University of Alberta

Al-PAM Assisted Filtration of Mature Fine Tailings from Oil Sands Developments

by

Aurangzeb Alamgir

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This thesis is dedicated to my parents, **Mr. Abdul Haq and Mrs. Rani** whose memories are the only asset I have in my life. May their souls rest in peace forever.

Dedicated to my wife Sobia Aurangzeb and to my immaculate love Uswa Zeb, Abdullah Zeb and Ibrahim Zeb whose presence brings me cheers and tranquility.

ABSTRACT

Improvement on existing tailings management technologies is pivotal for the sustainability of oil sands industry. Long term storage of oil sands tailings in tailing ponds is considered a serious environmental liability. Oil sands industry, with the collaboration of its research partners, has been striving to come up with cost effective and environmentally friendly technology to resolve mature fine tailings (MFT) issues.

Present research study explores a possibility to consolidate current and future inventory of MFT by using polymer aids as flocculants. Overall objective of this research is to expedite the densification of MFT by manipulating the consolidation process and using the optimum dosage of suitable polymers. The effect of residual bitumen removal from oil sands tailings, MFT dilution and manoeuvring the polymer addition mechanism are also investigated.

A novel approach of filtering the sediments is proposed and tested to achieve a maximum level of consolidation with a better recovery of useable water.

In this study, Al-PAM is identified to be a better flocculating agent than commercial Magnafloc1011 as filtration aid of diluted MFT. This class of polymer is expected to offer more viable approach for MFT disposal with a potential of putting an end to massive tailings ponds.

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Chapter 1 INTRODUCTION

The major accumulations of oil sands are distributed geographically in eight countries: Canada, Venezuela, USA, Trinidad, Madagascar, Albania, Russia and Romania. Over 95% of the known in place volumes occurs in Canada. The Athabasca oil sands deposit itself is the largest petroleum resource in the world. This discovery of massive oil sands reserve in Alberta has placed Canada in a sound position by holding the second largest reserve in the world after Saudi Arabia. Since conventional oil resources are exhausting so bitumen production from oil sands is gaining more attention and appreciation though the recovery of synthetic oil from tar sands is more challenging especially associated environmental issues. From the Canada's perspective there is no question whether or not this fuel source should be fully developed. Canada being a responsible country needs to respond to international calls regarding the environmental concerns more objectively. No doubt industry is vying to remove the tag of DIRTY OIL from our enviable source of energy but despite of all technical advancements especially in oil sands tailings management, it seems that the issue has not been fully addressed. More dedicated and joint efforts are the demand of hour to help industry flourish in a nation-wide acceptable manner.

Canada energy supply can be secured for more than 200 years if Alberta oil sands are fully utilized. Right now oil sands industry is the biggest single revenue generating source for Alberta. It has been estimated that there is about 1.7 trillion barrel of bitumen in these deposits [1]. Bitumen is recovered from the oil sands by either surface mining or by in-situ recovery methods. At present the surface mining is the process more extensively used to extract bitumen from oil sands. Mostly bitumen production is based on open pit mining. Typical bitumen recovery range is 88-95% depending on oil sands grade and origin.

Clark Hot Water Extraction (CHWE) is commercially used for the processing of oil sands ore to produce bitumen from oil sands ore [2]. CHWE is water intensive process and produces a huge volume of tailings, typically more than m³ of tailings are generated for production of each barrel of bitumen by mining operations [3]. In most of current commercial plants, tailings produced are pumped to large settling ponds referred to as tailings ponds. In tailings ponds, coarse solids settle quickly as sand beach while fine particles settle at extremely slow rate [4]. After an extended period of settling ultrafine solids form a stable suspension containing about 30 wt% solids, known as Mature Fine Tailings, MFT [5]. Further densification of MFT to a noticeable level could take decades if not centuries, leading to continuous accumulation of MFT at alarming rate. Containment of large volume of MFT is an industrial liability causing a great economic and environmental concern. Such a large volume of MFT adversely affects ecosystems and poses a risk to wild life in the surrounding area. To resolve MFT issues, the recently released ERCB directive [6] that sets the appropriate tailings management objectives for oil sands mines, requiring oil sands industry to: i) minimize and eventually eliminate long term storage of fluid tailings in the form of reclamation landscape; ii) create a solid landscape at the earliest opportunity to facilitate progressive reclamation; iii) reduce containment of fluid fine tailings in an external tailings disposal area during operation; iv) maximize intermediate process water recycle to increase energy efficiency and reduce fresh water intake; v) minimize resource sterilization associated with tailings ponds; vi) ensure that the liability for tailings is managed through reclamation of tailings ponds.

Slow consolidation rate of MFT has been identified as major handicap of the oil sands industry to its sustainable future. To develop environmentally friendly techniques to accelerate MFT consolidation

rate has stood out a real challenge for the industry. Among the many other technologies offering solution to MFT problem, the use of synthetic polymers as flocculants was also tried by the oil sands stakeholders to explore their applicability.

For better management of oil sands tailings in commercial oil sands operations, the settling characteristics of the fine solids must be improved by an economic and environmentally friendly approach. Several patents and reports describing techniques to increase the efficiency of the consolidation process are available in open literature. The proposed approaches can be summarized as: i) control slurry pH for the removal of suspended clay particles from water [7] [8]; ii) addition of flocculating agents to flocculate clay slimes from the extraction of Alberta oil sands [9]; iii) agglomeration of fines [8]; iv) bacterial enhanced-consolidation and biological dewatering of Athabasca oil sands sludge [10]; v) freeze thaw dewatering [11]; and vi) electrophoretically assisted gravitational settling [12].

These techniques can be applied individually or in combination to shift the segregation boundaries in composite tailings. The segregation characteristics have been manipulated by the addition of chemical additives. Tremendous efforts have been made jointly by government, industry and academics over the decades to investigate a variety of methods to de-water MFT. Through rigorous research and development initiatives a number of sound consolidation techniques have been evolved. Preliminary work aimed at reducing the oil sands tailings includes dry tailing filtration, centrifugation and other mechanical augmentation [13].

Composite Tailings (CT) process and Paste Technology are already in practice and have their own pros and cons. CT technology being employed by Suncor Energy and Syncrude Canada involves mixing a coarse tailings stream with a MFT stream and adding a coagulant to form slurry that rapidly releases water when deposited and binds the MFT in coarse tailings/ MFT deposit [14]. As a result of CT treatment, the slurry mix becomes non-segregating during transport, discharge and deposition. The solids retained within a homogenous and uniform deposit are initially soft and require Page | 3

containment. Over a short period of time an increase in strength to allow a relatively rapid reclamation is anticipated but CT containments require further reclamation to be converted into trafficable deposits [6]. Moreover use of gypsum results in increased salinity and sodium and sulphate content of recovered water [15].

Albian Sands Energy is the main user of Paste Technology to address oil sands tailings issue. In this technique, the fine tailings are flocculated by using synthetic and organic flocculants to produce a thickened material that seems to have the ability to consolidate to a dry landscape. It has been found that high molecular weight; medium charged anionic polymers are effective for flocculation of oil sands tailings. At low pH when clays tend to coagulate, the domain of a high initial settling rate and low solid content in sediment coincide. It has been also found that flocculation is much more efficient in the presence of divalent cations e.g. Mg²⁺ and Ca²⁺. Paste Technology offers warm water repossession for recycle in the bitumen extraction. The recovery of heat energy in the form of warm water reduces energy inputs and associated cost as well as diminishes the associated green house gases. Analytical analysis of recovered water reveals negligible effect of polymers on water chemistry [16]. Paste behaviour such as pumping, deposition and consolidation show that the paste could be pumped and piped for deposition. After being discharged, the paste forms a gentle slope (1.5-3%). The solids content and shear strength of the paste increased after deposition for a few days due to self weight consolidation and draining of water. Polymers flocculate the suspension through different mechanisms e.g. bridging and particle charge neutralization [17]. De-sanded Syncrude fine tailings were flocculated with Percol 727, the ISRs (slope of the initial linear portion of settling curve) were found low and the supernatant has relatively high solid content [18]. The effect of Al-PAM on flocculation of kaoline suspensions and mature fine tailings was already studied by some researchers. Their experiments revealed that staged polymer addition and stirring was beneficial to flocculation process [19].

The objective of this research study is to probe the potential of an in-house synthesized, organicinorganic hybrid polymer, Al-PAM as flocculating agent for MFT filtration, aiming at production of stackable solids and maximum recovery of the highest quality of process affected water for recycle. This is built on earlier studies [17] [20] where feasibility of filtration with proper filtration aids (flocculant) to treat as produced oil sands tailings was demonstrated. In one of the preceding studies [17], the filterability of the original oil sands tailings was found relatively low. It was proved that the flocculation of fines with a commercial anionic high molecular weight flocculant, partially hydrolyzed polyacrylamide (PAM), significantly improved the filterability by several orders of magnitude. Applying a similar flocculant to laboratory oil sands extraction tailings, a decreased filterability as compared with the case without flocculant addition was observed [20]. The observed reduction in filterability with the addition of commercial magnfloc1011 was attributed to its inability to flocculate ultrafine particles especially residual bitumen which blocks the pores of filter medium. Use of a cationic organic-inorganic hybrid polymer, Al-PAM improved the filterability significantly although the flocs formed by Al-PAM do not settle as fast as flocs formed by partially hydrolyzed PAM. This significant improvement is attributed to effective flocculation of ultrafine particles by Al-PAM as revealed by lower turbidity of supernatant of flocculated suspensions. These early studies demonstrated that filtration of the flocculated tailings is capable of producing stackable tailings of moisture content between 7 to 17 wt%, depending on the content of fine particles in the tailings [17] [20]. In addition, filtration allows a maximum amount of process water be recycled.

The filterability of the paste obtained as a result of polymer assisted flocculation whole oil sands tailings was examined in these studies [17] [20]. The filterability of paste was significantly higher than that of untreated original tailings [16]. The specific resistance to filtration, SRF, of the MFT suspension was also calculated and found two magnitudes lower than that without polymer addition [21]. The experiments to examine the effect of commercial Magnafloc and Al-PAM to improve the consolidation behaviour of model tailings, laboratory extraction tailings and tailings from paraffinic

froth treatment unit were conducted. It was found that Al-PAM improved the settling rate and filterability of froth treatment tailings significantly [20].

Not much work has been done to explore the prospects of pressure filtration to dewater flocculated MFT. For accelerated gravity settling and effective filtration, first step is to destabilize the MFT suspension, dilution assists MFT destabilization. In this study the performances of commercial magnafloc1011 and Al-PAM as flocculating aids for diluted MFT were compared and analysed. Sedimentation and filtration tests were conducted to assess settling and densification performance of polymers as MFT flocculating aids.

The ultimate aim of work is to demonstrate a novel process concept of MFT management and to identify the most favourable state of affairs for production of self-supportive deposits from MFT in terms of

- i) Type and dosage of polymer
- ii) Degree of MFT dilution
- iii) Process configuration

Chapter 2

MATERIALS AND EXPERIMENTS

Polymer assisted sedimentation has been long in use for flocculating the oil sands tailings. Filtration has been used traditionally for solid-liquid separation in many industries. First time filtration techniques was applied to oil sands tailings in mid 1990s on pilot scale tests. Filtration of coarse oil sands tailings requires high pressure and specific filtering media. In past, considering the huge inventory of tailings to be filtered and lack of stringent environmental regulations at that time, potential of filtration was not fully evaluated. In the view of current sterner environmental directive, oil sands tailings management groups are investigating the applicability of filtration process as an alternative of oil sands tailings disposal. Success of filtration to be implemented as commercially viable process depends upon its dewatering ability at affordable cost. In this research work simple laboratory-scale apparatus was used to evaluate the filterability of flocculated mature fine tailings. Since mature fine tailings is a stable suspension of fine clay and residual bitumen in water of complex chemistry so flocculation is essential to accelerate consolidation. Without any flocculating aid, gravity assisted settling is just marginal in MFT. Synthetic polymers are known for their best performance as flocculant. Polymer action is two folds one is to counteract the factors assisting the suspension formation and second to cause the particles come together to form agglomerate hereafter resulting in fast settling. Recovery of water from MFT by pressure filtration is labour intensive, costly and time consuming process. Addition of certain polymers is known to accelerate the filtration process by forming large, stable and dense flocs. Following sample of MFT and polymers were used during the course of current research work.

2.1 Mature Fine Tailings, MFT

The focus of current study was to test the concept of polymer assisted-filtration for treating MFT. For this purpose, an MFT sample from Syncrude Canada was used throughout the experiments. The composition of the original MFT sample was determined and results are given in Table 1.

Table 1	Composition	of Mature	Fine Tailings	(wt %)
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Water	Residual bitumen	Solid content	Fines content in solid
66	3	31	96*

* Particles of size < 44µm

The particle size distribution of the solids in MFT was determined using a Malvern Mastersizer 2000, Particle Size Analyzer. The results showed that 96% particles were smaller than 44 μ m and d₅₀ of the solid particles was 6.5 μ m.

For each set of tests, a subset of the samples was obtained by vigorously mixing the MFT using a mechanical mixer for 30 minutes prior to taking a representative sample of the original MFT under mixing into 3-L glass bottles.

2.2 Flocculants

In this study a commercial magnafloc1011 flocculant and in-house synthesized Al-PAM polymer were used as flocculants. Magnafloc1011, purchased from Ciba Specialty Chemicals, had an average molecular weight of about 17.5 million Daltons and ionic charge density of around 27% [22].

Al-PAM was synthesized in-house and its molecular weight was characterized by viscosity measurement. In Al-PAM molecule cationic core of $Al(OH)_3$ colloids get attached to negative sulphate ions from the initiator [23]. At 40 °C S₂O₈²⁻ combines with SO₃²⁻ to produce SO₄²⁻ which triggers the polymerization to yield $Al(OH)_3$ colloid particles [24]. In the preliminary work, Al-PAMs of different molecular weights and aluminum contents were used and the Al-PAM of intrinsic

viscosity of 750 cm/g was identified to perform the best. In the current study, this Al-PAM was used exclusively. Pertinent properties of both polymers are summarized in Table 2.

Properties	Al-PAM	Magnafloc1011
Structure	Al(OH) ₃ -PAM	Acrylamide-Acrylate Co-polymer
Molecular weight (Da)	$2.0 \mathrm{x} 10^{6}$	17.5x10 ⁶
Туре	Cationic	Anionic

 Table 2
 Characteristics of Polymeric flocculants used

2.3 MFT Dilution Water

Stable gel like structure of MFT does not allow proper addition of polymers for flocculation of the suspension. Addition of flocculants to raw MFT (31wt % solids) did not show any improvement on settling and filtration of the MFT. Even a dilution of MFT to 15 wt% solids with optimum dosage of flocculants did not exhibit any visible enhancement in both settling and filtration performance. Dewatering at measurable rates was observed only when the MFT was diluted to 10 wt% solids or less. Since water chemistry plays a crucial role in determining the consolidation behaviour of particles in a suspension so to rule out any effect of water chemistry on enhanced settling and filtration was used for MFT dilution. Tests were performed on raw MFT and MFT diluted to 15 wt%, 10 wt% and 5 wt% solids with the original MFT water unless otherwise stated.

2.4 Experimental Procedure

A detailed description of all the procedural steps involved in polymer addition, settling, filtration and calculation of suspension properties needs to be discussed and understood to ensure proper conduct of experiments and to get reproducible data.

2.4.1 Polymer Addition

The use of natural and synthetic polymers to destabilize the colloidal suspensions is a long practised technique. While synthesizing polymers, we have high degree of freedom to tailor them in terms of functional group, structure and molecular weight to suit a particular application as a flocculant. The only drawback of synthetic polymers is their high manufacturing cost and toxicity [24]. Preparation technique of polymer solution and the procedure for its addition to MFT suspension significantly affect its performance as flocculant so a well explained and understood method is to be used for stock solution preparation and its addition. For the experiments performed in this study stock solutions of 1000 ppm polymer concentration were prepared for both flocculants. To fully dissolve the polymers, the prepared magnafloc1011 stock solution was placed on a vibrating plate and Al-PAM solution on a mechanical shaker, both for 24 hours. The stock solutions were prepared one day prior to their use. For each set of tests fresh solution was used. MFT suspension was prepared by homogenizing 90 g of MFT slurry in a 250 mL beaker. The flocculation stock solutions were diluted to the desired concentration and added to the prepared MFT suspensions to a total of 100 g with pre-determined polymer dosage. In this study, the polymer dosages were expressed with reference to total suspension mass, unless otherwise stated. The diluted polymer solutions were added to MFT suspensions by following the three steps i.e. [25].

- Polymer stock solution was added at 0.1 mL/s addition rate to the prepared MFT suspension under agitation rate of 350 rpm
- The mixing was stopped as soon as polymer addition was complete
- The resultant suspension was transferred to a 100-mL graduated cylinder for settling measurements or 500-mL filter press for filtration tests

The extent to which flocculation could be achieved mainly depends upon polymer dosage. To maximize the efficiency of flocculation process as a whole, we need to establish the optimum dosage of polymer. It has been found that optimum dosage is function of particles surface area of the suspension to be flocculated. Fine particles suspension needs more polymer per unit weight of solid in the suspension to achieve a certain degree of flocculation.

For settling experiments, the cylinder was inverted three times and then placed on a bench. For most of the experiments filtration started instantaneously with the pouring of flocculated suspension to the filter press.



Figure 2.1 Mechanical stirrer

The term of polymer concentration w.r.t solids in suspension gives us a better idea where polymer is to be used more economically to achieve maximum consolidation. When the polymer dosage is given in g/ton of solid flocculated, it is easy to perceive how much cost would be involved to flocculate certain quantity of solid. To have a meaningful comparison of results with literature, the dosage of polymers has been expressed with respect to the total weight of the suspension not with respect solid in suspension. Mostly the polymer dosage was expressed with respect to total weight of the suspension but we can convert it with respect to the solids in suspension as follows.

50 ppm in MFT suspension of 5 wt% solids

Solids in 100 g of suspension = 5 g

Solids in 1 g of suspension = 5/100

Concentration of polymer with respect to solids in suspension = 50/(5/100) = 1000 ppm (g/ton) Similarly,

75 ppm in suspension of 10 wt% solids = 750 ppm (g/ton) with respect to solids in suspension 125 ppm in suspension of 15 wt% solids = 833 ppm (g/ton) with respect to solids in suspension 250 ppm in suspension of 30 wt% solids = 833 ppm (g/ton) with respect to solids in suspension

2.4.2 Settling Test

Quick formation of large and dense flocs with high mechanical strength is highly desirable and hence represents a better performance of polymer as flocculant leading to a rapid settling clear supernatant. For settling experiments, the cylinders with the flocculated suspensions were placed on a bench after inverting them three times. The height (h) of the mud line i.e. a clear supernatant-suspension interface was monitored as a function of settling time.

The settling curve was constructed by plotting normalized mud line height, h/H as a function of settling time (t), where H represents the initial height of the slurry. In general, the initial portion of settling curve was linear. The slope of this linear section of the settling was calculated and defined as initial settling rate (ISR). After the first five minutes of settling, 20 mL of supernatant was removed from the top of the graduated cylinder with the help of a syringe. The turbidity of this supernatant was measured with an HF-Micro laboratory turbidity meter (Matex Corp Ltd, NY, USA). Turbidity of the supernatant was expressed in Nephelometric Turbidity Unit (NTU).

The settling continued for one hour after which the entire supernatant was carefully removed. The sediment was weighed and then dried in an oven at 105 °C for 24 hours. The dried sediment was weighed again and its solid content was calculated. The effectiveness of a polymer as flocculant was quantified in terms of: i) initial settling rate (ISR) ii) turbidity of supernatant iii) solid content in the sediment after 1-hr settling

2.4.3 Filtration Test

A laboratory filter press of 500-mL capacity and 45.8-cm² filtration area was used in the filtration tests. Filtration tests were performed under a constant gauge pressure of 15 kPa. For each filtration test, the weight of the filtrate was continuously determined by an electronic balance interfaced with computer and recorded with custom-programmed filtration software. The cumulative mass of filtrate (m) was plotted as a function of filtration time (t), which is known as filtration curve. In general, initially the filtration rate (dm/dt) was relatively high and almost constant. As the filtration progressed to approach the break point, the filtration rate decreased sharply and approached zero to indicate completion of capillary filtration. In this study the filtration continued for one hour, after which the filter cake formed was dried in an oven at 105 °C to constant weight for moisture content analysis. The performance of polymers as filtration aid was evaluated in terms of initial filtration rate (i.e. the slop of the initial linear portion of the filtration curve), filtration time that was defined as the time to reach desired filter cake moisture content and resistance to filtration. For a better comparison with literature data, the specific resistance to filtration (SRF) was determined by following the procedures described in earlier studies [17]. The specific resistance to filtration is a quantitative measure of the filterability of a suspension. Assuming that the filter cake is incompressible and pressure drop is constant, the modified Darcy equation (Equation 2.1) could be used to calculate SRF.

$$t/V = (\mu_{\rm f.} SRF. c) V/(2. \Delta P.A^2) + (\mu_{\rm f.} R)/(\Delta P.A)$$
(2.1)

where

- $A = Area of the filter in m^2$
- $V = Collected filtrate volume in m^3$
- ΔP = Pressure drop in Pa
- $\mu_{f=}$ Viscosity of filtrate in Pa.s
- $R = Resistance of media in m^{-1}$
- c = Solid concentration in MFT suspension in kg/m³
- SRF = Specific cake resistance in m/kg



Figure 2.2 Laboratory filtration apparatus

2.4.4 Filtration of Sediments

A novel concept of coupling settling and filtration was proposed and tested to reduce filtration time and hence the load of filter press, the process showed enhanced Al-PAM performance. The idea was to thicken the diluted MFT by settling after flocculation, followed by filtration of the sediment aiming at reducing the volume liquid (filtrate) running through the filter cake and hence reducing the load on filter press and energy consumption for materials handling. This novel concept is referred to as flocculated aided two step filtration process that would be fully described in the next chapter. To test this concept, Al-PAM was added to diluted MFT suspension prior to settling. For most of the suspensions investigated in this study, one hour settling appeared to be sufficient to produce sediment with desired solids content. The thickened slurry (sediment) was filtered under the regular filtration conditions as used in filtration of flocculated MFT suspensions. Dewatering efficiency by filtration was measured in terms of filtration rate, filtration time and filter cake moisture content.

2.4.5 Water Recycle

A notable change in MFT treatment with the required dilution is the source of dilution water. In our flocculated aided two step filtration process, two streams of water were produced: supernatant in thickener and filtrate. Either of these two streams of water could be used for dilution of MFT. The tests were conducted to investigate suitability of supernatant as dilution water so that higher clarity filtrate could be recycled to bitumen extraction process.

Chapter 3

RESULTS AND DISCUSSION

In general effect of polymer addition on flocculation of raw MFT and MFT diluted to 15 wt% solids was negligible. When MFT was diluted to a higher dilution ratio, both settling and filtration rates of the diluted slurries improved significantly with increasing polymer dosages up to an optimal value after which a further increase in polymer dosage suppressed settling and filtration rates.

3.1 Settling3.1.1 Initial Settling Rate (ISR)

As shown in Figures 3.1 and 3.2, both commercial magnafloc1011 and in-house synthesized Al-PAM showed negligible effect on ISR of raw MFT. Dilution of MFT to 15 wt% solids also showed a little effect of polymer addition on its settling rate as it is evident from Figures 3.3 and 3.4. However, at dilution of MFT to 10 wt% and 5 wt% solids, polymer addition significantly improved the settling of diluted MFT; results are plotted as settling curves in Figures 3.5 - 3.8. The settling rates of MFT diluted to 10 wt% and 5 wt% solids were optimized with 100 ppm and 50 ppm magnafloc1011 addition that led to an ISR of 8.8 m/h and 28 m/h respectively. In case of Al-PAM 75 ppm and 50 ppm were identified as optimal dosages for MFT diluted to 10 wt% and 5 wt% solids respectively and the corresponding initial settling rates improved to 6.2 m/h and 18.2 m/h. Based on ISRs it is evident that at optimal dosages, magnafloc1011 is more effective than Al-PAM in flocculating MFT after proper dilution. Lower molecular weight of Al-PAM ($2x10^6$ Da) than that of magnafloc1011 ($17x10^6$ Da) appears to be the reason for its inferior performance while flocculating the diluted MFTs.



Figure 3.1 Settling curves of raw MFT (31 wt% solids) with MF1011 as flocculant



Figure 3.2 Settling curves of raw MFT (31 wt% solids) with Al-PAM as flocculant



Figure 3.3 Settling curves of diluted MFT (15 wt% solids) with MF1011 as flocculant



Figure 3.4 Settling curves of diluted MFT (15 wt% solids) with Al-PAM as flocculant



Figure 3.5 Settling curves of diluted MFT (10 wt% solids) with MF1011 as flocculant



Figure 3.6 Settling curves of diluted MFT (10 wt% solids) with Al-PAM as flocculant



Figure 3.7 Settling curves of diluted MFT (5 wt% solids) with MF1011 as flocculant



Figure 3.8 Settling curves of diluted MFT (5 wt% solids) with Al-PAM as flocculant

To have a close comparison of the performance of polymers at different dosages, ISRs of all the diluted MFT suspensions are plotted together for MF1011 in Figure 3.9 and for Al-PAM in Figure 3.10. As it is clear from these figures, both MF1011 and in-house synthesized Al-PAM could cause diminutive improvement on ISR of raw MFT. MFT diluted to 15 wt% solids also showed a little difference in settling behaviour with and without polymer addition. However, with MFT dilutions to 10 wt% and 5 wt% solids, polymer addition causes a major improvement on settling.



Figure 3.9 ISRs of MFT diluted to different factors with Magnafloc1011 as flocculant

The settling rates of MFT diluted to different factors were optimized by changing polymer dosage. For MFT diluted to 10 wt% solid, the fastest ISR was 8.8 m/h and 6.25 m/h for MF1011 at 100 ppm and Al-PAM at 75 ppm, respectively. In the case of 5 wt% solid suspension, the fastest ISR was 28 m/h and 18.2 m/h for magnafloc1011 and Al-PAM, respectively, both at 50 ppm. It is understandable that at optimal dosages, MF1011 is more effective than Al-PAM in flocculating MFT with same degree of dilution, if determined based on ISR.



Figure 3.10 ISRs of MFT diluted to different factors with Al-PAM as flocculant

3.1.2 Turbidity of Supernatant

Turbidity of the supernatant was expressed in NTU (Nephelometric Turbidity Unit). NTU is used as a surrogate for Total Suspended Solids (TSS). The higher, the NTU value is, the more turbid, the suspension is. Turbidity of supernatant was measured after five-minute settling of flocculated MFT suspensions. The supernatants from raw MFT and MFT diluted to 15 wt% solids remain highly turbid at all polymer dosages and their turbidities could not be measured by available turbidity meter. With proper dilution of MFT to 10 wt % and 5 wt% solids for both polymers, the turbidity of the decanted supernatant decreased with increasing polymer dosage up to an optimum value. A further increase in polymer dosage deteriorated water quality.



Figure 3.11 Turbidity of supernatant recovered from MFT diluted to 10 wt% solids with MF1011 as flocculant



Figure 3.12 Turbidity of supernatant recovered from MFT diluted to 10 wt% solids with Al-PAM as flocculant



Figure 3.13 Turbidity of supernatant recovered from MFT diluted to 5 wt% solids with MF1011 as flocculant



Figure 3.14 Turbidity of supernatant recovered from MFT diluted to 5 wt% solids with Al-PAM

In general turbidity values were lower for the supernatants recovered from MFT diluted to 5 wt% solids as compared to one that was taken from MFT with 10 wt% solids at their respective optimum dosage for both polymers. Slightly clearer water was recovered when Al-PAM was used as flocculant instead of magnafloc1011 in the same dosage. Turbidity measurements demonstrated that high dilution is favourable for producing better quality supernatant and Al-PAM is more effective than magnafloc1011 in flocculating fine particles despite magnafloc1011 could produce flocs that exhibit higher settling rate. How cationic nature of Al-PAM appears to facilitate flocculation of ultrafine particles is well explained in related literature [20]. In dominant mechanism of interaction, Al-PAM mainly reduces electric charges on the clay particles and bitumen globules and hence repulsion between negatively charged particles.



Figure 3.15 Turbidity of supernatant produced after settling of MFT with MF1011 as flocculant



Figure 3.16 Turbidity of supernatant produced after settling of MFT with Al-PAM as flocculant



Figure 3.17 Turbidities of supernatants recovered after sedimentation of diluted MFT with their respective optimum polymer dosages

The plots of turbidity vs. polymer dosage represent the performance of both MF1011 and Al-PAM on settling in terms of quantity of suspended solids in supernatant, water clarity. Results of experiments revealed that the optimum dosage for a particular suspension is same to achieve best quality of water as well as fastest ISR i.e. 100 ppm of MF1011 and 75 ppm Al-PAM for MFT diluted to 10 wt% solids and 50 ppm of both polymers for MFT diluted to 5 wt% solids, respectively.

After proper MFT dilution, turbidity of the decanted supernatant decreased with increasing polymer dosage up to optimum value suggesting the phenomenon of polymer overdosing. A further increase in dosage resulted in an increase in supernatant turbidity. For MFT diluted to 10 wt% solids, the lowest turbidity values were 162 NTU and 153 NTU for MF1011 at 100 ppm and Al-PAM at 75 ppm, respectively as shown in Figures 3.11& 3.12. In the case of MFT dilution to 5 wt% solids, the lowest turbidity values were 137 NTU and 127 NTU for MF1011 at 50 ppm and for both polymers as shown in Figures 3.13 & 3.14. Figures 3.15 & 3.16 show broad range variations in turbidity; here turbidity changes with solid concentration in suspension and polymer dosages for MF1011 and Al-PAM, respectively.



10 wt% solids175ppm, Al-PAM10

10 wt% solids 100ppm, MF1011

Figure 3.18 Supernatants produced after settling of MFT diluted to 10 wt% solids with optimum

dosages of polymer flocculants

Figure 3.17 summarizes the best case scenarios for each suspension with each polymer; it demonstrates that MFT dilution enhances the water quality in terms of suspended solid in ensuing supernatant. It is clear from relative values of turbidity at different dilution with their respective optimum dosages that high dilution is favourable for producing better quality supernatant and Al-PAM is more effective than MF1011 in flocculating fine particles especially residual hydrocarbons. In general Al-PAM produces relatively clearer supernatant as compared to magnafloc1011 performance at optimum dosage as shown in Figure 3.18. Dilution is expected to destabilize MFT structure and latter help flocculation.

Table 3	Initial	settling	rates	of	MFT	suspensions	and	turbidities	of	their	respective
	superna	atants at o	optimu	m p	olymer	dosages					

		ISR	Turbidity		
Polymers	Suspension solids content (wt %)	(<i>m/h</i>)	(NTU)		
Magnaflee 1011	10	8.8	162		
Magnajioc1011	5	28	135		
Al-PAM	10	6.25	156		
	5	18	127		

3.1.3 Solids Content of Sediment

Solid content of the sediment is another parameter to measure the performance of polymer as settling aid. Solid content of the sediment was determined after one hour of settling. Shorter settling time was not sufficient to produce sediment for most of the samples. Even an hour long settling, in case of raw MFT and MFT diluted to 15 wt% solids, could not yield sediment with maximum solid content as shown in Figures 3.19 & 3.20 irrespective of polymer dosage.



Figure 3.19 Solid content of sediment after settling of undiluted and diluted MFT with MF1011

as flocculant



Figure 3.20 Solid content of sediment after settling of undiluted and diluted MFT with Al-PAM as flocculant



Figure 3.21Solid content of the sediment formed by settling of MFT diluted to

10 wt% solids with MF1011 as flocculant



Figure 3.22Solid content of the sediment formed by settling of MFT diluted 5 wt% solids with
MF1011 as flocculant



Figure 3.23 Solid content of the sediment formed by settling of MFT diluted to 10 wt% solids with Al-PAM as flocculant



Figure 3.24 Solid content of the sediment formed by settling of MFT diluted to 5 wt% solids with Al-PAM as flocculant
The solid content of the sediments obtained from settling of 10 wt% and 5 wt% solids suspensions after flocculation with the corresponding optimum dosage of either polymer is the same at around 32-33 wt% solids as shown in Figures 3.21, 3.22, 3.23 & 3.24. The only difference is a shorter formation time of sediment for more diluted MFT. Within first hour of settling sediment reached to maximum solid content for 5 wt% and 10 wt% solids suspensions but when MFT was diluted to 15 wt% solids, the solid content of sediment was increasing even after one hour settling. Sediment was not formed when raw MFT was settled with any polymer dosage of either polymer. Table 4 suggests the consumption of Al-PAM is most economical for MFT suspension with 10 wt% solids to optimize the flocculation and hence solid content of the sediment. MFT diluted to 10 wt% solids stood out the most beneficial degree of dilution.



Figure 3.25 Sediments obtained under optimum conditions for Al-PAM (32 wt% solids)

These results show that use of the polymer in thickener is unlikely to release significant additional water from MFT. To produce stackable solids and release higher quality water from diluted MFT with flocculant addition, alternative enhanced dewatering techniques such as centrifugation or/and filtration are to be considered. In this study filtration was considered.

Weight of solid	Optimal polymer dosage	Optimal dosage	
_			Solid content in
		• • •	Sona content in
in suspension	pension with respect to total with respe		
			sediment (wt %)
(xxt 0/)	suspension (nnm)	solid (a/top)	
(wt %)	suspension (ppin)	sona (g/ton)	
5	50	1000	31.6
5	50	1000	51.0
10	75	750	32
15	125	833	25.6
20	250	0.22	20
30	250	833	30

Table 4Solid content of sediments obtained for different suspensions with optimum dosage of
Al-PAM

3.2 Filtration

Filtration tests were performed on laboratory scale filtration press. The performance of both polymers was measured in terms of initial filtration rate, filtration time and resistance to filtration. Since 10 wt% solids suspension of MFT was identified as appropriate dilution so most of the filtration tests were conducted with that slurry.

3.2.1 Filtration Rate

Filtration software plots the weight of filtrate (grams) vs. time (s) that was referred to as filtration curve. A comparison of filtration rates of the MFT suspensions with 5 wt% and 10 wt% solids with different polymer dosages are shown in Figure 3.26 when commercial magnafloc1011 was used as filtration aid. Results revealed that addition of magnafloc1011 adversely affects the filtration rate of MFT suspensions.

Typical filtration curves obtained with Al-PAM addition are shown in Figure 3.27. For a given suspension, filtration rate decreases with time and ultimately the filtration curve becomes parallel to time axis, indicating the completion of filtration. Although 5 wt% and 10 wt% solids suspensions

were mostly used for filtration tests yet Al-PAM was also tried on raw MFT and MFT diluted to 15 wt% solids. Even with optimum Al-PAM dosage, filtration rates of raw MFT and MFT diluted to 15 wt% solids was very slow. With further dilution, Al-PAM significantly improved filtration rate.



Figure 3.26 Filtration rate of MFT diluted to 10 wt% and 5 wt% solids with MF1011 as filtration aid

With MFT dilution to 10 wt% solids, filtration for 1000 s yielded 25 g of filtrate without polymer addition. Addition of 25 ppm, 50 ppm and 75 ppm of Al-PAM increased the filtration rate progressively, yielding 52 g, 67 g and 83 g filtrates, respectively when filtered for 1000 s.

A further increase in Al-PAM dosage to 100 ppm caused a slight decrease in filtration rate. In the case of dilution to 5 wt% solids, filtration for 1000 s yielded 35 g of filtrate without polymer addition. The addition of 25 ppm, 50 ppm, 75 ppm and 100 ppm yielded 74 g, 86 g, 65 g and 48 g of filtrate, respectively.



Figure 3.27 Filtration rate of MFT diluted to 10 wt% and 5 wt% solids with Al-PAM as filtration aid

Filtration results suggest that the optimum dosages of Al-PAM for MFT diluted to 5 wt% and 10 wt% solids are 50 ppm and 75 ppm respectively. Performance of Al-PAM as filtration aid on MFT diluted to 10 wt% and 5 wt% solids is shown in Figure 3.27. Filtration rates of MFT diluted to 10 wt% solids at its optimum dosages for the both polymers have been compared in Figure 3.28. The slope of the initial linear portion of the filtration curve is referred to as initial filtration rate, IFR. IFRs of MFT suspension having 10 wt% solids with various dosages of Al-PAM always excelled when compared with that of the same MFT suspension using same dosages of magnafloc1011 as

shown in Figure 3.28.



Figure 3.28 Filtration of MFT diluted to 10 wt% solids with different dosages of MF1011 and Al-PAM

3.2.2 Filtration Time

In the framework of this research, filtration time refers to the time for which filtration needs to continue to produce a cake with a preset moisture content. It was identified that a filter cake of 23 wt% moisture content produced from MFT is stackable and the filtration time to reach this moisture content in the cake was defined as filtration time. Strictly speaking, the moisture content could not be controlled to the same value for different experiments. In this study, it varied from 22 wt% to 23 wt% moisture.

The effect of MFT dilution on filtration time at their respective optimal Al-PAM dosage has been shown in Figure 3.29. For MFT diluted to 10 wt% solids, the shortest filtration time of 25 minutes

was achieved at 75 ppm Al-PAM. For MFT diluted to 5 wt% solids, the shortest filtration time of 19 minutes was recorded at 50 ppm Al-PAM.



Figure 3.29 Filtration time of diluted MFT with their respective optimal dosage of Al-PAM to produce a cake of 23 wt% moisture content

3.2.3 Specific Resistance to Filtration, SRF

Specific resistance to filtration of a suspension is an important parameter to measure the performance of a polymer as filtration aid. In deep bed filtration, rate of filtration declines with passage of time but SRF is supposed to remain the same throughout filtration. Ideally plot of t/V vs. V should be a straight line, provided that the filter cake is incompressible. In reality compaction of the filter bed occurs and slop of the plot is no longer constant and hence the SRF. Practically it is very difficult to determine average value of SRF. In fact the SRF increases as filtration progresses. It was suggested that the sedimentation during filtration can influence the measured value of average specific cake resistance [8]. Since MFT suspension with 10 wt% solids was identified as the best degree of dilution to optimize the effect of Al-PAM, the SRF values were calculated for that suspension at different polymer dosages. In our study typical filtration curves, t/V against V, were plotted and slope of the trend lines were determined as shown in Appendix A. These slope values are used to calculate the specific resistance to filtration as follows.

SRF = $(2. \Delta P.A^2) \times b / (\mu_f.c)$

where

SRF = Specific resistance to filtration

 $\Delta P = Pressure drop = 15 \times 10^3 Pa$

A = Area of filter = $45.8 \times 10^{-4} \text{ m}^2$

 μ_f = Viscosity of filtrate = 1× 10⁻³ Pa.s

c = Concentration of solid in suspension (kg/m³)

Mass of solids (kg)

Volume of water (m^3) + Volume of solids (m^3)

_	10
_	(0.09 + 10/2650)
=	106.64 kg/m^3

Density of water = 1000 kg/m^3

Density of solids = 2650 kg/m^3

 $b = Slop of t/V against V plot = t/V^2$

V= Volume of filtrate after time t (m^3)

Sample calculation:

Here is the calculation of SRF for MFT suspension diluted to 10 wt% solids with 75 ppm Al-PAM.

$$SRF = 2 \times 15 \times 10^{3} \times (45.8 \times 10^{-4})^{2} \times 8.98 \times 10^{10} / (1 \times 10^{-3} \times 106.64)$$

 $= 5.30 \times 10^{11} \text{ m/kg}$

The calculated SRF values are summarized in Table 5. SRF of MFT suspension diluted to10 wt% solids was calculated as 3.46×10^{12} m/kg when filtered without any polymer aid. The use of mangnafloc1011 caused an increase in average value of SRF no matter what dosage was employed. On the contrary to magnafloc1011, Al-PAM significantly decreased the SRF; minimum value was found when 75 ppm of Al-PAM was used i.e. 5.30×10^{10} m/kg.

Specific Resistance to Filtration, SRF MFT Suspension Slope of t/V vs. V plot (m/kg)No polymer aid $5.87 imes 10^{11}$ 3.46×10^{12} 25 ppm Magnafloc1011 9.94×10^{11} 5.86×10^{12} 50 ppm Magnafloc1011 1.96×10^{12} 1.16×10^{13} 75 ppm Magnafloc101 2.60×10^{12} 1.53×10^{13} 100 ppm Magnafloc1011 5.4×10^{12} 3.91×10^{13} 25 ppm Al-PAM 2.71×10^{11} 1.59×10^{12} 50 ppm Al-PAM 1.46×10^{11} 8.61×10^{11} 75 ppm Al-PAM 8.98×10^{10} 5.30×10^{11} 100 ppm Al-PAM 6.55×10^{11} 1.11×10^{11}

Table 5Calculated SRF of MFT suspensions diluted to 10 wt% solids at different polymer
dosages as filtration aids

3.3 Filtration of Sediments

Although flocculation-assisted filtration of diluted MFT by Al-PAM seems promising yet the filtration of a large volume of diluted MFT to a desirable cake moisture content of 23 wt% requires a considerably long filtration time. There was a need to reduce the filtration time to the level that is practically acceptable to industry. Here the idea was to filter a much smaller volume of sediments

after flocculation and thickening of diluted MFT. With this approach, the dilution can be accomplished by the clarified water recovered from the original MFT after flocculation and thickening without using water from external sources. The filtrate would represent a net water recovery from MFT. As shown in Figure 3.31, applying this concept to an MFT diluted to 10 wt% solid reduced filtration time from 25 minutes to 8 minutes to produce a cake of 23 wt% moisture, representing a significant time reduction. In the case of MFT dilution to 5 wt% solids, the filtration time was reduced from 19 minutes to 7 minutes. The shorter filtration time of the sediments as compared to straight filtration time could be anticipated as a majority of fluid (~2/3) in the diluted MFT would not run through the filter press, and any adverse effect of un-flocculated ultrafines remaining in suspensions (supernatant) could be avoided, leading to minimal blinder of filter cake and filter media.



Figure 3.30 Specific resistance to filtration (SRF) of MFT diluted to 10 wt% solids as a function of Al-PAM dosage

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As shown in Figure 3.32, the filtrate was clearer than water recovered after settling. In general the sediment, after flocculation and thickening, remained fluid. In contrast the filtration cake of 23 wt% moisture content is clearly shown in the inset of Figure 3.32 seems to be stackable. More interestingly, filtration of sediments could minimize fouling of filter media, which is major concern of practical application of filtration to oil sands tailings. The essence of the present study recommends that flocculation-assisted sediment filtration is a viable solution to treat existing inventory of MFT.

The shorter filtration time of the sediments could be accredited to MFT suspension getting fully flocculated in the form of sediment i.e. Flocculation gets completed before filtration starts .Only one third of MFT diluted volume is to be filtered.



Figure 3.31 Comparison of filtration time for diluted MFT and corresponding thickened sediments after flocculation at optimal Al-PAM dosage to produce cake (23 wt% moisture)



Figure 3.32 Comparison of release water clarity by thickener and filtration and fluidity of sediments and filter cake (inset)

3.4 Water Recycling

MFT dilution at first glance, may appear strange when the objective of MFT treatment aims at dewatering. However, if part of the clarified water could be used as dilution water, the process itself would generate net gain of water for recycling. As shown in Fig 3.33, filtration of sediment after flocculation and thickening produces two streams of water: clarified supernatant and filtrate. It is desirable to use the clarified water recovered from settling as MFT dilution water.

In this scheme recycle of any residual Al-PAM, if present in the clarified water, would reduce Al-PAM consumption per unit MFT treated. This hypothesis was tested by conducting the sediment filtration tests using the clarified water as MFT dilution water. The results in Figure 3.33 show a slight decrease in filtration time by diluting MFT with the clarified water (supernatant of settling) for the first two cycles, confirming the presence of residual Al-PAM in the clarified water and its beneficial effect on flocculation of diluted MFT. However, a slight increase in filtration time was observed for MFTs diluted to 10 wt% solids using the clarified water from the 3rd to 5th cycles. The observed increase in filtration time could be interpreted as an indication of continuous accumulation of residual Al-PAM in the clarified water, which may have exceeded the optimal dosage and hence affected the flocculation/filtration adversely. It is also suspected that the ultrafine particles get built up in the clarified water as the recycling progressed. The presence of ultrafine particles is known to have an advert effect on filtration performance. From this study, we have demonstrated that the flocculation assisted two-step filtration process as shown in Figure 4.1 is a vital alternative for treating large volume of MFTs from oil sands processing.

Table 6	Water recycling and utilization of residual polymer for MFT suspension diluted to 10
	wt% solids

	Time taken to produce filtration cake with 23 wt% moisture content					
Polymer dosage	(min)					
	Number of water recycle					
	1	2	3	4	5	6
75 ppm	10.5	10	9	11	13.5	
50 ppm	15	14	13	12.6	12.5	13

Different dosages of Al-PAM were used to evaluate the effect of water recycling on filtration time. When 50 ppm of Al-PAM was used on 10 wt% solid suspension, initial few recycles showed progressively shortening filtration time. It took more cycles before it started influencing the filtration negatively as compared to 75 ppm of Al-PAM.



Figure 3.33 Effect of water recycling on filtration time



Filtrate10 wt% solids 100ppm, Al-PAM Supernatant 10 wt% solids 75ppm Al-PAM Supernatant 10% solids 100 ppm, MF101





Figure 3.35 Filtration cake with 23% moisture



Figure 3.36 Oven dried filtration cake

3.5 Results analysis

Although commercial magnafloc1011 performed slightly better than Al-PAM in settling so far ISR is concerned but it could not boost dewatering of MFT by filtration as shown in Figure 3.26. MF1011 seemed increasing the specific resistance to filtration, probably because it emulsified the residual bitumen. In contrast to magnafloc1011 behaviour, Al-PAM was found effective in enhancing filtration of diluted MFT as it is obvious from its filtration curves in Figure 3.27. Initial filtration rate (IFR) and resistance to filtration (RTF) as a function of Al-PAM dosage at different MFT dilution ratios are shown in Figures 3.28 and 3.30 respectively. At 10 wt% solids suspension of MFT, increasing Al-PAM dosage up to 75 ppm significantly improved IFR and reduced SRF. A further increase in Al-PAM dosage to 100 ppm resulted in a slightly less significant improvement in both IFR and SRF. Without flocculant addition, for example, the SRF of MFT suspension diluted to 10wt% solids was determined to be 3.46×10^{12} m/kg. The addition of Al-PAM at its optimal dosage of 75 ppm reduced SRF significantly to 5.30×10^{11} m/kg. This value of SRF is comparable to the value of low fines whole tailings at optimal Al-PAM dosage of 10 ppm [20] indicating that with proper dilution and flocculation, filtration can be equally well applied to treating MFT.

One of the outcomes of settling experiments was turbidity measurements of the supernatants recovered from different MFT suspensions which revealed that an increase in Al-PAM dosage from 75 ppm to 100 ppm led to a slight increase in supernatant turbidity from 156 NTU to 170 NTU. It further reinforces that the presence of ultrafines remaining in suspension after flocculation is detrimental to filtration and emphasizes the importance of effective flocculation of ultrafines in improving filtration of flocculated suspensions i.e. diluted MFT in this case.

Since the objective of MFT filtration is to produce stackable solids with required solid content, the filtration results were also compared in terms of filtration time that was defined as time required to produce a filter cake of specified moisture content. In this study, it was identified that a filter cake

with 23 wt% moisture content produced from diluted MFT is stackable and the time to reach this moisture content is referred to as the filtration time.

The effect of MFT dilution on filtration time at optimal Al-PAM dosage is shown in Figure 3.29 for MFT diluted to 10 wt% solids, the shortest filtration time of 25 minutes was achieved at 75 ppm Al-PAM. For MFT diluted to 5 wt% solids, the shortest filtration time of 19 minutes was recorded at 50 ppm Al-PAM. Although the dilution of MFT to 5 wt% solids produced a filter cake of 23 wt% moisture at a slightly shorter filtration time at lower Al-PAM dosage but from practical prospective, MFT dilution to 10 wt% solid would represent an optimum dilution ratio to provide a better overall filtration performance. On the basis of treating a given volume of raw MFT, for example, dilution of MFT to 5 wt% solids would need 33% more Al-PAM dosage at 50% longer filtration time as compared to the case of MFT dilution to 10 wt% solids. Although the dilution of MFT to 5 wt% solids produced a filter cake of 23 wt% moisture at a slightly shorter filtration time at lower Al-PAM dosage yet MFT diluted to 10 wt% solids stayed best dilution to provide a better overall filtration performance as it could treat a larger volume of raw MFT (3 vs. 2 units of raw MFT) at a lower Al-PAM dosage (75 ppm vs. 100 ppm Al-PAM per unit volume of raw MFT). Exceptionally good performance of Al-PAM as filtration aid could be attributed to its molecular structure. Star like structure of Al-PAM [27] presents considerably larger area for clay particles attachment. Al-PAM necessitates the formation of large, spherical and dense flocs which do not chock filtering media. Highly cationic core of Al-PAM ensures effective bridging among emulsified bitumen droplets. Stable bitumen flocs were identified when extraction was done with Al-PAM addition [28]. Magnafloc1011 seems unfavourably affecting filtration due to its inability to flocculate residual hydrocarbons. Irregular clay flocs produced by mangafloc1011 block the pores of filtering medium [20]. On the other hand Al-PAM also alters the interfacial properties of bitumen (making more hydrophobic) and facilitates cohesion of bitumen droplets.

Chapter 4 CONCLUSIONS

Filtration experiments revealed the superior nature of Al-PAM as flocculating agent when used as filtration aid which could be rightfully attributed to molecular structure and chemistry of the polymer. An overview of research background to meet the tailings management objectives can give us a better understanding of Al-PAM performance as filtration aid. The usefulness of any polymer as filtration aid for MFT suspension probably stems from its ability to flocculate both residual bitumen and clay particles. Kotlyar group determined that sub micron particles of kaolinite and mica were the key crystalline components of the colloidal solids in the oil sands tailings, it was also discovered that colloidal particles are coated with polar organic matter [25] [29]. Superior flocculating performance of Al-PAM as compared to that of commercial magnafloc1011 is quite evident from the results of present study. MF1011 appeared increasing the specific resistance to filtration of the MFT suspension. In case of Al-PAM creation of dense, large and stable flocs could be attributed to electrostatic attraction between the positively charged core of Al-PAM molecule and oppositely charged fines and possible hydrogen bonding that exists between hydroxyl group on clay and amide group on the polymer surface [22] [30]. Moreover star-like molecular structure of Al-PAM offers extended surface area for the attachment of clay particles [23]. MFT used for this study contains 3% residual bitumen which is believed to be negatively affecting flocculation of the suspension. Asphaltene present in bitumen gets emulsified and encapsulates tiny droplets of water. Although asphaltene flocs are mechanically enough strong yet they contains substantial amount of water [31].

Al-PAM seems increasing the hydrophobicity of emulsified bitumen droplets which in turn helps them flocculate [30]. The nature of bitumen surface properties are mainly fashioned by pH of the suspension, generally bitumen droplets are negatively charged in alkaline solutions [32]. Long range repulsive interactions among emulsified bitumen droplets keep them apart constituting a stable suspension. Introduction of Al-PAM helps bridging the dispersed bitumen globules by attaching them around the periphery of its molecule due to highly cationic core. Consequently stable spherical flocs of bitumen are formed which are too large to fit into pores of the filtering media so enhance the filtration process. On the other side commercial magnafloc1011 did not show any ability to flocculate the residual emulsified bitumen. Two forces have been identified among coarse (sand) and fine (clay) particles present in MFT i.e. long range repulsive force and adhesion force. The relative strengths of these forces shape the overall interaction among sand and clay particles. Clay particles and silica don't experience adhesion force without polymer aid, the only force exists between them is long rang repulsion [33]. Al-PAM strengthens adhesion and suppresses long range repulsion resulting into overall attraction among clay and sands which flocculates them. A quantitative analysis of these forces was made and studied how the magnitudes of these forces vary with Al-PAM dosages [20]. Overdosing of polymer causes stearic stabilization of fine clay particles which leads to inhibition of filtration process [17]. Most of the researchers found that the polymer addition has negligible effect on water chemistry [34]. Presence of residual hydrocarbons is believed to have its role in stabilizing the MFT suspension. Water recovered from Al-PAM treated MFT may have some residual polymer that could restrict its use in subsequent bitumen extraction process so its chemical analysis is required.

A similar study was conducted on model tailings, laboratory extraction tailings and paraffinic froth treatment tailings [20]. The objective of their research work was to explore the potential of Al-PAM to improve the dewatering characteristics of real oil sands tailings. Previous study revealed the usefulness of Al-PAM as flocculant for settling and filtration of aforementioned kind of tailings [20]. To assess the applicability of her research work on real oil sands tailings Lina et al. continued her

work. Lina's experimental work is done on real fresh oil sands tailings mainly to determine the effectiveness of Al-PAM as filtration aid.

General understanding of the effect of residual hydro carbons can be summarized as:

- The MFT is stabilized by the water-soluble asphaltic acids present in the residual bitumen.
- The residual bitumen in MFT may have some adverse effect on the filtration by blinding the filter medium.
- Elimination of the fine bitumen drops must be considered while filtering the Mature Fine Tailings (MFT).

One of our group fellows successfully recovered the residual hydrocarbons from MFT by Column Floatation and then by Denver Cell [35]. To achieve a reasonable hydrocarbons recovery he had to dilute MFT to 10% solid before applying the recovery process. Actually present work is also an integral part of a broad range research activity aims at improving the dewatering characteristics of oil sands tailings. This endeavour is contemporary to another study [35] performed for hydrocarbons recovery and Lina's work on Al-PAM application on fresh oil sands tailings. In fact we were working on different aspects of same industrial problem. Luckily I got hydrocarbons free slurry from contemporary experiments being performed by fellow researcher so I was able to carry out settling and filtration experiments on MFT diluted to same degree before and after hydrocarbons recovery does not help improve MFT consolidation yet it paved the way for future research. The results of my experiments show the better response to flocculation of just diluted MFT as compared to hydrocarbons free slurry. We need to develop underlying scientific theory to support the observations, but at hand I can attribute this anomaly to the following factors:

• Reduction in overall d₅₀ during the hydrocarbons recovery process

- Only column floatation treated slurry of 80% hydrocarbon recovery was used. The rest of the unrecovered 20% hydrocarbons got emulsified in the treated MFT.
- Difference of water chemistry may have led to unexpected results.

In other study process water was used for MFT dilution prior to recovery process [35]. In this study, the water extracted by pressure filtration from same MFT was used for MFT dilution. When comparing these two slurries the variable of water chemistry was not accounted for.

Since hydrocarbons removal does not improve MFT consolidation, the emphasis was laid on determining the effect of polymers on just diluted MFT without removing the residual bitumen.

A variety of Al based PAMs could be prepared with varying flocculating capabilities. The compositions of Al-PAM synthesized in house were characterized by viscometry. The Al-PAM with best flocculating capability got the viscosity value 750g/cm that is the one I used throughout my work.

Since none of the polymer worked satisfactorily on raw MFT (31 wt% solids) so there was no option left except diluting the MFT to get polymer working. MFT diluted to 5 wt% and 10 wt% solids represent appropriate degree of dilution to highlight the effect of polymers as flocculants. MFT dilution may appear strange when the research aims at dewatering but the process runs in cycle, so once it gets started water not needs to be introduced externally. The superior nature of magnafloc1011as settling aid stood out from my experimental work. Settling as a sole consolidation process could not produce sediment with solid content more than what was in original raw MFT even under most favorable conditions. Moreover supernatant was too turbid to be safely recommended for subsequent bitumen extraction process. Magnafloc1011 simply does not help filtration so most of the experiments were performed on Al-PAM assisted filtration.

Al-PAM performance was measured in terms of polymer dosage, filtration rate, specific resistance to filtration, moisture content of the filtration cake and filtration time to get cake with least moisture.

Considering the above performance parameters, MFT diluted to 10 wt% solids stood out the best option to achieve objective of the work. When MFT diluted to 10 wt% solids was filtered with 75ppm of Al-PAM, a filtration cake with moisture content of 23% was formed after a 25minutes filtration. For the further reduction of filtration time a two stage dewatering technique was introduced. In the first stage MFT diluted slurry was flocculated and thickened by settling followed by filtration of sediments. Filtration time could be shortened considerably by this technique i.e. a filtration cake with 23 wt% moisture was formed in 10 minutes when 10 wt% solids slurry was filtered with 75ppm Al-PAM. Here we recover water in two streams i.e. supernatant and filtrate. Supernatant is used for dilution of subsequent batch of MFT whereas filtrate is net water recovery. Residual Al-PAM was suspected and then proved in first water stream. While we are using supernatant for MFT dilution residual Al-PAM automatically gets utilized. We may need to reoptimize the polymer dosage after certain number of water recycles. After couple of water recycles an adverse effect on filtration time was noted which could be attributed to accumulation of fines when supernatant is used over and over again for MFT dilution.

Enhancement of MFT dewatering requires destabilization of gel-like MFT structure and fine particles aggregation by improving attractive interactions among them. In present study, stable MFT structure was destroyed by MFT dilution while polymers were used to flocculate the solid particles. An ideal flocculant should have the capability to flocculate fine particles effectively, producing large and porous flocs of high water permeability. It appears that Al-PAM is capable of accomplishing these objectives due to its cationic nature of imbedded aluminum hydroxide colloids. The effective flocculation of ultrafine particles was confirmed by lower turbidity of supernatant after settling of diluted MFT with Al-PAM addition than with magnafloc1011 addition. MFT diluted to 10 wt% solids was found to achieve optimal results. Integrated with water management, the clarified water can be used to dilute raw MFT and clear filtrate generated for recycle in bitumen extraction, reducing

fresh water intake for the process. In Figure 4.1, the process diagram of this novel MFT management scheme is compared with conventional thickening or filtration processes.



Figure 4.1 Schematic flow diagram of a single stage filtration (plain section) and two stage (shadowed section) filtration of flocculated sediment

Chapter 5

RECOMMENDATIONS FOR FUTURE WORK

- Conduct a study to investigate the effect of different hydrocarbons recovering techniques on MFT characteristics.
- 2- Repeat the present research work by using process water instead of water extracted from MFT to assess the absolute efficacy of hydrocarbons removal on subsequent MFT dewatering process.
- 3- Carry a literature review to support the fact that magnafloc1011 is an excellent settling aid but fails to improve filtration.
- 4- Present study was conducted on high fines MFT (95 wt%, fines). A study needs to be made on comparative response of Mature Fines Tailings with different characteristics e.g. low fines MFT, high fines MFT, MFT with varying content of residual bitumen.
- 5- Study the correlation between filter pore size and filtration rate in context of hydrocarbons free slurry.
- 6- Probe the presence of residual polymer in recycling water (filtrate) and its influence on subsequent filtration process.
- 7- After a certain number of water recycles, residual polymer seems to deteriorate filtration process which could be attributed to the accumulation of fines. To rule out the adverse effect of fines accumulation, low fine MFT should be used to repeat the experiments

REFERENCES

- [1] Alberta Energy and Utilities Board, *Alberta's Energy Reserves and Supply Outlook 2006–2015*, 2006.
- [2] Clark, K.A., Pasternak, D.A., "Hot Water Separation of Bitumen from Alberta Bituminous Sand", *Industrial and Engineering Chemistry*, 24: p.1410-1416, 1932.
- [3] Peachey, B., "Strategic Needs for Energy Related Water Use Technologies", *Alberta's Environment Conference*, 2005.
- [4] Fine Tailings Fundamental Consortium (FTFC), "Advances in Oil Sands Tailings Research",
 Alberta Department of Energy, Edmonton, Alberta, 1995.
- [5] Cymerman, G., Kwong, T., Lord, T., Hamza, H., Xu, Y., "Thickening and Disposal of Fine Tails from Oil Sands Processing", *The 3rd UBC-McGill International Symposium on Fundamentals of Mineral Processing (CIM)*, Quebec City, 1999.
- [6] ERCB *Backgrounder on Draft Directive: "*Tailings Performance Criteria and Requirements for Oil Sands Mining Schemes", 2008.
- [7] Baillie, R.A., Malmberg, E.W., "Removal of Suspended Clay Particles from Water", U.S. Patents 3,487, 003, 1969.
- [8] Moschopedis, S.E., Parkash, S., Speigh, J.G., "Thermal Decomposition of Asphaltenes" *Fuel and Energy Journal*, 1977.
- [9] Kessick, M.A., "Structure and Properties of Oil Sands Clay Tailings", *Journal of Canadian Petroleum Technology, Alberta Research Council,* Edmonton, Alberta, 1979.
- [10] Li, X., Slaski, J.J., Feng, Y., Fung, M., "Evaluation of Capability of Aggregated Oil Sands Mine Tailings; Biological Indicators", *Journal of Canadian Petroleum Technology* 42(9): 47-50, 2003.

- [11] Rush, R.J., Stickney, A.R., "Natural Freeze-thaw Sewage Sludge Conditioning and Dewatering", Canada Environmental Protection Services, EPS 4-WP-79-1, 1979.
- [12] Flintoff, B.C., Plitt, L.R., "The Electrophoretic Clarification of Colloidal Suspensions", *Canadian Metallurgical Quarterly*, 1976.
- [13] Liu, J.K., Stephen J., Cymbalisty, L.M., "Filtration of Hot Water Extraction Process for Whole Tailings", *CA 1103184*, Canada, 1981.
- [14] Caughill, D.L., Morgenstern, N.R., Scott, J.D., "Geotechnics of Non Segregating Oil Sands Tailings", *Canadian Journal*, 30(5): p.800-812, 1993.
- [15] MacKinnon, M.D., Matthews, J.G., Shaw, W.H., Cuddy, R.G., "Water Quality Issues Associated with Composite Tailings Technology for Managing Oil Sands Tailings", *International Journal of Surface Mining, Reclamation and Environmental*, 2001.
- [16] Xu, Y., Cymerman, G., "Flocculation of Fine Oil Sands Tails", Proceedings of the UBC-McGill Bi-Annual International Symposium on Fundamentals of Mineral Processing, 3rd, Quebec City, Canada, 22-26, 1999.
- [17] Mpofu, P., Addai-Mensah, J., Ralston, J., "Flocculation and De-watering Behaviour of Smectite Dispersions: Effect of Polymer Structure Type", *Minerals Engineering*, 2004.
- [18] Sworska, A., Laskowski, J.S., Cymerman, G., "Flocculation of the Syncrude Fine Tailings, Effect of pH, Polymer Dosage and Mg²⁺ and Ca²⁺ Cations", *International Journal of Mineral Processing*, **60**(2): 143-152, 2000.
- [19] Ezeagwula, E. K., "Studies on Flocculation of Kaolin Suspensions and Mature Fine Tailings", M.Sc thesis, Department of Chemical and Material Engineering, University of Alberta Edmonton, 2008.
- [20] Wang, X., "Polymers Aids for Settling and Filtration of Oil Sands Tailings", M.Sc thesis, Department of Chemical and Material Engineering, University of Alberta Edmonton, 2010.

- [21] Xu, Y., Hamza, H., Matthews, J., "Enlargement of Fine Particles in the Oil Sands Industry Flocculation and Thickening, Particle Size Enlargement in Mineral Processing", Proceedings of the UBC-McGill Biennial International Symposium on Fundamentals of Mineral Processing, 5th, Hamilton, ON, Canada, 22-25, 2004.
- [22] Somasundaran, P., "Encyclopaedia of Surface and Colloid Science", 2nd edition, Vol. 4. CRC
 Press, Taylor & Francis Group, 2006
- Yang, W.Y., Qian, J.W., Shen, Z.Q., "A Novel Flocculant of Al (OH)₃₋ Polyacrylamide Ionic Hybrid", *Journal of Colloid and Interface Section*, 273(2): p. 400-410, 2004.
- [24] Yang, W.Y., Qian, J.W., Shen, Z.Q., Zhao, Xing-jun., "Synthesis and Characterization of Al(OH)₃ – PAM hybrid Flocculants", *Gaofenzi Cailiao Kexue Yu Gongcheng*, 20(1), 2004.
- [25] Kotlyar, L.S., Deslands, Y., Sparks, B.D., Hodama, H., Schuttle, R., "Characterization of Colloidal Solid from Athabasca Fine Tails", *NRC Publications Archives*, 41(3): p. 341-345, 1993.
- [26] Yim, S.S., Song, Y.M., "Problems in Measuring Average Specific Cake Resistance", Department of Environmental Engineering, Inha University, Korea, 2000.
- [27] Yang, W.Y., Qian, J.W., Shen, Z.Q., "A Novel Flocculant of AI(OH)₃-Polyacrylamide Ionic Hybrid", *Department of Polymer Science and Engineering Zhejiang University*, Hangzhou, China, 2004.
- [28] Kotlyar, L.S., Sparks, B.D., and Kodama, H., "Isolation and Characterization of Organic-rich Solids Present in Athabasca Tailings Pond Sludge", *AOSTRA Journal of Research*, 6(1), 1990.
- [29] Kotlyar, L.S., Sparks, B.D., Capes, C.E., Schutte, R., "Biwetted, Ultrafine Solids and Structure Formation in Oil Sands Fine Tailings", *Institute for Environmental Research and Technology*, National Research Council of Canada, Ottawa, Canada, 1995.
- [30] Long, J., Li, H., Masliyah, J.H., Xu, Z., "Novel Polymer Aids for Low-grade Oil Sands Ore Processing", *The Canadian Journal of Chemical Engineering*, 86(2): p. 168-176, 2008.

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- [31] Long, Y., Hamza, H., Dabros, T., Yang, X., Xu, Y., "Zone Settling Aid and Method for Producing Dry Diluted Bitumen with Reduced Losses of Asphaltenes", *Champion Technologies Inc.*, USA. Application: CA, 2006.
- [32] Yusa, M., "Mechanisms of Pelleting Flocculation", International Journal of Mineral Processing, 1977.
- [33] Long, J., Li, H., Masliyah, J.H., Xu, Z., "Role of Colloidal Interactions in Oil Sands Tailings Treatment", *AlChE Journal*, **52**(1), 2006.
- [34] Kotlyar, L.S., Sparks, B.D., Woods, J.R., "Understanding of Fundamentals: Key to Process Modification for Tailings Reduction", *Journal of Environmental Science and Health, Part A: Environmental Science Engineering*, A28 (10), 1993.
- [35] Thomas, T.E., "Hydrocarbons Recovery from Waste Streams of Oil Sands Processing", *M.Sc thesis, Department of Chemical/Materials Engineering,* University of Alberta, 2011.
- [36] Chase, R. P., "Settling Behaviour of Natural Aquatic Particulates", *Department of Geophysical Sciences*, University of Chicago, Illinois, USA, 1979.
- [37] Fine Tailings Fundamental Consortium (FTFC), "Advances in Oil Sands Tailings Research", Alberta Department of Energy, Edmonton, Alberta, Canada. 1995.
- [38] Kaminsky, H., "Characterization of an Athabasca Oil Sands Ore Process Stream", PhD Thesis, University of Alberta, Edmonton, Canada, 2008.
- [39] Kasongo, T., Zhou, Z., Xu, Z., Masliyah, J. H., "Effect of Clays and Calcium Ions on Bitumen Extraction from Athabasca Oil Sands Using Flotation", *The Canadian Journal of Chemical Engineering*, 78, 674 – 681, 2000.
- [40] Masliyah, J. H., Zhiang, Z., Xu, Z., Czarnecki, J., Hamza, H., "Understanding Water-based Bitumen Extraction from Athabasca Oil Sands", *The Canadian Journal of Chemical Engineering*, 82, 628-654, 2004.

APPENDIX A





Fig 1 t / V Vs. V plot for MFT diluted to 10 wt% solids without polymer





Fig 2 t / V Vs. V plot for MFT diluted to 10 wt% solids with 25 ppm Magnafloc1011





Fig 3 t / V Vs. V plot for MFT diluted to 10 wt% solids with 50 ppm of Magnafloc1011

d.



Fig 4 t / V Vs. V plot for MFT diluted to 10 wt% solids with 75 ppm of Magnafloc1011

e.



Fig 5 t / V Vs. V plot for MFT diluted to 10 wt% solids with 100 ppm of Magnafloc1011









t / V Vs. V plot for MFT diluted to 10 wt% solids with 50 ppm of Al-PAM





Fig 8 t / V Vs. V plot for MFT diluted to 10 wt% solids with 75 ppm of Al-PAM





Fig 9 t / V Vs. V plot for MFT diluted to 10 wt% solids with 100 ppm of Al-PAM