Understanding Two-step Polymer Flocculation of Oil Sands Tailings

by

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Abstract

In this study, a two-step flocculation method by combining anionic and cationic polymeric flocculants on the treatment of oil sands tailings was investigated. Compared to conventional flocculation by using a single anionic or cationic polymer, which has been a widely exploited procedure for flocculation of oil sands tailings and mineral tailings, the two-step flocculation with anionic Magnafloc 1011 (MF) and cationic chitosan showed an enhanced capacity in the treatment of oil sands tailings by improving the quality of released water, i.e. high clarity and low solid content, yet retaining a high settling efficiency. This improved flocculation performance is attributed to combined flocculation effects induced by bridging effect of the anionic polymer and charge neutralization of cationic polymer. The replacement of chitosan by a synthesized temperature responsive polymer, chitosan-g-PMEOMA (CgM), resulted in more water release and better consolidation. The CgM polymer chains adsorbed on solids at temperatures below the low critical solution temperature (LCST) become more hydrophobic at temperatures above LCST which results in particle aggregation by hydrophobic attraction. This work provides useful information and insights into the development of effective technologies for oil sands tailings treatment and settling of colloidal suspensions.

Preface

Chapter 2 of this thesis has been submitted for publication as Lu, Q.; Yan, B.; Xie, L.; Huang, J.; Liu, Y.; Zeng, H., "A Two-step Flocculation Process on Oil Sands Tailings Treatment Using Oppositely Charged Polymer Flocculants." Science of the Total Environment.

Chapter 3 of this thesis will be submitted for publication as Lu, Q.; Yan, B.; Huang, J.; Xie, L.; Liu, Y.; Zeng, H., "Dewatering of Oil Sands Tailings by Using a Thermo-sensitive Polymer Flocculant."

For the work of these two chapters, I was responsible for the experimental design and conduction, data analysis and integration, and the manuscripts composition. Dr. B. Yan and L. Xie assisted with the revision of the manuscripts. J. Huang assisted with the surface force measurements. Dr. J. Luo and Dr. B. Huang provided some suggestions for the revision of the paper manuscript. Dr. Y. Liu and Dr. H. Zeng involved with relevant concept formation as the supervisory authors. Dr. H. Zeng was the corresponding author and involved with the experiments and manuscripts.

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List of Acronyms

Al-PAM	Al(OH)3-polyacrylamide
APS	Ammonium persulphate
CgM	chitosan-g-PMEOMA
CT	Composite Tailings
DLVO	Derjaguin - Landau - Verwey - Overbeek
ET	Extraction Tailings
FBRM	Focused beam reflectance measurement
FT-IR	Fourier transform infrared
H-PAM	Hydrolyzed polyacrylamide
ISR	Initial settling rate
LCST	Low critical solution temperature
MF	Magnafloc 1011
MEOMA	2-(2-methoxyethoxy) ethyl methacrylate
NTU	Nephelometric turbidity units
NWR	Net water release
PAM	Polyacrylamide
PNIPAM	poly(N-isopropylacrylamide)
ppm	Parts per million
SLS	Static light scattering
SFA	Surface force apparatus
TEMED	tertramethylenediamine

Chapter 1 Introduction

1.1 Oil Sands Processing and Challenges in Tailings Management

Oil sands as a mixture of sand, clay, water, and a type of heavy oil referred to as "bitumen" have become one of the world's leading sources of non-conventional petroleum. Compared with the conventional crude oil, bitumen features a higher viscosity and specific gravity, lower hydrogen-to-carbon ratio, and higher nitrogen, sulphur and metal content. To recover bitumen from oil sands, a water-based extraction process pioneered by Dr. Karl Clark in 1920's has been commercially used by the majority of oil sands operators. [1-3]

Typically, the crushed oil sands are conditioned with alkaline hot water to prepare the slurry at the temperature of 40-55 ℃ for hydrotransport pipelines, where bitumen is liberated from sand grains and attached to air bubbles. The heat from hot water reduces the viscosity of bitumen and the caustic generates natural surfactant molecules from bitumen that facilitate bitumen liberation. The oil sands slurry with aerated bitumen, solids and water is fed into gravity separation vessels, where aerated bitumen floats to the top of the vessels as bitumen froth and solids settle to the bottom as extraction tailings. [4-6]

The recovered bitumen froth typically contains 60 wt% bitumen, 30 wt% water and 10 wt% solids. In froth treatment, the bitumen froth is de-aerated and diluted with organic solvent such as naphthenic or paraffinic diluent to reduce its viscosity and density, thereby accelerating solids and water removal from the organic phase of diluted bitumen.

In conventional froth treatment, naphtha is used to dilute bitumen froth at a relatively low diluent-to-bitumen ratio and typical bitumen products from this process contain 98 wt% bitumen, 1-2 wt% water and 0.5 wt% solids. In contrast, the bitumen products obtained through paraffinic froth treatment have lower levels of contaminates due to the formation of aggregates composed of emulsified water droplets, solid particles and precipitated asphaltenes. The obtained bitumen after solvent recovery is fed into upgraders to produce synthetic crude oil and the extraction tailings are discharged to tailings ponds for storage and management. [7-9]

In the extraction tailings, coarse solids settle quickly as the beaches along the tailings pond while fine solids remain suspended for long periods of time. After a few years, these suspended fine solids form a stable "gel-like" suspension with approximately 30 wt% fine solids and 70 wt% water, known as mature fine tailings (MFT) as illustrated in Figure 1.1. The fine solids in MFT may take several decades to settle and release the entrapped water, which has posed a significant challenge to the tailings management by oil sands industry. [10-14]

The accumulation of large volumes of MFT gives rise to various technical and environmental concerns, notably land reclamation, water recycling and environmental contamination, and therefore poses a significant management challenge to sustainable development of oil sands industry.[15] During the past half century of oil sands operations, approximately 830 million cubic meters of MFT have been accumulated in tailings ponds, covering an area of 176 square kilometres that have been more than tripled in size since 2005. [16-17] It has been estimated that the inventory of MFT will reach two billion cubic meters in 2034 if the current tailings management is not significantly improved.[18] The high inventory of MFT causes large extensions of land to be occupied by tailings ponds and large volume of water to be entrapped by fine solids, which cannot be used for several decades. Considering the sustainable development of oil sands industry, it is urgent to minimize and eventually eliminate the long-term tailings storage to create a trafficable landscape for progressive reclamation and ensure the process water can be recovered from the tailings and recycled to the extraction plant. Moreover, the water in tailings ponds contains large amounts of residual hydrocarbons, heavy metals (e.g., arsenic and mercury) and some other types of toxic materials, which have chronic effects on the wildlife and aquatic organisms surrounding the tailings ponds and further draw the attention of the public on the effective management of tailings ponds. [19-21]

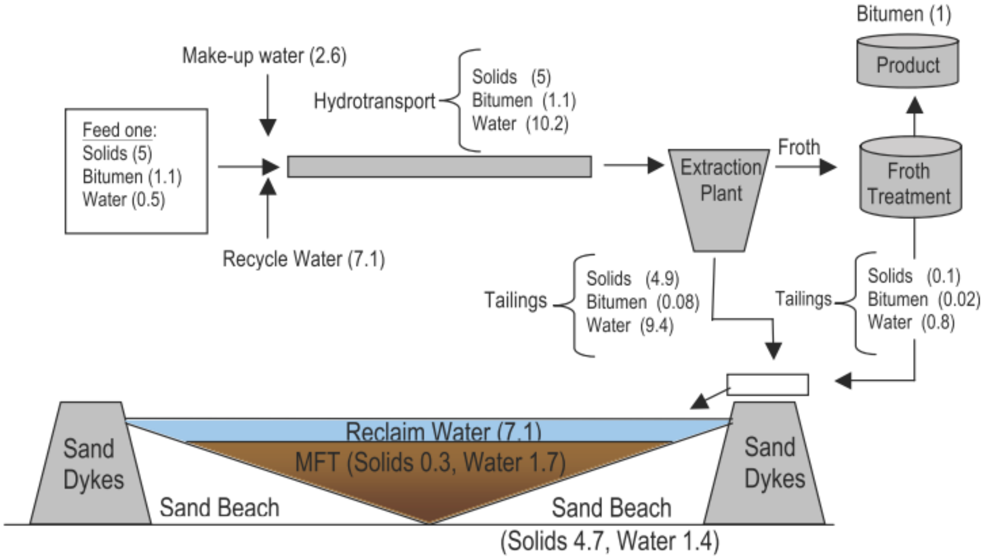

Figure 1.1 Schematic of typical oil sands tailings management (Number in parenthesis represents the relative volume of components used or generated during the production of one cubic meter of bitumen). [10]

1.2 Current Technologies for Tailings Treatment

Over the last few decades, much effort and significant progress has been made to develop the dewatering technologies to enhance the settling rate of fine solids and recover the maximum volume of water with appropriate quality for tailings treatment. [13, 22-27] The dewatering technologies such as filtration, centrifugation and natural drying have been tested for tailings treatment in laboratory scale but further work is still needed to perform commercial-scale operations. Composite tailings and thickened tailings are the only technologies that have been commercially used in large-scale operations to treat oil sands tailings.

1.2.1 Composite Tailings (CT)

Composite tailings (CT) process has been used for MFT treatment by oil sands operators such as Syncrude, Suncor and CNRL. In this process, MFT is mixed with the coarse sands from extraction tailings and treated with the coagulant aid such as gypsum to form a non-segregating mixture. With the calcium ions destabilizing the tailings suspension, fine solids and coarse sands consolidate into a non-segregating deposit with fast release of clear water. Inorganic coagulants have been proved to be effective to accelerate water release and land reclamation, but the presence of high amounts of divalent ions in the recovered water has a detrimental effect on the recovery of bitumen extraction and raises a challenge of scaling in process units and corrosion in metallurgy. Despite the negligible effect of polymeric coagulants on the water quality, the settling rate of the mixture and stability of the deposits are incomparable to the inorganic coagulants. All these negative impacts have been a challenge for sustainable implementation of the CT process, which stimulated the search for better alternatives. [10, 23, 28]

1.2.2 Thickened Tailings (TT)

Thickened tailings (TT) process is an effective solution for MFT treatment without introducing divalent ions to the recycled water stream. In this process, the high molecular weight polymeric flocculants are used to rapidly thicken fresh extraction tailings and recover warm water that can be readily recycled to the extraction process, therefore reducing energy cost and greenhouse gas emission. However, the sediments formed through the TT process still contain large volume of water that cannot be easily removed without the use of an external force due to the loosely packed structure of the aggregates (flocs). The polymeric flocculants are originally developed for other applications such as paper making, mining industry, and municipal and industrial wastewater treatment rather than oil sands tailings treatment, which could be the reason that the current flocculants are not sufficiently efficient to settle fine particles in oil sands tailings. The TT process has been successfully applied in other mining industries to obtain sediments with 50-70 wt% solids; therefore, it is believed that the optimal design of polymeric flocculants will facilitate fine solids to form the flocs with the compact structure, which can further enhance sediment densification and dewatering performance. [10, 29-30]

1.3 Stability of Colloidal System and DLVO Theory

The settling and sedimentation of oil sands tailings usually take several decades without any treatment, which arises from fine particles suspended in the tailings referred to as aluminosilicate clay particles. [5] The coagulants and flocculants can be used to destabilize fine particles and accelerate the settling. [30-31] To better understand the interaction mechanisms between suspended fine particles and the role of coagulants and flocculants in particle agglomeration, the theory of colloidal system is often used to explain the stability of fine particles and the destabilized role of coagulants and flocculants in the tailings as the size of fine particles is comparable to the range of the colloids. [32]

Despite a variety of compositions and structures of fine particles ranging from tetrahedral silicon-oxygen sheet to octahedron aluminum-oxygen or magnesium-oxygen sheet, the van der Waals force between fine particles such as kaolinite, illite or smectite in colloidal suspension is attractive, which is supposed to lead to an unstable colloidal system with the agglomeration of fine particles. [4] Unfortunately, these fine particles normally carry negative charges in alkaline condition, which causes repulsive electrical double layer force. Compared with the short-range van der Waals attraction that is only effective at distance below 10 nm, the electrical double layer repulsion is stronger even at distance over 10 nm, so an energy barrier is existed to inhibit the agglomeration of fine particles and therefore result in stabilization of colloidal suspension as shown in Figure 1.2. The balance between the van der Waals attraction and the electrical double layer repulsion will determine the stability of colloid system.

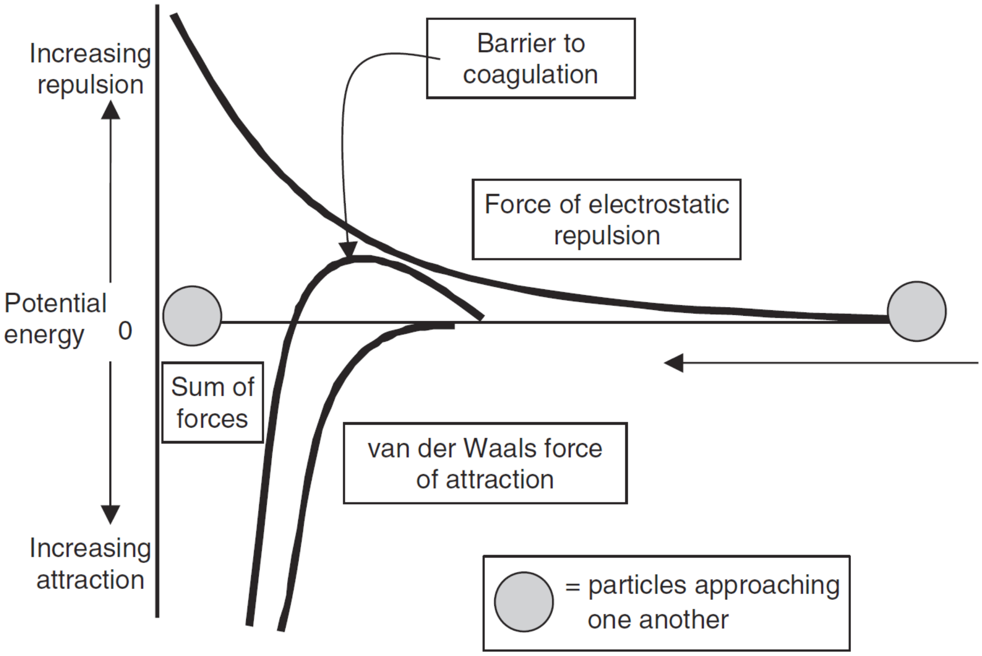

Figure 1.2 Schematic of the energy barrier for particle agglomeration due to the balance between van der Waals attraction and electrical double layer repulsion. [30]

The Derjaguin-Landau-Verwey-Overbeek (DLVO) theory is often used to describe the colloidal stability based on the assumption that the energy of a colloidal system is the sum of van der Waals energy and electrical double layer energy. If the net force between the particles is attractive, the system is unstable and the particles will agglomerate. In contrast, if the net force is repulsive, an energy barrier is existed to inhibit the particles approaching one another and agglomerating. In order to trigger the agglomeration of a stable colloidal suspension, it is necessary to reduce the energy barrier (e.g., coagulation) by compressing the electrical double layer repulsion or provide sufficient energy to overcome the energy barrier (e.g., flocculation) by bridging the gap between the particles. Once the energy barrier is jumped, the net interaction energy is attractive and the particles will agglomerate. [4] Therefore, it is of fundamental and practical importance to understand the DLVO theory including van der Waals and electrical double layer forces, which will facilitate to find effective approaches to overcome the barrier of agglomeration in tailings treatment.

1.3.1 Van Der Waals Force

The van der Waals force, named after Dutch physicist Johannes Diderik van der Waals, is the sum of the attractive or repulsive forces between molecules excluding those due to chemical bonds or electrostatic interaction. Three types of interactions contribute to the van der Waals force: dipole-dipole interaction (Keesom force), dipole-induced dipole interaction (Debye force) and instantaneous induced dipole-instantaneous induced dipole interaction (London dispersion force). The van der Waals force plays a critical role in many phenomena involving intermolecular forces such as surface tension and wetting film. [32]

The van der Waals force between two objects in a medium can be attractive or repulsive based on the comparison of refractive index and dielectric constant. If the parameters of the medium are lower or higher than those of two objects, the van der Waals force is attractive. On the other hand, if the parameters of the medium lie between those of two objects, the van der Waals force is repulsive. For example, in bitumen extraction, the van der Waals force between two bitumen droplets, between two solid particles or between a bitumen droplet and a solid particle in aqueous solution is attractive while the van der Waals force between an air bubble and a bitumen droplet or between an air bubble and a solid particle in aqueous solution is repulsive. Compared with other forces induced by chemical bonds or electrostatic interaction, the van der Waals force is relatively weak and the magnitude of the force dramatically decays with increasing the distance D between two objects. Typically, the van der Waals force between two atoms is proportional to D^{-7}. [32]

1.3.2 Electrical Double Layer Force

Most particles carry surface charges in aqueous suspension, which can be caused by different mechanisms such as preferential solution of surface ions, direct ionization of surface groups, substitution of surface ions and specific adsorption of ions. The schematic of double layer structure of a positively charged particle surface is demonstrated in Figure 1.3. The charged surface attracts oppositely charged ions referred to as counterions to the surface to compensate the surface charge and keep the system electrically neutral, so an electrical double layer develops near the charged surface in the solution.

The first layer, referred to as Stern layer, is the region between the charged surface and the Stern plane that is composed of immobile counterions adsorbed on the charged surface, in which the potential decreases linearly with increasing the distance. The potential at the charged surface and the Stern layer is called surface potential (Ψ_0) and Stern potential (Ψ_S), respectively. The second layer, referred to as diffusive layer, consists of mobile counterions that normally obey the Poison-Boltzmann distribution. [32]

The shear plane refers to as the plane that the ions and the ion bearing solution inside the diffusive layer move simultaneously with the particle in aqueous solution due to the Coulomb attraction between the charged surface and surrounding counterions. The slipping condition applies at the shear plane and the potential at the shear plane is known as the zeta potential. Since it's impossible to measure the surface potential or Stern potential by experimental instruments, the zeta potential is commonly used to characterize the surface charge of solid particles in colloidal system based on the electrophoresis phenomenon. When an electric field is applied across the suspension, charged particles are attracted towards the electrode of opposite charge and the electrophoretic mobility can be used to calculate the zeta potential through different equations depending on the particle size.

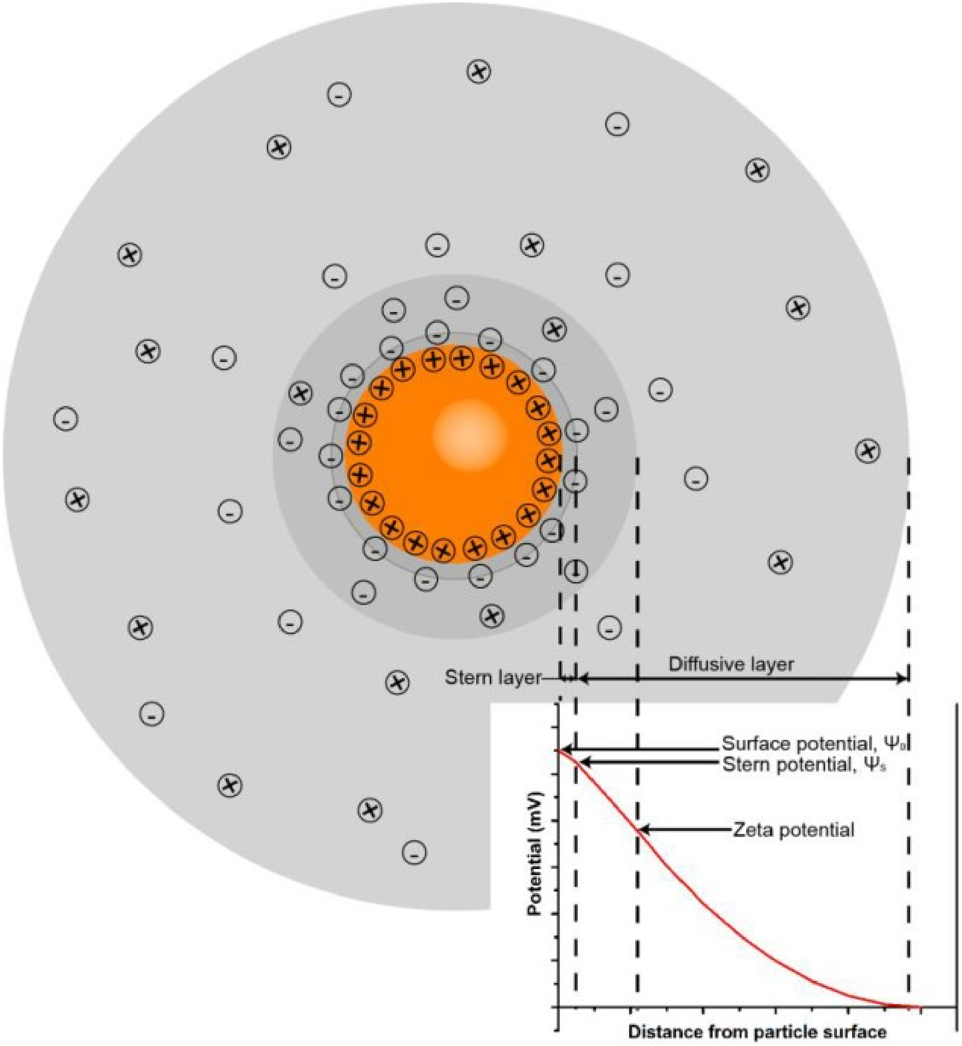

Figure 1.3 Schematic of double layer structure of positively charged particle surface. [33]

1.4 Coagulation and Flocculation

As mentioned above, the chemical reagents are widely applied to change the surface properties of colloidal particles and thus break the stable colloidal suspension state. The CT process is based on coagulation that can change the surface charges of colloidal particles and thus reduce the energy barrier and the TT process is based on flocculation that can bridge the gap between particles and thus provide sufficient energy to overcome the energy barrier. Coagulation and flocculation are two different concepts, but they are sometimes considered synonymously in certain conditions.

Coagulation is defined as the destabilization process of colloidal suspension to neutralize the surface charge or even induce a localised charge reversal of colloidal particles by adding the coagulants with highly opposite charge such as gypsum and quaternised polyamine based polymers. When the surface charge is neutralized or locally reversed, the electrical double layer repulsion is significantly suppressed or becomes attractive between the sites of varying opposite charges, which dramatically reduces the energy barrier of agglomeration and brings the suspended particles together. The small, compact and loosely bound structure makes the agglomerates to be highly sensitive to mechanical shear, which could be further improved by the "bridging" effect of flocculation. [30]

Flocculation usually refers to the formation of loosely packed flocs through the simultaneous adsorption of high molecular weight polymeric flocculants onto a number of colloidal particles and bridging the gap between the particles. In this process, the segments of polymeric flocculants are initially adsorbed onto one or more particles with the loops and tails extending beyond the range of electrical double layer repulsion in solution to overcome the energy barrier of agglomeration, which are then attached to other particles or to more sites on the same particle to form the flocs. [30]

The bridging force and steric force play a critical role in the flocculation of colloidal particles induced by polymeric flocculants. When two polymer-covered particles approach each other, the extended loops and tails on one particle will attach to another particle due to attractive bridging force. At the same time, the extending layers of polymer segments on both surfaces will overlap and repel each other due to repulsive steric force that arises from the increase in osmotic pressure and configurational constraints. The flocculation schematic of bridging effect and steric stabilization is illustrated in Figure 1.4. To greatly decrease repulsive steric force and increase attractive bridging force, the flocculation always has an optimum flocculant dosage corresponding to the maximum amount of polymers that can be utilized for flocculation and the optimum flocculation has been suggested to occur when half the surface area of the particles is covered with polymeric flocculants. An excess polymer dosage will result in high polymer coverage on particle surface and few available particle surfaces for attachment of polymer segments, thereby restabilizing the colloidal suspension. On the other side, a low polymer dosage is insufficient to lead to adequate bridging effects between the particles and thus inhibit the formation of flocs. Mixture condition has also been found to be critical for the flocculation of colloidal particles. Insufficient mixing may stabilize the colloidal suspension due to poor flocculation caused by local overdose and poor inter-particle bridging by secondary adsorption, while excessive mixing may cause the rupture of the formed flocs by extensive shear.

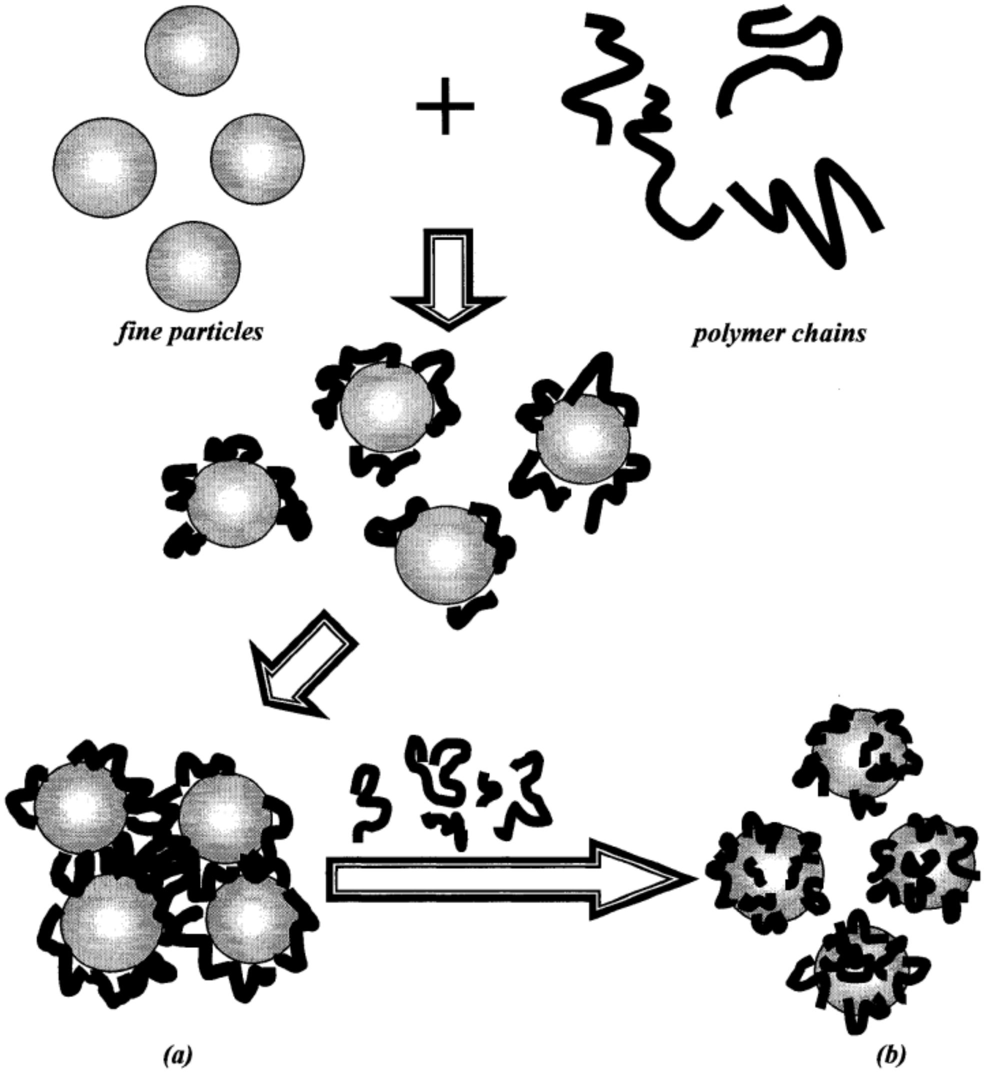

Figure 1.4 The flocculation schematic of (a) bridging effect and (b) steric stabilization induced by polymeric flocculants. [34]

1.5 Flocculation Materials

The polymeric flocculants cover a wide range of chemical types from natural polymers such as starch and guar gum to synthetic polymers based on acrylamide and its ionic counterparts. Compared with natural polymers, synthetic polymers are a type of more efficient flocculants that can be tailor made in terms of chemical structure and molecular weight to meet specific industrial applications. The majority of the commercial synthetic flocculants are based on polyacrylamide (PAM) and its derivatives, which can be classified into non-ionic PAM, cationic PAM and anionic PAM represented in Figure 1.5. [10, 30]

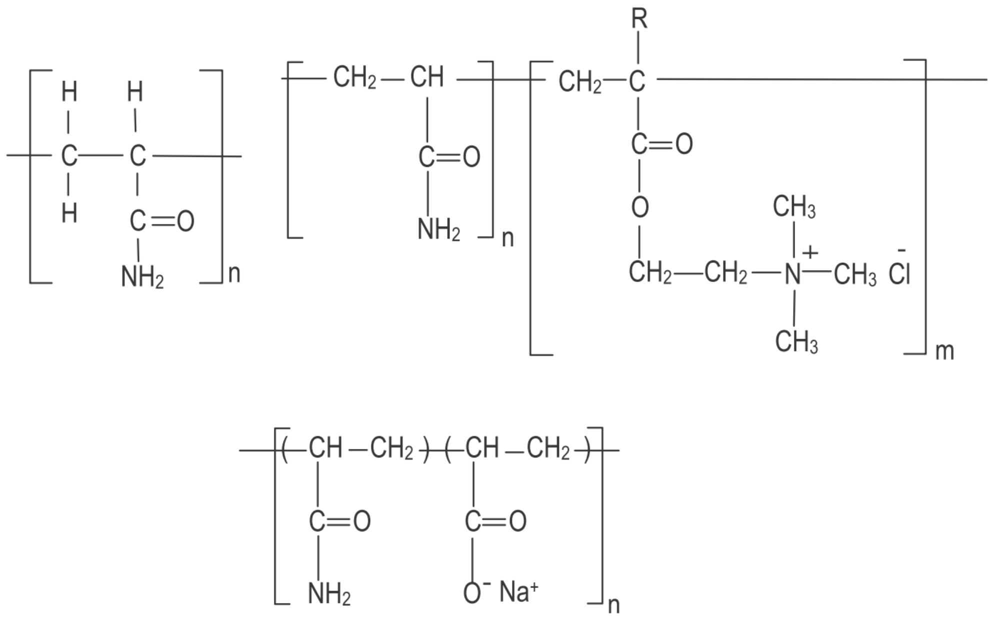

Figure 1.5 Chemical types of polymeric flocculants based on PAM and its derivatives (Clockwise from top left: non-ionic PAM, cationic PAM and anionic PAM). [10]

The non-ionic PAM is mostly used in mining industry to dewater the discarded slurry left after mineral flotation. The cationic PAM prepared by copolymerization of acrylamide with quaternary ammonium is used as retention aids in paper fabrication to bind inorganic fillers and fiber fines together with cellulose fibers, which prevents valuable fillers and fibers from draining with water. The anionic PAM prepared either by copolymerization of acrylamide with acrylic acid or by partial hydrolysis of non-ionic

PAM is widely used for removal of suspended solids in different industries including raw water clarification, thickening and dewatering of wastewater and sludge. As the commercial flocculants, the anionic PAM tends to be less expensive and of higher molecular weight. Most importantly, the negatively charged segments of anionic PAM allow the loops and tails to dangle away from the negatively charged solid surfaces, which makes it highly possible to form the bridging effect. [10]

1.6 Flocculation Application in Tailings Treatment

The flocculation performance of polymeric flocculants based on PAM has been reported to dewater the model suspensions and oil sands tailings. The properties of polymer (e.g., molecular weight and charge content) and suspension (e.g., solution pH and suspension type) are highly related to the dewatering performance in terms of settling rate and turbidity. [35-38] Although all types of PAM are effective to flocculate kaolinite suspensions, only PAM with very high molecular weight and anionic medium charge are able to flocculate oil sands tailings. However, the formed flocs still contain large volume of water and the supernatant water still contains high amounts of fine solids, which prevents the water recycling to the bitumen extraction process after tailings treatment.

Temperature sensitive polymers have been applied in various industrial operations such as mineral processing and wastewater treatment. With temperature rising above lower critical solution temperature (LCST), the conformation of polymer chains changes from an extended state to an agglomerated state, referred to as coil-globule transition, which induces the polymer change from water soluble and hydrophilic surface to water insoluble and hydrophobic surface. Therefore, temperature sensitive polymers are believed to show better dewatering performance due to the combined role of bridging effect and hydrophobic interaction at high temperature. Recently, the addition of poly(N-isopropylacrylamide) (PNIPAM) during bitumen extraction has been found to significantly improve the dewatering performance of oil sands tailings. [37] The development and application of temperature-sensitive polymers in tailings treatment is still in early stages, so more efficient polymers need to be designed to suit the specific requirement of oil sands tailings treatment.

1.7 Surface Forces Apparatus

Surface forces apparatus (SFA) has been widely used for direct measurements of intermolecular and surface forces, such as van der Waals, electrical double layer, steric and bridging interactions with angstrom resolution for separation distance and nanonewton force precision in both vapors and liquids. The SFA technique has provided significant mechanistic insights into the role of polymeric flocculants in the interactions between model clay surfaces. A schematic of typical SFA setup is shown in Figure 1.6. The main body of SFA includes micrometers, main stage with the single-cantilever spring (for SFA 2000), lower disk holder, upper disk holder with a piezoelectric tube, and a fully sealable chamber. [39-41]

In a typical SFA experiment, mica is commonly used as supporting substrate due to its molecularly smooth feature. Two back silvered (~45 nm) mica sheets were glued onto two cylindrical silica discs of radius 2 cm and mounted into the main chamber in a crossed-cylinder. Other materials such as SiO_2 and polymers have also been used as supporting substrates by modifying the mica surface by various physical or chemical methods such as spin coating, self-assembly, vapor deposition, Langmuir–Blodgett deposition, and surface initiated polymerization. [39-41]

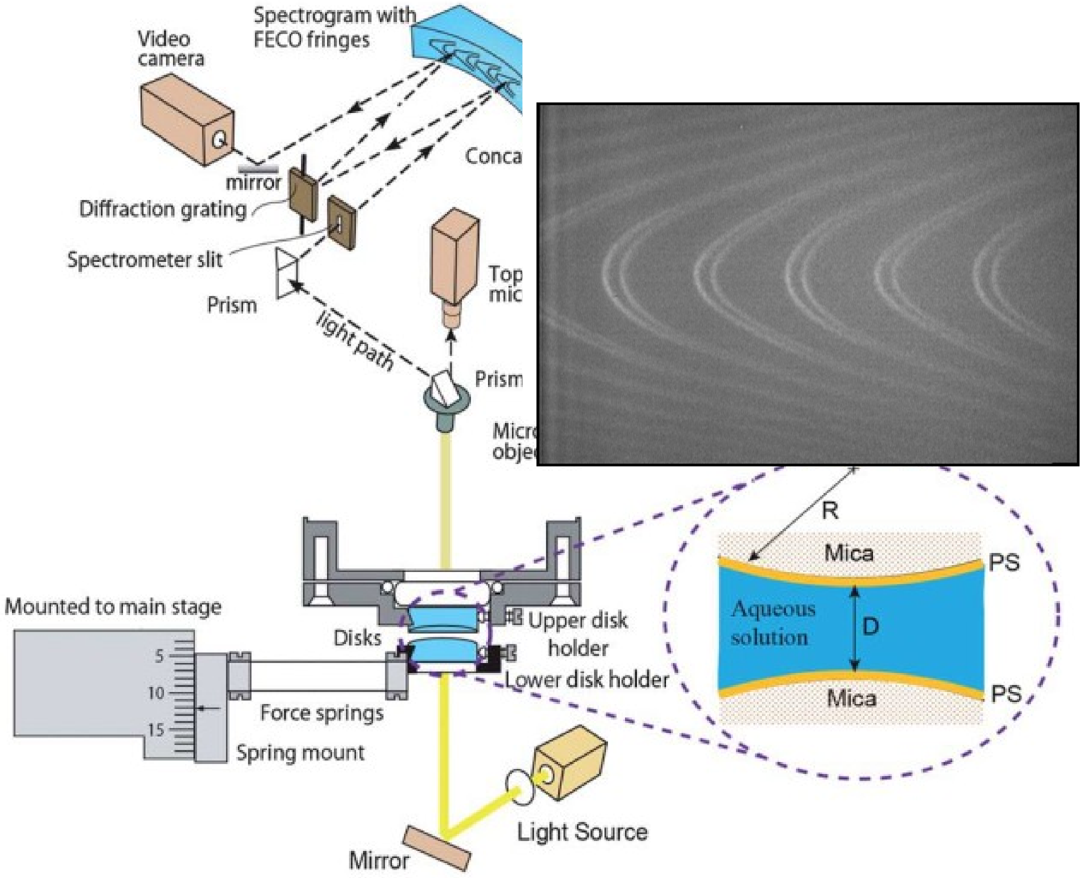

Figure 1.6 Schematic illustration of Surface Forces Apparatus for force measurement.

1.8 References

1. Giesy, J. P.; Anderson, J. C.; Wiseman, S. B., Alberta Oil Sands Development. Proceedings of the National Academy of Sciences 2010, 107, 951-952.

2. Czarnecki, J.; Radoev, B.; Schramm, L. L.; Slavchev, R., On the Nature of Athabasca Oil Sands. Advances in Colloid and Interface Science 2005, 114, 53-60.

3. Gray, M.; Xu, Z.; Masliyah, J., Physics in the Oil Sands of Alberta. Physics Today 2009, 62, 31-35.

4. Masliyah, J.; Czarnecki, J.; Xu, Z., Handbook on Theory and Practice of Bitumen Recovery from Athabasca Oil Sands. Vol. I. Theoretical basis 2010.

5. Masliyah, J.; Zhou, Z. J.; Xu, Z.; Czarnecki, J.; Hamza, H., Understanding Water - Based Bitumen Extraction from Athabasca Oil Sands. The Canadian Journal of Chemical Engineering 2004, 82, 628-654.

6. Shah, A.; Fishwick, R.; Wood, J.; Leeke, G.; Rigby, S.; Greaves, M., A Review of Novel Techniques for Heavy Oil and Bitumen Extraction and Upgrading. Energy & Environmental Science 2010, 3, 700-714.

7. Romanova, U. G.; Yarranton, H. W.; Schramm, L. L.; Shelfantook, W. E., Investigation of Oil Sands Froth Treatment. The Canadian journal of chemical engineering 2004, 82, 710-721.

8. Rao, F.; Liu, Q., Froth Treatment in Athabasca Oil Sands Bitumen Recovery Process: A Review. Energy & Fuels 2013, 27, 7199-7207.

9. Wu, J.; Dabros, T., Process for Solvent Extraction of Bitumen from Oil Sand. Energy & Fuels 2012, 26, 1002-1008.

10. Vedoy, D. R.; Soares, J. B., Water‐Soluble Polymers for Oil Sands Tailing Treatment: A Review. The Canadian Journal of Chemical Engineering 2015, 93, 888-904.

11. Wang, C.; Harbottle, D.; Liu, Q.; Xu, Z., Current State of Fine Mineral Tailings Treatment: A Critical Review on Theory and Practice. Minerals Engineering 2014, 58, 113-131.

12. Allen, E. W., Process Water Treatment in Canada's Oil Sands Industry: I. Target Pollutants and Treatment Objectives. Journal of Environmental Engineering and Science 2008, 7, 123-138.

13. Allen, E. W., Process Water Treatment in Canada's Oil Sands Industry: Ii. A Review of Emerging Technologies. Journal of Environmental Engineering and Science 2008, 7, 499-524.

14. Mikula, R. J.; Kasperski, K. L.; Burns, R. D.; MacKinnon, M. D., Nature and Fate of Oil Sands Fine Tailings. Advances in Chemistry Series 1996.

15. Chalaturnyk, R. J.; Don Scott, J.; Özüm, B., Management of Oil Sands Tailings. Petroleum Science and Technology 2002, 20, 1025-1046.

16. Grant, J.; Angen, E.; Dyer, S., Forecasting the Impacts of Oilsands Expansion; Pembina Institute, 2013.

17. Warmore, S., Tar Sends Oil and Pipeline Safety: Examining Regulatory Shortcomings. Wayne L. Rev. 2013, 59, 175.

18. Houlihan, R.; Haneef, M. In Oil Sands Tailings: Regulatory Perspective, Proceedings of the International Oil Sands Tailing Conference, Edmonton, Alberta, 2008.

19. Rogers, V. V.; Wickstrom, M.; Liber, K.; MacKinnon, M. D., Acute and Subchronic Mammalian Toxicity of Naphthenic Acids from Oil Sands Tailings. Toxicological Sciences 2002, 66, 347-355.

20. Kelly, E. N.; Short, J. W.; Schindler, D. W.; Hodson, P. V.; Ma, M.; Kwan, A. K.; Fortin, B. L., Oil Sands Development Contributes Polycyclic Aromatic Compounds to the Athabasca River and Its Tributaries. Proceedings of the National Academy of Sciences 2009, 106, 22346-22351.

21. Colavecchia, M. V.; Backus, S. M.; Hodson, P. V.; Parrott, J. L., Toxicity of Oil Sands to Early Life Stages of Fathead Minnows (Pimephales Promelas). Environmental Toxicology and Chemistry 2004, 23, 1709-1718.

22. Mikula, R.; Munoz, V.; Omotoso, O., Centrifugation Options for Production of Dry Stackable Tailings in Surface-Mined Oil Sands Tailings Management. Journal of Canadian Petroleum Technology 2009, 48, 19-23.

23. Matthews, J.; Shaw, W.; MacKinnon, M.; Cuddy, R., Development of Composite Tailings Technology at Syncrude. International Journal of Surface Mining, Reclamation and Environment 2002, 16, 24-39.

24. Beier, N.; Sego, D., The Oil Sands Tailings Research Facility. Geotechnical news 2008, 26, 72-77.

25. Rao, S. R., Flocculation and Dewatering of Alberta Oil Sands Tailings. International Journal of Mineral Processing 1980, 7, 245-253.

26. Dawson, R.; Sego, D.; Pollock, G., Freeze-Thaw Dewatering of Oil Sands Fine Tails. Canadian geotechnical journal 1999, 36, 587-598.

27. Powter, C.; Biggar, K.; Silva, M.; McKenna, G.; Scordo, E. In Review of Oil Sands Tailings Technology Options, Tailings and Mine Waste, 2011.

28. MacKinnon, M.; Matthews, J.; Shaw, W.; Cuddy, R., Water Quality Issues Associated with Composite Tailings (Ct) Technology for Managing Oil Sands Tailings. International Journal of Surface Mining, Reclamation and Environment 2001, 15, 235-256.

29. Boger, D., Personal Perspective on Paste and Thickened Tailings: A Decade On. Mining technology 2012, 121, 29-36.

30. Williams, P. A., Handbook of Industrial Water Soluble Polymers; John Wiley & Sons, 2008.

31. Mortimer, D. A., Synthetic Polyelectrolytes—a Review. Polymer International 1991, 25, 29-41.

32. Israelachvili, J. N., Intermolecular and Surface Forces: Revised Third Edition; Academic press, 2011.

33. Ji, Y. Fundamental Understanding of the Flocculation of Mineral Tailings in High Salinity Water. University of Alberta, 2013.

34. Emeka, K. Studies on Flocculation of Kaolin Suspensions and Mature Fine Tailings. University of Alberta, 2008.

35. Sworska, A.; Laskowski, J.; Cymerman, G., Flocculation of the Syncrude Fine Tailings: Part I. Effect of Ph, Polymer Dosage and Mg2+ and Ca2+ Cations. International journal of mineral processing 2000, 60, 143-152.

36. Li, H.; Long, J.; Xu, Z.; Masliyah, J. H., Flocculation of Kaolinite Clay Suspensions Using a Temperature ‐ Sensitive Polymer. AIChE journal 2007, 53, 479-488.

37. Li, H.; Long, J.; Xu, Z.; Masliyah, J., Synergetic Role of Polymer Flocculant in Low-Temperature Bitumen Extraction and Tailings Treatment. Energy & fuels 2005, 19, 936-943.

38. Li, H.; Long, J.; Xu, Z.; Masliyah, J. H., Effect of Molecular Weight and Charge Density on the Performance of Polyacrylamide in Low ‐ Grade Oil Sand Ore Processing. The Canadian Journal of Chemical Engineering 2008, 86, 177-185.

39. Israelachvili, J., et al., *Recent advances in the surface forces apparatus (SFA) technique.* Reports on Progress in Physics, 2010. **73**(3): p. 036601.

40.Israelachvili, J.N., *Intermolecular and surface forces: revised third edition*. 2011: Academic press.

41. Lu, Q., et al., *Understanding the molecular interactions of lipopolysaccharides during E. coli initial adhesion with a surface forces apparatus.* Soft Matter, 2011. **7**(19): p. 9366-9379.

Chapter 2 Two-step Flocculation for Treatment of Oil Sands Tailings

2.1 Introduction

Canada has the largest oil sands deposits in the world, and bitumen is being recovered by oil sands industry in two approaches: surface mining and thermally enhanced in situ extraction [1]. In surface mining, the recovery of bitumen from oil sands is normally achieved by the so-called Clark Hot Water Extraction Process, in which large amounts of hot and caustic water is used to separate bitumen from sands, resulting in the accumulation of fluid wastes referred to as oil sands tailings [1, 2]. Comprising water, sands, fine clays and bitumen residue, the tailings are discharged into surface tailings ponds [3, 4]. The accumulated oil sands tailings on site have resulted in over 176 km^2 of tailings ponds in Northern Alberta which will continue to increase with the continuing growth of oil sands exploration [5, 6], causing remarkable land disturbance and posing serious environmental and economic concerns as well as engineering challenges [7]. Therefore, water management is critical to the sustainable development of the Canadian oil sands, and it is highly desirable to develop efficient ways to enhance the settling of the solid particles in the tailings to recycle the water and reclaim the land where tailing ponds occupy [8].

Over the last two decades, much efforts has been devoted to development of technologies for oil sand tailings treatment including composite tailings, flocculation by polymers, fine tailings centrifuge and freeze/thaw method [9, 10]. Flocculation by polymers has been extensively explored and implemented by the oil sands industries due to its high efficiency in dewatering mineral tailings [11, 12]. Polymers (as flocculants) are normally employed to overcome the potential energy barrier between negatively charged solid particles in the oil sands tailings, and to bring these particles into the effective range of attractive van der Waals force and polymer bridging attraction, which triggers the destabilization and flocculation of suspended particles to form large sediments, or so-called flocs [13]. Depending on the properties of employed polymer flocculants and composition of tailing samples, different destabilization mechanisms such as bridging, charge patching and charge neutralization could be involved in the flocculation process [14]. Various types of polymer flocculants have been developed and exploited in paste technology for flocculation of oil sands tailings and most of them are derivatives of polyacrylamide (PAM) such as hydrolyzed polyacrylamide (HPAM) with 20-30% anionicity [15, 16], cationic hybrid Al(OH)3-polyacrylamide (Al-PAM) [17-20] and thermos-sensitive poly(N-isopropyl acrylamide) [21-23]. However, this widely explored flocculation technology based on a single polymer flocculant usually demonstrates unsatisfactory flocculation performances on oil sands tailing treatment. The specific and complex properties of oil sands tailings, i.e., alkalinity, residual bitumen and a wide size range of clay colloids, generally complicate the interactions of polymer-particle and particle-particle during flocculation and undermine the performance of the polymer flocculant. Thereby most polymers fail to simultaneously enhance (1) the settling rate of suspended solid particles and (2) the clarity of released water during the treatment of oil sands tailings, which are two major criteria for evaluation of flocculant performance [24]. Therefore, it is of both fundamental and practical importance to explore and develop a novel flocculation strategy for oil sands tailings treatment with fast settling rate as well as sufficient dewatering capacity, which will not only greatly accelerate the recovery of water from oil sands tailings but also significantly reduce the operating cost in the tailings management and eliminate environmental footprint of oil sands production [25].

It is noted that treatment of mining tailings or pulp sludge from food and paper industries generally appears to be a multi-component flocculation procedure. Compared to using a single polymer flocculant, the multi-component flocculation procedure has demonstrated improved flocculation performance on treating these industrial tailings. For example, a study by Xiao et al. revealed that a two-component system consisting of both cationic micro-particles and anionic polymers as retention aids in papermaking process could improve flocculation efficiency and led to better retention performance than that using either individual component [26, 27]. Peng and Lu applied two oppositely charged polymers to the sedimentation of copper flotation tailings and showed improved settling rate and supernatant clarity [28]. Similar results were shown in a recent study that treating positively charged alumina suspension by two-polymer based flocculation procedure could greatly lower final cake moisture and increase filtration rate [29]. However, little effort has been devoted to exploring a multi-component flocculation procedure on oil sands tailings treatment. Meanwhile, most polymer flocculants used are synthetic and little attention has been paid to usage of natural biodegradable polymers as effective flocculants for oil sands tailings treatment.

Herein, we developed a new two-step flocculation process for the treatment of oil sands tailings by using two oppositely charged polymers, i.e. an anionic polyacrylamide and a natural biodegradable polymer, namely chitosan. The new process demonstrated an outstanding flocculation performance in treating extraction tailings directly from oil sands extracting plants in Northern Alberta, which not only greatly enhanced the clarity of released water but also achieved high settling efficiency. In addition, our flocculation process is benign and friendly to the environment because of the application of chitosan, a biocompatible and biodegradable natural polymer. To explore the underlying flocculation mechanisms, we adopted focused beam reflectance measurement (FBRM), zeta potential and surface force measurements to monitor changes in the number and size as well as surface charges of flocs during flocculation process.

2.2 Materials and Methods

2.2.1 Materials

Extraction tailings (ET) were provided by Canadian Natural Resources LTD, which consist of water (73.0-74.0 vol%), solids (26.0-27.0 vol%) and bitumen residues (0.10-0.25 vol%) with a pH of 8.6-8.9 at 20℃. The solids in the tailings were centrifuged, dried and characterized by X-ray diffraction (XRD, Rigaku, Japan). Laser diffraction (Mastersizer 2000, Malvern) was employed to determine the particle size of tailing particles in slurry. The microstructure of dried fine particles was examined through SEM (Zeiss EVOMA 15) and FE-SEM. The water of tailings were filtered and subjected to Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for the measurement of ion concentrations.

Two oppositely charged polymers, Magnafloc-1011 (Percol 727, Ciba, UK) and chitosan (Sigma, Canada), were employed as polymer flocculants in the two-step flocculation process developed. Magnafloc-1011 (MF) is a partially hydrolyzed polyacrylamide with an anion charge density of 27 mol% and has a high molecular weight of around 1.75×10^7 Dalton. Chitosan is a natural abundant cationic polymer with a molecular weight of 60,000 to 80,000 g/mol at a concentration of 1 wt % in 1% acetic acid solution.

2.2.2 Settling Tests

Polymer dosages were expressed on the basis of tailings weight. The stock solutions of MF and chitosan were prepared one day earlier at a concentration of 500 ppm in Milli-Q water and 2000 ppm in 1% acetic acid solution, respectively. The settling tests followed a procedure reported previously [30]. Briefly, 90 mL extraction tailings samples were transferred into a 250 mL standard baffled beaker and homogenized at 600 rpm for 2 min. Then the agitation speed was decreased and kept at 300 rpm when a desired amount of polymer stock solution was added to the slurries. For our two-step flocculation process, anionic polymer MF was added first to the slurries to induce a primary flocculation and followed by the cationic polymer (i.e. chitosan) stock solution within 10 seconds. Agitation was immediately stopped after polymer addition to avoid floc breakage. The resulted mixture was transferred into a 100 ml graduated cylinder followed by 5 times inversion. Changes in solid/liquid interface (mudline) were recorded as a function of settling time. The mudline height (h) was plotted vs. time (t) to determine the initial settling rate (ISR) (m/h) from the initial slope of the plot, as shown in Figure 2.1. After settling for 30 min, supernatants were withdrawn from the cylinder for turbidity and zeta potential measurement by Micro-100 Turbidimeter (Fisher, US) and Zeta Nano ZSP (Malvern, UK), respectively. For solid content measurements, 20 g of supernatant was dried in an oven at 120 °C overnight. The solid content of supernatants was calculated as dry mass over wet mass.

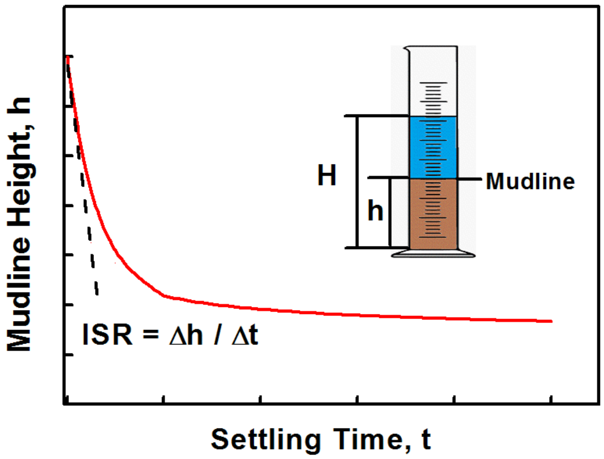

Figure 2.1 Schematic of ISR calculation based on the settling results of mudline height vs. settling time.

2.2.3 Focused Beam Reflectance Measurement

Particle size distribution and aggregate dimensions of suspensions at all stages of flocculation process was monitored by Focused Beam Reflectance Measurement, FBRM G400 PVC (Mettler-Toledo Auto Chem, USA). The FBRM probe focal plane was positioned 5 cm above the bottom of a 600 mL beaker. In each experiment, 20 ppm of anionic MF was added to 200 mL tailings sample in the beaker and followed by 100 ppm, 200 ppm and 400 ppm chitosan, respectively at a constant mixing speed of 300 rpm. The polymer addition process followed the same procedure as settling tests except that the agitation continued for 10 minutes after polymer addition. Total counts and square-weighted mean chord length were recorded at a scan rate of 2 s over the range of 1-1000 μm during the experiment. The square weighted mean chord length distribution monitors changes in particle dimensions in real time. The total counts indicate particle number in the suspension [31, 32].

2.2.4 Surface Force Measurements by Surface Forces Apparatus

A surface forces apparatus (SFA) was employed to probe the interactions between two model clay surfaces (i.e. fresh cleaved mica) in the presence of MF and chitosan solutions. The detailed experiment setup of SFA has been reported elsewhere [33]. Briefly, a thin mica sheet was glued upside down onto a cylindrical silica disk with the back surface coated with a thin layer of ~50 nm silver. The multiple-beam interferometry (MBI) optical technique by employing fringes of equal chromatic order (FECO) was used to monitor the surface separation in real time. The two curved mica surfaces (with radius R) were then mounted into the SFA chamber in a crossed-cylinder geometry, of which the interaction is locally equivalent to the interaction between a sphere of radius R approaching a flat surface based on the Derjaguin approximation when the surface separation D is much smaller than R [34, 35]. Polymer solution was then injected between the two mica surfaces. The forces between the two surfaces were determined based on the Hooke's law by measuring the deformation of the double cantilever force springs.

For SFA measurements, 20 ppm MF was prepared in 800 ppm NaCl solution, which was the approximate measured salt concentration of extraction tailings, and 200 ppm chitosan was prepared in 800 ppm NaCl and 1% acetic acid solution. For MF coating, mica surface was dipped into 20 ppm MF solution for 90 min, followed by a thorough rinsing with Milli-Q water to remove unbounded MF.

2.3 Results and Discussion

2.3.1 Characterization of Extraction Tailings

The XRD patterns of minerals in Extraction Tailings are shown in Figure 2.2. Quartz (SiO_2) and nacrite ($Al_2Si_2O_5(OH)_4$, a polymorph of kaolinite) are the major mineral phases. Figure 2.3 shows the morphology of dried tailings particles with stacked thin plate layers by FE-SEM. The particle size distribution of tailings slurry is shown in Figure 2.4. The D_{10}, D_{50} and D_{90} of the solid particles are 29.9 nm, 223 nm and 18.9 µm. The subscript number represents the volume fraction at or below the specific size. For example, D_{50} = 161 nm indicates that 50% particles are smaller than 161 nm. The ion concentrations are summarized in Table 2.1, in which the most abundant ions in Extraction Tailings are Na and K.

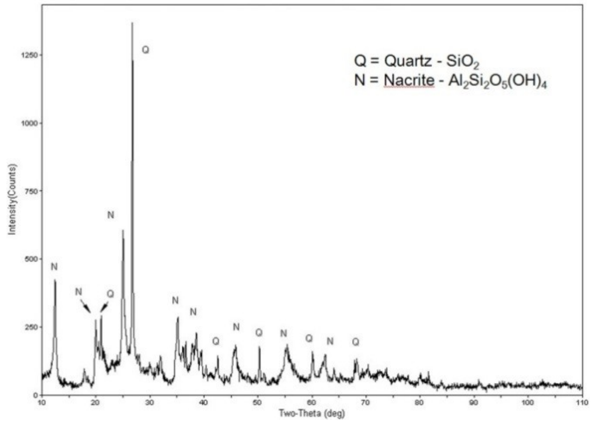

Figure 2.2 XRD patterns of ET clay solids.

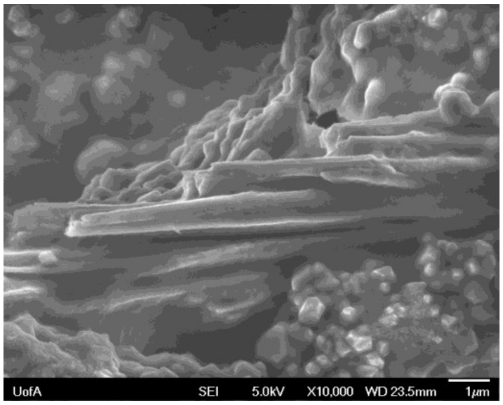

Figure 2.3 FE-SEM of freeze-dried ET solids.

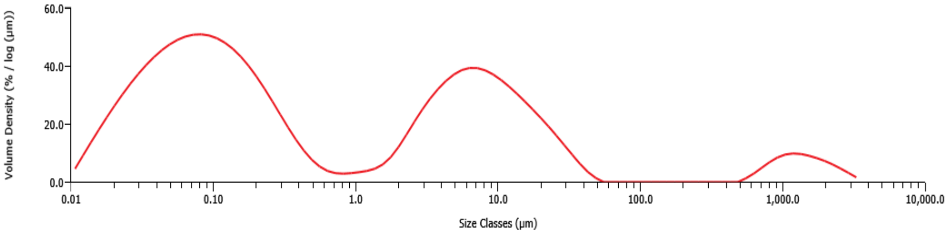

Figure 2.4 Particle size distribution of ET suspension.

Table 2.1 Ion concentrations (ppm) of ET water.

Ions	**Na**	**K**	**B**	**Mg**	**Ca**	**Ba**	**Sr**	**Li**
Concentration in ppm	811	13.9	3.53	2.65	2.80	0.291	0.241	0.243
Ions	**Mo**	**Al**	**Rb**	**Cr**	**Cu**	**Mn**	**Se**	
Concentration in ppm	0.0751	0.0205	0.0216	0.017	0.0134	0.0153	0.0102	

2.3.2 Flocculation using Single Polymer Flocculant

The flocculation performance of using a single polymer flocculant (i.e. MF or chitosan) on treating extraction tailings was investigated first and the results are shown in Figure 2.5 and Figure 2.6, respectively. It is noted that the two polymers display different flocculation performances on extraction tailings. As shown in Figure 2.5, MF exhibited excellent settling ability on the exaction tailings: with an optimal polymer dosage at 20 ppm, a high ISR value of 10.26 m/h was achieved, which is appealing for fast settling of oil sands tailings. However, MF failed to improve the quality of released water. At all polymer dosages applied, turbidity of supernatants was very high which indicates that there were still a large amount of fine particles left in the released water. As shown in Figure 2.5B, 1.51 wt% solid remained in the supernatant after treating the extraction tailings by 20 ppm MF. Although the solid content decreased significantly after treatment by MF, no apparent clarity difference in supernatants between untreated and treated tailings was observed due to the remaining large amount of solids in MF treated tailings as shown in the inset photo of Figure 2.5B. On the other hand, chitosan was able to significantly enhance the clarity of released supernatants with increasing chitosan dosage (Figure 2.6). After treating extraction tailings with 600 ppm of chitosan, the released supernatant showed a very low turbidity value of 15 NTU. Unfortunately, chitosan itself had relatively weak settling ability on the extraction tailings. Even treated by 600 ppm of chitosan, the ISR value was as low as 1.27 m/h. These results were consistent with previous reports [36].

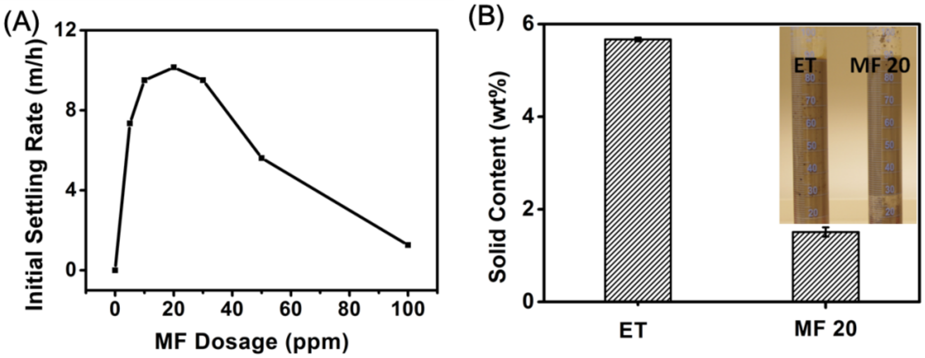

Figure 2.5 Flocculation performance of MF on extraction tailings (ET). (A) Initial settling rate (ISR) as a function of MF dosage, (B) solid content in released supernatants after settling for 30 min for untreated extraction tailings and that treated by 20 ppm of MF. The photograph taken 30 min after settling test is shown as the inset graph.

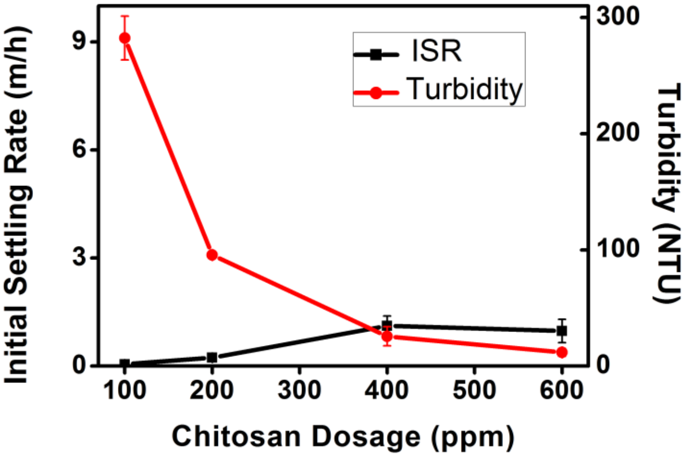

Figure 2.6 ISR and Turbidity of supernatant as a function of chitosan dosage. Turbidity of supernatant was measured after 30 minutes of settling test.

2.3.3 A two-step flocculation procedure with two oppositely charged polymers

The settling tests of the oil sands extraction tailings using a single polymer (i.e. MF or chitosan) showed unsatisfactory results. Therefore, we developed a new two-step flocculation process by combining these two polymers (i.e. MF and chitosan), and expected it would improve the flocculation performance on the extraction tailings in terms of settling efficiency and turbidity of released water. To maintain a fast settling on extraction tailings, MF was applied first at its optimal dosage of 20 ppm. Then different dosages of chitosan solution were added to the above mixture to induce further flocculation. It turned out this two-step flocculation process inherits the merits of both polymers on treating the extraction tailings. As shown in Figure 2.7A, at all the testing conditions, the two-step flocculation process could maintain more than 50% ISR of that in the flocculation process treated by 20 ppm of MF alone; at the same time, the turbidity of released supernatants after 30 min was appreciably low. Under an optimized condition, for example, after treating the extraction tailing by 20 ppm of MF followed by 200 ppm of Chitosan, the turbidity of the resultant supernatant was extremely low with a value of 71 NTU while the ISR value was maintained as high as 7.7 m/h. The above results indicated that quite low solid content of fine particles remained in the released supernatant, which can be easily discerned from a huge difference in the clarity between supernatants treated by two different flocculation processes as shown in Figure 2.7B. It was found that the solid content in the supernatant after the two-step flocculation process was dramatically low, only 0.16 wt%, as compared to 1.51 wt% after flocculation using MF alone.

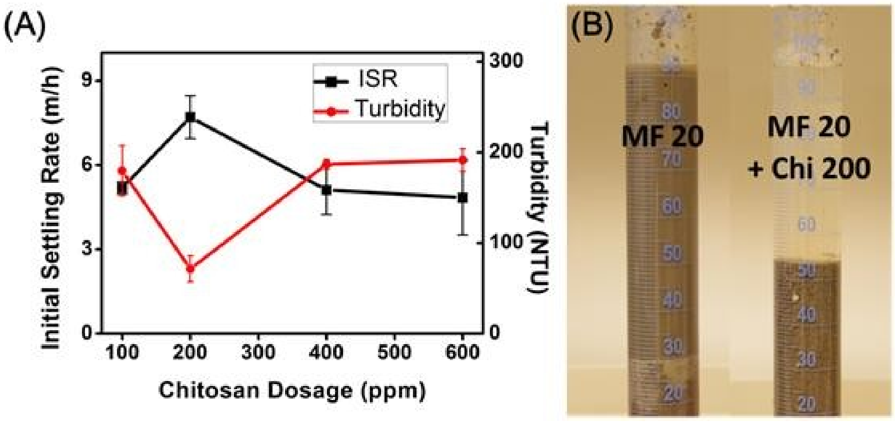

Figure 2.7 (A) ISR and turbidity of supernatants of oil sands extraction tailings settled using a two-step flocculation process with 20 ppm of MF followed by different dosages of chitosan. (B) Image shows the clarity of supernatants (viz. released water) of extraction tailings after treatment by two different flocculation processes: left one for the flocculation using 20 ppm MF and the right one for the two-step flocculation using 20 ppm of MF and 200 ppm of chitosan. Photograph was taken after 30 minutes of settling test.

2.3.4 Zeta potential and FBRM measurements

All the results shown above indicate that our developed two-step flocculation processes could significantly enhance the quality of released water as well as achieve an excellent settling rate on flocculation of oil sands extraction tailings. This phenomenon was mainly attributed to the fact that the subsequent addition of chitosan after MF could facilitate the further agglomeration and settlement of the unflocculated fines dispersed in tailing samples, thus leading to a clearer supernatant production without the detriment of settling efficiency. To better understand and explore the destabilization mechanisms involved in the new flocculation process, zeta potential measurements have been conducted and the whole flocculation process has been monitored through FBRM measurements.

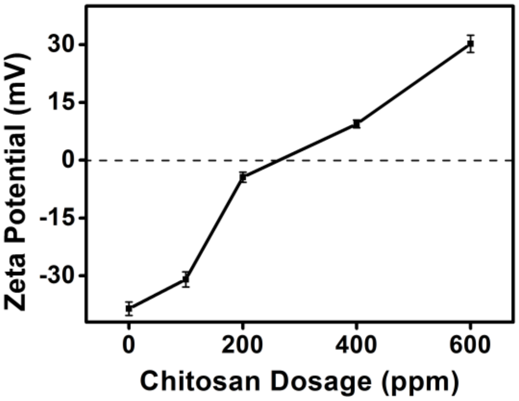

Figure 2.8 Zeta potential of tailing particles suspended in the supernatants after 30 minutes treatment with 20 ppm of MF followed by different dosages of chitosan in the two-step flocculation process.

Zeta potential of tailing particles in released supernatants after 30 min settling was measured and is shown in Figure 2.8. After 20 ppm of MF treatment, there was no significant change in zeta potential as compared to that in the blank bare tailing samples: -38.6 mV vs. -39 mV. These results also indicated that MF destabilized tailing particles mainly by bridging mechanism and left a large amount of fine particles in released supernatant, which agreed with the turbidity and solid content measurements. However, once chitosan was introduced into the system right after the addition of MF, a significant change in the charge property of the tailing particles was observed. The zeta potential of tailing particles in supernatants gradually changed from -38.6 mV to +30.2 mV as the chitosan dosage increased from 100 ppm to 400 ppm, suggesting that the positively charged chitosan polymer chains could bond to negatively charged tailing particles. It is noted that adding 200 ppm of chitosan could almost neutralize the surface charges of tailing particles, leading to a zeta potential value of -4.4 mV, which was quite close to zero (the iso-electric point of the suspension). The dosage was the same condition that resulted in the maximum ISR in the two-step flocculation process. These observations verified that chitosan employs charge neutralization mechanism to destabilize tailing particles in the second step. Through adsorption of the cationic chitosan onto negatively charged particles, the surface charge density of the particles could be changed, weakening the electric double layer repulsion and thereby destabilizing the suspended particles.

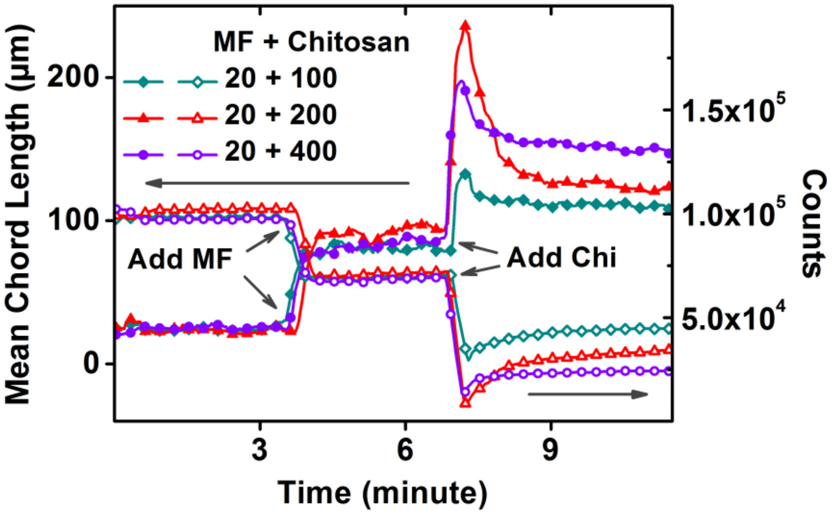

Figure 2.9 Counts and square weighted mean chord length versus time in two-step flocculation using a fixed dosage of MF at 20 ppm with varied chitosan dosage (100, 200, 400 ppm). The constant mixing speed was 300 rpm.

FBRM measurements monitored the changes in the number and size of the particles during the two-step flocculation process, as the counts and square weighted mean chord length of FBRM were sensitive to changes in number and size of the flocs. Formation of large flocs diminished particle species in the tailings mixture and suggested an increase of square weighted mean chord length and a decrease of counts in FBRM. FBRM measurements were conducted under the same condition for settling tests. The corresponding changes in square weighted mean chord length and total counts of oil sands tailing treated by these two polymers were recorded and the results are summarized in Figure 2.9. It is evident from the sequent changes of square weighted mean chord length and total counts in Figure 2.9 that the developed flocculation process using MF and chitosan clearly showed two steps of flocculation of the solid particles in the oil sands tailings. In the first step, MF triggered a preliminary flocculation by bridging coarse particles into large flocs and decreasing the number of particles, which was demonstrated by the increase of square weighted mean chord length and decrease of total counts. Subsequent addition of chitosan further led to a significant alteration in particle size and particle number. For example, with an addition of 200 ppm chitosan, square weighted mean chord length of the system was apparently changed from 85 to 220 micrometer with an obvious decrease of the total count from 7.5×10^4 to 1000, indicating a further aggregation of the unsettled fines together with the flocs formed during the first step. These results also indicated subsequent introduction of chitosan could significantly improve the clarity of released supernatant. The FBRM results were in consistent with the settling results. As in settling tests, the highest ISR was achieved by 20 ppm MF and 200 ppm chitosan, which was exactly the same condition to reach the largest size and lowest total counts in FBRM measurement.

It is also interesting to note that different dosages of chitosan produced different flocs in terms of mechanical strength. As shown in Figure 2.9, flocs induced by MF were quite strong and tolerant to external mechanical force: even after 3 min agitation, no obvious change was found in the particle size and counts during the first step of flocculation; whereas the flocs induced by chitosan in the second step were larger in volume but less compact than its counterparts from MF, which could be easily broken down under agitation. After addition of chitosan, if agitation continues, formed flocs swiftly broke down and thus resulted in a continuous decrease of square weighted mean chord length, particularly for 200 ppm chitosan mediated flocculation, which showed the sharpest decrease of particle size under agitation. However, it is still worth to note that even under continuous agitation final equilibrated flocs still possesses a larger size than that treated only by MF. This phenomenon was most likely attributed to the different destabilization mechanisms of MF and chitosan, namely bridging and charge neutralization mechanisms. According to previous studies [37], charge neutralization normally forms flocs of larger size but more susceptible to shear stress than bridging effect does.

2.3.5 Surface Force Measurements

To probe the adsorption behavior and interaction forces of the two polymers on tailings particle surfaces in the two-step flocculation, surface force measurements were carried out between model mica surfaces in polymer solutions. Mica surface has similar silicate structure as kaolinite, a major clay component in tailings solids. The force-distance profiles between two mica surfaces in different polymer solutions are shown in Figure 2.10. As in Figure 2.10A, when two mica surfaces were brought closer in 20 ppm MF solution, ~14 nm of polymer was detected and confined between the two mica surfaces, indicating a soft layer of MF polymer (~7 nm under confinement) was successfully coated on each mica surface. The repulsive force measured was mainly due to steric interaction of the extended MF polymer chains adsorbed on mica. Figure 2.10B shows the force-distance profile for two mica surfaces interacting in 200 ppm chitosan, and an adhesion of F/R value ~ -4 mN/m was measured which indicates the weak bridging adhesion of chitosan on the two mica surfaces, mainly due to electrostatic attraction. Figure 2.10C shows the force-distance profile between two mica surfaces coated with a layer of MF interacting in 200 ppm chitosan solution. To mimic the two-step flocculation process, the two mica surfaces were firstly coated with a layer of MF by dipping in 20 ppm MF solution for 90 minutes which were then washed by pure water. An adhesion of F/R value at -31 mN/m was measured with confined polymer thickness of around 17 nm in Figure 2.10C, suggesting the addition of chitosan could strongly enhance the bridging attraction between MF-absorbed particle surfaces. The surface force results in Figure 2.10 are in consistent with the settling tests and FBRM results that the addition of chitosan in the two-step flocculation could lead to the formation of large aggregates and further facilitate the settling process by improving the clarity of the released water.

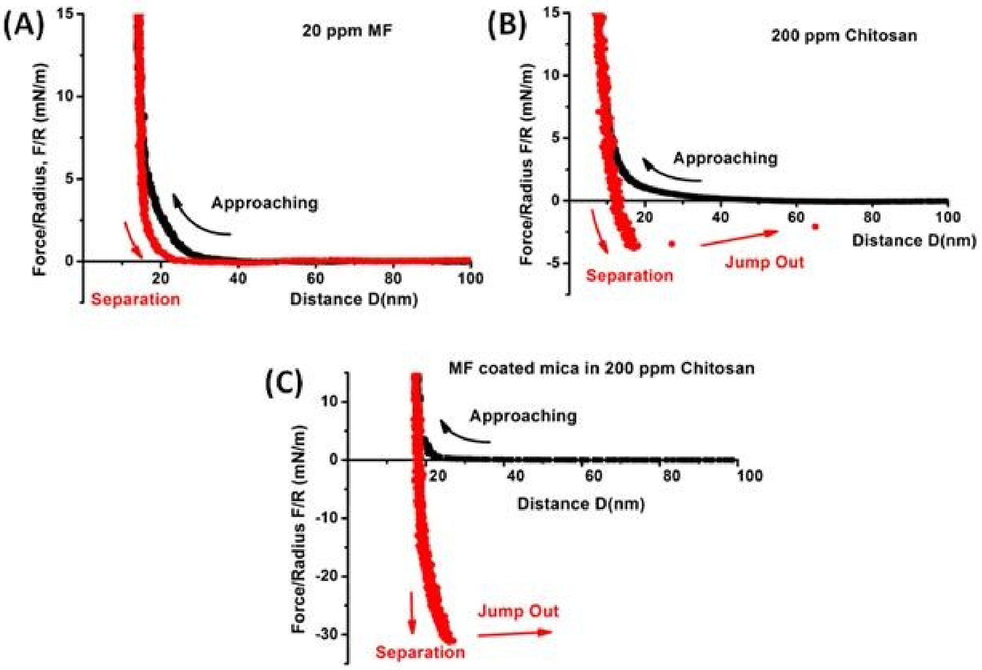

Figure 2.10 Force-distance profiles between (A) mica surfaces in 20 ppm MF solution, (B) mica surfaces in 200 ppm chitosan solution, and (C) MF coated mica surfaces in 200 ppm chitosan solution. All polymers were prepared in 800 ppm NaCl solution, which was the measured salt concentration of extraction tailings.

2.3.6 Destabilization Mechanisms

Based on the above results, a flocculation mechanism is proposed to explain the enhanced settling performance of the developed two-step flocculation process (Figure 2.11): (1) bridging of fine solids by anionic polyacrylamide polymer (i.e. MF), and (2) further aggregation and flocculation mediated by charge neutralization of the cationic polymer (i.e. chitosan). The preliminary bridging flocculation induced by anionic polyacrylamide only results in partial collection of fine particles into some dense flocs and leaves a large amount of free fine solids, thereby triggering a fast settling but retaining a high turbidity (see Case 1 in Figure 2.11). Subsequent addition of cationic polymer will further aggregate and flocculate the remaining fine particles together with the formed flocs, which significantly eliminates the fine solids in the supernatants as well as increases floc size. Due to its specific characteristics of the neutralization mechanism, dosage of cationic polymers applied plays an important role in the final flocculation performance. Either insufficient or excessive application of cationic polymers will fail to aggregate or flocculate the remaining fine particles. If chitosan is applied insufficiently, then partial aggregation of particles in the system will occur, leaving suspended fines in the supernatant (Case 2 in Figure 2.11). On the other hand, if chitosan is added in excess, then extra chitosan chains will bring in extra electrical repulsion among particles, resulting in smaller flocs (Case 4 in Figure 2.11). Only at a suitable applied dosage of chitosan that completely or nearly neutralizes negatively charged particles will result in a fast settling rate and a low solid content of the supernatant (Case 2 in Figure 2.11).

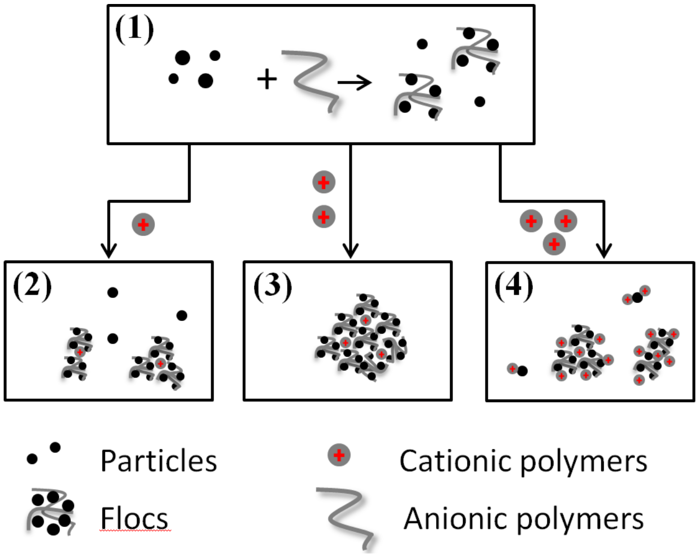

Figure 2.11 A schematic for proposed flocculation mechanism involved in the two-step flocculation process: (1) small flocs formed from MF bridging, leaving fine solids

unsettled; (2) adsorption of a small (insufficient) amount of chitosan onto particle surfaces induces incomplete flocculation; (3) complete neutralisation by chitosan forms large flocs; (4) excessive positive chitosan re-stabilizes the system through electrical repulsion.

2.4 Conclusion

In summary, a two-step flocculation process has been developed for the treatment of oil sands tailings by using two oppositely charged polymers MF and chitosan. Compared to incompetency in treating oil sands tailings using widely-applied flocculation process based on a single polymer flocculant, this two-step process could not only significantly improve the quality of released water by dramatically enhancing the turbidity of supernatant and reducing solid content of supernatant but also maintained a comparably high settling rate. The turbidity of released supernatant was as low as 71 NTU while maintaining a high ISR of 7.7 m/s. The enhanced flocculation performance is attributed to the successive flocculation caused by two polymers, as supported by surface force measurements: (1) bridging of fine solids by anionic polyacrylamide, and (2) further aggregation and flocculation mediated by charge neutralization of the cationic polymer. In addition, the two-step flocculation adopting natural biopolymer (i.e., chitosan) is more environmentally friendly as compared to using synthetic polymer flocculants. Our results provide insights into the development of novel technologies for oil sands tailings treatment.

2.5 Acknowledgements

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2.6 References

1. Allen, E.W., Process water treatment in Canada's oil sands industry: I. Target pollutants and treatment objectives. Journal of Environmental Engineering and Science, 2008. 7(2): p. 123-138.

2. Giesy, J.P., J.C. Anderson, and S.B. Wiseman, Alberta oil sands development. Proceedings of the National Academy of Sciences, 2010. 107(3): p. 951-952.

3. Chalaturnyk, R.J., J. Don Scott, and B. Özüm, Management of oil sands tailings. Petroleum Science and Technology, 2002. 20(9-10): p. 1025-1046.

4. Scott, A.C., et al., Ozonation of oil sands process water removes naphthenic acids and toxicity. Chemosphere, 2008. 71(1): p. 156-160.

5. Gosselin, P., et al. Environmental and health impacts of Canada's oil sands industry. 2010: Royal Society of Canada Ottawa, Ontario, Canada.

6. Kelly, E.N., et al., Oil sands development contributes elements toxic at low concentrations to the Athabasca River and its tributaries. Proceedings of the National Academy of Sciences, 2010. 107(37): p. 16178-16183.

7. Mamer, M., Oil sands tailings technology: Understanding the impact to reclamation. 2010.

8. Yergeau, E., et al., Next-generation sequencing of microbial communities in the Athabasca River and its tributaries in relation to oil sands mining activities. Applied and environmental microbiology, 2012. 78(21): p. 7626-7637.

9. Jeremy Boswell, M.D., Oil Sand Tailings Technology Development Roadmap, D. Cowan, Editor. 2012, Alberta Innovates – Energy and Environment Solutions.

10. Xu, Y., T. Dabros, and J. Kan, Filterability of oil sands tailings. Process Safety and Environmental Protection, 2008. 86(4): p. 268-276.

11. Farkish, A. and M. Fall, Rapid dewatering of oil sand mature fine tailings using super absorbent polymer (SAP). Minerals Engineering, 2013. 50: p. 38-47.

12. Gray, M., Z. Xu, and J. Masliyah, Physics in the oil sands of Alberta. Physics Today, 2009. 62(3): p. 31-35.

13.Tripathy, T. and B.R. De, Flocculation: a new way to treat the waste water. 2006.

14. O'Shea, J.-P., G.G. Qiao, and G.V. Franks, Temperature responsive flocculation and solid–liquid separations with charged random copolymers of poly (N-isopropyl acrylamide). Journal of Colloid and Interface Science, 2011. 360(1): p. 61-70.

15. Wang, S., Fundamental Study on Polymer Flocculation Behavior in Saline Solutions. 2014, University of Alberta.

16. Wang, C., et al., Current state of fine mineral tailings treatment: A critical review on theory and practice. Minerals Engineering, 2014. 58: p. 113-131.

17. Alagha, L., et al., Adsorption kinetics of a novel organic–inorganic hybrid polymer on silica and alumina studied by quartz crystal microbalance. The Journal of Physical Chemistry C, 2011. 115(31): p. 15390-15402.

18. Alamgir, A., et al., Al-PAM assisted filtration system for abatement of mature fine tailings. Chemical Engineering Science, 2012. 80: p. 91-99.

19. Wang, S., L. Alagha, and Z. Xu, Adsorption of organic–inorganic hybrid polymers on kaolin from aqueous solutions. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2014. 453: p. 13-20.

20. Guo, L., Understanding Al-PAM assisted oil sands tailings treatment. 2012, University of Alberta.

21. Wang, Y., et al., Temperature-responsive hyperbranched amine-based polymers for solid–liquid separation. Langmuir, 2014. 30(9): p. 2360-2368.

22. Long, J., et al., Improving oil sands processability using a temperature-sensitive polymer. Energy & Fuels, 2011. 25(2): p. 701-707.

23. Li, H., et al., Enhancing treatment and geotechnical stability of oil sands fine tailings using thermo - sensitive poly (n - isopropyl acrylamide). The Canadian Journal of Chemical Engineering, 2015. 93(10): p. 1780-1786.

24. Sworska, A., J. Laskowski, and G. Cymerman, Flocculation of the Syncrude fine tailings: Part I. Effect of pH, polymer dosage and Mg2+ and Ca2+ cations. International journal of mineral processing, 2000. 60(2): p. 143-152.

25. Vedoy, D.R. and J.B. Soares, Water‐soluble polymers for oil sands tailing treatment: A Review. The Canadian Journal of Chemical Engineering, 2015. 93(5): p. 888-904.

26. Xiao, H., Z. Liu, and N. Wiseman, Synergetic effect of cationic polymer microparticles and anionic polymer on fine clay flocculation. Journal of Colloid and Interface Science, 1999. 216(2): p. 409-417.

27. Sang, Y. and H. Xiao, Clay flocculation improved by cationic poly (vinyl alcohol)/anionic polymer dual-component system. Journal of Colloid and Interface Science, 2008. 326(2): p. 420-425.

28. Peng, F. and Z. Lu, POLYMER FLOCCULATION AND COAGULATION FOR SEDIMENTATION OF COPPER FLOTATIONTAILINGS. Minerals & metallurgical processing, 1998. 15(1): p. 14-20.

29. Glover, S.M., G.J. Jameson, and S. Biggs, Dewatering properties of dual-polymer-flocculated systems. International journal of mineral processing, 2004. 73(2): p. 145-160.

30. Ji, Y., et al., Effect of solution salinity on settling of mineral tailings by polymer flocculants. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2013. 430: p. 29-38.

31. Owen, A., et al., The impact of polyacrylamide flocculant solution age on flocculation performance. International journal of mineral processing, 2002. 67(1): p. 123-144.

32. Alfano, J.C., et al., Polyelectrolyte-induced aggregation of microcrystalline cellulose: reversibility and shear effects. Journal of Colloid and Interface Science, 2000. 223(2): p. 244-254.

33. Israelachvili, J., et al., Recent advances in the surface forces apparatus (SFA) technique. Reports on Progress in Physics, 2010. 73(3): p. 036601.

34. Li, L., et al., Mussel-inspired antifouling coatings bearing polymer loops. Chemical Communications, 2015. 51(87): p. 15780-15783.

35. Zhang, L., H. Zeng, and Q. Liu, Probing Molecular and Surface Interactions of Comb-Type Polymer Polystyrene-graft-poly (ethylene oxide)(PS-g-PEO) with an SFA. The Journal of Physical Chemistry C, 2012. 116(33): p. 17554-17562.

36. Hogg, R., The role of polymer adsorption kinetics in flocculation. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 1999. 146(1): p. 253-263.

37. Jarvis, P., et al., A review of floc strength and breakage. Water Research, 2005. 39(14): p. 3121-3137.

Chapter 3 Dewatering of Oil Sands Tailings by Using a Thermo-sensitive Polymer Flocculant

3.1 Introduction

The colloidal stability governed by various surface forces including van der Waals force, electrical double layer force, bridging force, and some other forces plays a critical role in a wide range of engineering processes such as froth flotation, wastewater treatment and tailings management [1-3]. In tailings treatment, fine solids are settled and consolidated to be separated from tailings water, which is determined by the solid settling related to the size and density of formed aggregates as well as sediment consolidation relied on low mechanical strength for easy compaction [4, 5]. Nevertheless, the negatively charged surfaces inhibit the approach and aggregation of fine solids due to strongly repulsive electrical double layer interaction [2]. To destabilize the colloidal suspension, polymeric flocculants, mainly polyelectrolytes based on high molecular weight, ionic or nonionic polyacrylamide (PAM), have been extensively used to facilitate the solid/liquid separation through bridging mechanism, where the polymer chains are adsorbed to multiple solid surfaces, resulting in the formation of large flocs with loosely bounded structure [6, 7, 8]. Despite their high settling rate, the strongly attractive bridging interaction inside the flocs dramatically impedes sediment consolidation due to considerable mechanical strength, thereby causing a large amount of water to be trapped in the flocs [9-11].

Over the past few decades, significant progress has been achieved with respect to the polymer design to effectively solve the challenge of sediment consolidation and water release [12]. The temperature responsive polymers have been successfully developed to flocculate model clays such as silica and kaolin by manipulating the interaction between clay particles through altering surface hydrophobicity with the temperature [11, 13]. Below the lower critical solution temperature (LCST), the hydrophilic polymers are adsorbed to solid surfaces, which inhibits the aggregation of fine particles by steric repulsion [14]. Once the temperature rises above the LCST, the adsorbed polymer molecules become hydrophobic, leading to the aggregation of fine solids by hydrophobic interaction and the formation of compact sediment with a large volume of released water [14, 15]. The solid/liquid separation using temperature responsive polymers has attracted much attention, yet the basic understanding of the flocculation of temperature responsive polymers on oil sands tailings still remains limited, particularly for mature fine tailings (MFT) [11, 16, 17]. It was reported that the addition of poly(N-isopropylacrylamide) (PNIPAM) during the bitumen extraction process at 40 ºC effectively accelerated the solids settling, but the optimal settling rate of ~2.5 m/h was far lower than that flocculated by anionic PAM [18].

The recently developed two-step flocculation process has enabled high settling rate and low solid content for oil sands tailings treatment [19, 20]. By introducing the bridging mechanism by anionic PAM and charge neutralization mechanism by cationic chitosan, lower solid content of supernatants and similar settling rate can be achieved as compared to anionic PAM flocculation on oil sands tailings. Therefore, it is possible to realize high settling rate, low solid content, compact sediment bed and high water release in oil sands tailing treatment by replacing the cationic chitosan with a cationic temperature responsive polymer in the two-step flocculation process.

In this work, a chitosan based chitosan-g-PMEOMA (CgM) was synthesized as the cationic temperature responsive polymer for the two-step flocculation process due to its naturally cost-effective and environment-friendly property [21-23]. The flocculation performances on the diluted MFT in terms of initial settling rate, and turbidity of released water were investigated by two-step settling test using cationic CgM and anionic PAM, which were compared with single flocculation by anionic PAM. The effect of temperature on sediment was studied through sediment consolidation and filtration by pressure filtration in terms of filtration rate, turbidity of filtrated water, solid content and shear yield stress of filter cake. The force interaction as a function of time between model clay surfaces in polymer solution was investigated using surface force apparatus (SFA). This work provides useful information and new insights into oil sands tailings treatment and other related engineering operations.

3.2 Materials and Methods

3.2.1 Materials

All the chemicals were purchased from Sigma-Aldrich unless specified. Chitosan with a molecular weight of 6×10^5 to 8×10^5 g/mol was purchased from Acros Organics and used as received without further purification. Magnafloc-1011 (MF) purchased from Ciba Specialty Chemicals is a negatively charged copolymer of acrylamide and sodium acrylate with 27% charge density and molecular weight of 1.75×10^7 g/mol. The polymer stock of MF was prepared at a concentration of 0.5 g/L in Milli-Q water for settling tests.

MFT provided by Syncrude Canada Ltd was diluted to a solid content of 5 wt% as the demonstrating tailings in this study. The solids in the tailings were centrifuged, dried and characterized by X-ray diffraction (XRD, Rigaku, Japan). Laser diffraction (Mastersizer 2000, Malvern) was used to determine the particle sizes of tailings suspensions. The microstructure of dried fine particles was examined through SEM (Zeiss EVO MA 15) and FE-SEM. The supernatants of tailings were filtered and subjected to Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for the measurement of ion concentrations.

3.2.2 Synthesis of chitosan-g-PMEOMA (CgM)

2 g chitosan was dissolved in 100 mL 1 wt% acetic acid and the solution was stirred for 30 min to obtain a homogeneous state; thereafter, 1.5 g 2-(2-methoxyethoxy) ethyl methacrylate (MEOMA) was added to the solution with Argon continuously purged to remove oxygen. As 0.2 mL tetramethylenediamine (TEMED) was added as the accelerator, a white precipitate was formed immediately and re-dissolved by an extra addition of 0.5 mL acetic acid. After additional 30 min Argon purging, 0.05 g ammonium persulfate (APS, pre-dissolved in 1 mL Milli-Q water) was injected into the solution to initiate the polymerization of MEOMA. The reaction was stopped after 6 hrs of stirring at room temperature and the obtained polymer solution was used as obtained without further purification and diluted to 2 g/L for settling tests.

3.2.3 Polymer Characterization

The Fourier transform infrared (FT-IR) spectra of CgM and chitosan were obtained using a NicoletiS50 FTIR instrument (Thermo Scientific, Canada). The molecular weight of CgM was determined by static light scattering (SLS) using a Zetasizer Nano (Malvern Instruments Ltd., UK). The LCST of CgM was determined at 50% transmittance of the solution at 550 nm when 0.1 wt% polymer solution was continuously recorded by UV−vis spectrometer at a heating rate of 0.5 °C/min.

3.2.4 Settling Test

The tailings samples and polymer solutions were pre-cooled in 4 ºC freezer for over three hours prior to settling tests. In each settling test, 100 mL diluted MFT was agitated under 600 rpm for 2 min to obtain uniform slurry and a desired amount of polymer solution was then added to the slurry under 300 rpm agitation at room temperature. If a second polymer was required, the second polymer solution was added 10 s after the addition of first polymer to achieve a uniform state. Thereafter, mixing was immediately stopped to avoid breakage of flocs and the mixture was then transferred into a 100 mL graduated cylinder. The cylinder was inversed for 5 times and the height of the mud line was monitored as a function of time to obtain the settling curve. The cylinder was then placed in water bath at either 4 ºC (below LCST) or 50 ºC (above LCST) for sedimentation. Initial settling rate (ISR, in m/h) was calculated from the initial slope of the settling curve as described in a previous report [24]. After settling for 5 min, supernatants were taken out for turbidity (in NTU) measurement using a Micro-100 Turbidimeter (Fisher Scientific, USA). In this work, all the polymer dosages were calculated based on the unit of gram polymer per litter undiluted MFT.

3.2.5 Filtration Test

The sediments were kept in water bath at 4 ºC or 50 ºC prior to filtration tests. Each filtration test was conducted by a laboratory vacuum filtration set for 10 min under a constant pressure of 40 kPa. The cumulative volume of filtrate water was plotted as a function of filtration time. The formed filter cake was dried in an air-vented oven at 105 ºC to determine the final moisture content. The performance of filtration was evaluated in terms of initial filtration rate (mL/s), turbidity of filtrated water, solid content (wt%) and yield stress (Pa) of filter cake.

3.2.6 Shear Strength

The shear strength (yield stress) measurements of filtrate cakes were performed on a C-VOR Bohlin® stress-controlled rheometer using a stainless steel vane that was equipped with a four-bladed paddle with the diameter of 25 mm and an outer cup with the diameter of 50 mm and depth of 60 mm. The samples were loaded and sheared at a constant rate of 0.1 per second for 2 min.

3.2.7 Measurement of Interaction Force Using Surface Forces Apparatus

Interaction forces between two model mica surfaces and CgM coated mica surfaces in MF and CgM solutions were investigated by a Surface Forces Apparatus (SFA). As described in Chapter 2, two mica sheets were glued onto cylindrical silica disks and then mounted in the chamber in a crossed-cylinder configuration. The two cylindrical mica disks of radius R were locally equivalent to a sphere of radius R interacting with a flat surface or, two spheres of radius 2R when the surface separation distance D was much smaller than R. The separation distance D was determined by fringes of equal chromatic order (FECO) in a multiple beam interferometry (MBI) [25-28].

3.3 Results and Discussion

3.3.1 Characterization of MFT

The mature fine tailings from Syncrude Ltd were characterized to contain 4.58 wt% bitumen, 31.7 wt% solids and 63.72 wt% water as shown in Table 3.1. The XRD patterns of tailings solids demonstrated that quartz, kaolinite and nacrite are the major mineral phases as summarized in Table 3.2. Figure 3.1A shows the FE-SEM image of dried tailing particles, which clearly demonstrated that the particles of MFT formed stacked thin plate layers. Figure 3.1B shows the SEM of sieved tailing solids less than 53 micron. It was found that the solids of tailings formed flaky plates in the scale of ~2 microns in diameter, and aggregated into different sizes of compact and claylike masses. The energy-dispersive X-ray spectroscopy analysis (EDX) coupled with the SEM demonstrated an abundant content of Si and Al (Si:Al ≈ 1.5:1). Particle size analyzer (Mastersizer) was employed to measure the size of suspended particles in tailings, 93.48% of which were smaller than 44 micron as shown in Figure 3.2. The ion concentrations of tailings water were summarized in Table 3.3, in which the most abundant ions were Na, K, Ca and Mg.

Table 3.1 The composition of MFT.

MFT composition	wt%
solids	31.7
bitumen	4.58
water	63.72

Table 3.2 Major mineral composition of MFT solids from XRD measurement.

Major mineral phases	Formula
Quartz	SiO_2
Kaolinite	$Al_2Si_2O_5(OH)_4$
Nacrite	$Al_2Si_2O_5(OH)_4$

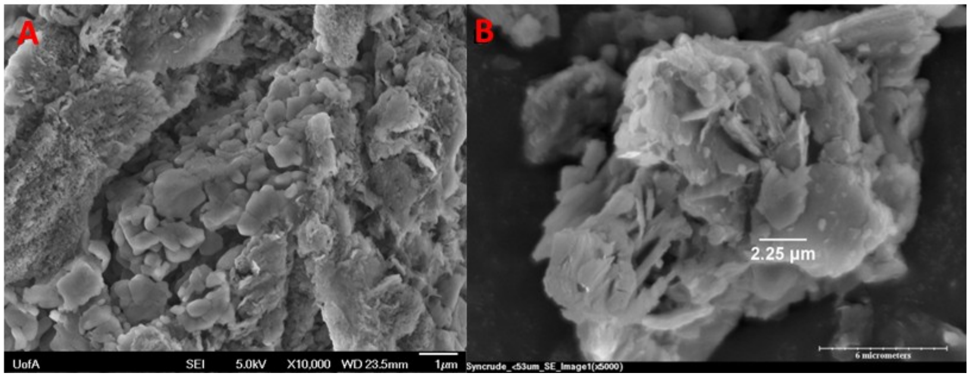

Figure 3.1 (A) FE-SEM of freeze-dried MFT solids, (B) SEM of sieved dry MFT solids.

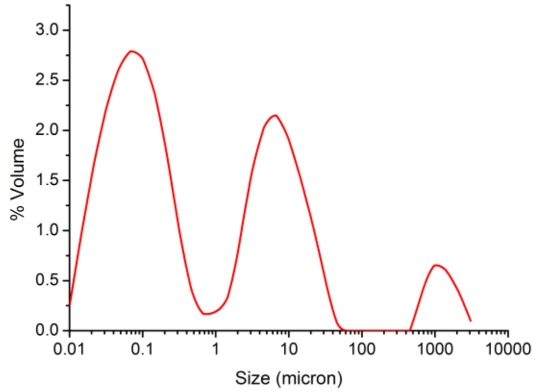

Figure 3.2 Particle size distribution of MFT suspension.

Table 3.3 Ion concentrations (ppm) of MFT water.

Ions	**Na**	**K**	**B**	**Mg**	**Ca**	**Ba**	**Sr**	**Li**
Concentration in ppm	824	13.5	3.86	8.84	13.3	0.340	0.558	0.198
Ions	**Mo**	**Al**	**Rb**	**Cr**	**Cu**	**Mn**	**Se**	
Concentration in ppm	0.0144	0.0652	0.0232	0.0241	0.0127	0.0146	0.0046	

3.3.2 Characterization of chitosan-grafted-PMEOMA

The CgM was synthesized according to a modified procedure as demonstrated in Figure 3.3. The molecular weight of the synthesized CgM was determined to be 1.64×10^6 g/mol by SLS measurement, which has been more than doubled the molecular weight of chitosan, indicating that PMEOMA has been successfully grafted to chitosan backbones. The FT-IR spectra of chitosan and CgM in Figure 3.4 clearly shows a broad peak at 3363 cm^{-1} attributed to the stretching vibrations of O−H and N−H as well as a small peak at 2850 cm^{-1} assigned to the C−H stretching vibrations from saccharide groups of chitosan. Compared to chitosan, it is evident that a strong absorption peak at 1725 cm^{-1} arising from the -COO- strong stretching vibrations of PMEOMA and an increased absorbance intensity of -C-O-C- at 1028 cm^{-1} and 1066 cm^{-1} can be observed for the spectrum of CgM, which further confirmed the successful grafting of PMEOMA to chitosan backbones. As shown in Figure 3.5, The LCST of the synthesized CgM was determined to be 23-43 ºC by UV−vis spectrometer; therefore, CgM is soluble in aqueous solution with the hydrophilic structure at 4 ºC, which becomes hydrophobic and insoluble at 50 ºC.

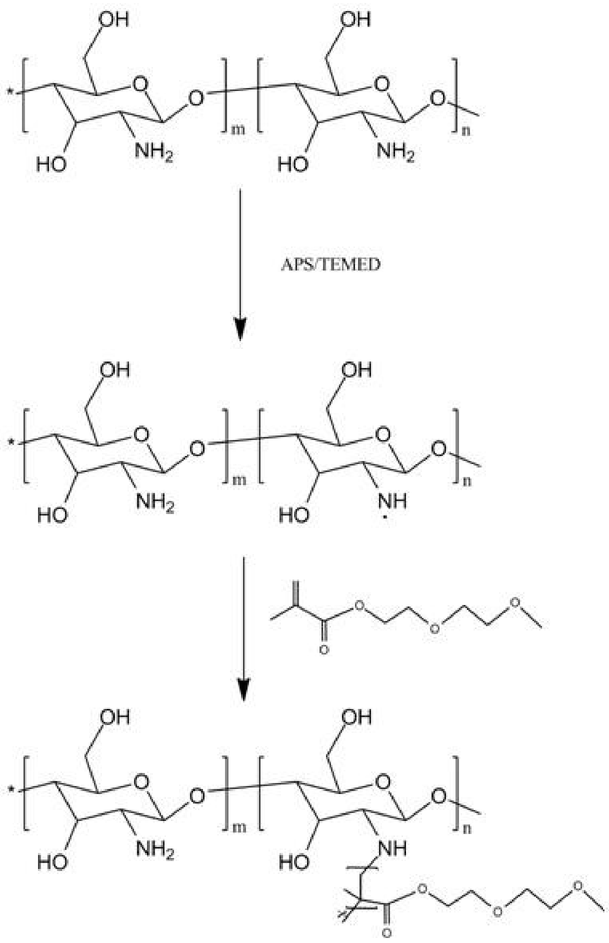

Figure 3.3 Schematic of the synthesis of chitosan-grafted-PMEOMA (CgM).

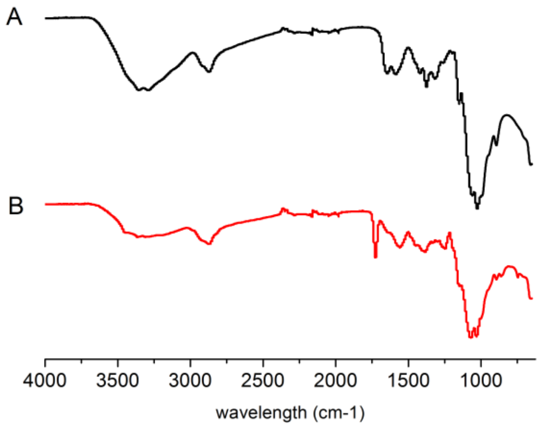

Figure 3.4 FT-IR spectra of (A) chitosan and (B) CgM powder samples.

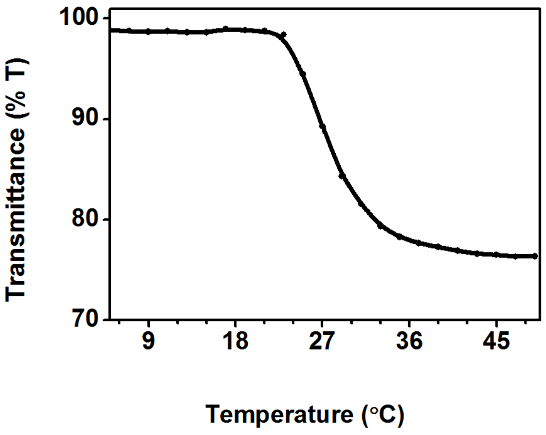

Figure 3.5 Lower critical solution temperature (LCST) of CgM.

3.3.3 Settling performance of single flocculation

The settling of diluted MFT was first conducted using single flocculation to compare the effect of different polymers on flocculation performance. As a temperature responsive polymer, the settling performance of CgM highly relies on the temperature of flocculation. Since CgM is soluble in aqueous solution at temperatures lower than LCST, it was added to diluted MFT at 4 ºC. The mixture of CgM and diluted MFT was subsequently placed in water bath at 4 ºC and 50 ºC, respectively. The impact of temperature on the initial settling rate (ISR) is as illustrated in Figure 3.6.

The flocculation at 4 ºC showed a very low ISR that slightly increased to 0.05 m/h with increasing the polymer dosage. In contrast, a higher ISR was observed for flocculation at 50 ºC at all polymer dosages and the maximum ISR reached 0.15 m/h at the dosage of 1.18 g/L. The enhanced ISR was arising from the adsorbed polymers through charge neutralization mechanism that became hydrophobic at 50 ºC and facilitated the aggregation of fine solids by hydrophobic attraction. Despite the enhanced settling performance at 50 ºC, the ISR of CgM was still far lower than the case of MF single flocculation with the maximum ISR of 15.22 m/h at the optimal dosage of 0.2 g/L, which was most probably due to the shorter range of hydrophobic interaction between polymer-covered solids as compared to bridging interaction between fine solids in MF polymer solution.

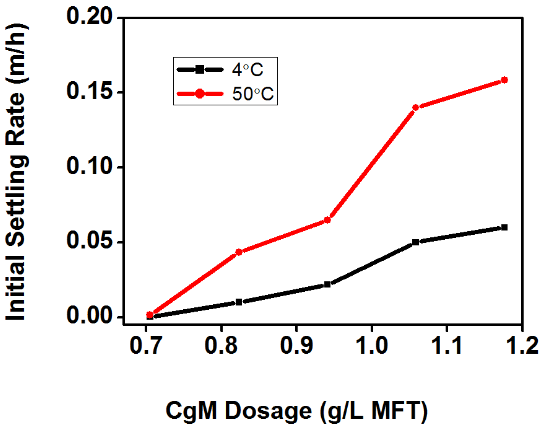

Figure 3.6 ISR of diluted MFT as a function of CgM dosage by single flocculation at different temperatures.

3.3.4 Settling performance of two-step flocculation

In two-step flocculation, cationic CgM was added in diluted MFT followed by the addition of anionic MF at 4ºC. Herein, the optimal dosage of MF at 0.2 g/L was chosen while the dosage of CgM varied, and the ISR and turbidity of supernatant is shown in

Figure 3.7A. The turbidity of supernatant continuously decreased as the dosage of CgM increased. The ISR was observed to be over 11 m/h at all CgM dosages and a maximum ISR of 19.44 m/h was achieved at the dosage of 0.83 g/L. As shown in Figure 3.7B, the subsequent placement of the mixture in water bath at 4 ºC and 50 ºC played negligible role in the ISR because sedimentation by the two-step flocculation happened very fast and could be completed within one minute before the temperature of sediment got changed.

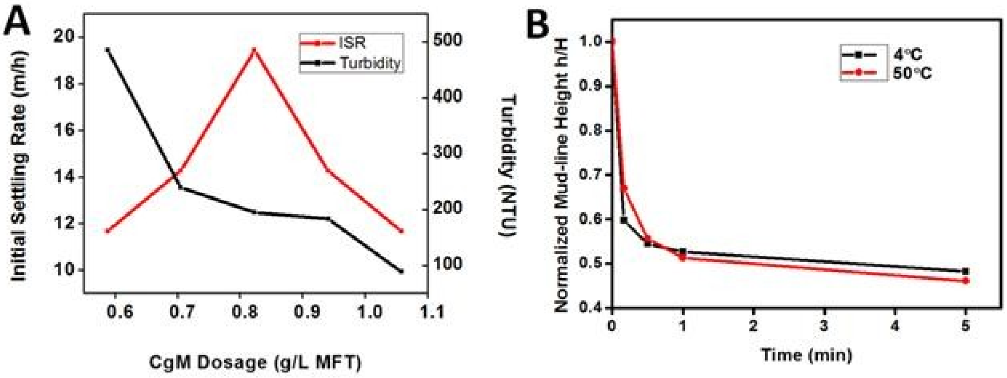

Figure 3.7 (A) ISR and turbidity as a function of CgM dosage by two-step flocculation. The dosage of MF was controlled at 0.2 g/L. (B) Settling curve of 0.83 g/L CgM followed by 0.2 g/L MF at 4 ºC and 50 ºC.

A further comparison of ISR and turbidity by two-step flocculation and MF single flocculation within 5 minutes of flocculation in Table 3.4 demonstrated that the optimal ISR achieved by two-step flocculation was 28% higher than MF single flocculation, and a dramatic elimination of suspended solids in supernatant was measured for two-step flocculation. Single flocculation by MF had negligible effect on the clarity of supernatant, and the turbidity cannot be measured due to large amount of remaining fine solids in the supernatant, which could be observed from the unclear sediment line in Figure 3.8. The enhanced ISR and clarity of two-step flocculation were attributed to the charge neutralization mechanism where the adsorbed cationic CgM induced a localized charge reversal on negatively charged solid surfaces and the formation of small aggregates through the interaction between sites of opposite charges on different particles. The addition of MF further bridged small aggregates into large aggregates (Figure 3.8 right) to facilitate a high settling rate and low solid content of supernatant, which was consistent with our observation in Chapter 2.

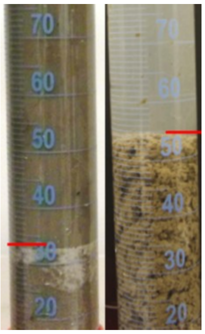

Figure 3.8 Photograph showing sediment bed line (red line) and supernatant by MF single flocculation (left) and two-step flocculation (right) using the optimal dosage at 4 ºC.

Table 3.4 Comparison of ISR and solids content of supernatant by MF single flocculation and two-step flocculation using optimized dosage at 4 ºC. Measurement of solid content was done in 5 minutes of polymer addition.

	MF	Two-step at 4 ºC
ISR in m/h	15.22	19.44
Solid content in supernatant	1.401%	0.037%

The effect of temperature on consolidation and sedimentation time of two-step flocculation with the optimal dosage was investigated by staying at 4 ºC and 50 ºC for 2 hrs. The comparison in the turbidity of supernatants is shown in Figure 3.9 and Table 3.5. Sedimentation at 50 ºC for 2 hrs dramatically removed suspended solids in supernatants and led to a better supernatant clarity with the turbidity of 15 NTU as compared to 239 NTU for 4 ºC. The lower solid content of supernatant after sedimentation at 50 ºC indicates the aggregation and settling of residual CgM-adsorbed particles through hydrophobic interaction at above LCST.

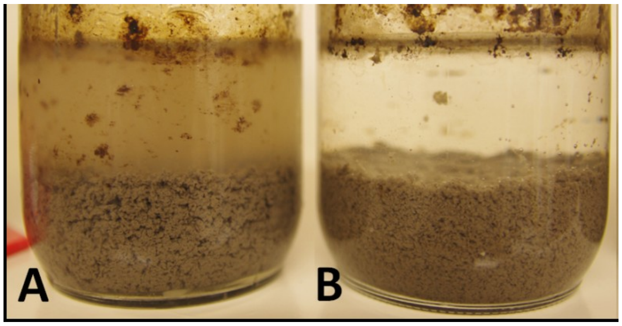

Figure 3.9 Diluted MFT treated by two-step flocculation followed by placing at (A) 4 ºC for 2 hrs; and (B) at 50 ºC for 2 hrs.

Table 3.5 Impact of temperature on turbidity of supernatant and solid content of sediments by two-step induced flocculation.

	Two-step at 4ºC	**Two step at 50ºC**
Turbidity in NTU	239	15
Solid content in sediments	20.83%	23.49%

The effect of temperature on sediment solid content and floc formation of two-step flocculation is illustrated in Table 3.5 and Figure 3.10. After two hrs, solid content of sediments at 50 ºC was higher than that at 4 ºC. The structure of flocs formed before and after sedimentation at 4 ºC was similar, but the size of flocs formed after sedimentation at 50 ºC was significantly reduced, which was in consistent with the loosely bound structure after sedimentation at 4 ºC and compact structure after the sediment at 50 ºC in Figure 3.10. The enhanced consolidation and reduced floc size by temperature change were most probably because CgM-adsorbed particles inside the flocs became hydrophobic when the temperature was risen above the LCST, and the hydrophobic particles bridged by MF started to approach each other and squeeze the water out of the flocs through hydrophobic interaction, thereby leading to a compact structure of flocs with high solid content.

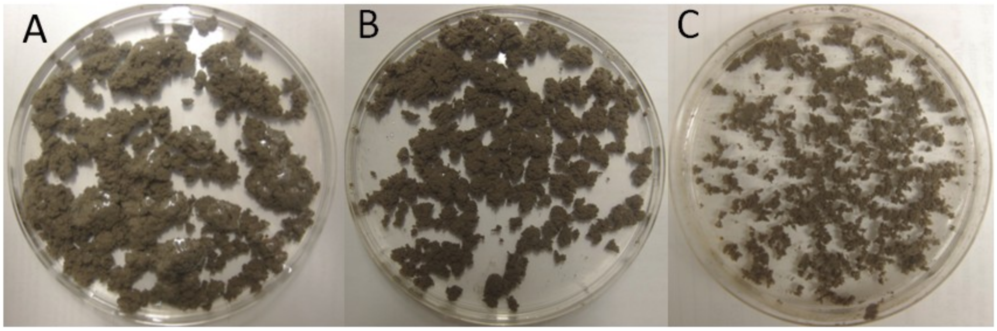

Figure 3.10 The flocs in tailings water (A) right after polymer addition, (B) after sedimentation at 4 ºC for 2 hrs, and (C) after sedimentation at 50 ºC for 2 hrs.

3.3.5 Effect of temperature on filterability of sediments

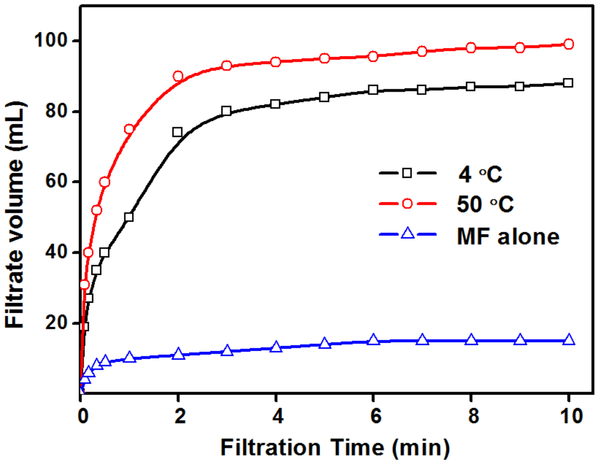

Figure 3.11 Volume of filtrated water as a function of time.

Because filtration is a universal process in solid/liquid separation operations, the impact of temperature on the filterability of two-step flocculation was investigated by pressure filtration tests and the performance was compared to MF single flocculation. Before filtration tests, two-step flocculated diluted MFT at the optimal dosage of CgM and MF was placed in water bath at 4 ºC and 50 ºC for 2 hrs, while MF single flocculated diluted MFT was placed in room temperature for 2 hrs. The filtrated water volume as a function of time is presented in Figure 3.11, which demonstrates that the sediments from two-step flocculation were filtrated much faster than MF single flocculation. In fact, the addition of MF to diluted MFT formed a gel-like structure, blocking the pores of filter cake and hindering water to pass through the cake. After 10 minutes of filtration, large volume of water still remained in the funnel for MF flocculated diluted MFT. Comparing the two-step flocculated tailings at different temperatures, 50 ºC treated sediments released more water than the case of 4 ºC after 10 min of filtration. A further comparison in initial filtration rate in Figure 3.12A clearly shows that sediments treated at 50 ºC achieved a faster initial filtration rate than the other two cases.

The turbidity of filtrated water was very high for MF single flocculation in Figure 3.12B and the turbidity of filtrated water from two-step flocculation at 50 ºC was the lowest of the three, indicating that suspended fine solids were eliminated by the flocculation effect of CgM at above LCST. Solid content and shear yield stress of filter cake are shown in Figure 3.12C and D. After 10 minutes of filtration, solid content of filter cake from two-step flocculated sediments at 4 ºC (30.8 wt%) showed no big difference to MF single flocculated sediments (28.6 wt%). However, by increasing the temperature above LCST, the solid content was improved to 50.6 wt%. Changes in temperature also significantly influenced the vane shear yield stress of filter cakes, which reflected the stackability of the resulted solid waste. The yield stress of cake from sediments at 50 ºC was 1267 Pa, whereas the yield stress was 191 Pa for at 4 ºC and 181 Pa for MF single flocculation.

The significantly improved performance in filtration demonstrated that the filtration-assisted consolidation of sediments from two-step flocculation became much easier when the flocculated diluted MFT was placed in 50 ºC for 2 hours prior to filtration. It is hypothesized that the polymer chains of hydrophilic CgM and MF molecules bind water molecules and fine solids through hydrogen bonding at the temperatures below the LCST, resulting in loose yet highly strong structures of aggregates with large volume of entrapped water, which cannot be easily recovered even under pressure filtration. The polymer chains of CgM coil up when the temperature rises above the LCST, exposing hydrophobic groups to solid surfaces and thus weakening the intermolecular attraction with water molecules in the flocs. As a result, the entrapped water can be released and the large flocs can be split into small and compact flocs, which allow more water recovery and higher solid content in filter cakes.

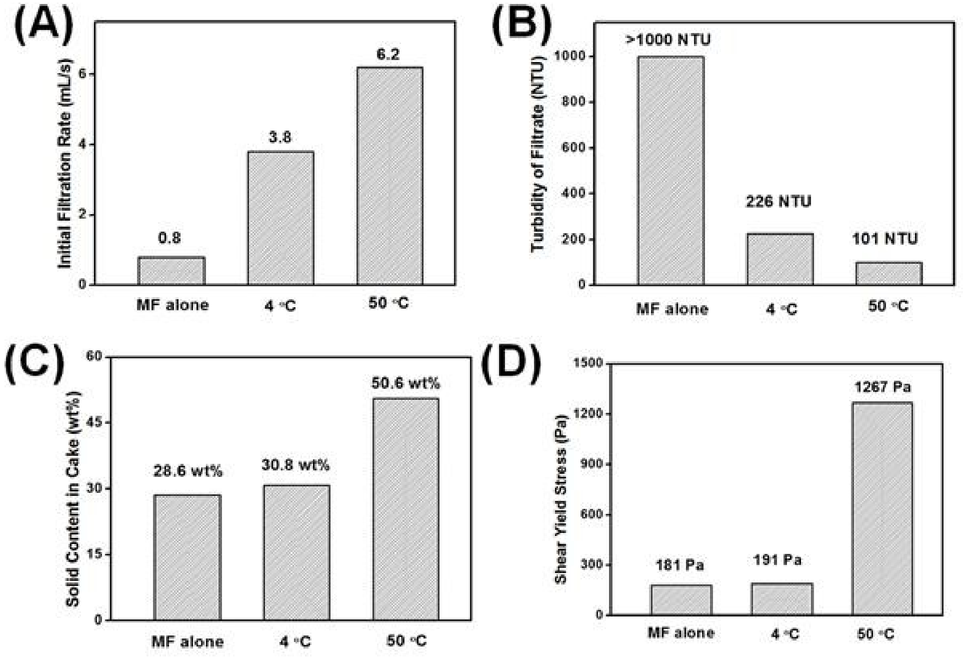

Figure 3.12 Filtration results of two-step flocculation after sedimentation at 4 ºC and 50 ºC for 2 hrs, in comparison with MF single flocculation: (A) initial filtration rate in mL/s, (B) turbidity of filtrated water in NTU, (C) solid content in filter cakes in wt%; (D) shear stress of filter cakes in Pa.

3.3.6 Surface Force Measurements

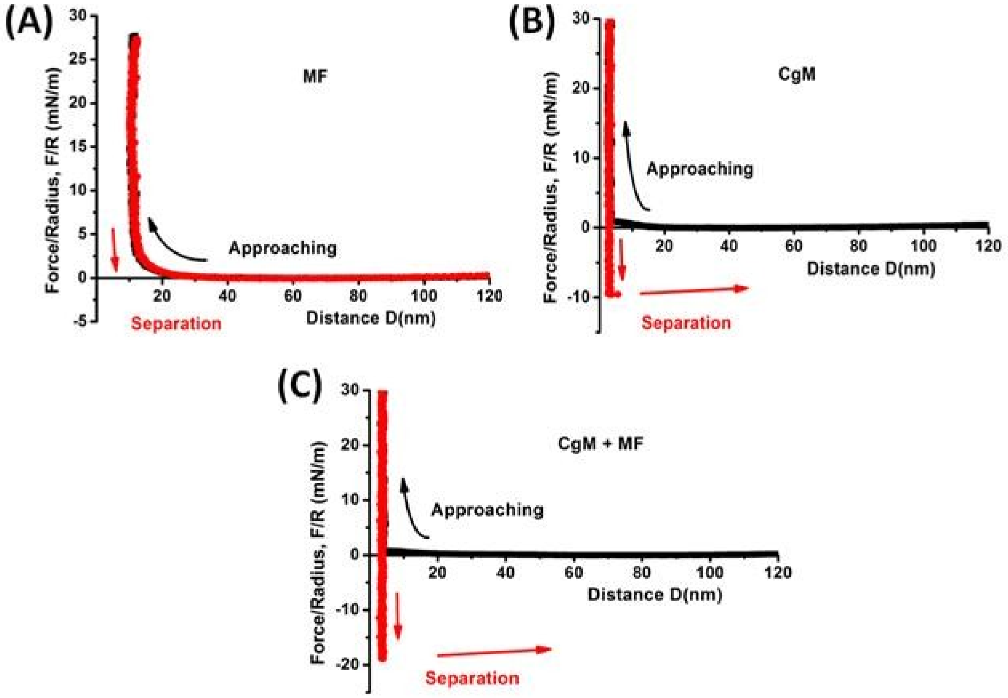

Figure 3.13 Force-distance profiles between (A) mica surfaces in 0.2 g/L MF solution, (B) mica surfaces in 0.83 g/L CgM solution, and (C) CgM coated mica surfaces in 0.2 g/L MF solution. All polymers were prepared in 800 ppm NaCl solution, which was the measured salt concentration of MFT.

The adsorption behavior and interaction forces of the two polymers on tailings particle surfaces during the two-step flocculation were investigated by conducting force measurements between two model mica surfaces, which has similar surface composition of clay particles in tailings, in the two polymer solutions at room temperature. Figure 3.13 shows the force-distance profiles between two mica surfaces in different polymer solutions. Pure repulsive force with a confined layer thickness of ~9 nm was measured when two mica surfaces were brought closer in 0.2 g/L MF solution, as shown in Figure

3.13A, because a full coverage of MF chains on two mica surfaces resulted in both steric interaction and electrostatic repulsion between the extended MF polymer chains adsorbed on mica. The force-distance profile of mica surfaces in 0.83 g/L CgM solution is shown in Figure 3.13B. An adhesion of F/R ~ -10 mN/m was measured, indicating the weak bridging effect of CgM on surfaces due to electrostatic attraction. Figure 3.13C shows the force-distance profile between two mica surfaces coated with a layer of MF interacting in 0.83 g/L CgM solution. A stronger adhesion of F/R ~ -19 mN/m was observed between CgM coated mica surfaces in MF solution, suggesting MF induced a strong bridging effect due to the electrostatic interaction of MF and CgM coated mica surfaces. This observation is in consistence with our settling test in which two-step flocculation of CgM and MF yielded a better settling performance.

3.4 Conclusion

An eco-friendly temperature responsive polymer chitosan-g-MEOMA (CgM) was synthesized as the cationic polymer in the two-step flocculation process for flocculation of diluted MFT. By adjusting the temperature below LCST, CgM can adsorb to fine solids through charge neutralization and the CgM-adsorbed particles can be bridged by MF to form the flocs with loosely bound structure in two-step flocculation to induce higher settling rate as compared to single flocculation of MF. The enhanced flocculation performance is attributed to the successive flocculation with the charge neutralization and bridging effect caused by two polymers, which is supported by surface force measurements. Once a sediment bed has formed, the temperature can be raised to above LCST so that CgM become hydrophobic and insoluble, which allows more water recovery and higher solid content in sediments as well as enhanced filtration performance.

Therefore, enhanced consolidation of sediments can be achieved by feasible techniques such as temperature switching and filtration. The concept of using the cationic polymer with temperature stimulation in two-step flocculation for rapid settling and easy consolidation in the treatment of diluted MFT could offer valuable information for significant improvement in oil sands tailings treatment and other solid-liquid separation operations. In addition, the thermo-responsive CgM is chitosan based flocculant, which is a biocompatible and biodegradable polymer that reduces the impact of polymer flocculation on aqua environment.

3.5 References

1. Masliyah, J., J. Czarnecki, and Z. Xu, Handbook on Theory and Practice of Bitumen Recovery from Athabasca Oil Sands. Vol. I. Theoretical basis, 2010.

2. Williams, P.A., Handbook of industrial water soluble polymers. 2008: John Wiley & Sons.

3. Nguyen, A. and H.J. Schulze, Colloidal science of flotation. Vol. 118. 2003: CRC Press.

4. Dimitrova, R.S. and E.K. Yanful, Factors affecting the shear strength of mine tailings/clay mixtures with varying clay content and clay mineralogy. Engineering Geology, 2012. 125: p. 11-25.

5. Franks, G.V., C.V. Sepulveda, and G.J. Jameson, pH ‐ sensitive flocculation: Settling rates and sediment densities. AIChE journal, 2006. 52(8): p. 2774-2782.

6. Tripathy, T. and B.R. De, Flocculation: a new way to treat the waste water. 2006.

7. Kitchener, J., Principles of action of polymeric flocculants. British Polymer Journal, 1972. 4(3): p. 217-229.

8. Wang, C., et al., *Current state of fine mineral tailings treatment: A critical review on theory and practice.* Minerals Engineering, 2014. **58**: p. 113-131.

9. Sworska, A., J. Laskowski, and G. Cymerman, Flocculation of the Syncrude fine tailings: Part I. Effect of pH, polymer dosage and Mg2+ and Ca2+ cations. International journal of mineral processing, 2000. 60(2): p. 143-152.

10. Mpofu, P., J. Addai-Mensah, and J. Ralston, Temperature influence of nonionic polyethylene oxide and anionic polyacrylamide on flocculation and dewatering behavior of kaolinite dispersions. Journal of Colloid and Interface Science, 2004. 271(1): p. 145-156.

11. Sakohara, S., E. Ochiai, and T. Kusaka, Dewatering of activated sludge by thermosensitive polymers. Separation and purification technology, 2007. 56(3): p. 296-302.

12. Vedoy, D.R. and J.B. Soares, Water‐soluble polymers for oil sands tailing treatment: A Review. The Canadian Journal of Chemical Engineering, 2015. 93(5): p. 888-904.

13. O’Shea, J.-P., G.G. Qiao, and G.V. Franks, Temperature responsive flocculation and solid–liquid separations with charged random copolymers of poly (N-isopropyl acrylamide). Journal of Colloid and Interface Science, 2011. 360(1): p. 61-70.

14. O’Shea, J.-P., G.G. Qiao, and G.V. Franks, Solid–liquid separations with a temperature-responsive polymeric flocculant: effect of temperature and molecular weight on polymer adsorption and deposition. Journal of Colloid and Interface Science, 2010. 348(1): p. 9-23.

15. Li, H., J.P. O'Shea, and G.V. Franks, Effect of molecular weight of poly (N‐isopropyl acrylamide) temperature‐sensitive flocculants on dewatering. AIChE journal, 2009. 55(8): p. 2070-2080.

16. Lu, H., et al., *Temperature-and pH-Responsive Benzoboroxole-Based Polymers for Flocculation and Enhanced Dewatering of Fine Particle Suspensions.* ACS applied materials & interfaces, 2015. **7**(49): p. 27176-27187.

17. Wang, Y., et al., *Temperature-responsive hyperbranched amine-based polymers for solid–liquid separation.* Langmuir, 2014. **30**(9): p. 2360-2368.

18. Long, J., et al., Improving oil sands processability using a temperature-sensitive polymer. Energy & Fuels, 2011. 25(2): p. 701-707.

19. Jeeravipoolvarn, S., et al. *Sedimentation and consolidation of in-line thickened fine tailings*. in *Proceedings of 1 st International Oil Sands Tailings Conference*. 2008.

20. Yuan, X. and W. Shaw, *Novel processes for treatment of Syncrude fine transition and marine ore tailings.* Canadian Metallurgical Quarterly, 2007. **46**(3): p. 265-272.

21. Lubian, L.M., Concentrating cultured marine microalgae with chitosan. Aquacultural engineering, 1989. 8(4): p. 257-265.

22. Morales, J., J. De La Noüe, and G. Picard, Harvesting marine microalgae species by chitosan flocculation. Aquacultural engineering, 1985. 4(4): p. 257-270.

23. Wang, J.-P., et al., Synthesis and characterization of a novel cationic chitosan-based flocculant with a high water-solubility for pulp mill wastewater treatment. Water Research, 2009. 43(20): p. 5267-5275.

24. Ji, Y., et al., Effect of solution salinity on settling of mineral tailings by polymer flocculants. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2013. 430: p. 29-38.

25. Zhang, L., et al., *Effect of polycarboxylate ether comb-type polymer on viscosity and interfacial properties of kaolinite clay suspensions.* Journal of Colloid and Interface Science, 2012. **378**(1): p. 222-231.

26. Zhang, L., H. Zeng, and Q. Liu, *Probing Molecular and Surface Interactions of Comb-Type Polymer Polystyrene-graft-poly (ethylene oxide)(PS-g-PEO) with an SFA.* The Journal of Physical Chemistry C, 2012. **116**(33): p. 17554-17562.

27. Lim, C., et al., *Nanomechanics of Poly (catecholamine) Coatings in Aqueous Solutions.* Angewandte Chemie International Edition, 2016. **55**(10): p. 3342-3346.

28. Huang, J., et al., *Understanding nanorheology and surface forces of confined thin films.* Korea-Australia Rheology Journal, 2014. **26**(1): p. 3-14.

Chapter 4 Conclusions and Future Work

4.1 Major Conclusions

A two-step flocculation process with a cationic chitosan and an anionic polyacrylamide (MF) was developed for dewatering of oil sands tailings in this work. The performance of the two-step flocculation process on oil sands extraction tailings was firstly investigated by using two commercial polymer flocculants. An in-home synthesized thermo-responsive cationic polymer was also used to substitute chitosan in the two-step flocculation to treat diluted MFT. The settling tests, turbidity measurements of supernatants and filtration tests were conducted to evaluate the efficiency of two-step flocculation in comparison with single polymer flocculation. The interaction mechanism of the two-step flocculation was studied through zeta potential, FBRM and surface force measurements.

The major findings and conclusions of this thesis are summarized as follows:

1) Single polymer flocculation on extraction tailings by MF resulted in high ISR but extremely low clarity of supernatants; whereas single flocculation by chitosan resulted in high clarity of supernatants but low ISR.

2) Two-step flocculation of extraction tailings using MF followed by chitosan achieved both high ISR and high clarity at the optimal polymer dosage.

3) In two-step flocculation, the polymer chains of added MF bridged the larger solids in the tailings into flocs, leaving considerable amounts of fine solids in

supernatants. The positively charged chitosan added in the second step of flocculation with proper dosage neutralized negatively charged solid surfaces (with adsorbed MF chains), stimulating a second step of agglomeration. The formation of ultra-large aggregates from small flocs and suspended fines resulted in a fast settling rate and a low solid content of supernatants.

4) The in-house synthesized CgM is a thermo-resposive polymer with LCST of 23-43 ºC, which is insoluble in aqueous solution at temperatures above LCST and is soluble and postively charged below LCST.

6) Single-step flocculation of 5 wt% diluted MFT using CgM showed temperature dependent settling behavior but the ISR remained very low at all dosages.

7) Two-step flocculation of diluted MFT using CgM followed by MF in proper dosage resulted in high ISR as well as high clarity of the released water.

8) By increasing the temperature of two-step flocculated sediments (using CgM and MF) to above LCST, more water release and higher sediment solid content were achieved, indicating a better consolidation performance.

9) Filtration test of two-step flocculated sediments by CgM and MF demonstrated that increasing the temperature of sediment above LCST significantly improved filtration rate, turbidity of filtrated water, solid content and yield stress of filtrated cake.

10） The surface force measurements using SFA demonstrated the mechanism of successive flocculation of (1) bridging of fine solids by anionic polyacrylamide, and (2) further aggregation and flocculation mediated by charge neutralization of the cationic polymer.

4.2 Contributions to the Original Knowledge

Although two-step flocculation for solid/liquid separation has been studied in model tailings systems for various wastewater treatments, the direct use of this process for oil sands tailings treatment was not reported. The mechanism of two-step flocculation using two oppositely charged polymers has been proposed but was not investigated. This work is the first study on the intermolecular and surface interaction mechanism of two-step flocculation. In addition, the use of eco-friendly polymer chitosan is firstly reported for oil sands tailings treatment. A novel thermal sensitive polymer CgM was synthesized and used as one component to directly flocculate diluted MFT, which demonstrated great sedimentation rate as well as good consolidation. Because chitosan is a naturally abundant biodegradable polymer, the introduction of chitosan based CgM in MFT treatment would not only lower the dosage and cost of flocculants but also benefit environmental applications by reducing the toxicity from flocculation.

4.3 Suggestions for Future Work

1) Oil sands extraction tailings and diluted MFT were used in this work. However, the two-step flocculation could be tested for many kinds of wastewater and mining tailings from different industries.

2) The interaction mechanism of thermal responsive two-step flocculation could be further studied by surface forces apparatus (SFA) and Quartz Crystal Microbalance with Dissipation (QCM-D) by switching temperatures below and above LCST.

3) The chemical structure and component ratio of CgM could be optimized to lower the LCST of the polymer, thereby lowering the energy cost in practical applications.

Bibliography

1. Giesy, J. P.; Anderson, J. C.; Wiseman, S. B., Alberta Oil Sands Development. Proceedings of the National Academy of Sciences 2010, 107, 951-952.

2. Czarnecki, J.; Radoev, B.; Schramm, L. L.; Slavchev, R., On the Nature of Athabasca Oil Sands. Advances in Colloid and Interface Science 2005, 114, 53-60.

3. Gray, M.; Xu, Z.; Masliyah, J., Physics in the Oil Sands of Alberta. Physics Today 2009, 62, 31-35.

4. Masliyah, J.; Czarnecki, J.; Xu, Z., Handbook on Theory and Practice of Bitumen Recovery from Athabasca Oil Sands. Vol. I. Theoretical basis 2010.

5. Masliyah, J.; Zhou, Z. J.; Xu, Z.; Czarnecki, J.; Hamza, H., Understanding Water - Based Bitumen Extraction from Athabasca Oil Sands. The Canadian Journal of Chemical Engineering 2004, 82, 628-654.

6. Shah, A.; Fishwick, R.; Wood, J.; Leeke, G.; Rigby, S.; Greaves, M., A Review of Novel Techniques for Heavy Oil and Bitumen Extraction and Upgrading. Energy & Environmental Science 2010, 3, 700-714.

7. Romanova, U. G.; Yarranton, H. W.; Schramm, L. L.; Shelfantook, W. E., Investigation of Oil Sands Froth Treatment. The Canadian journal of chemical engineering 2004, 82, 710-721.

8. Rao, F.; Liu, Q., Froth Treatment in Athabasca Oil Sands Bitumen Recovery Process: A Review. Energy & Fuels 2013, 27, 7199-7207.

9. Wu, J.; Dabros, T., Process for Solvent Extraction of Bitumen from Oil Sand. Energy & Fuels 2012, 26, 1002-1008.

10. Vedoy, D. R.; Soares, J. B., Water - Soluble Polymers for Oil Sands Tailing Treatment: A Review. The Canadian Journal of Chemical Engineering 2015, 93, 888-904.

11. Wang, C.; Harbottle, D.; Liu, Q.; Xu, Z., Current State of Fine Mineral Tailings Treatment: A Critical Review on Theory and Practice. Minerals Engineering 2014, 58, 113-131.

12. Allen, E. W., Process Water Treatment in Canada's Oil Sands Industry: I. Target Pollutants and Treatment Objectives. Journal of Environmental Engineering and Science 2008, 7, 123-138.

13. Allen, E. W., Process Water Treatment in Canada's Oil Sands Industry: Ii. A Review of Emerging Technologies. Journal of Environmental Engineering and Science 2008, 7, 499-524.

14. Mikula, R. J.; Kasperski, K. L.; Burns, R. D.; MacKinnon, M. D., Nature and Fate of Oil Sands Fine Tailings. Advances in Chemistry Series 1996.

15. Chalaturnyk, R. J.; Don Scott, J.; Özüm, B., Management of Oil Sands Tailings. Petroleum Science and Technology 2002, 20, 1025-1046.

16. Grant, J.; Angen, E.; Dyer, S., Forecasting the Impacts of Oilsands Expansion; Pembina Institute, 2013.

17. Warmore, S., Tar Sends Oil and Pipeline Safety: Examining Regulatory Shortcomings. Wayne L. Rev. 2013, 59, 175.

18. Houlihan, R.; Haneef, M. In Oil Sands Tailings: Regulatory Perspective, Proceedings of the International Oil Sands Tailing Conference, Edmonton, Alberta, 2008.

19. Rogers, V. V.; Wickstrom, M.; Liber, K.; MacKinnon, M. D., Acute and Subchronic Mammalian Toxicity of Naphthenic Acids from Oil Sands Tailings. Toxicological Sciences 2002, 66, 347-355.

20. Kelly, E. N.; Short, J. W.; Schindler, D. W.; Hodson, P. V.; Ma, M.; Kwan, A. K.; Fortin, B. L., Oil Sands Development Contributes Polycyclic Aromatic Compounds to the Athabasca River and Its Tributaries. Proceedings of the National Academy of Sciences 2009, 106, 22346-22351.

21. Colavecchia, M. V.; Backus, S. M.; Hodson, P. V.; Parrott, J. L., Toxicity of Oil Sands to Early Life Stages of Fathead Minnows (Pimephales Promelas). Environmental Toxicology and Chemistry 2004, 23, 1709-1718.

22. Mikula, R.; Munoz, V.; Omotoso, O., Centrifugation Options for Production of Dry Stackable Tailings in Surface-Mined Oil Sands Tailings Management. Journal of Canadian Petroleum Technology 2009, 48, 19-23.

23. Matthews, J.; Shaw, W.; MacKinnon, M.; Cuddy, R., Development of Composite Tailings Technology at Syncrude. International Journal of Surface Mining, Reclamation and Environment 2002, 16, 24-39.

24. Beier, N.; Sego, D., The Oil Sands Tailings Research Facility. Geotechnical news 2008, 26, 72-77.

25. Rao, S. R., Flocculation and Dewatering of Alberta Oil Sands Tailings. International Journal of Mineral Processing 1980, 7, 245-253.

26. Dawson, R.; Sego, D.; Pollock, G., Freeze-Thaw Dewatering of Oil Sands Fine Tails. Canadian geotechnical journal 1999, 36, 587-598.

27. Powter, C.; Biggar, K.; Silva, M.; McKenna, G.; Scordo, E. In Review of Oil Sands Tailings Technology Options, Tailings and Mine Waste, 2011.

28. MacKinnon, M.; Matthews, J.; Shaw, W.; Cuddy, R., Water Quality Issues Associated with Composite Tailings (Ct) Technology for Managing Oil Sands Tailings. International Journal of Surface Mining, Reclamation and Environment 2001, 15, 235-256.

29. Boger, D., Personal Perspective on Paste and Thickened Tailings: A Decade On. Mining technology 2012, 121, 29-36.

30. Williams, P. A., Handbook of Industrial Water Soluble Polymers; John Wiley & Sons, 2008.

31. Mortimer, D. A., Synthetic Polyelectrolytes—a Review. Polymer International 1991, 25, 29-41.

32. Israelachvili, J. N., Intermolecular and Surface Forces: Revised Third Edition; Academic press, 2011.

33. Ji, Y. Fundamental Understanding of the Flocculation of Mineral Tailings in High Salinity Water. University of Alberta, 2013.

34. Emeka, K. Studies on Flocculation of Kaolin Suspensions and Mature Fine Tailings. University of Alberta, 2008.

35. Sworska, A.; Laskowski, J.; Cymerman, G., Flocculation of the Syncrude Fine Tailings: Part I. Effect of Ph, Polymer Dosage and Mg2+ and Ca2+ Cations. International journal of mineral processing 2000, 60, 143-152.

36. Li, H.; Long, J.; Xu, Z.; Masliyah, J. H., Flocculation of Kaolinite Clay Suspensions Using a Temperature ‐ Sensitive Polymer. AIChE journal 2007, 53, 479-488.

37. Li, H.; Long, J.; Xu, Z.; Masliyah, J., Synergetic Role of Polymer Flocculant in Low-Temperature Bitumen Extraction and Tailings Treatment. Energy & fuels 2005, 19, 936-943.

38. Li, H.; Long, J.; Xu, Z.; Masliyah, J. H., Effect of Molecular Weight and Charge Density on the Performance of Polyacrylamide in Low ‐ Grade Oil Sand Ore Processing. The Canadian Journal of Chemical Engineering 2008, 86, 177-185.

39. Israelachvili, J., et al., *Recent advances in the surface forces apparatus (SFA) technique.* Reports on Progress in Physics, 2010. **73**(3): p. 036601.

40.Israelachvili, J.N., *Intermolecular and surface forces: revised third edition*. 2011: Academic press.

41. Lu, Q., et al., *Understanding the molecular interactions of lipopolysaccharides during E. coli initial adhesion with a surface forces apparatus.* Soft Matter, 2011. **7**(19): p. 9366-9379.

42. Allen, E.W., Process water treatment in Canada's oil sands industry: I. Target pollutants and treatment objectives. Journal of Environmental Engineering and Science, 2008. 7(2): p. 123-138.

43. Giesy, J.P., J.C. Anderson, and S.B. Wiseman, Alberta oil sands development. Proceedings of the National Academy of Sciences, 2010. 107(3): p. 951-952.

44. Chalaturnyk, R.J., J. Don Scott, and B. Özüm, Management of oil sands tailings. Petroleum Science and Technology, 2002. 20(9-10): p. 1025-1046.

45. Scott, A.C., et al., Ozonation of oil sands process water removes naphthenic acids and toxicity. Chemosphere, 2008. 71(1): p. 156-160.

46. Gosselin, P., et al. Environmental and health impacts of Canada's oil sands industry. 2010: Royal Society of Canada Ottawa, Ontario, Canada.

47. Kelly, E.N., et al., Oil sands development contributes elements toxic at low concentrations to the Athabasca River and its tributaries. Proceedings of the National Academy of Sciences, 2010. 107(37): p. 16178-16183.

48. Mamer, M., Oil sands tailings technology: Understanding the impact to reclamation. 2010.

49. Yergeau, E., et al., Next-generation sequencing of microbial communities in the Athabasca River and its tributaries in relation to oil sands mining activities. Applied and environmental microbiology, 2012. 78(21): p. 7626-7637.

50. Jeremy Boswell, M.D., Oil Sand Tailings Technology Development Roadmap, D. Cowan, Editor. 2012, Alberta Innovates – Energy and Environment Solutions.

51. Xu, Y., T. Dabros, and J. Kan, Filterability of oil sands tailings. Process Safety and Environmental Protection, 2008. 86(4): p. 268-276.

52. Farkish, A. and M. Fall, Rapid dewatering of oil sand mature fine tailings using super absorbent polymer (SAP). Minerals Engineering, 2013. 50: p. 38-47.

53. Gray, M., Z. Xu, and J. Masliyah, Physics in the oil sands of Alberta. Physics Today, 2009. 62(3): p. 31-35.

54.Tripathy, T. and B.R. De, Flocculation: a new way to treat the waste water. 2006.

55. O'Shea, J.-P., G.G. Qiao, and G.V. Franks, Temperature responsive flocculation and solid–liquid separations with charged random copolymers of poly (N-isopropyl acrylamide). Journal of Colloid and Interface Science, 2011. 360(1): p. 61-70.

56. Wang, S., Fundamental Study on Polymer Flocculation Behavior in Saline Solutions. 2014, University of Alberta.

57. Wang, C., et al., Current state of fine mineral tailings treatment: A critical review on theory and practice. Minerals Engineering, 2014. 58: p. 113-131.

58. Alagha, L., et al., Adsorption kinetics of a novel organic–inorganic hybrid polymer on silica and alumina studied by quartz crystal microbalance. The Journal of Physical Chemistry C, 2011. 115(31): p. 15390-15402.

59. Alamgir, A., et al., Al-PAM assisted filtration system for abatement of mature fine tailings. Chemical Engineering Science, 2012. 80: p. 91-99.

60. Wang, S., L. Alagha, and Z. Xu, Adsorption of organic–inorganic hybrid polymers on kaolin from aqueous solutions. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2014. 453: p. 13-20.

61. Guo, L., Understanding Al-PAM assisted oil sands tailings treatment. 2012, University of Alberta.

62. Wang, Y., et al., Temperature-responsive hyperbranched amine-based polymers for solid–liquid separation. Langmuir, 2014. 30(9): p. 2360-2368.

63. Long, J., et al., Improving oil sands processability using a temperature-sensitive polymer. Energy & Fuels, 2011. 25(2): p. 701-707.

64. Li, H., et al., Enhancing treatment and geotechnical stability of oil sands fine tailings using thermo‐sensitive poly (n‐isopropyl acrylamide). The Canadian Journal of Chemical Engineering, 2015. 93(10): p. 1780-1786.

65. Sworska, A., J. Laskowski, and G. Cymerman, Flocculation of the Syncrude fine tailings: Part I. Effect of pH, polymer dosage and Mg2+ and Ca2+ cations. International journal of mineral processing, 2000. 60(2): p. 143-152.

66. Vedoy, D.R. and J.B. Soares, Water‐soluble polymers for oil sands tailing treatment: A Review. The Canadian Journal of Chemical Engineering, 2015. 93(5): p. 888-904.

67. Xiao, H., Z. Liu, and N. Wiseman, Synergetic effect of cationic polymer microparticles and anionic polymer on fine clay flocculation. Journal of Colloid and Interface Science, 1999. 216(2): p. 409-417.

68. Sang, Y. and H. Xiao, Clay flocculation improved by cationic poly (vinyl alcohol)/anionic polymer dual-component system. Journal of Colloid and Interface Science, 2008. 326(2): p. 420-425.

69. Peng, F. and Z. Lu, POLYMER FLOCCULATION AND COAGULATION FOR SEDIMENTATION OF COPPER FLOTATIONTAILINGS. Minerals & metallurgical processing, 1998. 15(1): p. 14-20.

70. Glover, S.M., G.J. Jameson, and S. Biggs, Dewatering properties of dual-polymer-flocculated systems. International journal of mineral processing, 2004. 73(2): p. 145-160.

71. Ji, Y., et al., Effect of solution salinity on settling of mineral tailings by polymer flocculants. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2013. 430: p. 29-38.

72. Owen, A., et al., The impact of polyacrylamide flocculant solution age on flocculation performance. International journal of mineral processing, 2002. 67(1): p. 123-144.

73. Alfano, J.C., et al., Polyelectrolyte-induced aggregation of microcrystalline cellulose: reversibility and shear effects. Journal of Colloid and Interface Science, 2000. 223(2): p. 244-254.

74. Israelachvili, J., et al., Recent advances in the surface forces apparatus (SFA) technique. Reports on Progress in Physics, 2010. 73(3): p. 036601.

75. Li, L., et al., Mussel-inspired antifouling coatings bearing polymer loops. Chemical Communications, 2015. 51(87): p. 15780-15783.

76. Zhang, L., H. Zeng, and Q. Liu, Probing Molecular and Surface Interactions of Comb-Type Polymer Polystyrene-graft-poly (ethylene oxide)(PS-g-PEO) with an SFA. The Journal of Physical Chemistry C, 2012. 116(33): p. 17554-17562.

77. Hogg, R., The role of polymer adsorption kinetics in flocculation. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 1999. 146(1): p. 253-263.

78. Jarvis, P., et al., A review of floc strength and breakage. Water Research, 2005. 39(14): p. 3121-3137.

79. Masliyah, J., J. Czarnecki, and Z. Xu, Handbook on Theory and Practice of Bitumen Recovery from Athabasca Oil Sands. Vol. I. Theoretical basis, 2010.

80. Williams, P.A., Handbook of industrial water soluble polymers. 2008: John Wiley & Sons.

81. Nguyen, A. and H.J. Schulze, Colloidal science of flotation. Vol. 118. 2003: CRC Press.

82. Dimitrova, R.S. and E.K. Yanful, Factors affecting the shear strength of mine tailings/clay mixtures with varying clay content and clay mineralogy. Engineering Geology, 2012. 125: p. 11-25.

83. Franks, G.V., C.V. Sepulveda, and G.J. Jameson, pH ‐ sensitive flocculation: Settling rates and sediment densities. AIChE journal, 2006. 52(8): p. 2774-2782.

84.Tripathy, T. and B.R. De, Flocculation: a new way to treat the waste water. 2006.

85. Kitchener, J., Principles of action of polymeric flocculants. British Polymer Journal, 1972. 4(3): p. 217-229.

86. Sworska, A., J. Laskowski, and G. Cymerman, Flocculation of the Syncrude fine tailings: Part I. Effect of pH, polymer dosage and Mg2+ and Ca2+ cations. International journal of mineral processing, 2000. 60(2): p. 143-152.

87. Mpofu, P., J. Addai-Mensah, and J. Ralston, Temperature influence of nonionic polyethylene oxide and anionic polyacrylamide on flocculation and dewatering behavior

of kaolinite dispersions. Journal of Colloid and Interface Science, 2004. 271(1): p. 145-156.

88. Sakohara, S., E. Ochiai, and T. Kusaka, Dewatering of activated sludge by thermosensitive polymers. Separation and purification technology, 2007. 56(3): p. 296-302.

89. Vedoy, D.R. and J.B. Soares, Water‐soluble polymers for oil sands tailing treatment: A Review. The Canadian Journal of Chemical Engineering, 2015. 93(5): p. 888-904.

90. O'Shea, J.-P., G.G. Qiao, and G.V. Franks, Temperature responsive flocculation and solid–liquid separations with charged random copolymers of poly (N-isopropyl acrylamide). Journal of Colloid and Interface Science, 2011. 360(1): p. 61-70.

91. O'Shea, J.-P., G.G. Qiao, and G.V. Franks, Solid–liquid separations with a temperature-responsive polymeric flocculant: effect of temperature and molecular weight on polymer adsorption and deposition. Journal of Colloid and Interface Science, 2010. 348(1): p. 9-23.

92. Li, H., J.P. O'Shea, and G.V. Franks, Effect of molecular weight of poly (N‐isopropyl acrylamide) temperature‐sensitive flocculants on dewatering. AIChE journal, 2009. 55(8): p. 2070-2080.

93. Lu, H., et al., *Temperature-and pH-Responsive Benzoboroxole-Based Polymers for Flocculation and Enhanced Dewatering of Fine Particle Suspensions.* ACS applied materials & interfaces, 2015. **7**(49): p. 27176-27187.

94. Wang, Y., et al., *Temperature-responsive hyperbranched amine-based polymers for solid–liquid separation.* Langmuir, 2014. **30**(9): p. 2360-2368.

95. Long, J., et al., Improving oil sands processability using a temperature-sensitive polymer. Energy & Fuels, 2011. 25(2): p. 701-707.

96. Jeeravipoolvarn, S., et al. *Sedimentation and consolidation of in-line thickened fine tailings*. in *Proceedings of 1 st International Oil Sands Tailings Conference*. 2008.

97. Yuan, X. and W. Shaw, *Novel processes for treatment of Syncrude fine transition and marine ore tailings.* Canadian Metallurgical Quarterly, 2007. **46**(3): p. 265-272.

98. Lubian, L.M., Concentrating cultured marine microalgae with chitosan. Aquacultural engineering, 1989. 8(4): p. 257-265.

99. Morales, J., J. De La Noüe, and G. Picard, Harvesting marine microalgae species by chitosan flocculation. Aquacultural engineering, 1985. 4(4): p. 257-270.

100. Wang, J.-P., et al., Synthesis and characterization of a novel cationic chitosan-based flocculant with a high water-solubility for pulp mill wastewater treatment. Water Research, 2009. 43(20): p. 5267-5275.

101. Ji, Y., et al., Effect of solution salinity on settling of mineral tailings by polymer flocculants. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2013. 430: p. 29-38.

102. Zhang, L., et al., *Effect of polycarboxylate ether comb-type polymer on viscosity and interfacial properties of kaolinite clay suspensions.* Journal of Colloid and Interface Science, 2012. **378**(1): p. 222-231.

103. Zhang, L., H. Zeng, and Q. Liu, *Probing Molecular and Surface Interactions of Comb-Type Polymer Polystyrene-graft-poly (ethylene oxide)(PS-g-PEO) with an SFA.* The Journal of Physical Chemistry C, 2012. **116**(33): p. 17554-17562.

104. Lim, C., et al., *Nanomechanics of Poly (catecholamine) Coatings in Aqueous Solutions.* Angewandte Chemie International Edition, 2016. **55**(10): p. 3342-3346.

105. Huang, J., et al., *Understanding nanorheology and surface forces of confined thin films.* Korea-Australia Rheology Journal, 2014. **26**(1): p. 3-14.