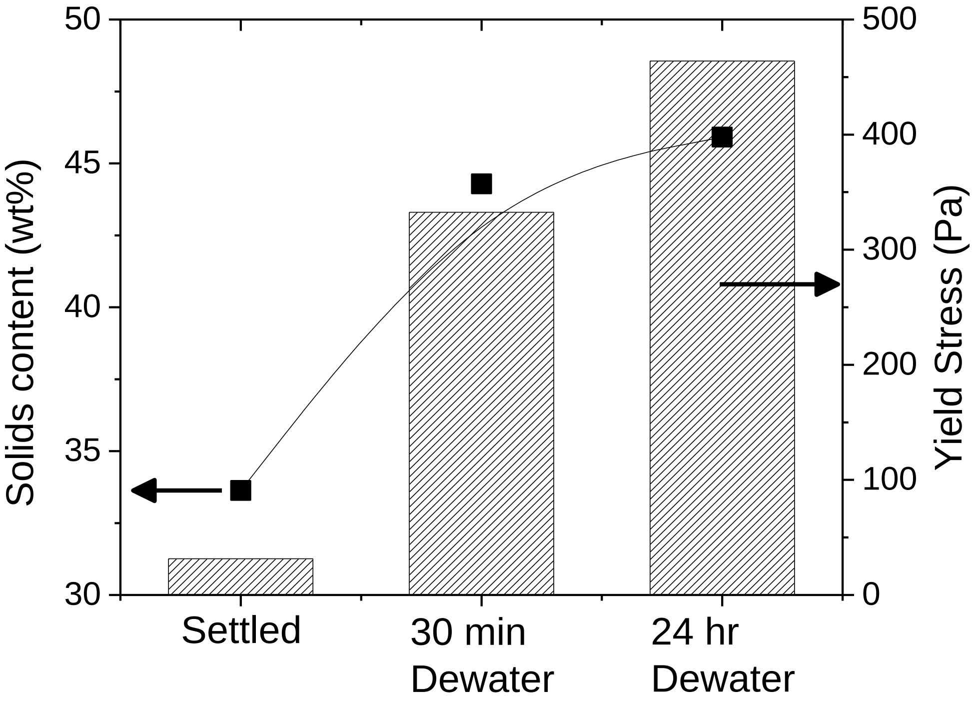

Figure A-17: Solid content and yield stress of sediment formed by treated sand method before and after drainage (Experiments conducted by Mr. Ian Osborn)

It is unclear at this point why the treated sand, without additional polymer failed to attract fines. It is possible that a very small amount of fines were attached but the amount was too small to be noticed. It is also possible that the attachment of fines was too weak and the shear that results from the fast settling of sand grains was too strong for the fines to remain attached. More work will be needed to determine the underlying issue, as well as to improve the process to the point where it would become a viable tailings treatment option.

A.4 Conclusions

- pDADMAC has been shown to flocculate oil sand fine tailings at sufficient dosage and tailings dilution.
- The presence of sand enhances settling of flocculated tailings and the sand does not appear to segregate from the fines at the optimum dosage.
- Pretreating the sand with polymer has been shown to reverse the charge of the sand and the polymer does not appear to desorb from the sand after rinsing.
- In spite of this, sand pretreated with polymer does not appear to provide suitable conditions to flocculate with the majority of fines in FFT, with performance most likely related to excess polymer solution remaining after vacuum filtration of the sand sediment.

Future Work:

The interactions between polymer treated sand and fines will need to be investigated to better understand how much, if any, fines attach to the treated sand and how strong the attachment is.

The same procedure should be attempted with polymers of different charge densities and molecular weights to make the process function as intended. In addition, the effect of different mixing regimes should be examined to determine if mixing affects the adsorption of polymer onto the sand or the attachment of fine tailings onto the treated sand.

A.5 References:

[1] E. S. Hall, E. L. Tollefson, Can. J. Chem. Eng. 1982, 88, 812.

[2] Soane, D. W. 2nd International. Oil Sands Tailings Conference, Edmonton, Alberta 2010 p. 135.

Appendix B: Supplemental data

Model tailings

Procedure:

The desired amount of bitumen was dissolved in ~ 50 mL of toluene and this solution was then mixed with the desired amount of clay. The toluene was allowed to evaporate overnight and the resulting bitumen coated clays were used to prepare 5 wt% suspensions in process water. The suspensions were agitated overnight and settling tests were conducted using the standard procedure.

Results:

The results of these tests are shown in Figure B-1. The settling rate is substantially lower for bitumen coated clays than for the uncontaminated control sample. This indicates that the presence of bitumen on clays hinders flocculation and settling. The settling rate for coated clays is essentially the same for all bitumen contents investigated. For this method bitumen should be deposited in an even layer on all clay surfaces. The settling data indicates that the thickness of the bitumen layer does not impact the settling rate and that any amount of contamination on the surface hinders the adsorption of polymer.

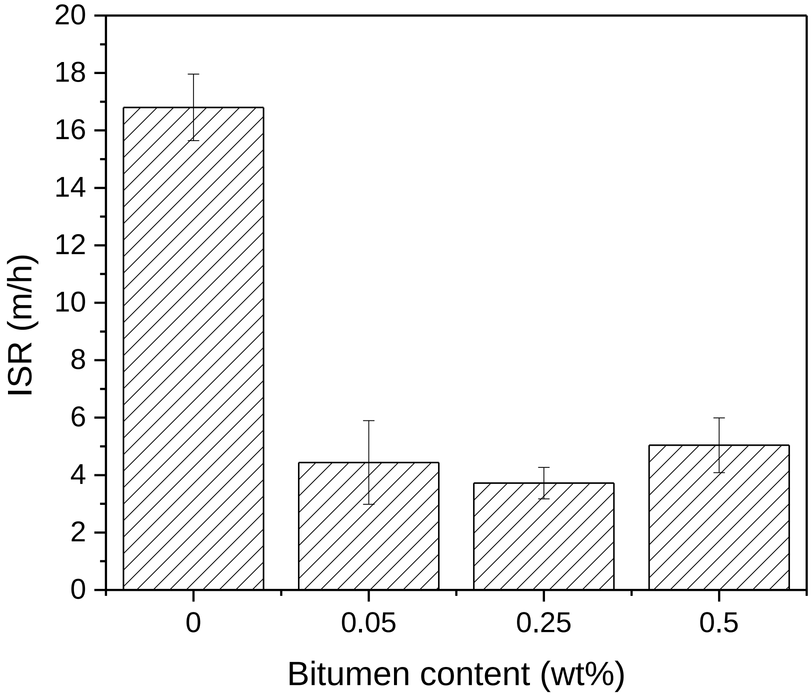

Figure B-1: Settling rate vs. bitumen content for model tailings (bitumen coated kaolin in process water, 5 wt% suspension, bitumen content as a fraction of total slurry mass; 50 ppm Hychem)

<u>QCM-D Analysis of interactions between polymer and fine tailings particles</u>

Procedure:

Syncrude MFT was diluted 3:1 with deionized water and allowed to settle for 2 days. The resulting supernatant was decanted and centrifuged at 15000 rpm for 20 min. The resulting sediment is shown in Figure B-2. Light and dark fractions were carefully separated with a spatula. The particle size distribution and relative organic content of the two fractions were determined by Mastersizer and TGA as described in Chapters 3 and 4. For QCM-D analysis, the following procedure was used. First, background solution (0.1 µm filtered process water, pH 8.2), was pumped over an alumina sensor to establish a baseline. Next, a 500 ppm polymer solution (in filtered process water) was pumped until steady state was attained. After the polymer layer was deposited background solution was pumped again to remove any un-adsorbed polymer present. Finally, suspensions of 0.01 wt% solids in process water were pumped. The flow rate used in all cases was 0.15 mL/min. The shift in resonant frequency and dissipation were monitored for as long as was practical. Typically the experiment ran for 4 hr. In addition, to study the particle interaction with the sensor surface without the presence of polymer the same experiments were repeated without the polymer addition step. To ensure that particle deposition did not occur due to gravitational settling the QCM-D unit was inverted for all experiments.

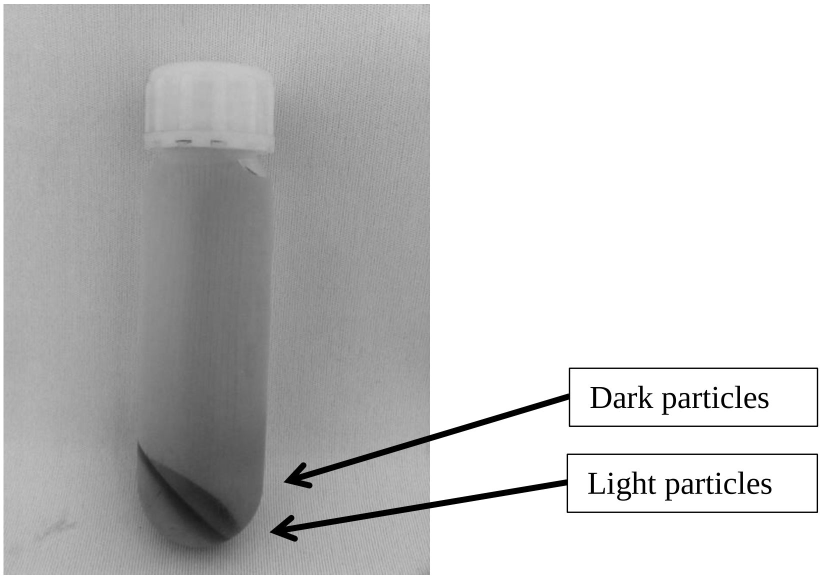

Figure B-2: Fine particles obtained from MFT

Results:

As shown in Figure B-3, the particle size distributions for both particle fractions are almost identical. As well, the majority of the particles have a size of approximately 100 nm. The TGA results are shown in Figure B-4. These results show that the dark fraction has significantly larger amounts of organic matter present. QCM-D results are shown in Figures B-5 through B-8. The frequency and dissipation data (Figure B-5) for the particle adsorption onto polymer is very unusual. The dissipation reading increases significantly, indicating the particles and polymer form a very loose, extended layer. However, the frequency reading does not behave as expected. When the mass of the adsorbed layer increases the frequency reading typically decreases (i.e. becomes more negative) however, in this case the frequency reading increases. This may indicate a loss in mass, however other overtones not depicted here follow the same trend and even cross the axis which would not be possible if the results were due to desorption. The exact reason for this behavior is not know at this time. The results can be modelled, however, and the results are shown in Figure B-6. The dark particles show a greater mass uptake than the light particles. This may be due to the fact that organic contaminated particles have been shown to aggregate with one another to a greater extent than particles with less contamination. This contention is supported by the results in Figures B-7 and B-8. Both particle fractions interact very strongly with the alumina surface most likely due to the aggregation mechanism described in Chapters 2 and 3. The mass uptake is even greater than without the polymer layer, most likely due to electrostatic repulsion. The adsorption of dark particles is also greater in this case. A possible explanation for the unusual behavior seen with the polymer-particle system is that some particles attach to the polymer and become part of that layer. However, the majority of particles aggregate with each other, forming a second layer which does not fully couple with the first, resulting in large changes in dissipation and unusual frequency behavior.

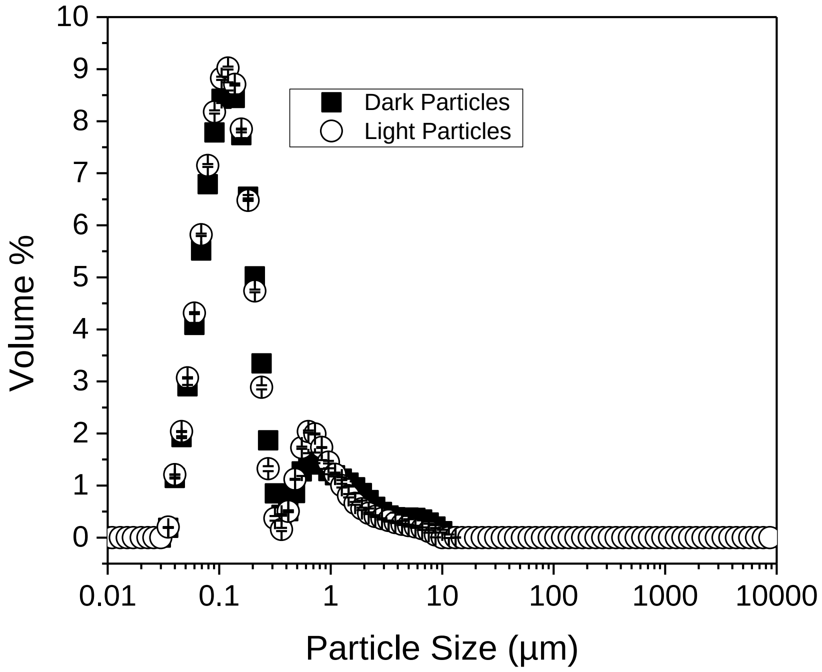

Figure B-3: Particle size distribution of fine particles obtained from MFT

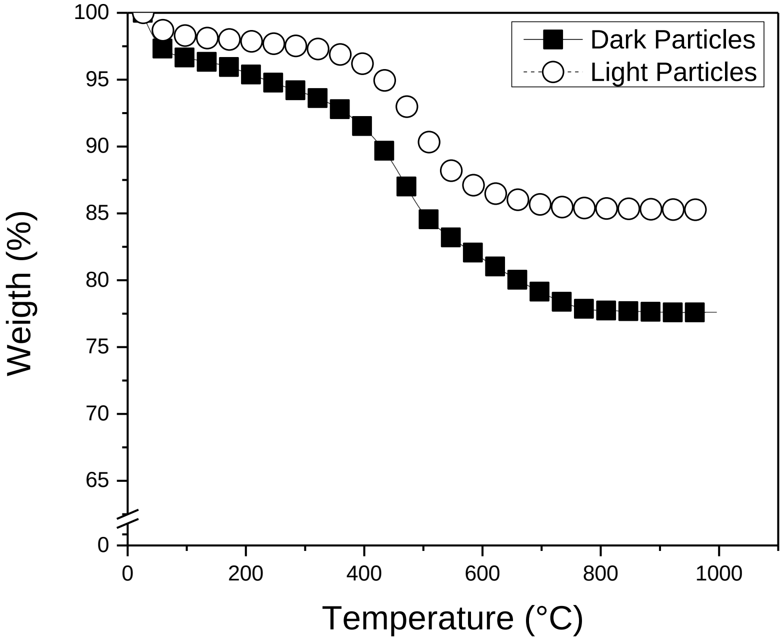

Figure B-4: TGA profile of fine particles obtained from MFT

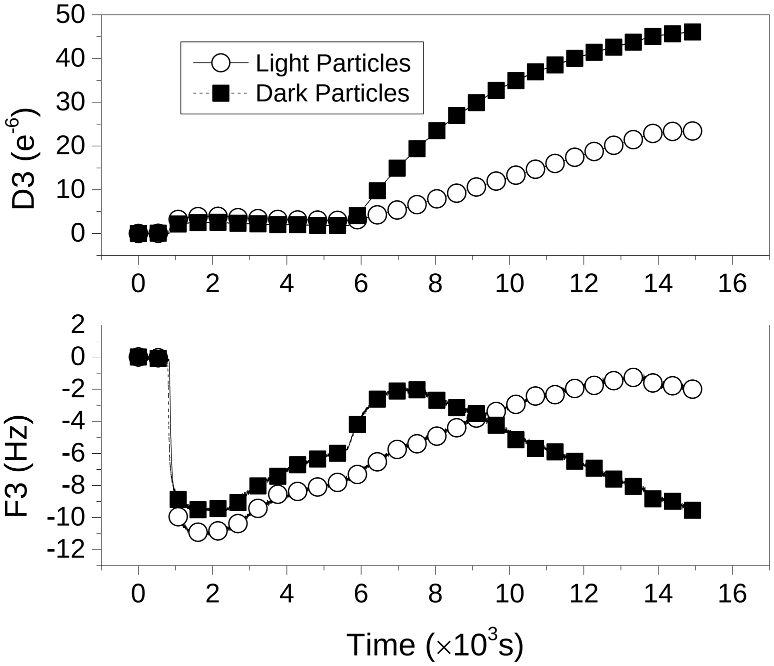

Figure B-5: Frequency and dissipation measurements of attachment of fine particles to adsorbed polymer flocculant layer (AF246; 500 ppm solutions at pH 8.5 on alumina surface), as a function of time.

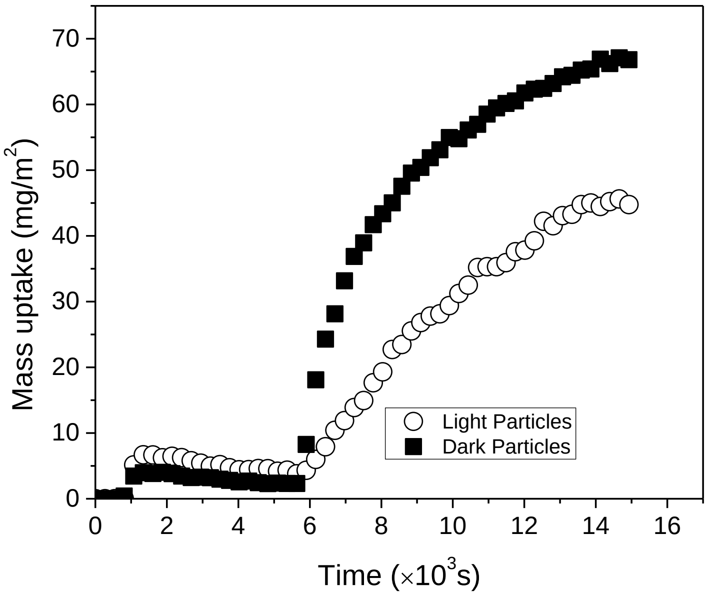

Figure B-6: Calculated mass uptake of attachment of fine particles to adsorbed polymer flocculant layer (AF246; 500 ppm solutions at pH 8.5 on alumina surface), as a function of time.

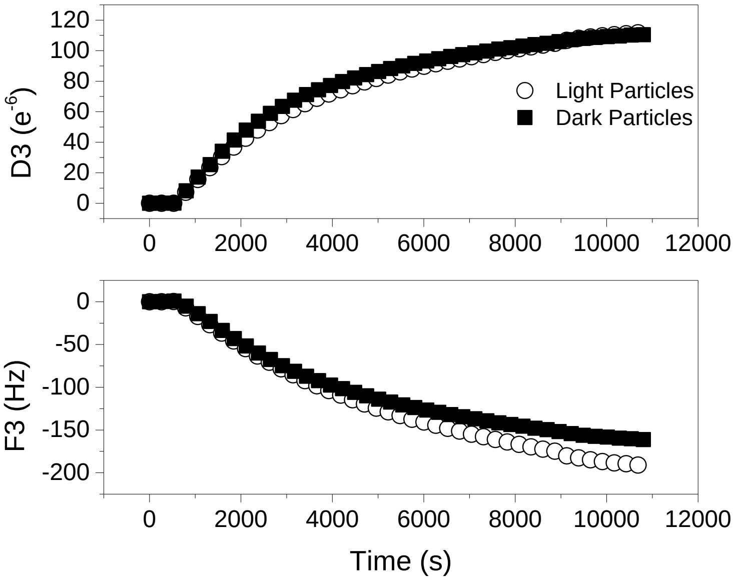

Figure B-7: Deposition of fine particles (0.01 wt% in process water, pH 8.5) on alumina surface as a function of time.

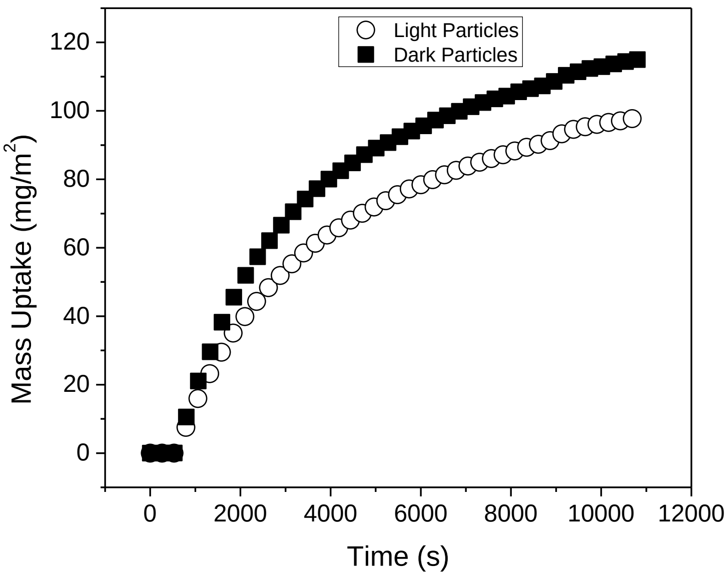

Figure B-8: Calculated mass uptake of fine particles (0.01 wt% in process water, pH 8.5) on alumina surface as a function of time.

<u>Properties of supernatant solids:</u>

Procedure:

During settling tests, approximately 30 mL samples of supernatant were extracted after 5 min of settling. These samples were centrifuged to separate solids to determine the solids content of the supernatant. The particle size and mineralogy of these solids were also characterized using the same methods described in Chapters 3 and 4.

Results:

Figure B-9 shows the supernatant solids content and corresponding initial settling rate. The solids content of the supernatant approximately corresponds to the observed settling rate, with higher settling rates having somewhat lower solids content. The particle size distribution (Figure B-10) shows that the majority of particles are approximately 1 µm. This agrees with the theory discussed in Chapter 2 which stated that high molecular weight polymers are not generally effective at flocculating very fine (<1 µm) particles. The mineralogy data (Figure B-11) shows that the majority of the supernatant is silica and there are significantly lower amounts of clays present than in the bulk tailings. This agrees with the QCM-D data shown in Chapter 3, which showed that the polymer used has a very low affinity for silica.

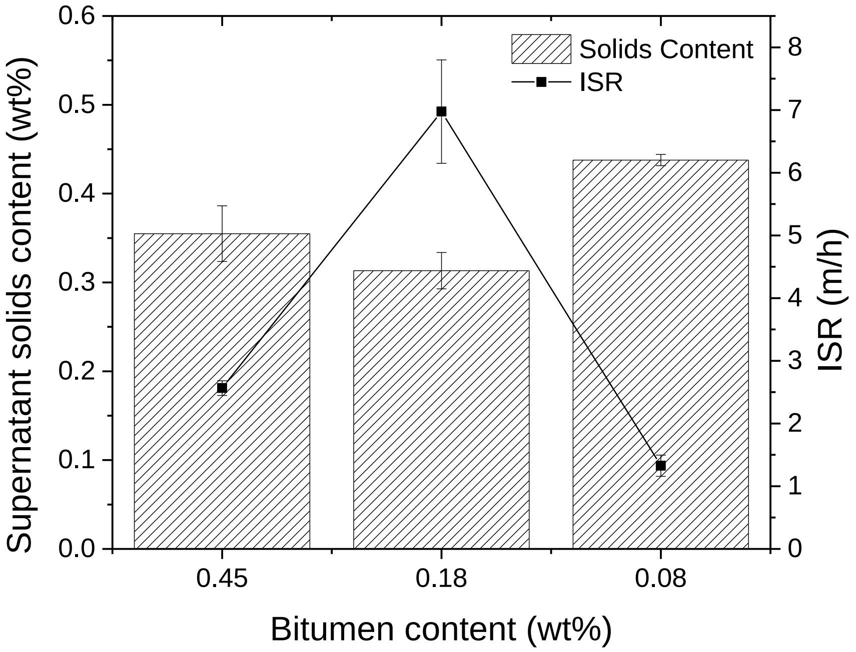

Figure B-9: Supernatant solids content of selected tailings samples

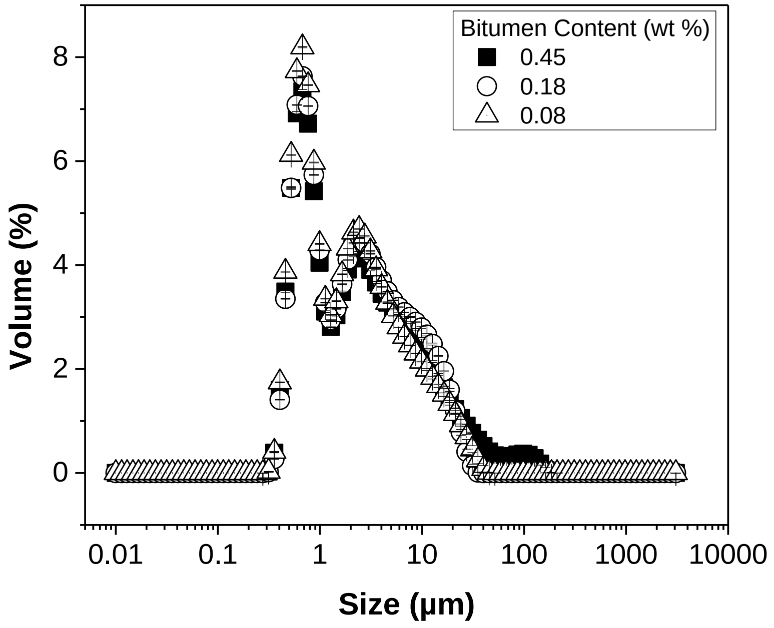

Figure B-10: Particle size distribution of supernatant solids

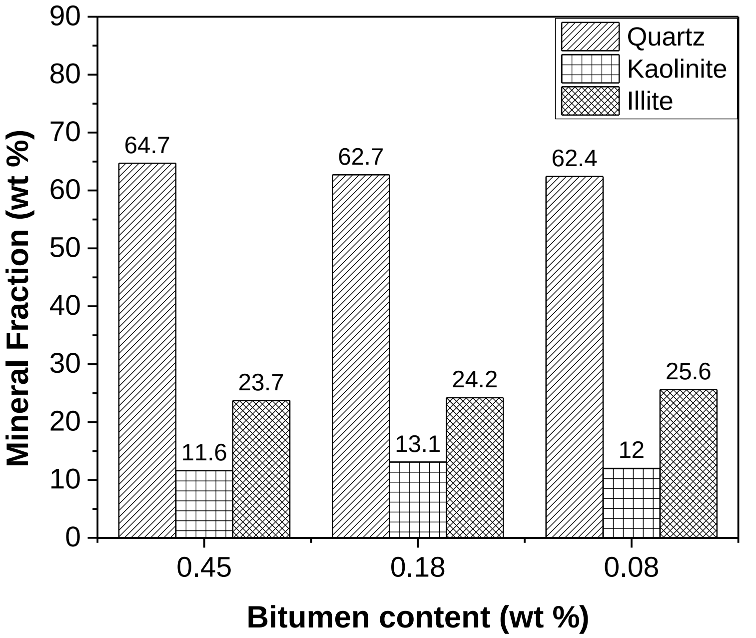

Figure B-11: Mineralogy of supernatant solids

FTIR of tailings solids:

Procedure:

Tailings samples of varying bitumen content were prepared using Denver cell extraction as described in Chapter 3. Solids were separated from water and residual bitumen by Dean-Stark extraction. The collected solids were crushed with a mortar and pestle to break up any lumps present. Fourier-transform Infrared Spectroscopy was used to analyze the samples to detect organic matter present on the particle surfaces. The powder samples were mixed to approximately 5 wt% with KBr powder and formed into a pellet. The analysis was performed with a Biorad FTS600 in the mid-IR range with a resolution of 4 cm^{-1}.

Results:

The spectra obtained are shown in Figures B-12 to B-14. Peaks in the ranges of 3800 – 3600 cm^{-1} and 1150 – 650 cm^{-1} indicate the presence of alumina and silica which is expected as the samples contain primarily clays and silica particles. Peaks at 3000 – 2800 cm^{-1} and 1380 cm^{-1} correspond to aliphatic groups, i.e. –CH3. The presence of ketones and carboxylic acids are also indicated as shown in Figure B-13 (Adegoroye et al, 2010). With lower original bitumen content (greater bitumen extraction), the relative heights of the peaks corresponding to the presence of organic matter decrease indicating an overall reduction in the amount of organic matter contaminating the surfaces. This is not unexpected as organic matter is likely to increase surface hydrophobicity and therefore contaminated particles are more likely to be removed with the froth during flotation.

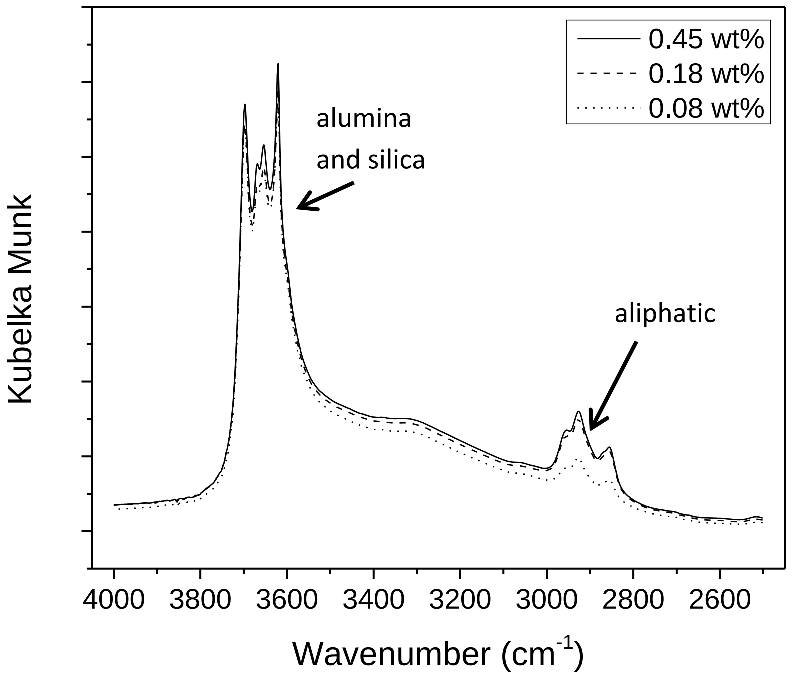

Figure B-12: FTIR results for extraction tailings solids; 4000 cm^{-1} - 2500 cm^{-1}

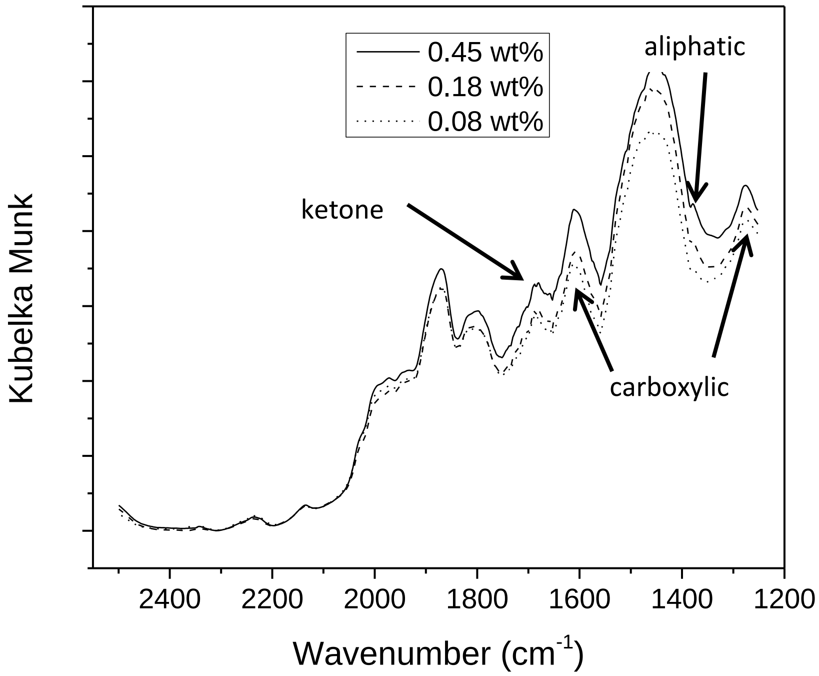

Figure B-13: FTIR results for extraction tailings solids; 2500 cm^{-1} - 1250 cm^{-1}

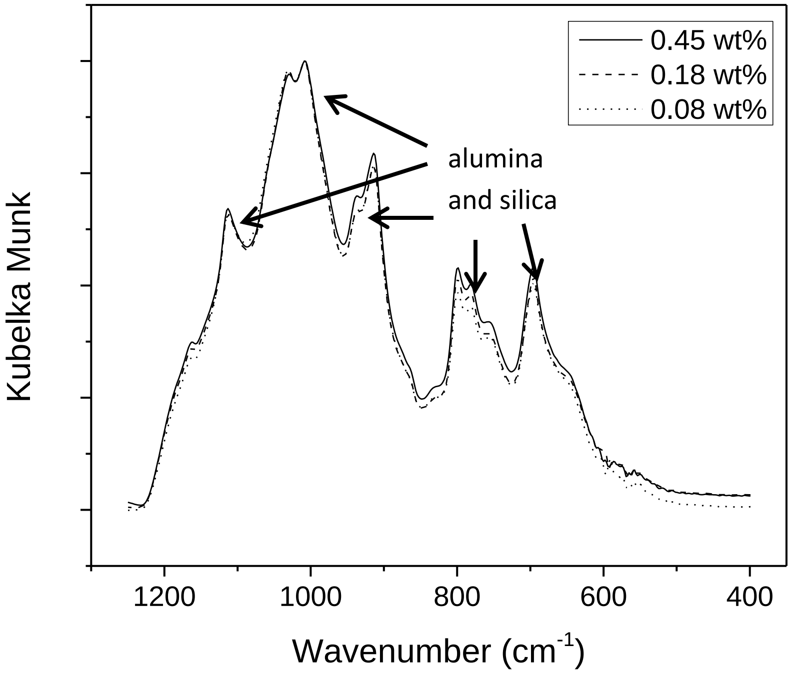

Figure B-14: FTIR results for Extraction Tailings Solids; 1250 cm^{-1} - 400 cm^{-1}

Tailings rheology following Denver cell mixing:

Procedure:

Samples of toluene washed tailings were prepared as described in Chapter 3. An 800 g portion of these tailings was mixed at 1200 rpm in the Denver cell for a period of 20 min as with previous extraction tests. No air was introduced during this process. Within 1 hr of mixing the viscosity of the tailings with and without mixing was measured using a TA instruments ARG2 rheometer with a cup and bob geometry. The diameter of the cup and bob were 30 mm and 28 mm respectively. The length of the bob was 42 mm. Approximately 25 mL of each sample was used; enough to fill the geometry. Viscosity was measured from a shear rate of 0.01 s^{-1} to 50 s^{-1} at room temperature.

Results:

As shown in Chapter 4, the settling rate of flocculated tailings decreases following long periods (20 min) of Denver cell mixing. It was speculated that the long period of intense mixing cause some type of rheological change in the tailings that affected how the tailings flocculated. To determine if this was the case the viscosity of tailings with and without Denver cell mixing were measured. The results of the viscometry experiments are shown in Figure B-15. Initially the unmixed sample shows higher viscosity of approximately 15 Pa·s, while the mixed sample has an initial viscosity of approximately 6 Pa·s. Both samples show shear thinning behavior with the viscosity decreasing significantly as the shear rate increased. Furthermore, after a shear rate of approximately 0.1 s^{-1} the viscosities of both samples are approximately the same which would indicate that the rheological properties of the two samples are very similar. From these results it is difficult to determine if any substantial rheological changes occur after extended periods of mixing in the Denver cell that would account for differences in settling observed previously.

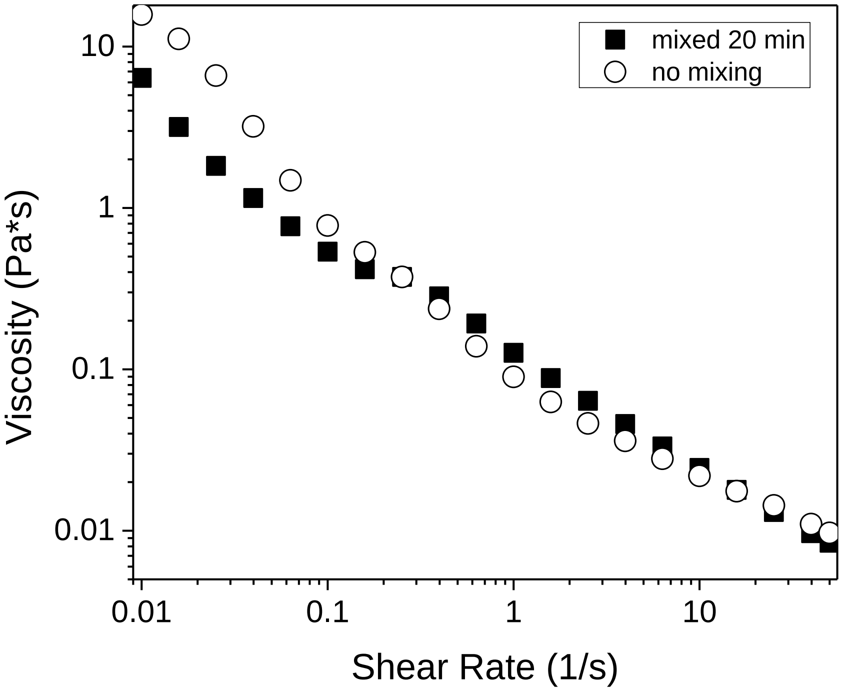

Figure B-15: Viscosity of toluene washed tailings with and without Denver cell mixing