Understanding and Developing New Methods for Treating Oil Sands Tailings

by

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Abstract

Management of oil sands tailings from bitumen extraction operations remains a challenge for mineable oil sands producers. Promoting fine solids settling in tailings ponds is key to treating oil sands tailings. Present study explores two methods of tailings treatment – ATA process and polymer assisted CT process.

ATA (Anchor-Tether-Activator) process involves anchor of particles usually coarse solids with tethering polymer and adding an activator polymer to tailings slurry. MF1011 was used as activator polymer, while in-house synthesized Al-PAM and commercially available pDADMAC were used as tethering polymers. Both Al-PAM and pDADMAC were able to produce non-segregated tailings, but the initial settling rate was higher with the use of Al-PAM while the turbidity of supernatant was lowest with the use of pDADMAC.

A novel method for treating oil sands tailings using only coarse sand and tethered polymer pDADMAC was developed. This new process is capable of producing clear water for extraction and sediment bed of high yield stresses at significantly reduced consumption of polymers.

T*his thesis is dedicated*

to

my parents

Acknowledgement

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Chapter 1 Introduction

1. Introduction

1.1 Background

The warm-water extraction process used to recover bitumen from oil sands produces large volumes of slurry waste tailings, composed of sand, silt, clay and a small amount of residual bitumen, with the total solids content in the range of 45 to 55 wt.%. Upon discharge to the tailings pond, solids stratification results in the formation of dykes and beaches by the coarse fraction ((FTFC), 1995), while the fines remain suspended and accumulate to form a sludge of approximately 30 to 35 wt.% solids, often referred to as Mature Fine Tailings (MFT) (Kasperski, 1992; and MacKinnon M. M., 2001). The gradual accumulation of MFT and the trapping of process water create numerous challenges for effective and responsible tailings management. It is estimated that the volume of fine tails is increasing at a rate of about 0.1 m^3/ton of processed oil sand and the growth of MFT is approximately 0.06 m^3/ton of processed oil sand (Nelson L. G., 1995). In addition to more surface mining leases granted to operators such as Total E&P Canada, Imperial Oil, etc., there remains great pressure to treat legacy MFT and introduce innovative approaches and technologies that can reduce the accumulation of tailings, and return tailings sites back to a sustainable environment.

Water management and the reclamation of tailings ponds are some of the pressing issues facing the industry. On average 4 barrels of fresh water is consumed to produce one barrel of bitumen (Nelson R. , 2006). In addition to fresh water, the recycle process water accounts for approximately 75% of the total water consumed in the warm water extraction process. With the formation of water-trapping suspensions, such as MFT, recovery and recycle of process water, and the safe containment of ‘unrecoverable’ water have become an engineering challenge. By the very nature of the sedimentary formations, and millions of years of underground water flow through the oil formations, the connate water contains a complex mixture of ions such as sodium, calcium, magnesium and chlorides. The continual recycle of process water and the addition of process aids such as caustic (NaOH) lead to the gradual accumulation of dissolved ions the recycle water (Kasongo, 2000). High salinity water can lead to various operational problems, including poor extraction recovery and froth quality, scaling/fouling of pipelines and process equipment, and environmental concerns regarding seepage. Therefore, with continued recycle of process-affected water, technologies or approaches to reduce the ion concentration are required (Beier, 2009).

Oil sands tailings also contain a residual amount of fugitive bitumen which can influence the settling, consolidation and dewatering properties of tailings, as well as introduce operational complexities (Sobkowicz, 2009). Hydrological and geochemical studies performed in the area of the Athabasca Oil Sands have also indicated the accumulation of heavy metals in tailings that pose an environmental concern (MacKinnon M. M., 2001), with the release at elevated concentrations of metals and other elements reported in surface and groundwater ((FTFC), 1995).

The accumulation of tailings is a direct result of the surface mining method used to extract bitumen. It has been estimated that if bitumen production by surface mining continues to grow as expected, Syncrude - one of the largest operators in northern Alberta - will produce an estimated one billion cubic meters of fine tailings by 2025, and Suncor will accumulate 800 million cubic meters by 2033 (Houlihan, 2008). At present, it is estimated that the tailings ponds occupy a total land area of more than 130 km^2 (Alberta, Alberta's Oil Sands. Fact Sheets - Tailings management, 2010). Provision for the containment of fluid fine tailings represents a direct incremental operating cost and continues to be a source of major logistical and environmental concern (BGC Engineering Inc., 2010).

There are many objectives in tailings management, all centered on water, whether it is release or recycle, or safe containment and treatment. The first stage, release and recycle, is achieved through rapid sedimentation and consolidation of the fines and clays. While the increased recycle reduces the total stored volume, it also reduces the dependency on river water intake. If rapid recycling of process water can be achieved and heat retained in the water, it will lower the energy requirement of the process and hence, reduce GHG emissions. Furthermore, with significant water removal a high density, self-supportive cake is produced, that can be deposited back into the mine for gradual reclamation, minimizing the land disturbance from oil sands operations. It is therefore highly desirable to rapidly and efficiently remove water from oil sands tailings.

Commercially, Consolidated Tailings (CT) technology has been practiced to produce non-segregated thickened tailings (NST). In this process, MFT is mixed with cyclone underflow coarse solids from the bitumen extraction plant, together with gypsum to form NST. The tailings are then discharged to the pond at a desired sand to fines ratio (SFR) for optimal consolidation and geomechanical performance (Jacob H. Masliyah, 2011; and MacKinnon M. H., 1995). Because the CT mixture contains ~ 60 wt.% water, the initial deposit exhibits a low yield stress. Also, the addition of gypsum increases the calcium content in the recycle water that can have a detrimental effect on bitumen extraction (Kasongo, 2000). Hence, alternative tailings treatment technologies to improve the transformation of fluid fine tailings a thickened, trafficable deposit remain of great interest.

1.2 Research Objectives

In the present study, two methods for tailings management were investigated. The first method called ATA (Anchor-Tether-Activator) process was studied using commercial polymers (MF1011 and pDADMAC) and an in-house synthesized polymer Al-PAM. This process requires mixing of flocculated fine tailings with an anionic polymer and subsequent addition of a cationic polymer to anchor particles, i.e. sand (Soane, 2010). The settling performance was evaluated by initial settling rate, turbidity of supernatant and sediment solids content. The mechanism by which the ATA process successfully treats fine tailings was studied by QCM-D (Quartz Crystal Microbalance with Dissipation) and zeta potential measurements. The research was extended to develop a novel NST strategy for treating fine tailings. Using a single anionic polymer (pDADMAC), coating of coarse sand particles which are used as seeding to flocculate the fine clays, was shown to be an attractive alternative to existing tailing strategies.

This thesis is divided into six chapters:

Chapter 1: This chapter gives a general introduction and background to mineable oil sands processing and the research objectives of the current study,

Chapter 2: Provides a review on the most relevant literature considering oil sands tailings treatment techniques.

Chapter 3: Describe the materials and methods that were used throughout the study. Equipment operational procedures are also described in this chapter.

Chapter 4: This chapter discusses the settling performance observed using ATA process. Also described in this chapter is the mechanism of the ATA process determined using zeta potential and QCM-D measurements.

Chapter 5: This chapter contains the novel technique developed to settle oil sands tailings using single cationic polymer and sand. Results based on the settling tests and hypothesized mechanism using polymer assisted CT process are reported in this chapter.

Chapter 6: Overall project conclusions are presented along with suggestions for future research directions.

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2. Literature Review

2.1 Introduction

Crude bitumen, a type of heavy oil, is characterized by very high viscosities, high densities and a low hydrogen to carbon ratio in comparison to conventional crude oils (NEB, 2004). This crude bitumen must be treated to convert into "synthetic crude oil" before it can be fractionated in traditional refineries to produce gasoline, heating oils and diesel fuels (Xu, 2011). The crude bitumen and the rock matrix where it is found, together with any associated mineral material other than natural gas, are called oil sands. Oil sands deposits are found throughout the world. The major accumulations of oil sands are distributed in eight countries: Canada, Venezuela, USA, Trinidad, Madagascar, Albania, Russia and Romania (Xu, 2011). Over 95% of the known in-place oil (bitumen) in oil sands is found in Canada, specifically in Northern Alberta (Chalaturnyk, et. al., 2002). With initial established reserves estimated at 176.7 billion barrels, Alberta ranks second only to Saudi Arabia in terms of oil reserves. In Alberta, these deposits are located specifically in three regions – Athabasca Wabiskaw-McMurray, Cold Lake Clearwater and Peace River Bluesky-Gething. These three regions occupy an area of about 140,000 km^2 (Energy Resources Conservation Board, 2009). Among the three deposits, the Athabasca deposit is the largest deposit containing an initial volume of crude bitumen of about 223 billion cubic meters. Essentially more than half of the bitumen reserves in this deposit are contained within the Lower Cretaceous Wabiskaw- McMurray Formation. In this deposit, there is about 20.7 billion cubic meters of crude bitumen that has overburden less than 65 meters which makes it suitable for bitumen extraction by surface mining technologies. This is unlike the rest of Alberta's bitumen, where in-situ methods are required (Kasperski, 2001). For the surface-mining method, 2 ton of mined oil sands ore will produce a tailings stream volume of 3.3 m^3, of which the solids content is in the range 40-55 wt.% (Jeeravipoolvarn, et.al., 2008).

2.2 Bitumen Extraction Process

The commercial bitumen extraction process incorporates the basic science developed by Dr. Karl Clark in collaboration with the Research Council of Alberta almost a century ago. The Clark Hot Water Extraction (CHWE) process uses hot water and chemical additives (NaOH) to separate and float bitumen from conditioned ore (Clark & Pasternack, 1932). Adaptations of this method, lower temperature operations, are currently used to achieve greater than 90% bitumen recovery at temperatures in the range from 45 ^{o}C to 70 ^{o}C and pH between 7.8 and 8.6. By adding small quantities of NaOH, the naphthenic-type compounds (partly aromatic, containing oxygen functional groups such as phenolic, carboxylic and sulphonic types) present in bitumen become water-soluble and act as surfactants (Baptista & Bowman, 1969). It is believed that these surfactants play a critical role in bitumen recovery by influencing surface properties, such as wettability and surface tension, of oil sands components (Xu, 2011). The wettability of solids determines how easily bitumen can be separated from sand grains, an essential step for bitumen recovery while the shape of a bitumen droplet on a sand grain or of an air bubble on a bitumen surface in process water is largely determined by interfacial tension. (Xu, 2011).

Figure 2.1 shows the generalized processing scheme for oil sands extraction. The mined oil sand is first crushed and mixed with water to form slurry that is transported to the extraction plant via a hydrotransport pipeline. The dynamic environment during transport aids the liberation and separation of bitumen from the sands grains prior to reaching the primary separation vessel (PSV). In the PSV, aerated bitumen floats from the slurry to form a bitumen froth (60 wt.% bitumen, 30 wt.% water and 10 wt.% solids) which is then de-aerated using steam. The de-aerated bitumen is then diluted with solvents, either paraffinic (hexane) or naphtha, to reduce the bitumen viscosity and density which improve separation of bitumen from water and solids. In the case of naphtha addition, the diluted bitumen froth is centrifuged in a scroll type centrifuges at 250G where the coarse solids are removed as a cake that is subsequently fed to a naphtha recovery unit (NRU) to recover associated solvent in the solids cake. In case of paraffinic solvent addition, asphaltenes, a high molecular weight constituent of bitumen are precipitated out, which act as flocculant to the emulsified water droplets and fine solids in diluted froth. A counter-current three stage bitumen-diluent mixer/settler is employed. No centrifuges are used for paraffinic froth treatment process. The solvent-free bitumen that contains some residual solids is then sent to upgrading. At the upgrading facilities, bitumen's light ends are removed in a vacuum distillation unit and sent to refineries for further processing (Xu, 2011).

The waste material from the extraction process, which is mostly water and solids with a small fraction of organics is sent to the tailings pond for further treatment and ultimate disposal. Upon discharge of tailings, the coarse solids (sand) settle fast to form beaches along the pond edge, while the fines (mainly silts and clays) settle slowly to form a fine tailings zone that after two to three years of consolidation is considered to be mature fine tailings (MFT). After reaching nearly 30 wt.% solids, MFT forms a stable gel that traps a substantial quantity of water. The water trapped could potentially be used as recycle water if it can be separated. (Xu, 2011)

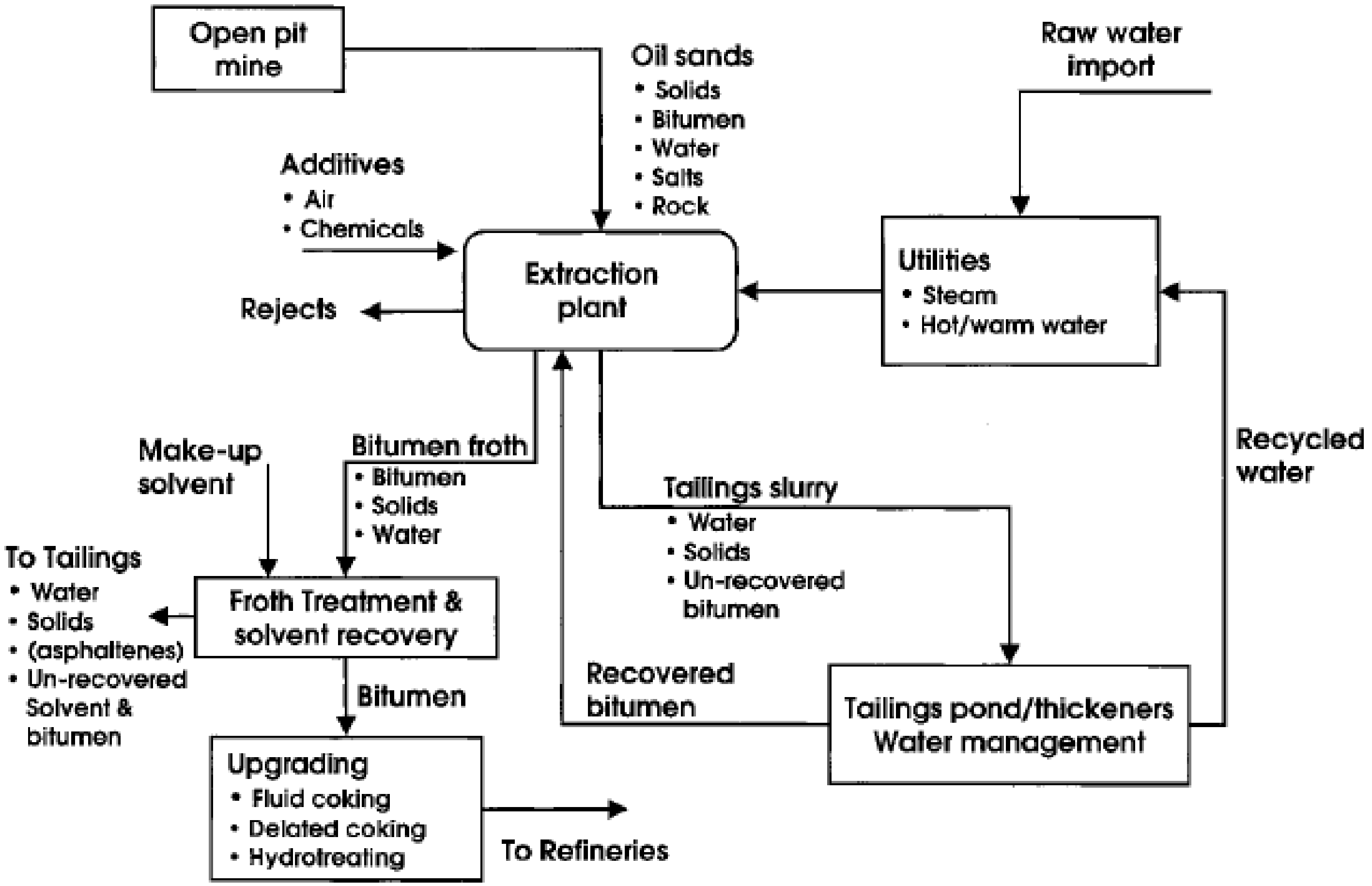


Figure 2.1 Generalized scheme for oil sands processing (Xu, 2011)

2.3 Conventional Method of Tailings Disposal

Disposal of whole tailings into large pond results in the coarse particles settle out to form dykes and beaches, while the fines and residual bitumen flow into the pond as a thin fine tailings stream at approximately 8wt% solids. As the thin fine tailing stream advances, particle settling leaves a nearly sediment-free supernatant water layer that can be recycled back to the extraction process. A schematic cross section of an oil sands tailings pond is shown in Figure 2.2 (Jeeravipoolvarn, et. al., 2008)

With time, three distinct zones develop in the tailing ponds as shown in Figure 2.2. The top 1 to 3 m of the pond is referred to as free water that is recovered and pumped back to the extraction. The second layer referred to as the immature fine tailings zone is a transition zone of water and settling particles of approximate thickness, 1 to 2 m. The third layer referred to as the MFT zone is a layer of silts, clays, fine sands, bitumen and water, where consolidation and dewatering are prevented by the formation of a gel-network and low hydraulic conductivity. The depth of the MFT zone can vary between 15 to 20 m. Below the MFT the sandy material accumulates forming a dense packed pond base, with a total pond depth approaching almost 50 m. (Guo, 2009)

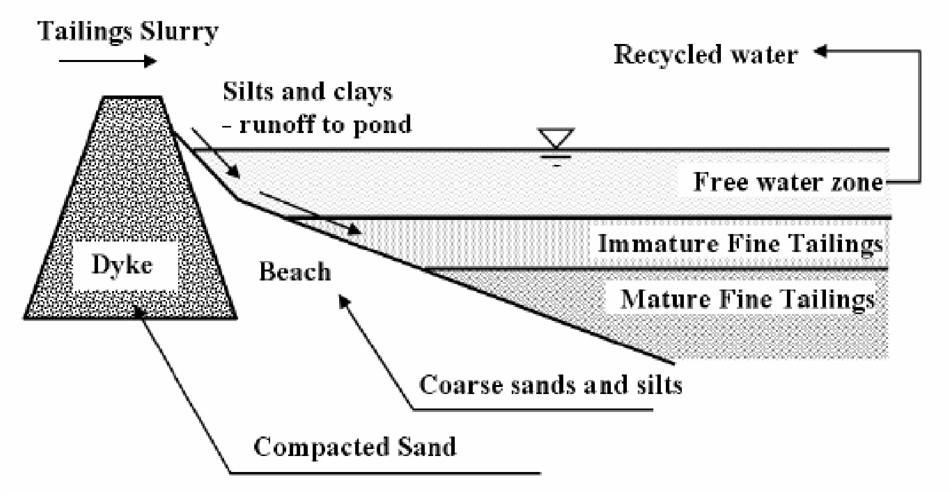


Figure 2.2 Schematic of an oil sands tailings basin (FTFC, 1995)

2.4 Initiatives for Tailings Management

2.4.1 Government of Alberta

For better management of oil sands tailings in commercial operations, Energy Resourced Conservation Board, ERCB, recently published Directive 074 that incorporates several key objectives:

- Minimize and eventually eliminate long-term storage of fluid tailings in the reclamation landscape,
- Create a trafficable landscape at the earliest opportunity to facilitate progressive reclamation,
- Eliminate or reduce containment of fluid tailings in an external tailings disposal area during operations,
- Reduce on site stored volumes of process-affected waste water,
- Maximize intermediate process water recycling to increase energy efficiency and reduce fresh water import,

- Minimize resource sterilization associated with tailings ponds, and

- Ensure that the liability for tailings is managed through reclamation of tailings ponds. (Energy Resources Conservation Board, 2009)

2.5 Industrial Process for Tailings Management

Over the past several years various attempts have been made to increase the rate of fine tails settling to allow for water recycling and to reduce the volume of MFT (Kasperski, 1992). The methods employed include treatment of MFT with lime, inorganic flocculants and polymers, as well as pH control and freeze-thaw cycles (FTFC, 1995). The following section outlines two of the industrial methods that are currently being used.

2.5.1 Consolidated/Composite Tailings (CT) Process

The CT process was developed at the University of Alberta by J.D Scott and M.F. Chichak (Caughill, et. al., 1993). CT technology involves mixing densified extraction tailings (coarse sand from cyclone underflow of tailings, CUT) and MFT with a coagulant (typically gypsum) to produce non-segregating tailings (NST). This NST would be subsequently discharged into tailings pond to form a rapid consolidating deposit. The CT process is designed to run at an average of 20% fines (4:1 sand to fines ratio) to produce a slurry density of approximately 60% solids. (BGC Engineering Inc., 2010) Figure 2.3 shows the simplified process flow diagram for the formation of NST.

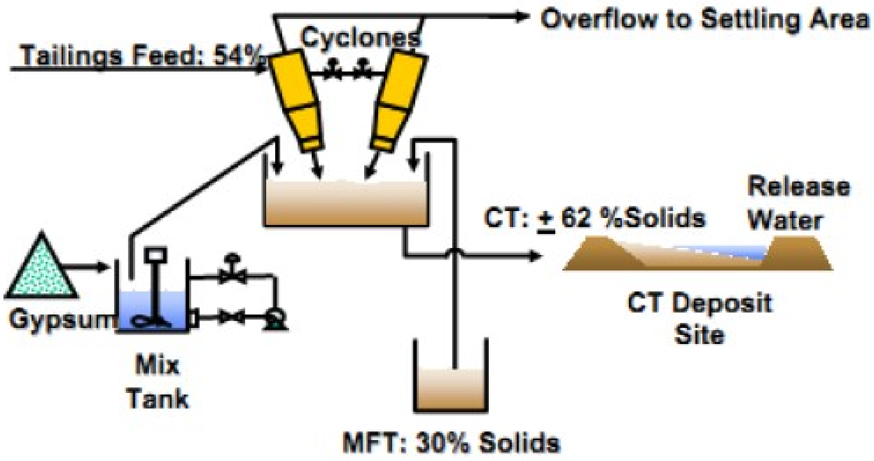


Figure 2.3 Schematic Flow Chart of Composite Tailings Process (Xu, 2011)

In commercial operations, Suncor was the first, in 1995, to apply the CT process on a commercial basis in its Pond 5 (Suncor, 2009). Syncrude conducted a NST field demonstration in 1995, followed by the CT prototype in 1997-1998. (MacKinnon M. , 1999)

The successful implementation of the CT process has led to a reduction in MFT inventory. This is evident in the reduced volumes of MFT of Leases 17/22 of Syncrude Canada Ltd. (Ezeagwula, 2008) Due to its low cost and high consolidation rates, CT remains the primary tailings management technique for existing and future plans of several operators, with continued effort to assess and improve deposit performance.

However there are several drawbacks with the CT process. The addition of gypsum results in significant changes to the water chemistry. Chemical analysis of the water released from CT process has revealed high concentrations of ions such as Ca^{2+}, Na^{+}, Cl^{-} and SO_4^{2-} (MacKinnon M. M., 2001). The recycled water containing high concentrations of Ca^{2+} has been shown to have negative impact on bitumen extraction process (Ezeagwula, 2008), and (Kasongo, et. al., 2000). Some studies have shown that CT process releases H_2S by anaerobic reduction of SO_4^{2-} with the residual bitumen in the tailings (Kasongo, et. al., 2000).

2.5.2 Thickened Tailings/Paste Technology

Thickened Tailings (TT) technology or Paste Technology (PT), involves rapid settling of suspended fines within a process vessel called a thickener with the help of chemical aids usually flocculants. The water released after the use of flocculants is suitable for reuse and can be recycled to the extraction plant with very little heat losses. Hence, this process reduces the consumption of natural gas required to warm the process water and in turn reduces GHG emissions. The flocculated fines are able to settle quickly and form a stable solid bed that can be deposited in tailings pond for land reclamation.

The most important factors influencing the performance of PT is the choice of flocculant(s) and the type of thickener. The choice to commercially implement PT to manage fine tailings is ultimately dependent upon the ability to achieve the necessary tailings deposition requirements. It must also be cost competitive relative to other tailings management options (Yuan & Lahaie, 2009)

Thickeners have a rake mechanism that transports bed material to the underflow, assists dewatering of the bed material and scrapes away deposits from the base. (BGC Engineering Inc., 2010). It is estimated that it takes about half an hour for a thickener to increase the solids content of suspended fines to 30%, whereas it takes a few years to achieve the same solids content through gravity settlement in a tailings pond (Devenny & Nelson, 2009). High molecular weight polymers can further increase the solids content. According to Cymerman (1999), polymers like Percol 727 (also known as Magnafloc 1011) or Percol LT27A, both high molecular weight and medium charge density anionic polymers, were found to be most effective in flocculation of the fines tailings at pH 8.5.

Currently, only Shell Muskeg River is using PT to consolidate fine tailings using a thickener. Recently, Syncrude has conducted several large scale thickened tailings evaluations (Fair, 2008).

In summary, PT is a very promising technique to deal with fine tailings. It produces water with no change in ion concentration that can be recycled back to the extraction plant for bitumen extraction. The resulting water is warm and hence reduces the consumption of energy. The solids after the thickening process are very stable and can be deposited without further treatment. Since the tailings are contained in the thickener, there are no concerns of process water polluting groundwater reserves.

Although promising, PT has several limitations. PT does not provide any solution to the existing inventory of MFT. In the study by Alamgir, et.al. (2012), it was found that commercially available anionic MF1011 and lab synthesized cationic $Al(OH)_3$-PAM were ineffective in treating raw MFT. No filter cake was formed even after 1 hr of filtration. PT is capital intensive since it requires design, construction and maintenance of thickener. Continuous requirement of polymers only adds to operating cost of PT technology.

2.6 Recent Developments in Tailings Management

Since no single strategy has been able to completely solve the tailings management issue, research is being done on development of new methods and technologies to resolve the issue. Other methods such as centrifugation, filtration, electrical treatment, etc. are being considered. This section describes some of the novel methods that have recently been considered.

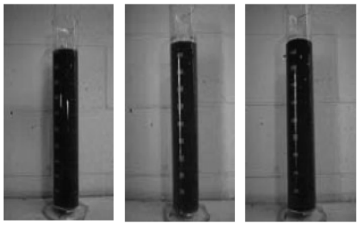
2.6.1 Dual Polymer Flocculation/Coagulation

Conventional processing of tailings, obtained from transition and marine oil sands ores, by a single flocculant or a single coagulant were found to be ineffective in settling (Yuan & Shaw, 2007). For example, when a single anionic flocculant was used to treat such tailings, thickener overflow resulted in about 1-4 wt.% solids, which is above the acceptable range of 0.5 wt.%. When a single coagulant (C) was used, the initial settling rate recorded was only 0.4 m/h. The initial settling rate increased to 35.8 m/h when a flocculant (F) was used, but the turbidity of supernatant was too high as seen in Figure 2.4. The combination of coagulant-flocculant (CF) decreased initial settling rate to 10 m/h with no significant improvement in the turbidity of supernatant.

Hence alternative methods such as: Coagulation-Flocculation-Coagulation (CFC), Flocculation-Coagulation (FC), and Flocculation-Coagulation-Flocculation (FCF) were developed and found to produce superior results. At appropriate dosages of coagulant and flocculant, it was found that the CFC was very successful in tailings management, resulting in a very clear supernatant (nearly 0.05 % solids) but relatively poor initial settling rate (nearly 3 m/h). Ultimately, FCF was able to outperform CFC and FC processes, resulting in very high initial settling rates and relatively clean supernatant (nearly 0.10% solids). Figure 2.4 shows the detailed results obtained with different techniques on tailings.

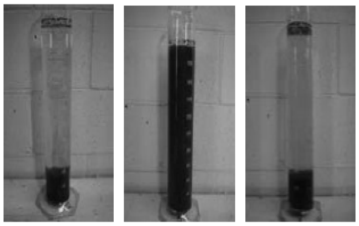
Processes	CF	C	F
Coagulant g/t	600	600	0
Flocculant g/t	100	0	100
Coagulant g/t	0	0	0
Feed solids%	4%	4%	4%
O/F solids% at 10 min	0.87%	0.76%	1.05%
O/F pH	8.52	8.83	8.52
U/F solids% at 60 min	28.5%	11.5%	39.2%
U/F SFR	0.4	0.30	0.30
ISR, m/hr	9.6	0.4	35.8

Pictures at 60 min



Processes	CFC	CFC	FC
Coagulant g/t	300	200	0
Flocculant g/t	100	100	100
Coagulant g/t	300	200	600
Feed solids%	4%	4%	4%
O/F solids% at 10 min	0.06%	0.82%	0.07%
O/F pH	8.71	8.65	8.62
U/F solids% at 60 min	22.6%	27.0%	22.0%
U/F SFR	0.37	0.39	0.39
ISR, m/hr	2.9	2.0	1.2

Pictures at 60 min



Processes	FCF	FCF	FCF
Flocculant g/t	250	250	250
Coagulant g/t	250	250	250
Flocculant g/t	60	60	60
Feed solids%	4.68%	2.84%	3.30%
O/F solids% at 10 min	0.13%	0.12%	0.11%
O/F pH	8.26	8.28	8.26
U/F solids% at 60 min	21.91%	19.54%	20.97%
U/F SFR	0.04	0.05	0.05
ISR m/hr	33.9	37.8	35.1

Pictures at 60 min

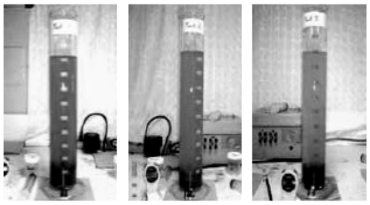


Figure 2.4 Results from different techniques on tailings (Yuan & Shaw, 2007).

FCF was able to outperform because of the formation of large flocs. It was proposed that the initial addition of flocculant binds the relatively large particles by bridging mechanism, resulting in bimodal size distribution with formation of larger flocs and extremely fine particles left in dispersion. The addition of the cationic coagulant collapses the electric double layer around the extremely fine particles and makes them aggregate. Then, the small dose of flocculant added binds the larger flocs with the coagulated fines so that they settle as one unit, which results in high initial settling rates.

2.6.2 Addition of Sand

Flocculation of whole oil sands tailings using slaked lime and high molecular weight anionic polyacrylamide polymer was studied by Hamza and Kessick in 1996. It was found that the addition of sand increased the settling rates at low polymer dosages. Figure 2.5 shows the settling rates of flocculated tailings with and without sand incorporation.

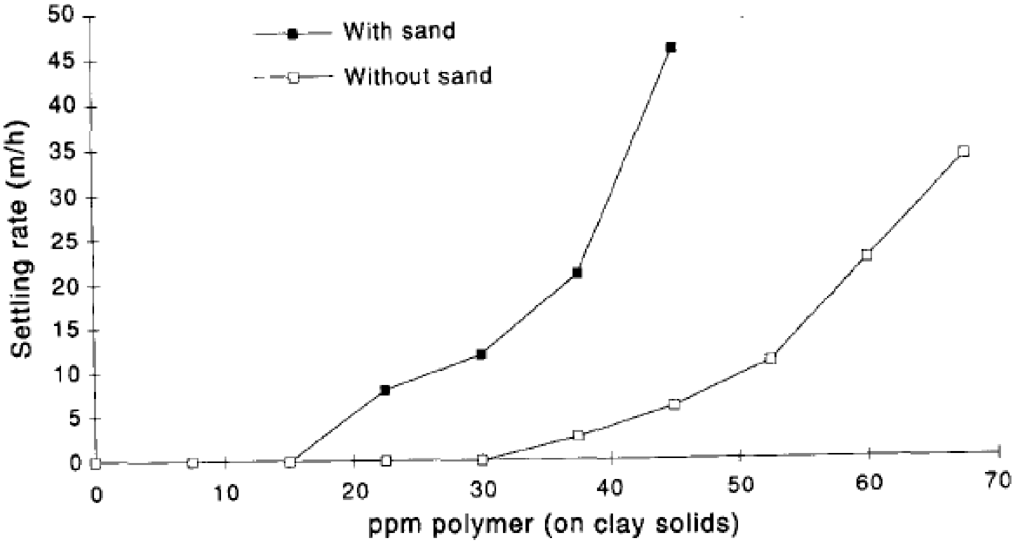


Figure 2.5 Settling rates of flocculated tailings with and without sand incorporation. (Hamza & Kessick, 1996)

The resulting composite sand-clay particles settle and dewater rapidly, resulting in a clear supernatant. When the sediment was hand squeezed, it further dewatered, resulting in a stackable material with 40-83 wt% solids. It is projected that if the procedure were to be performed on a large scale, actual compression settling would become very much significant, particularly since the sand fraction would be distributed evenly throughout the sludge. (Hamza & Kessick, 1996)

2.6.3 ATA Technique

In 2010, Soane Energy developed a novel approach to tailings management, called Anchor-Tether-Activator (ATA) process, using surface active polymers and coarse particles (Soane, 2010). The ATA process uses surface-active polymers to flocculate the fines with heavier sand particles, so that the fines can be separated from the aqueous environment and compacted into a stable solid. The ATA process, shown in Figure 2.6, comprises of three steps: 1) an Activator polymer is added to the fine tailings stream; 2) a Tether polymer is added to the anchor particles, usually sand; and 3) an Anchor particle that is coated with the Tether polymer. In this process, fine tailings stream is flocculated using the activator polymer. Tethered polymer is added to the anchor particles and mixed with the flocculated tailings slurry. The fines and coarse particles form a tailings-anchor particle complex that settles rapidly to produce a clear supernatant. (Soane, 2010)

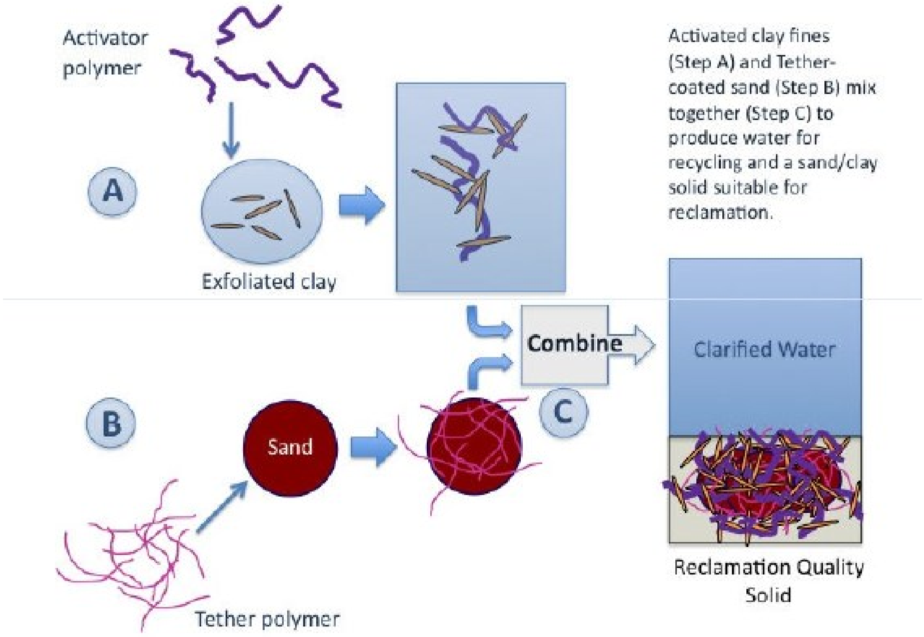


Figure 2.6 Schematic of the ATA mechanism. (Soane, 2010)

2.7 Mechanism of Polymer-Particle Interactions

The behavior of fine particles in a suspension (tailings) is strongly influenced by the electrical charge on the particle surface. Each fine particle normally carries a similar charge, which is usually negative (Hunter & Liss, 1979). This similar charge causes adjacent particles to repel each other and leads to stabilization of the suspension. All particles exert mutual attraction forces, known as London-Van der Waals forces, which are effective only at short distances of separation. However, the electrostatic repulsion of the surface charges opposes the particles from coming close enough for these attraction forces to take effect. The following sections describe the origins and nature of these forces and their effect on suspension stability.

2.7.1 The Electrical Double Layer

The charge on the surface of particles in solution can be best explained using electric double layer model (Masliyah & Bhattacharjee, 2006).

Figure 2.7 shows the structure of electric double layer for a negatively charged surface according to the Stern model. In this model, positively charged ions (counter ions) are attracted to the surface while the negatively charged ions (co-ions) are repelled from the surface. The electric double layer is made up of charged surface neutralized by excess of counter ions and co-ions distributed in a diffused manner in the medium (Shaw, 1992).

Stern layer is the region between the particle surface and the Stern plane. As can be seen from Figure 2.7, the presence of positively charged counter ions near the surface of negatively charged surface produces an electrical potential across the diffuse layer. This potential is highest at the surface and decreases linearly to the end of the Stern layer, resulting in Stern potential ψs. Beyond the Stern potential, the potential decreases exponentially away from the Stern plane.

Shear plane refers to the plane that the ions and the ion bearing solution move around the particle. The slipping condition applied at the shear plane and the potential at the shear plane is known as zeta potential ζ. The potential in the double layer region depends on the type of electrolyte and their concentrations.

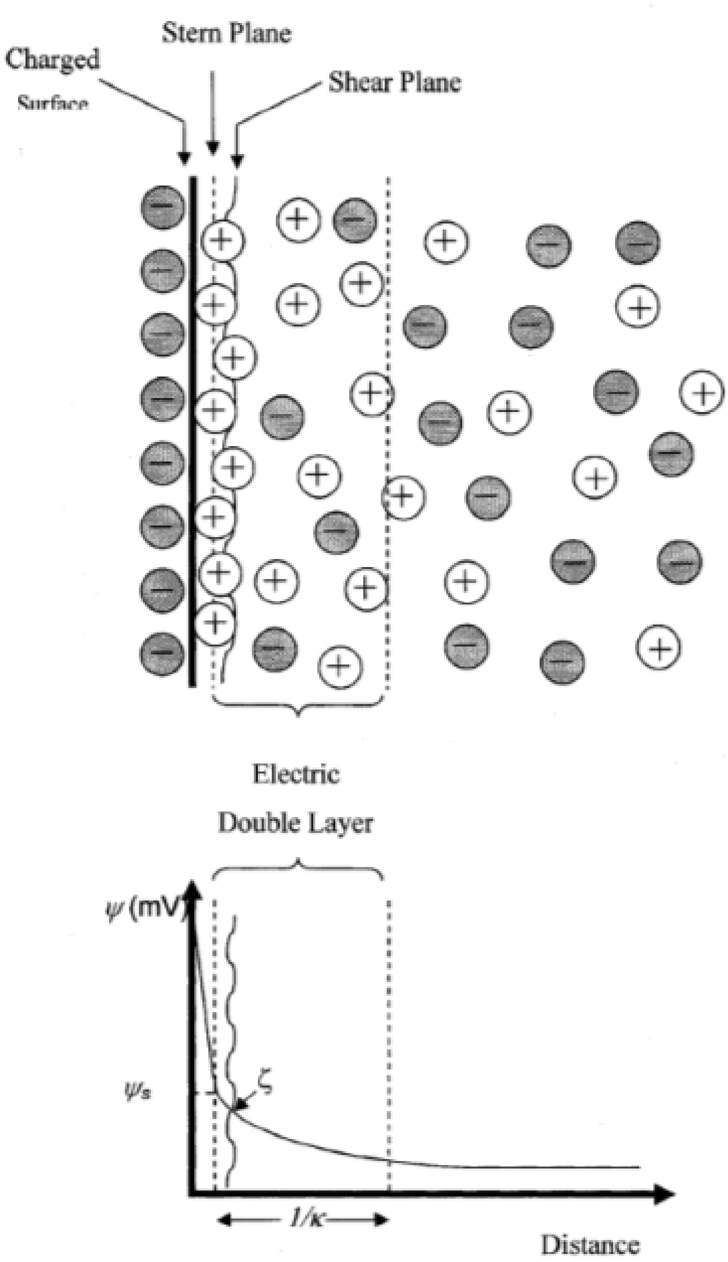


Figure 2.7 Schematic illustration of an electric double layer across a negatively charged surface and profile of electric potential distribution away from the surface. (Masliyah & Bhattacharjee, 2006)

2.7.2 DLVO Theory

Derjaguin and Landau in 1941 (Derjaguin & Landau, 1941) and Verway and Overbeek in 1948 (Verway & Overbeek, 1948) were able to predict the stability of colloidal suspensions using the double layer theory. This theory became known as famous DLVO theory.

DLVO theory takes into account only electrostatic repulsion and Van der Waals attraction forces to determine the ability of the system to remain stable or coagulated. It suggests that the stability of the suspension is determined by total interaction energy, V_T given by

$$V_T = V_A + V_R$$

where V_A is the van der Waals attractive force, and V_R is the electrostatic repulsion force.

For two spherical particles of the same size, the van der Waals force is given by (Shaw, 1992):

$$V_A = -\frac{Aa}{12D}$$

where A is the Hamaker constant, a is the particle radius and D is the distance between the spherical particles

The electrical double layer repulsive force is given by:

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

where ε is the permeability of the solvent, ζ is zeta potential, and κ is called the Debye-Huckel parameter, which is a function of ionic composition.

According to the DLVO theory, if the net interaction between the particles is attractive, the system is unstable and particles would coagulate and settle down rapidly. In order to cause the particles to coagulate, it is necessary to provide sufficient kinetic energy to overcome the energy barrier. On the other hand, if the net interaction between the particles is repulsive, the system is stable and the particles remain dispersed. Figure 2.8 shows energy profile of two particles at varying distance between them.

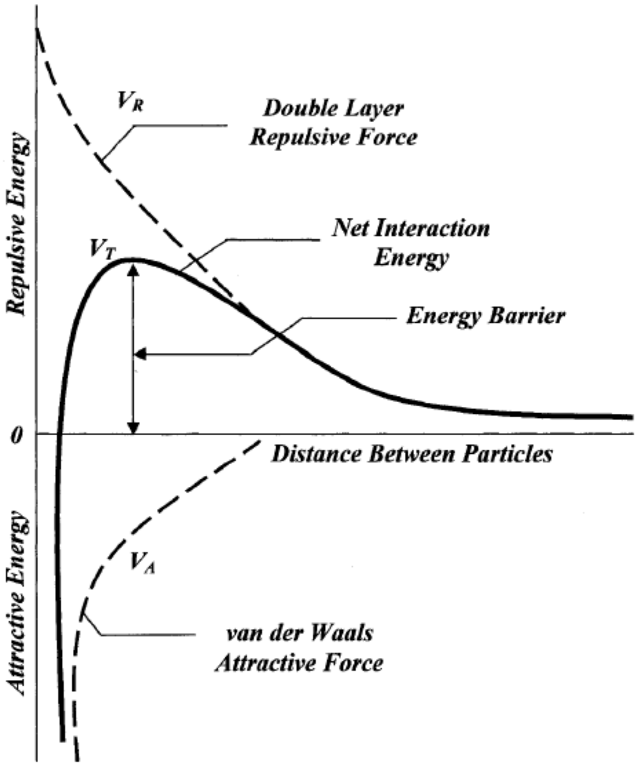


Figure 2.8 Schematic diagram of the variation of free energy with particle separation according to DLVO theory. (Masliyah & Bhattacharjee, 2006)

2.7.3 Mechanism of Particle Aggregation

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

2.7.3.1 Double Layer Compression

Double layer compression involves adding salts like KCl, NaCl, etc. to the suspension (i.e. increasing the ionic strength of the solution). When enough counter ions are added to the suspension, the double layer is compressed until there is no longer an energy barrier. At this time, van der Waals attractive forces dominate and the particles are able to agglomerate. Reagents like Alum, Lime and multivalent ions are effective for this purpose (Hogg , 2000).

2.7.3.2 Surface Charge Neutralization

Charge neutralization involves reduction of the net surface charge (zeta potential) of the particles in the suspension. As the net surface charge diminishes, the diffuse layer thickness surrounding the particles is reduced and energy required to move the particles into contact is minimized. Charge neutralization is accomplished by addition of coagulants such as $CaCO_3$. Coagulants have a strong tendency to adsorb onto the particle surface. The tendency of the coagulants to adsorb is usually attributed to both poor coagulant-solvent interaction and a chemical affinity of the coagulant for the particle surface (Amritharajah, et. al., 1999).

2.7.3.3 Bridging Mechanism

Flocculation by bridging is the most important mechanism of agglomeration (Sworska, et. al., 2000). When optimum dosage of polymer is added, the polymer chains adsorb onto particles in such a way that the individual chain can become attached to two or more particles, thereby bridging them together. Bridging mechanism requires particle surface to be available for polymer chain attachment. When polymer concentration is lower than optimum, there are insufficient bridging links between polymer chains and particles, and thus there exists unlinked particles in the supernatant of the suspension. On the other hand, when excess polymer is added, there is no longer sufficient particle surface available for the attachment of polymer segments, and this leads to re-stabilization of the suspension (also known as steric stabilization). Hence there exists an optimum dosage of the polymer at which the particles are sufficiently covered with polymer chains, leading to destabilization of the suspension (Tridib & Bhudeb, 2006). An illustration of the bridging mechanism and steric stabilization is shown in Figure 2.9.

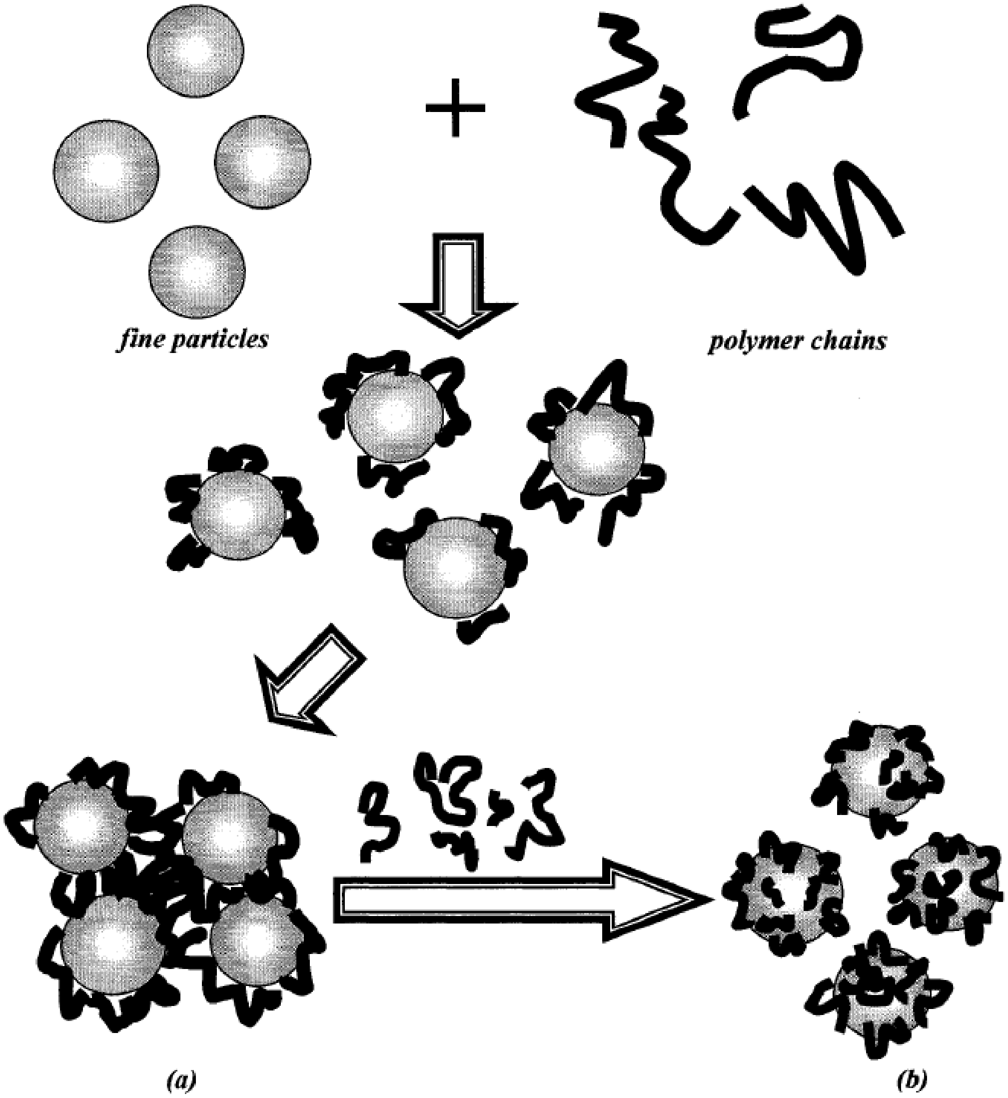


Figure 2.9 Schematic illustration of (a) bridging flocculation, (b) re stabilization by adsorbed polymer (steric stabilization) (Tridib & Bhudeb, 2006)

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3. Materials, Methods and Equipment

3.1 Polymers

There were three polymers used in this study and following section lists their properties:

1. Magnafloc 1011 (MF 1011) is an anionic commercial polymer purchased from Ciba Specialty Chemicals, Switzerland. It is a copolymer of acrylamide and sodium acrylate with high molecular weight of about 17.5 Million Daltons. It is a linear polymer with a medium charge density of about 27%.

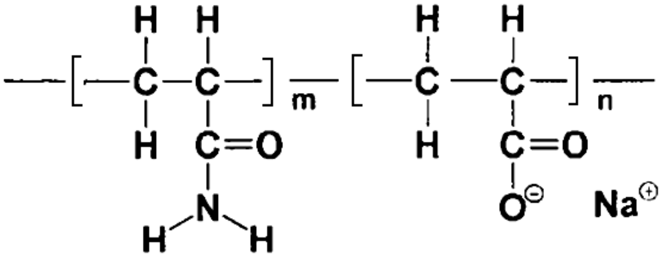


Figure 3.1 Structure of MF 1011

2. $Al(OH)_3$-polyacrylamide (Al-PAM) is a novel organic-inorganic cationic polymer synthesized in our laboratory. The structure of Al-PAM is star shaped with slightly positively charged $Al(OH)_3$ colloid in the centre attached to PAM chains. The molecular weight of Al-PAM used in this

study is about 1.6 Million Daltons. Detailed procedure of the synthesis of Al-PAM is described in Section 3.2.

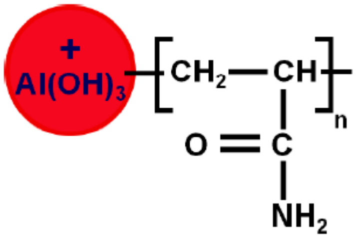


Figure 3.2 Structure of Al-PAM

3. Poly(diallyldimethylammonium chloride) (pDADMAC) is a cationic polymer purchased from Sigma-Aldrich (20 wt.% in solution). It is formed from free-radical polymerization that yields a structure, in which the quaternary ammonium groups are on rings along the backbone of the polymer chain. pDADMAC is also a linear polymer with a molecular weight of 400,000 - 500,000 Daltons.

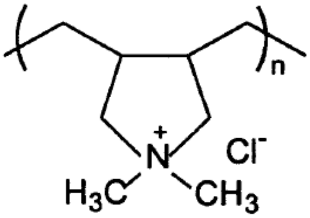


Figure 3.3 Structure of pDADMAC

Table 3.1 summarizes the properties of the polymers used in this study.

Table 3.1 Summary of properties of polymer used in this study

Polymer	Intrinsic Viscosity (mL/g)	Molecular Weight (Da)	Type
MF1011	13968	17.5×10^6	Anionic
Al-PAM	587	1.6×10^6	Cationic
pDADMAC	N/A	400,000-500,000	Cationic

3.2 Synthesis of Al-PAM

The synthesis of Al-PAM involves three steps, namely;

1. Preparation of $Al(OH)_3$ colloid,
2. Formation of Al-PAM polymer, and
3. Purification and characterization of Al-PAM.

3.2.1 Preparation of $Al(OH)_3$ Colloid

Aluminum hydroxide colloids, $Al(OH)_3$, were prepared by adding ammonium carbonate solutions into excess aluminum chloride solutions under vigorous mixing. The formation reaction of $Al(OH)_3$ colloids is:

$$2AlCl_3 + 3(NH_4)_2CO_3 + 3H_2O \longrightarrow 2Al(OH)_3 + 6NH_4Cl + 3CO_2$$

29 mL of 1.54 M ammonium carbonate solution was added to 60 mL of 0.6 M aluminum chloride solution in a 250 mL baffled beaker under continuous agitation of 500 rpm. The addition of ammonium carbonate solution was

maintained at 0.13 g/min using a Master FLEX C/L mini pump. After the completion of the reaction, the colloidal suspension was stirred for 1 hour at 300 rpm using IKA RW20 digital stirrer. Using Brookhaven Zeta PALS, the size and zeta potential of the formed colloids were determined to be 65 nm and 29 mV at pH 5.6, respectively.

3.2.2 Formation of Al-PAM Polymer

The next step involved the polymerization of acrylamide monomer in $Al(OH)_3$ colloid suspension using a redox initiator. 4.5 g acrylamide monomer was dissolved in 25.5 mL of $Al(OH)_3$ colloid suspension in a three neck round bottom flask. 2 mL of 1g/L $(NH_4)_2S_2O_8$ and 2 mL of 0.5 g/L $NaHSO_3$ solutions were added drop-wise into the round bottom flask using a glass funnel. The temperature of the reaction was maintained at 40 ^{o}C using oil bath. The flask was protected from light by covering with aluminum foil. The reaction continued until a transparent gel was formed, which took about 6 to 8 hrs.

3.2.3 Purification and Characterization of Al-PAM

The gel was diluted to 10 wt% using Milli-Q® water and placed in the shaker for 2-3 days until the gel was completely dissolved. In order to remove the unreacted monomer and initiators, dissolved gel was purified using acetone. The dissolved gel was drop-wise added to acetone (5 times the volume of polymer) to precipitate the polymer. Finally the precipitated polymer was transferred to a Teflon dish and kept in vacuum oven overnight at 60^{o}C.

The characterization of Al-PAM involves calculating the aluminum content and intrinsic viscosity of the polymer. Atomic absorption spectroscopy (AAS) was used to determine aluminum content of the polymer. This technique relies on the Beer-Lambert law to determine the concentration of a specific element in a sample. The electrons of the atoms are promoted to higher energy orbitals by absorbing light at a particular wavelength. Each element absorbs radiation of specific wavelengths. During an atomic absorption test, a known amount of energy is passed through the atomized sample by measuring the intensity of light remained at characterization wavelength after absorption, the concentration of the element is determined.

Ubbelohde viscometer (CANNON 75-J953) was used to measure the reduced viscosity at five different concentrations. The intrinsic viscosity of the polymer was determined by the intercept calculated using the linear fit as shown in Figure 3.4. The viscosity-mean molecular weight of the polymer was calculated using the intrinsic viscosity and Mark-Houwink equation. Table 3.2 lists the properties of Al-PAM.

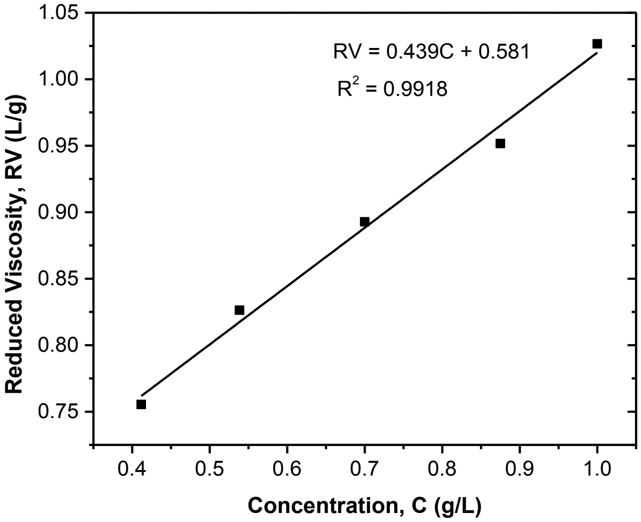


Figure 3.4 Reduced viscosity versus concentration of Al-PAM in aqueous solutions.

Table 3.2 Properties of Al-PAM

	Al content (wt.%)	Intrinsic Viscosity (mL/g)	Molecular Weight (Daltons)
Al-PAM	0.18	581	1.6×10^6

3.3 Sand and Tailings

1. Ottawa Sand – Ottawa Sand (trade name Sil-7030) was purchased from Sil Industrial Minerals, Edmonton, Canada. The d_{50} of the Ottawa Sand was found to be 202.4 micron.
2. Tailings - Oil sands tailings used in this study was obtained from Syncrude Canada Ltd. The bitumen, solids and water content of the

tailings was found using Dean Stark analysis to be 2 wt.%, 16.25 wt.%, and 81.75 wt.%, respectively.

The particle size distribution of the sand and tailings is shown in Figure 3.5. The d_{50} of tailings and sand was found to be 7 and 202.4 µm, respectively.

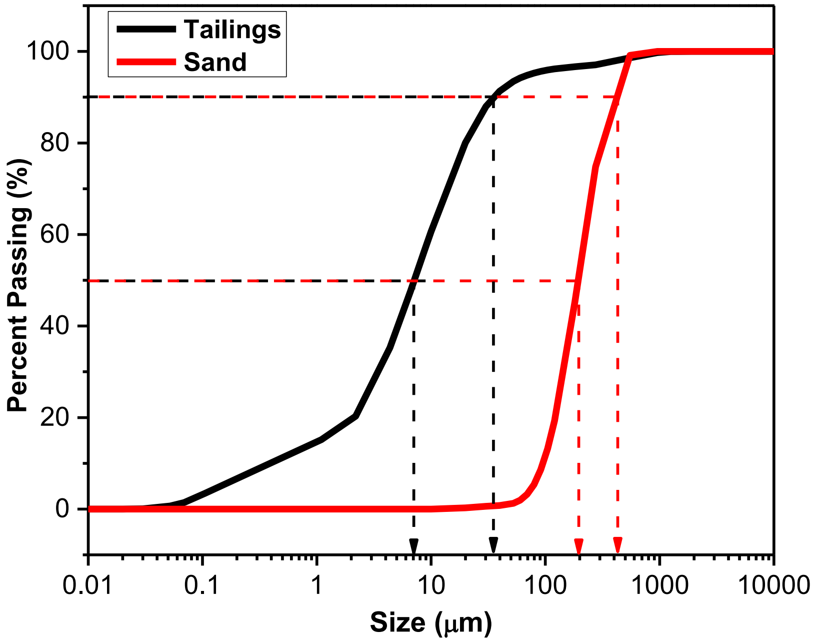


Figure 3.5 Particle size distribution of sand and tailings used in this study.

3.4 Process Water

The process water was supplied by Syncrude Canada Ltd. Table 3.3 shows the composition of major ions present in the process water.

Table 3.3 Composition (mg/L) of major ions in PW.

PW	Mg^{2+}	Ca^{2+}	Na^{+}	K^{+}	Cl^{-}	NO_3^{-}	SO_4^{2-}	HCO_3^{-}
mg/L	18.6	32.5	475.2	18.9	290.1	3.3	111.8	558.6

3.5 Mixing Tools

Several different mixing tools were used in this study for homogenizing the samples. This section contains details of mixing techniques employed for this study.

3.5.1 Polymer Solutions

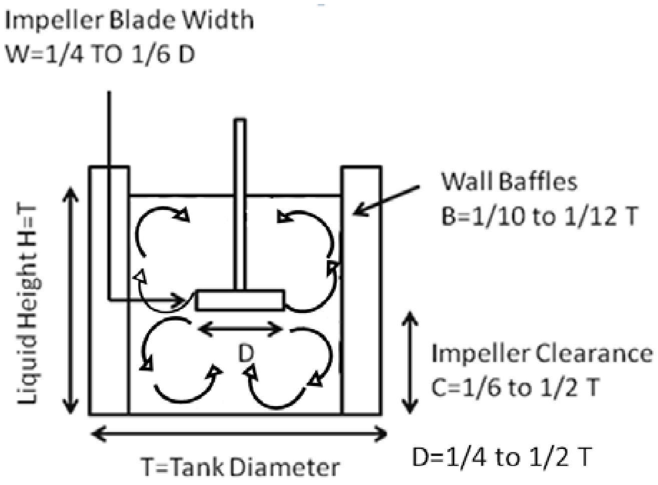
1000 ppm stock solutions of polymers in DI water were prepared two days prior to experiments. The stock solutions were discarded within five days of opening. Heavy duty Eberbach shaker (two-speed, Eberbach 6010 Shaker, Eberbach Labtools, USA) was used for mixing. In this study, all the polymer dosages are represented as ppm, i.e. parts per million (milligrams of polymer flocculant per kilogram of slurry).

3.5.2 Tailings Stock

Tailings obtained from Syncrude were stored in 20 L pails. The tailings were thoroughly mixed using a mechanical stirrer and then transferred to 4-L glass jars. The tailings in the jar were used as stock and mixed at 700 rpm for an hour with IKA RW20 overhead mixer prior to any experiments. This was done to ensure that the tailings were completely homogenous before samples were removed using 25 mL plastic pipette.

3.5.3 Tailings Slurry

Using a plastic pipette, tailings samples were removed from tailings stock and dispensed in a 250-mL beaker. In order to achieve optimum mixing, the beaker was equipped with a homemade baffle. An axial flow 4 blade impeller with a diameter of 3.8 cm was used to provide agitation. Standard geometrical configurations of beaker, baffle and impeller used in this project are shown below in Figure 3.6.



Here T= 7.5 cm, C= 2.5 cm, B= 0.6 cm, D= 3.5 cm, and W= 0.7 cm.

Figure 3.6. Geometrical configuration of the beaker, baffle and impeller used in this project.

3.6 Criteria for Settling Performance

The effectiveness of polymer flocculant for tailings treatment was determined by measuring three key parameters:

1. Initial settling rate (ISR),
2. Turbidity of the supernatant, and
3. Solids content of the sediments.

3.6.1 Initial Settling Rate

Initial settling rate (ISR) is used to evaluate the performance of settling characteristics of the tailings. It is calculated by plotting normalized mud-line height (h/H) versus time (t), where h is the mud-line height at time t and H is the initial mud-line height. Figure 3.7 shows a schematic diagram of a typical settling curve. The suspension mud-line is the interface between supernatant and settling flocs. The mud-line descends with time during settling. The initial slope of the settling curve is taken as initial settling rate.

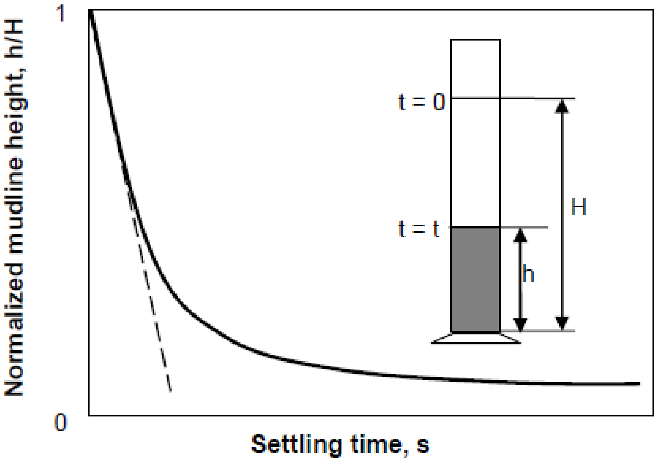


Figure 3.7 Schematic diagram of a typical settling curve.

3.6.2 Turbidity of Supernatant

After 2 minutes of settling, about 30 mL of supernatant was decanted from the graduated cylinder and used to measure turbidity using Turbidimeter (HF Scientific DRT-15CE Portable Turbidimeters, Fisher Scientific). Turbidity of supernatant is expressed in Nephelometric Turbidity Unit (NTU). The higher, the NTU value is, the more turbid, the suspension is.

3.6.3 Solids Content in the Sediments

At the end of settling, the supernatant was completely removed using a 25 mL pippete and sediment bed was weighed. The sediment was then dried overnight in vacuum oven at 100 ^{o}C and re-weighed to calculate the solids content.

3.7 Zeta Potential Measurement

Zeta potential measurements were conducted using Malvern ZetaSizer Nano ZS. The instrument uses the electrophoretic mobility of the particles to calculate zeta potential. When an electric field is applied across an electrolyte, charged particles in the electrolyte are attracted towards the electrode of the opposite charge. The velocity of the particles in a unit electric field strength is referred as electrophoretic mobility. The software calculates zeta potential using the following Henry equation:

$$U_E = \frac{2\varepsilon\zeta f(\kappa a)}{3\eta}$$

where U_E is electrophoretic mobility, ζ is zeta potential, ε is dielectric constant, η is viscosity and $f(\kappa a)$ is called Henry's function. The Henry's function is effectively the ratio of the particle radius to the electrical double layer thickness as κ and a represent the thickness of double layer and the radius of particles, respectively. For large values of κa (i.e. when the particles are much larger than the double layer thickness), Henry's function approaches 1.5. This is known as

Smoluchowski approximation. Henry’s function approaches 1 for small values of κa also known as Huckel approximation. (Masliyah & Bhattacharjee, 2006). For this study, it was assumed that the particles are larger than the electrical double layer and hence Smoluchowski approximation was used.

In this study, a suspension of 0.5 wt.% silica powder (obtained from Fiber Optic Centre, New Bedford, MA) in process water was made. The average size of silica particles was 0.5 microns. The suspension was mixed by a mechanical mixer for 24 hours before measurements. The pH of the suspension was maintained at 8.5.

3.8 Quartz Crystal Microbalance with Dissipation (QCM-D)

QCM-D (Q-sense E4 system, Sweden) was used to measure the adsorption of polymers on quartz crystal sensors coated with silica (QSX 303). The quartz crystals used in this study were 14 mm in diameter and AT-cut with shear oscillation of 5 MHz fundamental frequency. A quartz crystal sensor is a thin piezoelectric plate with gold electrodes on each side. When an AC voltage is applied to the electrodes, the crystal oscillates at a specific resonance frequency, which is recorded by the instrument at 5, 15, 25, 35, 45, 55, and 75 Hz. A shift in oscillation frequency is related to the mass adsorbed on the surface of the crystal. In addition to the frequency, the instrument also monitors changes in dissipation energy, which is a result of energy loss due to viscous dissipation when oscillating the crystal with the adsorbed materials. Shifts in dissipation during adsorption provide an indication of the rigidity of the adsorbed layer. A small dissipation shift indicates a rigid and compact adsorbed layer (Alagha et.al., 2011).

Prior to any experiment, the crystal was soaked in ethanol and sonicated for 10 minutes. After blow-drying with nitrogen, the crystal was exposed to a UV radiation for 20 minutes to remove any organic contaminants. The crystal was then placed on the O-ring of the flow module, which was later mounted on the temperature controlled chamber platform. Before measuring the fundamental frequencies, background solution was pumped for about 30 minutes. The flow rate throughout the experiment was maintained at 0.15 mL/min by an IPC-N peristaltic pump (Ismatec, Switzerland).

All experiments were conducted at pH of 8.5 and temperature of 22^{o}C (± 0.02). The polymer stock solutions were diluted using filtered process water to 100 ppm. Voigt model, which was provided by QCM-D software (Q-tool) was used to calculate the mass uptake of the polymers on silica surface (Alagha, et.al., 2011). The third and fifth overtones were used to calculate the mass adsorbed and expressed in milligrams of adsorbed material per square meter of surface area of the crystal.

3.9 Viscometer

Yield stress of the sediments was measure using a rotational viscometer HAAKE VT 550 (Thermo Fisher Scientific, USA). A rotational speed is set and the resistance to the flow of the sample is measured in terms of torque. From the torque, the set speed, and geometry factors of the applied sensor, rheological properties such as viscosity and shear stress are determined. Yield stress is the minimum stress at which the sample starts to flow. According to Nguyen and Boger (1983), a vane technique is the optimal method for determining the yield stress. This is not only because the geometrical shape eliminates any possibility of wall slip, but also insertion of vane into the sample causes least disturbance. A torque versus time response is used to determine the maximum torque obtained when the vane is rotated at a very low constant speed (0.014/s), as shown in Figure 3.8.

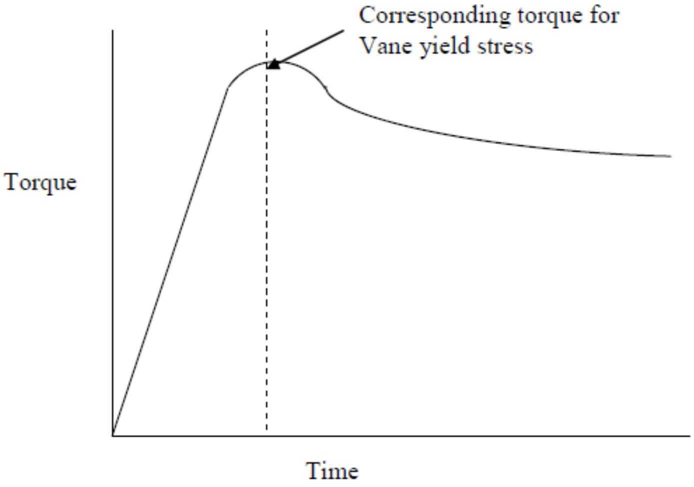


Figure 3.8 Torque versus time curve for the vane yield stress measurement

Nguyen and Boger (1983) developed the following relation that converts the maximum torque to yield stress of the sample:

$$\tau_V = \frac{T_m}{\frac{\pi D_V^3}{2}\left[\frac{H_V}{D_V} + \frac{1}{3}\right]}$$

where τ_v is the yield stress, T_m is the maximum torque, H_v is the height of the vane, and D_v is the diameter of the vane.

In this study, FL100 was used as the vane which has a diameter of 22 mm and height of 16 mm. For these tests, custom made settling columns that incorporated detachable section were used. The detachable section enabled yield stress measurement to be conducted on the formed sediment, thus eliminating any handling issues.

3.10 Zeta Potential of Sand

Zeta potential of coarse sand was measured using Anton Paas SurPASS Electrokinetic Analyzer. Unlike Zeta Sizer Nano ZS, the SurPASS calculates zeta potential by measuring the streaming potential of the sample. In this technique, electrolyte is forced to pass through the sample, which disrupts the diffuse layer, creating a potential difference (i.e streaming potential). This streaming potential is used to calculate zeta potential using the Helmholtz-Smoluchowski equations:

$$\zeta = \frac{dU}{dp} \times \frac{\eta}{\varepsilon \times \varepsilon_0} \times \frac{L}{A \times R}$$

$$\zeta = \frac{dl}{dp} \times \frac{\eta}{\varepsilon \times \varepsilon_0} \times \frac{L}{A}$$

where ζ is zeta potential, dU/dp is slope of streaming potential versus pressure, dl/dp is slope of streaming current versus pressure, η is electrolyte viscosity, ε_0 is permittivity of vacuum, ε is dielectric constant of electrolyte, L is length of streaming channel, A is cross-section of streaming channel, R is Ohm resistance inside the measuring cell.

Before any measurement, the electrodes were calibrated for pH and conductivity. About 2 grams of sand (sieved to 75 microns) was used to fill the cylindrical cell. After mounting the sample, process water was passed through the sand to perform flow check. The flow check was done to ensure the pressure within the cell was no more than 400 mbar. The cell was then rinsed with process water for 500 seconds. The measurements were conducted at pH 8.5 and temperature of 22^{o}C.

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Zhu, R.; Liu, Q.; Xu, Z.; Masliyah, J. H.; Khan, A. (2011) Role of Dissolving Carbon Dioxide in Densification of Oil Sands Tailings. *Energy & Fuels, 25* (5), 2049-2057.

4. Settling Behavior and Mechanism of ATA Process

After transferring the tailings slurry into a 250 mL beaker, the slurry was mixed for 2 min at 500 rpm. At the end of 2 minutes, the agitation was lowered to 350 rpm and the MF1011 was dropwise added to the slurry to the required dosage. Since the flocculation was very sensitive to shear rate, agitation was stopped as soon as the addition of polymer was completed. Polymer (Al-PAM or pDADMAC) was added to sand-water suspension in the same way as described above. The flocculated tailings suspension was then added to the sand-water suspension and stirred at 350 rpm for 30 seconds. Figure 4.1 shows the generalized schematics of the procedure for ATA process.

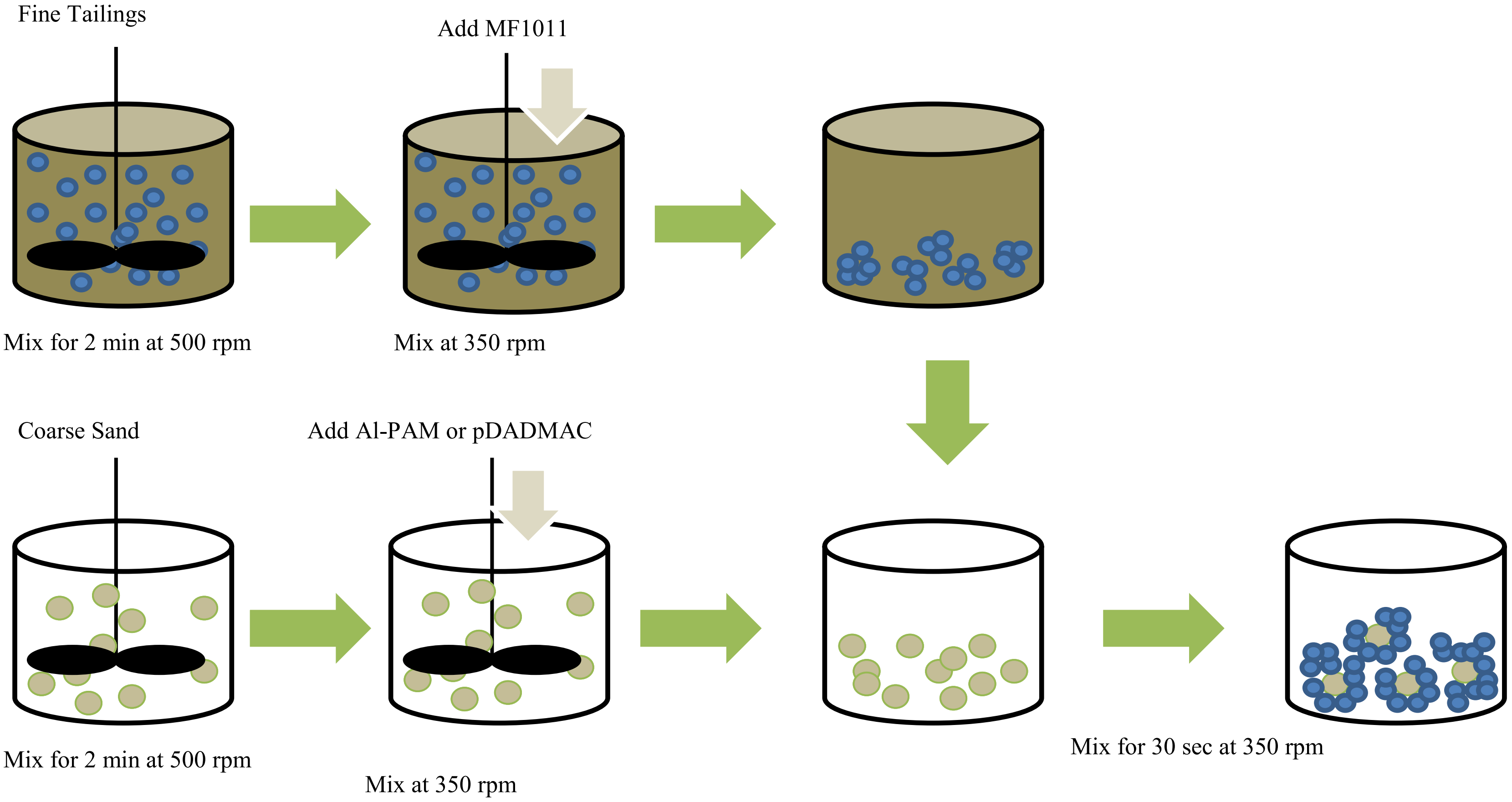

Figure 4.1 Schematics of the mixing procedure for ATA process.

4.1 Optimum Dosage of MF1011 in the Tailings

In order to find the optimum dosage of MF1011, various concentrations of MF1011 were added to the tailings. Figure 4.2 shows the initial settling rate as a function of the polymer dosage at pH 8.5. It can be seen that increasing concentration of MF1011 in tailings, increases ISR from 0 m/h to almost 7 m/h at 75 ppm. Beyond 75 ppm, any further addition of MF1011 decreases the ISR. This effect of overdosing is most likely the result of an increase in electrostatic and electrosteric repulsion between clay particles fully covered by MF1011 molecules at high dosages. At pH 8.5, both clay and bitumen carry a net negative charge (Wang, 2010). MF1011 is an anionic polymer that binds to clay particles by hydrogen bonding only. With the increase in dosage of MF1011, more polymer molecules can bind to clay particles and hence there is an initial increase in ISR when dosage was increased from 0 ppm to 75 ppm. When any additional polymer was added, electrosteric repulsion dominates between the polymer-loaded clay particles, resulting in decrease in ISR from 6.84 m/h at 75 ppm to 3.6 m/h at 200 ppm.

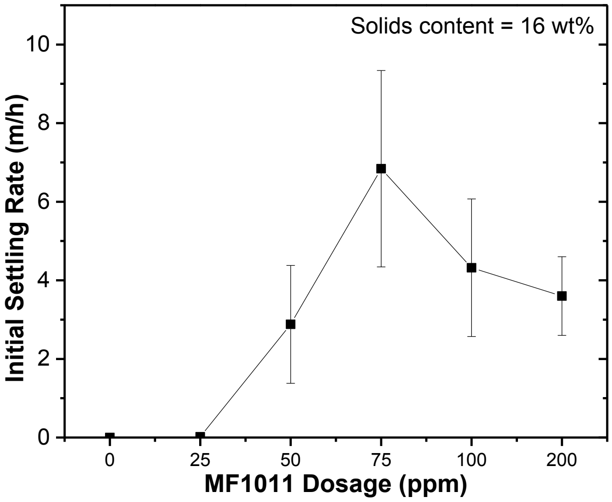

Figure 4.2 Initial settling rate as a function of MF 1011 dosages in fine tailings

Turbidity of supernatant was measured after 2 minutes of settling. The results are shown in Figure 4.3. The supernatant of tailings alone was too high to be accurately measured by the instrument. Even at 25 ppm of MF1011 the turbidity was well above 1000 NTU. The turbidity started to improve beyond 50 ppm. As seen from Figure 4.2, the turbidity of supernatant was lowest (544 NTU) at 75 ppm. Further addition of MF1011 did not significantly improve the turbidity of supernatant.

Solids content of sediments was measured after 1 hour of settling and the results are shown in Figure 4.4. The solid content in sediment bed increases with the increase in the MF1011 dosage to about 28% at 75 ppm.

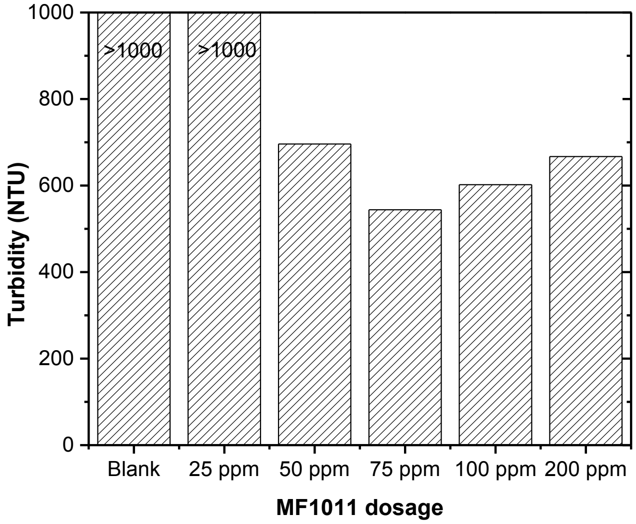

Figure 4.3 Turbidity of supernatant at various dosages of MF1011 in fine tailings

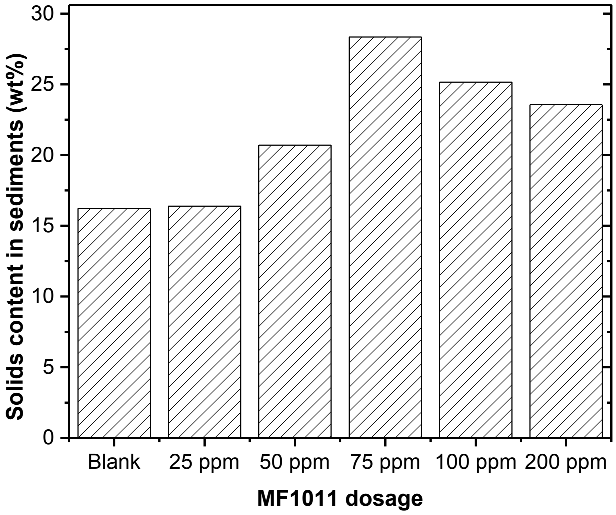

Figure 4.4 Solids content of sediments at various dosages of MF1011 in fine tailings

From Figures 4.2, 4.3 and 4.4, it can be seen that at 75 ppm, ISR was highest, turbidity was lowest. Hence 75 ppm is the optimum dosage of MF1011 for treating fluid fine tailings.

4.2 75 ppm MF1011 in Tailings and Al-PAM in Sand

With concentration of MF1011 in tailings fixed at 75 ppm, various dosages of Al-PAM were added to the sand and the settling performance of the mixture was measured. The total solids content of the slurry was maintained constant at 16 wt% which was the original solids content of the tailings.

Figure 4.5 shows the ISR at various dosages of Al-PAM in sand at SFR 0.25, 0.5 and 1. At a given SFR, ISR increases with the addition of Al-PAM. For example, at SFR 0.5 ISR increased from 10.08 m/h at 20 ppm to 29.52 m/h at 200 ppm. This increase in ISR can be attributed to the increase in the surface coverage of sand with Al-PAM. With the increase in Al-PAM concentration, more sands are covered with Al-PAM, and hence better to bind with fines. It is also noticed that ISR increased when SFR was increased from 0.25 to 0.5. At 100 ppm Al-PAM in sand, ISR was found to be 14.2 m/h, and 24.8 m/h, at SFR 0.25 and 0.5, respectively. But the ISR decreased slightly when SFR was increased to 1. This finding suggests that there exists an optimum sand concentration at which ISR is maximum. For this study, it was determined to be SFR 0.5.

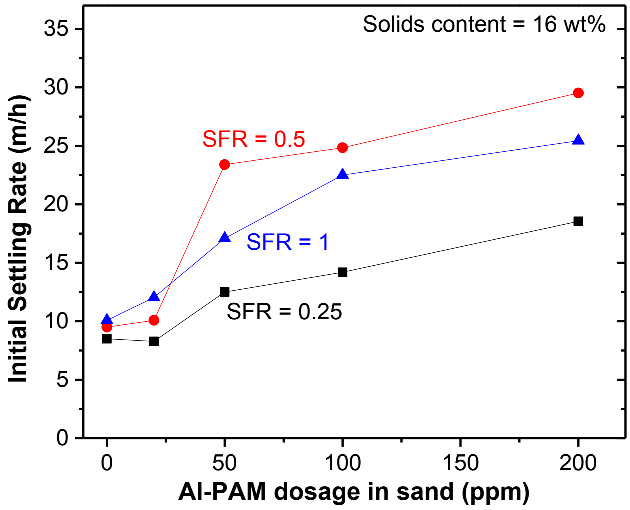

Figure 4.5 Initial settling rate of ATA process with the addition of 75 ppm MF1011 in fine tailings and various dosages of Al-PAM in sand at SFR 0.25, 0.5 and 1.

Figure 4.6 shows the turbidity of supernatant after 2 minutes of settling. Increasing the Al-PAM concentration decreased the turbidity of supernatant. At SFR 0.25, the turbidity was highest at 20 ppm Al-PAM (475 NTU) but it decreased to 222 NTU when concentration of Al-PAM was increased to 200 ppm. This was because at 200 ppm more Al-PAM was able to bind to sand particles leading to decrease in sand-clay repulsion and thus resulting in clear supernatant.

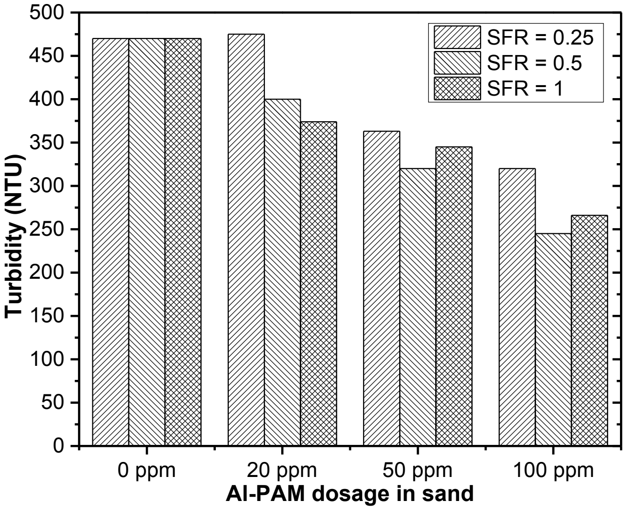

Figure 4.6 Turbidity of supernatant of ATA process with the addition of 75 ppm MF1011 in fine tailings and various dosages of Al-PAM in sand at SFR 0.25, 0.5 and 1.

Solid content of sediments were measured after 1 hour of settling and the results are shown in Figure 4.7. At a given SFR the solid content increased slightly with the increase in Al-PAM dosages. As expected, the overall solids content increased with SFR, as coarse sand allowed formation of more compact sediment than fine particles. Over the SFR studied, Al-PAM concentration was found to have minimal impact on solids content of sediments.

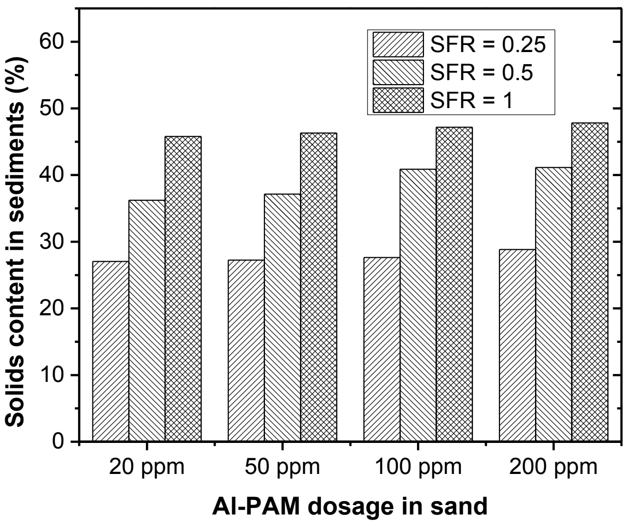

Figure 4.7 Solids content in sediments of ATA process with the addition of 75 ppm MF1011 in fine tailings and various dosages of Al-PAM in sand at SFR 0.25, 0.5 and 1.

4.3 75 ppm MF1011 in Tailings and pDADMAC in Sand

With the concentration of MF1011 fixed at 75 ppm, various dosages of pDADMAC were added to the sand and settling performance was measured. The total solids content of the slurry was maintained constant at 16 wt% which was the original solids content of the tailings.

Figure 4.8 shows the initial settling rate as a function of pDADMAC dosages in sand at SFR 0.25, 0.5 and 1. At a given SFR, ISR increases with increasing the concentration of pDADMAC. At SFR 0.25, ISR rose from 8.5 m/h at 0 ppm to 18.55 m/h at 200 ppm. This increase in ISR can be attributed to the increase in surface coverage of sand with PDADMAC. With the increase in pDADMAC concentration, more sand is covered and hence is able to bind to fines. As seen with the Al-PAM addition, the ISR increased when SFR was increased from 0.25 to 0.5. At SFR 1, a decrease in ISR was recorded as seen in Figure 4.8. Thus, there exists an optimum sand concentration in the ATA process and it was found to be SFR 0.5.

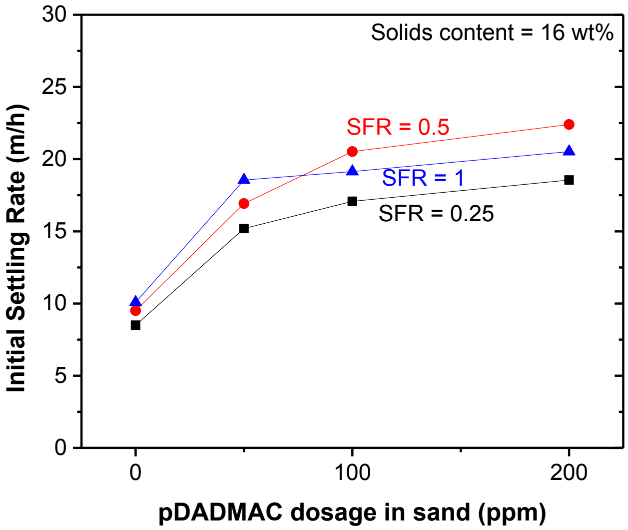

Figure 4.8 Initial settling rate of ATA process with the addition of 75 ppm MF1011 in fine tailings and various dosages of pDADMAC in sand at SFR 0.25, 0.5 and 1.

Turbidity of supernatant was recorded after 2 minutes of settling and the results are shown in Figure 4.9. The turbidity decreased from the initial 470 NTU to less than 100 NTU when only 50 ppm pDADMAC was added. This decrease was most likely due to the bind of pDADMAC to sand particles, thereby reducing the electrostatic repulsion between sand-clay particles and thus resulting in clear supernatant.

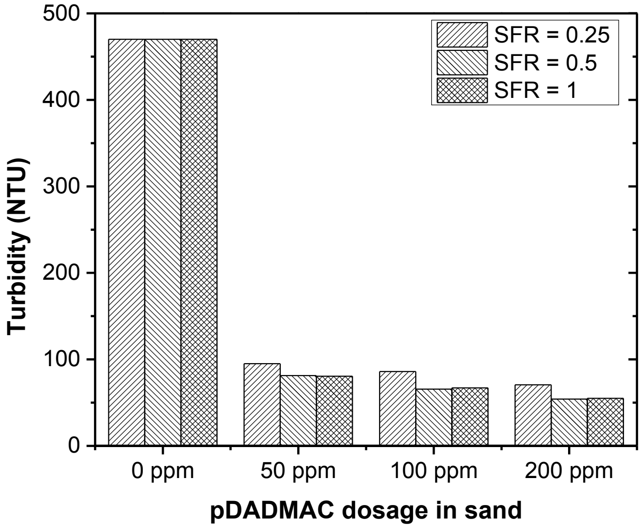

Figure 4.9 Turbidity of supernatant of ATA process with the addition of 75 ppm MF1011 in fine tailings and various dosages of pDADMAC in sand at SFR 0.25, 0.5 and 1.

Figure 4.10 shows the solid content in sediments of ATA process with the addition of 75 ppm MF1011 in fine tailings and various dosages of pDADMAC in sand at SFR 0.25, 0.5 and 1. As expected, an increase in SFR results in coarse sand forming more compact sediment bed and hence an increase in solids content.

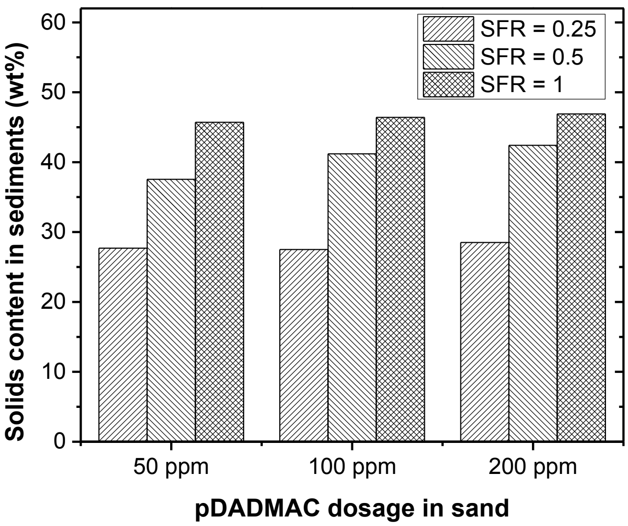

Figure 4.10 Solid content in sediments of ATA process with the addition of 75 ppm MF1011 in fine tailings and various dosages of pDADMAC in sand at SFR 0.25, 0.5 and 1.

4.4 Comparison of performance with Al-PAM and pDADMAC in sand

Figure 4.11 shows the comparison of ISR with the addition of Al-PAM and pDADMAC in sand at SFR 0.5. ISR is higher when Al-PAM is added to the sand than pDADMAC. Since ISR is a function of size of aggregates, this result indicates that the aggregates formed using Al-PAM will be larger than using pDADMAC. This is most likely because of the difference in the bridging mechanism of the two polymers. A more detailed discussion about the mechanism of the two polymers would be described in the next section.

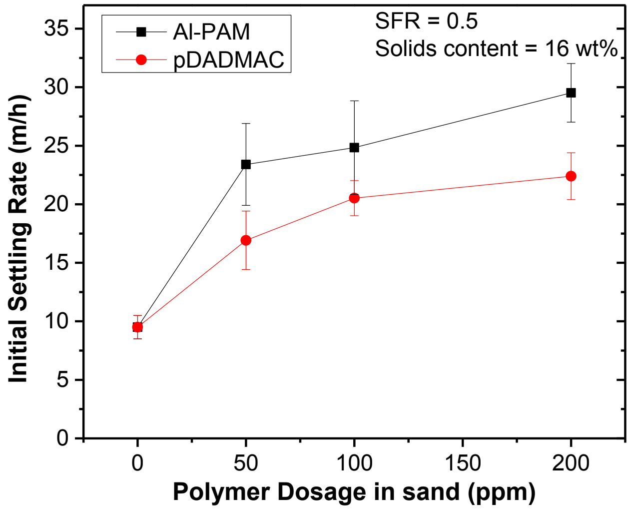

Figure 4.11 Comparison of ISR in the ATA process with the addition of Al-PAM and pDADMAC in sand at SFR 0.5.

As seen in Figure 4.12, the turbidity of supernatant was significantly lower when pDADMAC was added to the sand than Al-PAM. At 100 ppm Al-PAM in sand the turbidity of supernatant was found to be 245 NTU, in comparison to turbidity of 65.7 NTU when pDADMAC was added to the sand. The turbidity of supernatant was always lower with the addition of pDADMAC than Al-PAM. The results suggest a stronger flocculation of fines on pDADMAC activated sand than on Al-PAM activated sand. Hence pDADMAC is more favorable than Al-PAM to reduce the turbidity of supernatant.

Figure 4.13 shows the comparison of solid content in sediment bed with the addition of Al-PAM and pDADMAC in sand at SFR 0.5. No significant change in solids content was observed with the addition of Al-PAM or pDADMAC at a given SFR. This finding suggests that both polymers are capable of producing compact sediment bed using ATA process.

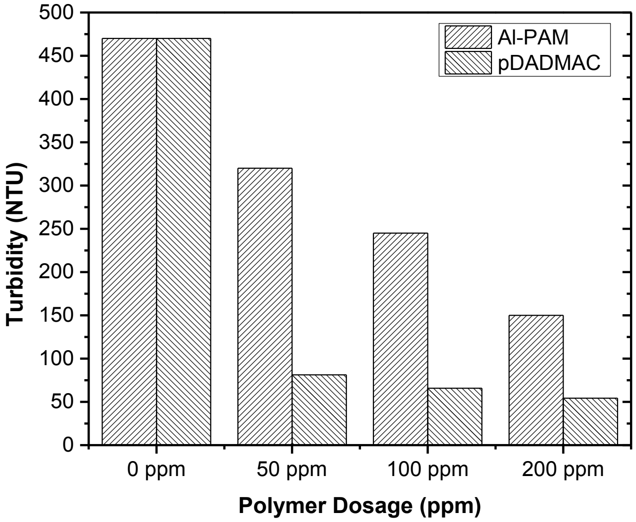

Figure 4.12 Comparison of turbidity of supernatant in the ATA process with the addition of Al-PAM and pDADMAC in sand at SFR 0.5.

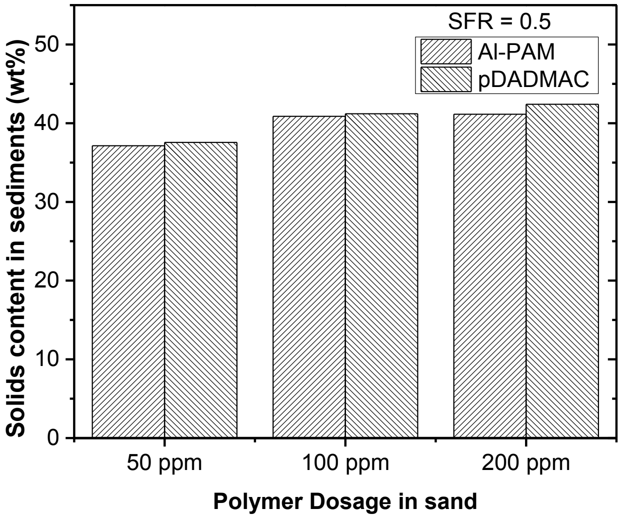

Figure 4.13 Comparison of solid content in sediment in ATA process with the addition of Al-PAM and pDADMAC in sand at SFR 0.5.

Figure 4.14 is the photograph of the settling columns using 50, 100 and 200 ppm Al-PAM and pDADMAC at SFR 0.5. The blank contains 75 ppm MF1011 and no cationic polymer in sand. The left hand side columns are when Al-PAM is added, while the right hand side columns contain pDADMAC in sand. This figure shows that both Al-PAM and pDADMAC are excellent choices for forming NST using ATA process. But the turbidity is significantly better with the use of pDADMAC in sand.

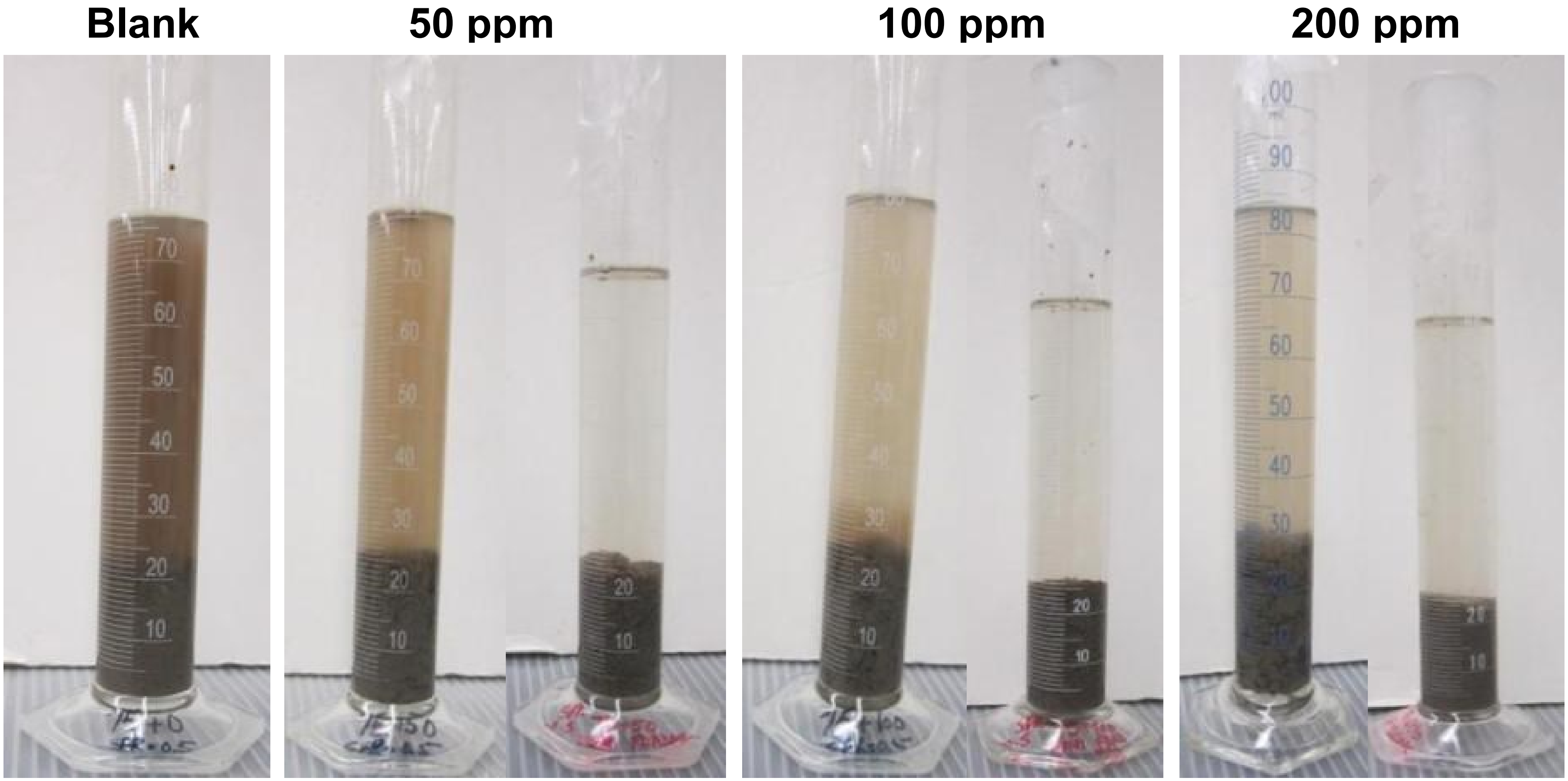

Figure 4.14 Photograph of settling columns with the addition of Al-PAM (left) and pDADMAC (right) in sand at various dosages and SFR 0.5.

4.5 Mechanism of ATA process

To study the change in surface properties of sand due to the addition of Al-PAM and pDADMAC, zeta potential measurements were conducted. Figure 4.15 shows the zeta potential of silica at various dosages of Al-PAM and pDADMAC. The zeta potential of silica at pH 8.5 is -35 mV. This result is consistent with the isoelectric point of silica at pH 3.5 (Kosmulski, 2001). With the addition of 100 ppm Al-PAM, the zeta potential of silica increases to 0.5 mV. On the other hand, the addition of 100 ppm pDADMAC causes a complete charge reversal of silica by raising its zeta potential to 32.5 mV. When a cationic polymer (like Al-PAM or pDADMAC) is added to the silica suspension, electrostatic forces of attraction develops between the silanol (-SiO) groups and polymer, which results in the adsorption of the polymer on the sand and hence a reduction in zeta potential of silica (Long, 2006a). The extent of reduction in zeta potential of silica depends on the strength of electrostatic forces. In case of Al-PAM, the $Al(OH)_3$ colloid is highly cationic (nearly 30 mV), which bind to the surface of silica due to electrostatic force of attraction and hence makes the surface of silica less negative (Alagha et.al., 2011). On the other hand, pDADMAC is a strong polyelectrolyte with very high charge density (~6meq/g) (Terhi Saarinen, 2009). The strong electrostatic adsorption of amine group $^{+}N(CH_3)_3$ of pDADMAC on silica causes the complete charge reversal of sand. This phenomenon is consistent with the results from other studies (Penta et.al., 2011). Thus it can be concluded that pDADMAC has a higher affinity for silica than Al-PAM. But in order to study the adsorption characteristics of these polymers on silica and interaction with MF1011, QCM-D studies were conducted.

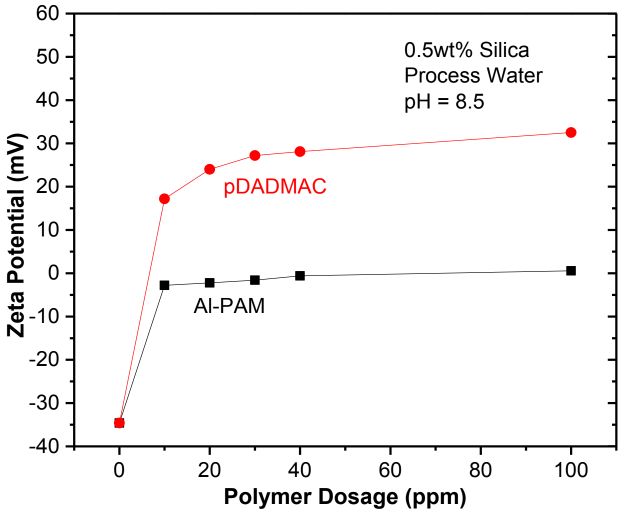

Figure 4.15 Variation of zeta potential of silica with the addition of varying dosage of Al-PAM and pDADMAC at pH 8.5.

Adsorption kinetics of 100 ppm Al-PAM/MF1011 and pDADMAC/MF1011 on silica surface are shown in Figure 4.16 and Figure 4.17, respectively. The corresponding mass adsorbed as calculated using Voight model is shown in Figure 4.18. In this set of experiments, the background solution of DI water at pH 8.5 was pumped for about 30 minutes before polymer was injected. After the addition of cationic polymer, process water was used to rinse any free molecules that were not adsorbed on surface.

As seen in Figure 4.16, there is a rapid decrease in frequency by 30 Hz upon switching from background solution to 100 ppm Al-PAM. This frequency shift corresponds to a mass adsorbed of 5.65 mg/m^2 on silica surface. The driving force of Al-PAM adsorption on silica surface is both the electrostatic attraction between positively charges $Al(OH)_3$ colloidal particles in Al-PAM and negatively charged deprotonated silanol groups on silica surface and hydrogen-bond formation (Alagha et.al., 2011). The combination of the two forces results in an irreversible adsorption, as indicated by a negligible change in frequency when Al-PAM was washed with process water. When 100 ppm MF1011 was pumped, there was a small but noticeable decrease in frequency by 5 Hz, suggesting adsorption of anionic MF1011 on silica surface pre-adsorbed by Al-PAM. A relatively low change in ΔD indicates the formation of a rigid layer of coiled Al-PAM molecules on the surface. Since the polymer is not able to completely cover the surface of the silica, it leads to the formation of pancake like structure. Linear anionic molecules of MF1011 then adsorb weakly on slightly cationic Al-PAM due to electrostatic attraction.

When 100 ppm pDADMAC was pumped, as seen in Figure 4.17, a more significant decrease in frequency (nearly 120 Hz) and increase in dissipation was observed. Using Voigt model, the mass uptake of pDADMAC on silica was was calculated to be 38.38 mg/m^2. The reason for such a rapid increase in mass adsorption is due to the large difference in the opposite surface charge densities between the silica and pDADMAC molecules. Washing this layer with process water did not cause any change in frequency or dissipation. The absence of change in frequency during the rinsing process is an indication of the quasi-irreversibility of the adsorption process. This irreversibility may be related to the thermodynamics of the polymer adsorption process, which is accompanied by the release of counter ions from the polymer and the surface into the solution (Eduardo Guzman, 2009). It is hypothesized that the silanol groups on silica surface are attracted to the amine groups of pDADMAC to form a stable configuration for the adsorption of pDADMAC. Once pDADMAC is deposited, there will be some amine groups exposed to the bulk liquid. These are then free to attract the negatively charged MF1011 molecules, resulting in a shift of frequency by 18 Hz. A rapid decrease in frequency indicates pDADMAC adsorbs very fast on silica surface, causing a complete coverage of the surface. This is followed by a change in conformation of the polymer due to an increase in electrostatic repulsion between the polymer strands and release of water molecules from the adsorbed layer. As a result, they form a brush-like pattern with the polymer strands protruding more into the solution. This type of conformation allows more molecules to adsorb, forming a thicker but more loosely packed polymer layer, characterized by a rapid increase in dissipation. Anionic MF1011 can bind to this highly cationic polymer layer due to electrostatic attraction.

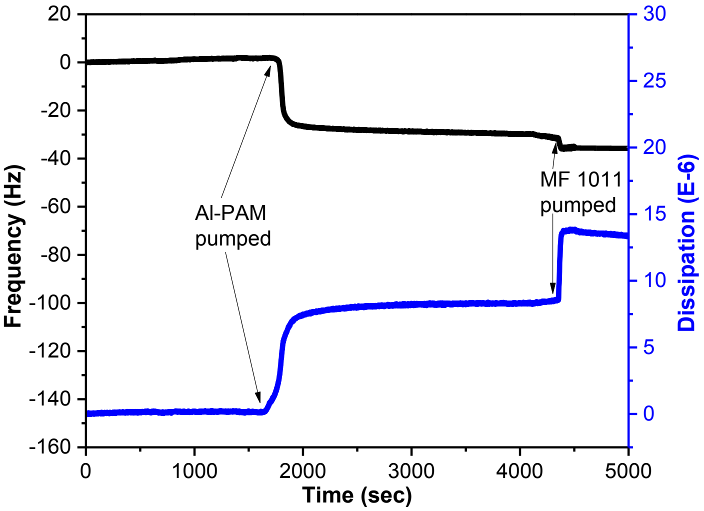

Figure 4.16 Change in frequency and dissipation of bilayer system of Al-PAM/MF1011 on silica surface at pH 8.5.

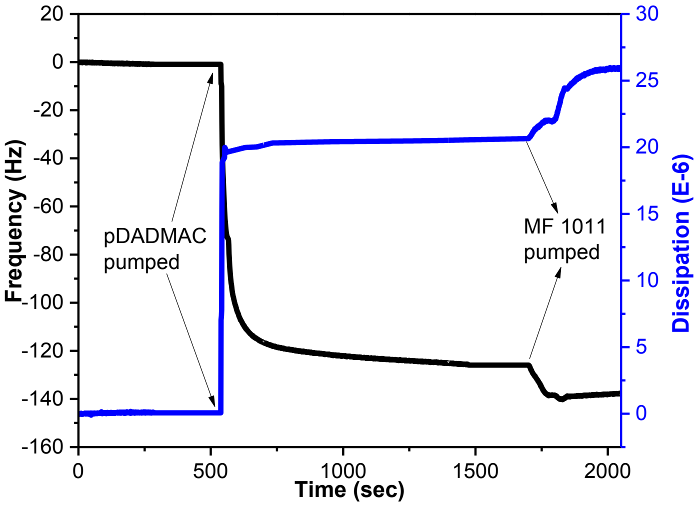

Figure 4.17 Change in frequency and dissipation of bilayer system of pDADMAC/MF1011 on silica surface at pH 8.5.

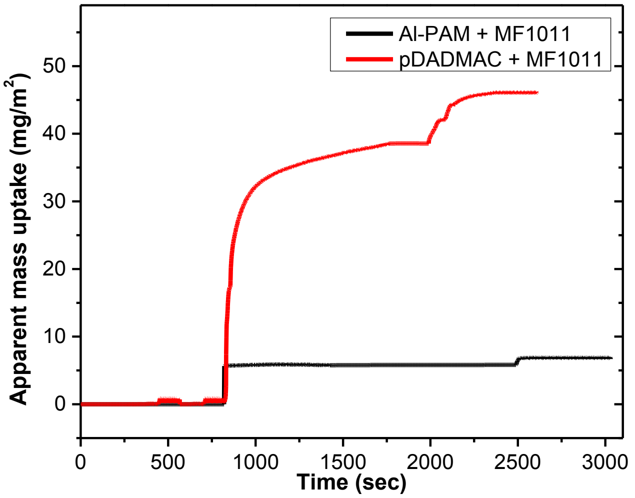

Figure 4.18 Cumulative mass adsorbed with the presence of Al-PAM/MF1011 and pDADMAC/MF1011 on silica at pH 8.5.

Using the above zeta potential measurement and QCM-D studies, Figures 4.19 and 4.20 show a possible mechanism of the ATA process using Al-PAM and pDADMAC. The initial settling rate is a function of the size of aggregates. As seen from Figure 4.19, Al-PAM does not completely cover the surface of silica. This leads to the formation of patches of Al-PAM covering sand which can bind not only to the negatively charged clay particles but also to negatively charged sand. On the other hand, the surface of silica is completely covered with the addition of highly cationic pDADMAC as seen in Figure 4.20. When negatively charged clay particles are added, sand covered with pDADMAC strongly binds to clay particles. The electrostatic repulsion between the two completely covered sand particles dominates and prevents any further bridge formation between sand particles. Due to this conformation, the size of aggregates is larger with the addition of Al-PAM in sand and hence the initial settling rate is higher with Al-PAM than with pDADMAC. Since pDADMAC is significantly more cationic than Al-PAM, it is able to attract negatively charged fines more strongly and hence resulting in clearer supernatant than Al-PAM.

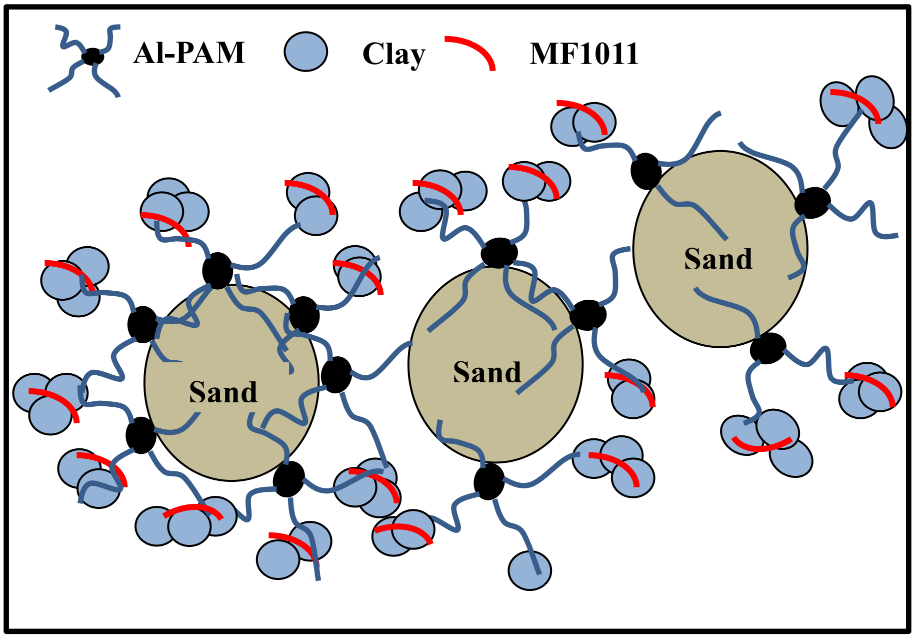

Figure 4.19 Proposed mechanism of formation of flocs with addition of Al-PAM on sand.

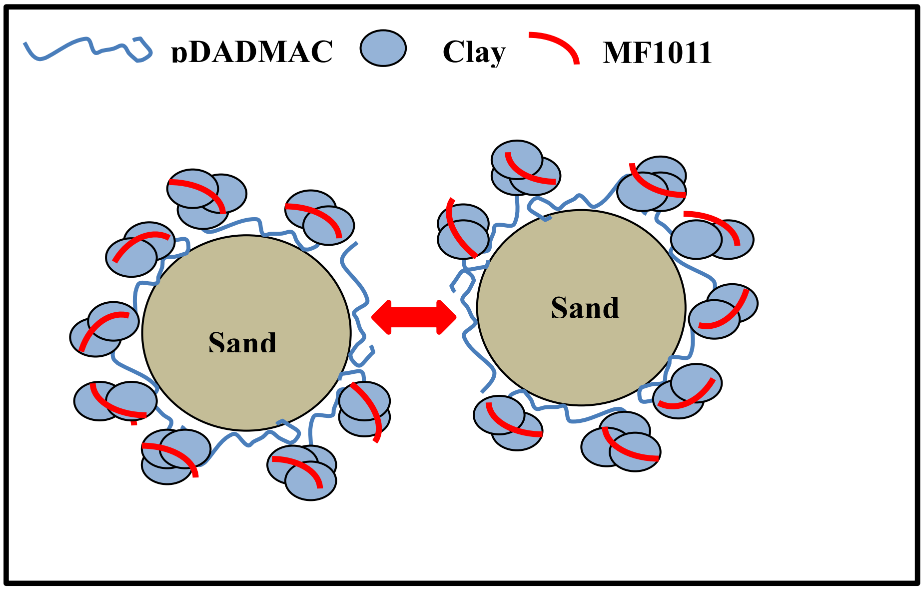

Figure 4.20 Proposed mechanism of formation of flocs with addition of pDADMAC on sand.

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5. A Novel Polymer assisted CT process

Although ATA process is promising for settling oil sands tailings, it could be very expensive due to its use of large amount of dual polymers. ATA process requires two polymers – an anionic polymer which is able to interact with the clays and a cationic polymer which is able to interact with the sand. In a large industrial scale, cost of these polymers could be enormous and hence there is a need for better methods to treat oil sands tailings. A new method was proposed using one polymer to activate sand particles followed by mixing with tailings fines.

5.1 Schematic of Polymer Assisted CT Process

Figure 5.1 shows the schematic for polymer assisted CT process. In this method, 15 g sand is first mixed with 100 g pDADMAC (10g/L) for one hour in the mechanical mixer IKA RW20. After covering sand with pDADMAC, the pDADMAC was removed with pipette. In order to remove any residual polymer in the system, sand is rinsed with DI water for 5 times. The coated sand was then mixed with oil sands tailings at 350 rpm for 30 seconds. The solids content of the entire slurry was maintained constant at 16 wt% by adding process water to the sand.

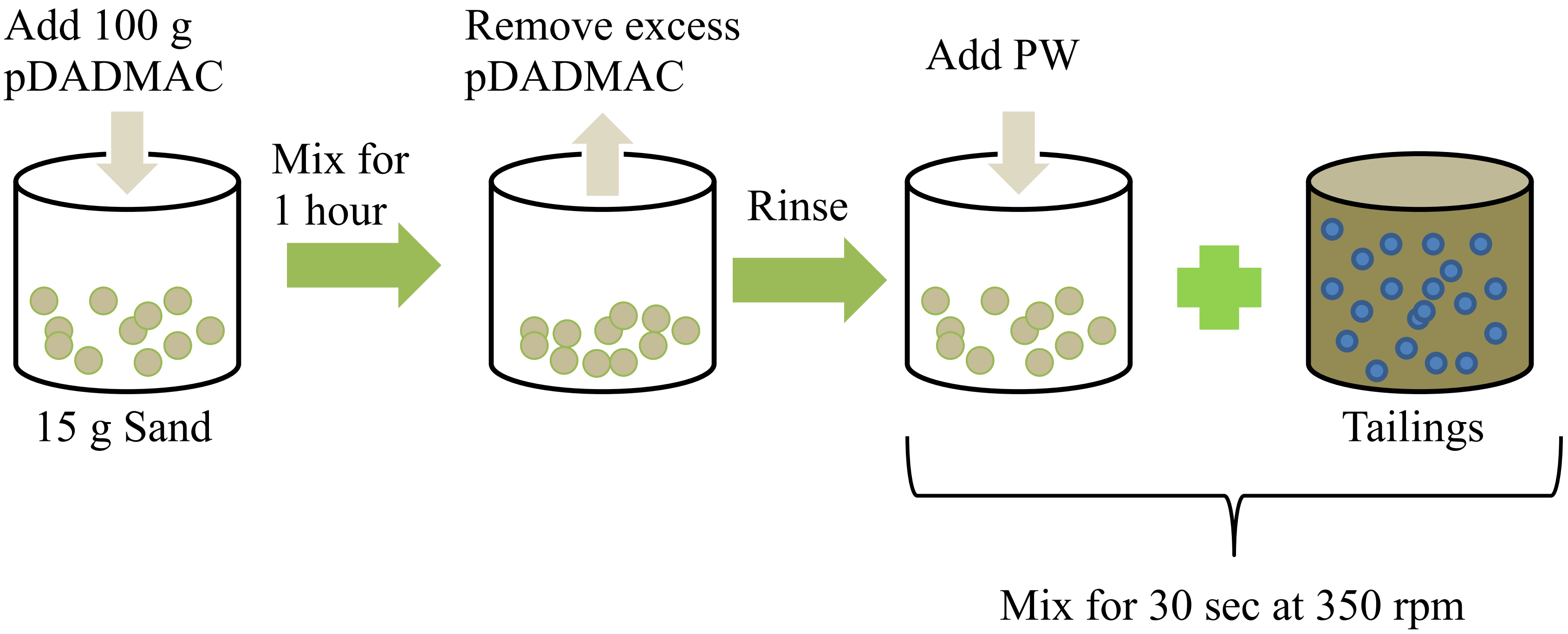


Figure 5.1 Schematic for polymer assisted CT process

5.2 Need for Dilution

When pDADMAC coated sand was added to the raw tailings (solids content of 16 wt%), no visible settling was observed even after one hour. Hence the decision was made to dilute the tailings to 10 wt% solids using process water. Even though the tailings were diluted to 10 wt% solids, the total solids content of the slurry (tailings and sand) was kept constant at 16 wt%.

5.3 Settling Performance Using Polymer Assisted CT Process

Figure 5.2 shows the initial settling rate at SFR 1, 2, and 4. As seen in Figure 5.2, initial settling rate increases with the addition of sand. The initial settling rate increased from 0.75 m/h at SFR 1 to 3.2 m/h at SFR 4. This result shows that increasing the mass fraction of sand enhances the settling of the fines. It is hypothesized that when the mass fraction of pDADMAC coated sand is increased, more fines are attracted to the sand thus improving ISR.

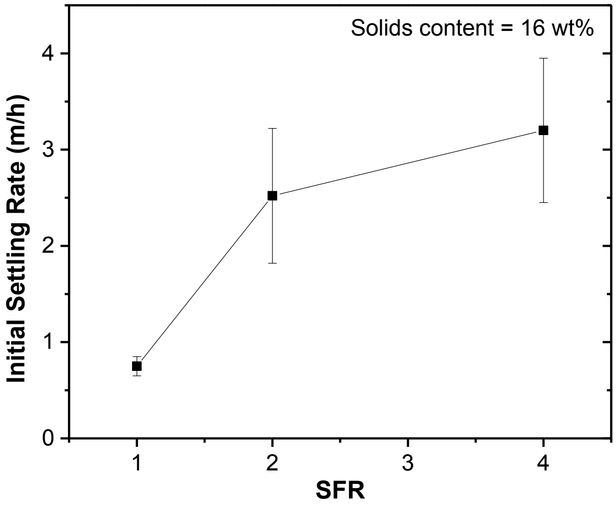


Figure 5.2 Initial Settling Rate at different sand concentrations.

Turbidity of the supernatant was measured after 2 minutes of settling and the results are shown in Figure 5.3. The turbidity of supernatant significantly reduced with the increase in the addition of sand. The turbidity of supernatant was extremely poor at SFR 1. This result is consistent with low ISR seen above, hence indicating that insufficient sand at SFR 1 was available to attract fines. At SFR 2, the turbidity of supernatant reduced to 20 NTU. The turbidity increased to nearly 65 NTU at SFR 4.

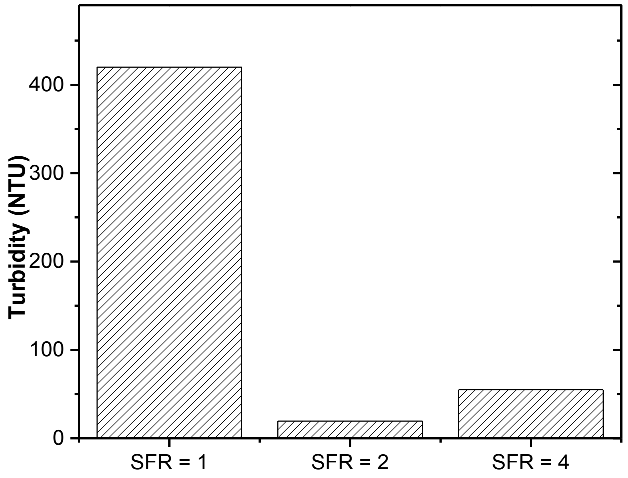


Figure 5.3 Turbidity of supernatant after 2 minutes of settling.

Figure 5.4 shows the solids content in sediments after 1 hour at different sand concentrations. As expected, increasing sand concentrations increased the solids content in the sediments. The solids content in sediment bed increased from 46.4 wt% at SFR 1 to 59.3 wt% at SFR 4. The overall solids content increased with SFR as coarse sand was able to form more compact sediment than fine particles.

Another aspect of the tailings treatment is to form trafficable solid deposits which can be used for land reclamation purposes. To determine if the solids are self contained, yield stress was measured. Figure 5.5 shows the yield stress of the sediments after settling. The yield stress of the bed was 70.18 Pa, 104.1 Pa, and 179.58 Pa at SFR 1, 2, and 4, respectively. As the SFR increases, surface area of sand covered with pDADMAC increases. The fines are now able to bind to sand more effectively, resulting in larger and robust flocs with high yield stresses.

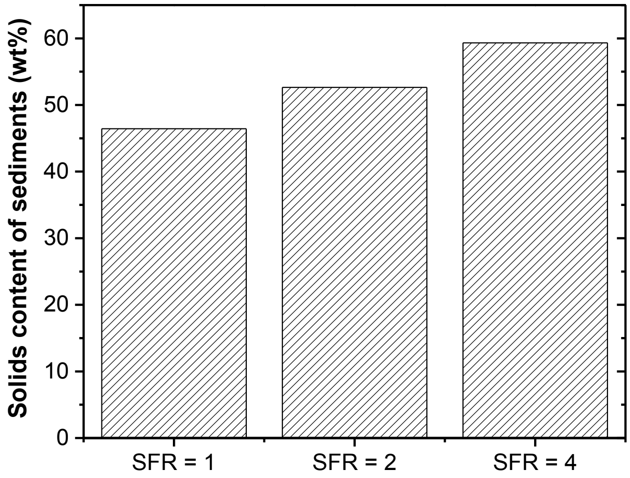


Figure 5.4 Solids content in sediments at different sand concentrations.

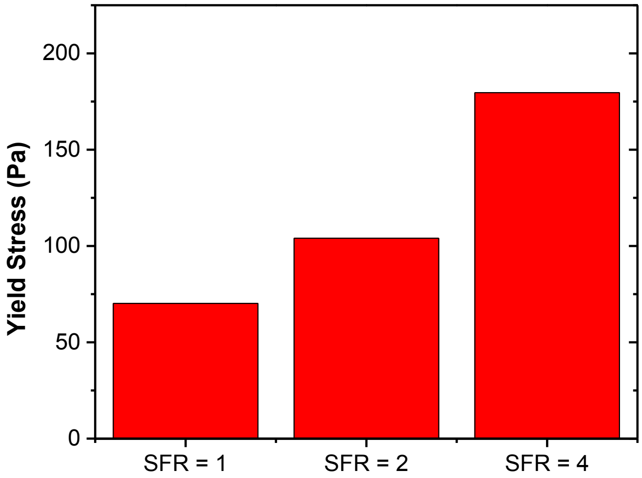


Figure 5.5 Yield Stress of sediments after 1 hour of settling at various SFR

5.4 Mechanism of Polymer Assisted CT Process

Sand alone is not able to enhance settling of fine oil sands tailings. It is only when the sand is coated with pDADMAC, the sand is able to bind to the fines. Hence it is hypothesized that the mechanism of the polymer coated CT process is the change is surface properties of sand brought about by the addition of pDADMAC, as shown in Figure 5.6. When sand is coated with pDADMAC, the surface of the sand is completely covered with pDADMAC. This layer of pDADMAC is now able to attract fines and form large aggregates which settle easily due to gravity.

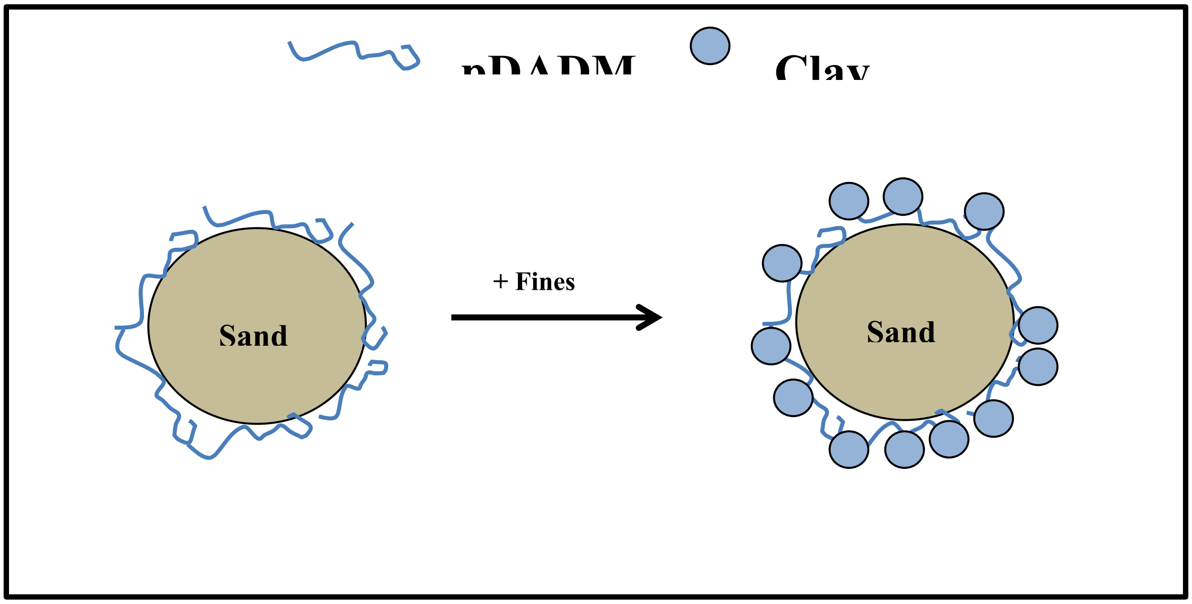


Figure 5.6 Proposed mechanism of polymer assisted CT process

To study the change in surface properties of sand due to the addition of pDADMAC, zeta potential of sand was measured before and after coating. The results of the zeta potential measurements are shown in Figure 5.7. At pH 8.5, the zeta potential of sand was found to be -45.6 mV. When the sand was coated with pDADMAC, zeta potential increased to nearly 54 mV. Even with rinsing three times with process water, the zeta potential remained almost constant. This result shows that positively charged pDADMAC was able to adsorb strongly on the surface of sand (Penta et.al., 2011). pDADMAC was not only able to reverse the charge on sand but also formed a strong layer which remained on sand even after washing. It is believed that it is this layer of pDADMAC that attracts the fines.

Although changes in zeta potential of sand measured by SurPass is useful in determining the interaction of pDADMAC and sand, the zeta potential measurements do not truly reflect the actual amount of pDADMAC adsorbed. QCM-D was employed to study the adsorption behavior of pDADMAC. Figure 5.8 shows the mass adsorption of fines on silica surface pre-adsorbed by pDADMAC. Silica sensor was chosen to simulate the surface of sand. After rinsing the silica sensor with background solution, 100 ppm pDADMAC (diluted from 1000 ppm stock solution using process water) was pumped. A sharp reduction in frequency was observed. Using Voigh model, it was determined that the mass uptake of pDADMAC on silica was 40.47 mg/m^2. Process water was used to rinse any free molecules of pDADMAC from silica surface. When no change in frequency was observed, suspension of 0.1 wt% fines in process water was pumped, which resulted in a further increase in mass adsorbed on surface of silica. Generally the combination of electrostatic attraction and hydrogen bonding results in the rapid and strong adsorption (Terhi Saarinen, 2009). These forces resulted in adsorption of fines on pDADMAC coated silica surface, suggesting that deposition of fines can be enhanced using pDADMAC.

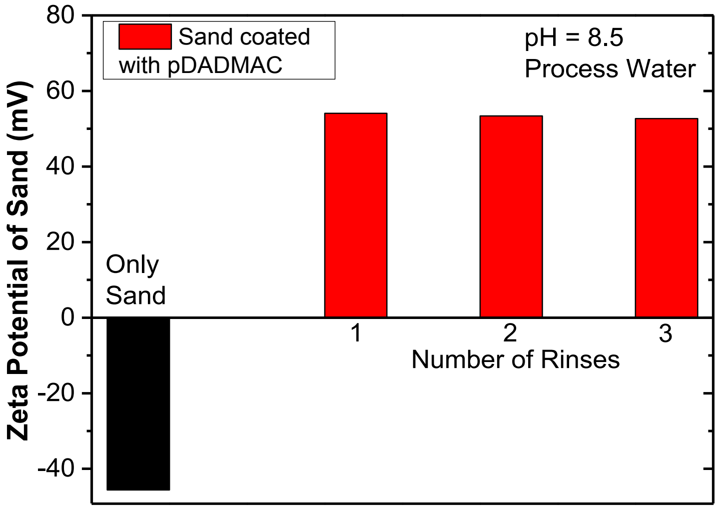


Figure 5.7 Zeta potential of sand using SurPASS

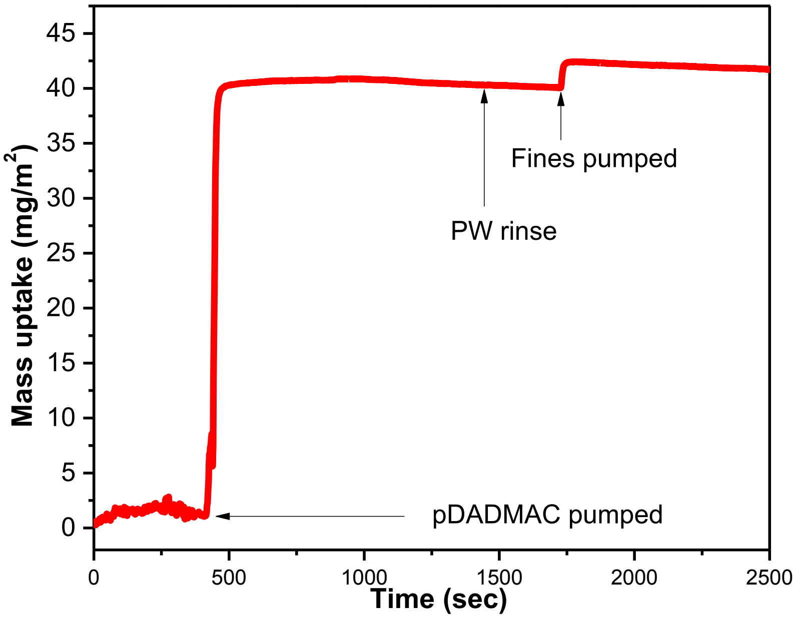
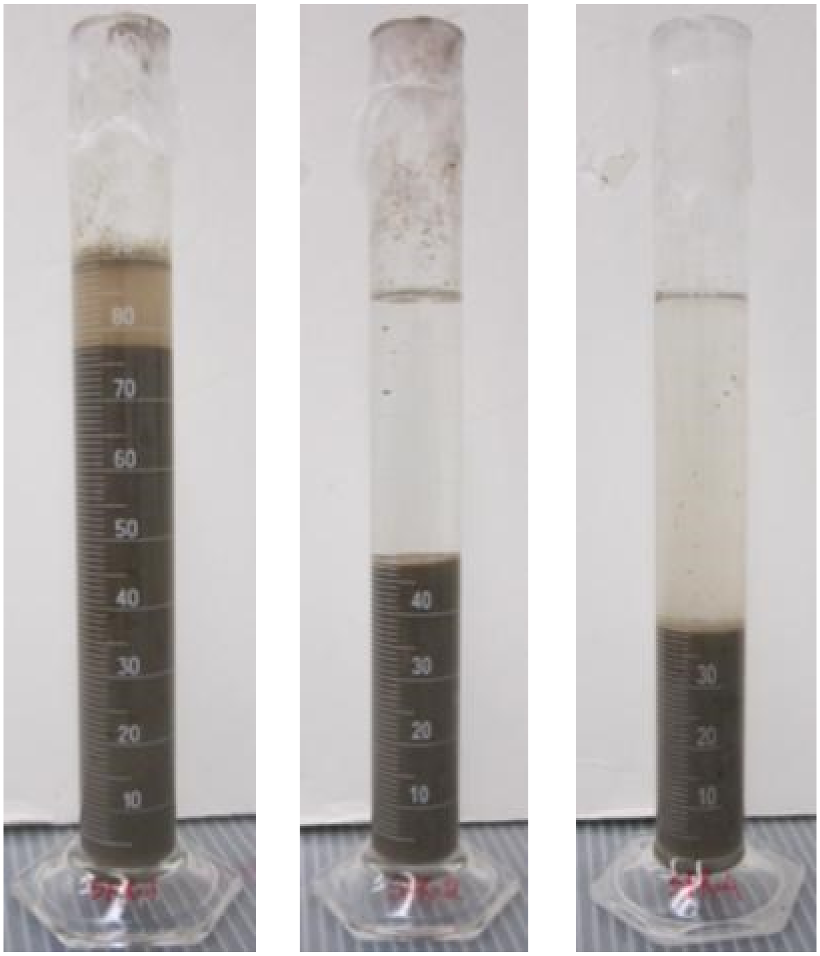


Figure 5.8 Mass uptake of fines on pDADMAC adsorbed silica surface.

5.4 Anomalies and future research

1. As shown in photographs of Figure 5.9, non-segregating tailings were formed using only one cationic polymer. No visible distinction between sand and fines can be observed. However, if the fines were completely adsorbed onto the treated sand, it is expected that the resulting settling rate would be higher as the sand-laden flocs would settle at a rate similar to the sand (> 20m/h). Instead, the observed settling rates are much lower than this, thus indicating that some fines may be flocculating separately from the sand. Further work is in progress to understand this phenomenon.

2. Although the sand was rinsed with DI water to remove any excess polymer, it is possible that trace amounts of pDADMAC may still be present in the system. Further work is in progress to understand the effect of trace polymer in formation of NST.



SFR = 1 **SFR = 2** **SFR = 4**

Figure 5.9 Settling columns after 2 minutes of settling at SFR 1, 2, and 4.

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6. Conclusions and Recommendations

6.1 Conclusions

ATA process uses combination of two oppositely charged polymers. Anionic polymer MF1011 was used to activate fines in the tailings while cationic polymers Al-PAM and pDADMAC were added to the coarse sand. Zeta potential, QCM-D, initial settling rate and turbidity of supernatant were used to better understand the mechanism of the ATA process.

100 ppm Al-PAM was able to cause charge neutralization of silica by increasing the zeta potential of silica from -35 mV to 0.5 mV. On the other hand, 100 ppm pDADMAC caused a charge reversal by raising the zeta potential of silica to 32.5 mV. Due to the difference in charges of two polymers, there was a significant difference in mass adsorption of the two layers on silica surface. 100 ppm pDADMAC led to an adsorbed mass of 38.55 mg/m^2 on silica surface while 100 ppm Al-PAM only 5.81 mg/m^2 was adsorbed from 100 ppm Al-PAM solutions. The mass uptake on both polymers increased further when MF1011 was pumped. But the mass adsorption was higher when silica was coated with pDADMAC. This result shows that the interaction of sand with fines is stronger for pDADMAC/MF1011 than Al-PAM/MF1011. Thus, the turbidity of supernatant was significantly reduced when sand was coated with pDADMAC. At optimum dosages (50 ppm pDADMAC and 200 ppm Al-PAM), turbidity of

supernatant was reduced to 81.3 NTU and 150 NTU, respectively. On the other hand, initial settling rate with the addition of Al-PAM was higher (nearly 30 m/h) than that of pDADMAC (nearly 20 m/h). Unlike pDADMAC, Al-PAM did not completely cover the surface of sand. As a result, electrostatic repulsion between sand particles was reduced and sand particles were able to bind to each other to form bigger aggregates.

A novel method for treatment of oil sands tailings using only a single polymer and sand was developed. In this method, sand was coated with pDADMAC and mixed with tailings to produce non-segregated tailings and clear supernatant. SFR 2 was found to be the optimum sand concentration, which produced an initial settling rate of about 2 m/h and clear supernatant of 20 NTU turbidity. Although the QCM-D studies indicate that electrostatic attraction between the amine groups of pDADMAC and clay particles in tailings leads to formation of dense aggregates, more investigation needs to be conducted to better understand the mechanism.

6.2 Recommendations for future research

To better understand the mechanism of polymer assisted CT process, following are recommendations for future research:

1. Study the effect of charge density, and molecular weight of polymer on settling behavior,
2. Study the effect of residual polymer in tailings water on bitumen extraction,

3. Measure the interaction forces between clays and sand with polymer at various dosages.

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