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EXECUTIVE SUMMARY

The main objective of this proposal is to develop the strategy to connect microstructure and rheology of flocculated mature fine tailings (MFT) systems. In order to achieve this goal, several important breakthroughs were made. We were the first to non-invasively visualize oil sands tailings samples in 4D (via laser scanning confocal microscopy), which is extremely challenging, due to the inherent complex nature of tailings systems.¹ The project contributed significantly towards better understanding of the complex interactions of clay, bitumen and polymers in tailings systems, as well as development of technical tools required to interpret results. With the platform established through this work we helped bridge the gap in understanding the link between the polymer-particle interactions leading to the favorable sediment structure that would ensure efficient dewatering and consequent sediment strength development. Several new polymers, synthesized by Soares' group were tested. By establishing such a link, the structural parameters estimated from the 3D images can serve as improved performance indicators over the traditionally used initial settling rates, water release and water turbidity which do not provide any connection between the floc structure and the flocculation performance. Therefore, the outcomes of this project can have a direct impact of providing more sustainable and effective solutions for remediation of oil sands tailings, giving a way to oil sand operators an improved social license to operate in Alberta and strengthen its commitment to environmental responsibility and innovation, and in making environmental quality an integral element of business.

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1 INTRODUCTION

Project conception, objectives, overall execution, HQP's trained, major results achieved, and relevance to the oil sands industry and IOSI research themes.

The main objective of this proposal is to develop the strategy to connect microstructure and rheology of flocculated mature fine tailings (MFT) systems. This link can in turn enable identifying suitable polymers to accelerate oil sands tailings reclamation.

In order to reach this goal, we posed several fundamental questions: *What is the role of polymer/clay interfacial properties in the destabilization of colloidal systems? How do shape, size and surface properties of clay affect their dispersion and organization in 3D? What is the role of polymer molecular structure, ionic charges, chemical composition, and rheology in the process? What role do clay dispersion and location play in stability of colloidal suspension?*

We also defined several subprojects including:

- a) Design experimental methods to visualize the spatio-temporal distribution of fine clays in colloidal systems under shear using a confocal-rheology instrument;
- b) Synthesize fluorescently labeled flocculants. Both commercial flocculants and novel polymers developed by Soares's group will be considered;
- c) Enable linking between polymer structure, flocculated MFT microstructure and rheology by extracting of the important structural parameters from 3D images.

Throughout the project 6 graduate and 3 undergraduate students were trained. The project enabled deepening of mechanistic understanding of particle-flocculant interactions and its link to the resulting floc structure, which is essential for developing tailings treatments with enhanced consolidation rates. A non-invasive, in-situ visualization of the floc formation and the consequent sediment microstructure via tri-dimensional laser scanning confocal microscopy (LSCM) was achieved for the first time and the quantitative link between the flocculation conditions, polymer structure, and bulk properties of the resulting sediment structures was established. The developed method has a great potential to be implemented in industry for polymer screening as well as predictive models for consolidation efficiency of flocculated tailings.

2 BACKGROUND

Adding water-soluble polymers such as polyacrylamides (PAM) to oil sands tailings make them settle faster, facilitating land reclamation.^[2-4] Despite the large volume of literature published on this topic, the fundamental aspects of polymer/tailings interactions remains unclear. This is partly due to the complexity of interactions that occur in this system, and partly due to the lack of reliable experimental techniques to measure these interactions dynamically. Consequently, there are no reliable design rules to tailor polymer properties to treat oil sands tailings. To complicate this problem even further, tailings themselves depend on mining source, ageing, depth in the pond and other factors. A polymer flocculant that works well for one tailings sample may not exhibit the same behavior for another tailings sample. Most particles (approximately 90% w/w) in oil sand tailings are smaller than 44 μm , with significant fractions as small as 0.1 to 1 μm . Fine tailings are silicates with a negative surface charge surrounded by an electrical double layer. According to the DLVO theory, the stability of colloidal suspension is governed by the surface potential ξ (determined by the particle charge density) and the distance at which the repulsive potential drops to the predetermined value of ξ .^[5] Precipitation of this suspended material can be achieved, in principle, by lowering the repulsive electrostatic forces between particles, which can be achieved by adding salts or by adding acids to lower the surface charge density. Other forces such as steric repulsion, Van der Waals forces, and hydration affect colloidal particles in suspension and determine the final settled volume, hydraulic conductivity, and stability of the suspension. Methods to increase the settling rate try to affect these forces and destabilize the colloidal suspension. Mature fine tailings have a solid content of 30-40% w/w.^[6,7] Reaching this solid content may take several years, and the subsequent sedimentation is even slower. The settling of MFT can be promoted by adding sand in the presence of a binding agent such as calcium sulfate or polymers. The resulting mixture is called consolidated tailings (CT). Colloidal particles in a dilute suspension were subjected to a centrifugal force field in an analytical ultracentrifuge equipped with an optical system to track the movement of the sedimenting boundary in real time.^[8] The approach was suitable for this application, as it predicted the rate of clear water production, total time for sedimentation and consolidation, and the maximum concentration of solids. However, these experiments could not reveal interactions at the mesoscale, which lead to the changes in bulk properties of the tailings. Imaging technologies such as magnetic resonance imaging, X-ray computed tomography, and laser-scanning confocal microscopy (LSCM) are opening up a vast 3D morphology world for a wide variety of samples, from biological cells to semiconductor devices. The advantage of fast image acquisition has been fully exploited to image medical and biological specimens where natural movements occur without external potentials, such as natural movements in cells. Most of the poorly understood phenomena in engineering applications arise from non-equilibrium states or when the systems are under the influence of some external force.

In this project we used the state-of-the-art hybrid confocal-rheology equipment to image sample morphology in 4-D under well-defined macroscopic flow fields. Rheology can effectively probe the structure and responses of soft materials, and it has been applied extensively to study the flocculation efficiency as well as consolidation of tailings systems. Bulk material properties, quantified as elastic moduli for solids or viscosity for liquids can be calculated from measurements of stress and strain. Through the unique setup, we were able to understand the effect of polymer structure ranging from typically used PAM flocculants, to the new class of polymers with hydrophobic backbone and hydrophilic grafts. These findings will provide a foundation for the development of new theories and new technological applications for oil sands tailings reclamation.

3 EXPERIMENTAL

3.1 Materials

Mature fine tailings used for flocculation in this study were provided by Innotech tailings sample bank. The composition, determined by the Dean Stark method, showed around 32 wt% of mineral solids content with 4–5wt% bitumen. Water phase pH was measured at 7.7. Prior to the flocculation, the MFT sample was diluted to 5-20 wt% clay content by the addition of DI water. The low density MFT flocculation is a more consistent process where the bitumen-clay interactions and the floc formation are easier to monitor in real time.

Aside from the typically used Flopam A3338 polyacrylamide flocculant, Soares's group synthesized a range of polymers differing in their chain length, functionality, and polymer structure.

In particular, ethylene propylene diene terpolymer grafted with poly(methyl acrylate) (EPDM-g-PMA) was studied in detail by changing the polymer hydrophilicity. EPDM backbone was kept the same, while the percent of PMA grafting efficiency is varied from 30, 40 to 50%. The interesting part of these polymers is that their hydrophobic backbone could aid water repelling while hydrophilic PMA groups can aid bridging clay particles. by changing the extent of grafting efficiency of PMA

Name	Structure	M _w (Dalton)
Matmac-graft-chitosan		1.5
Poly(acrylamide-co-vinylbenzyl trimethylammonium chloride)		1-2
EPDM-g-PMA		2.5-10
FloPAM		16

3.2 LSCM imaging of the tailings sediments

Image data was acquired using an inverted SP8X Leica confocal microscope equipped with 11000 Hz resonant scanner. The real-time MFT flocculation was monitored *in situ* at 1000 ppm dosage of Ca²⁺ ions and polymer flocculant. For the ease of performing the *in-situ* imaging, the flocculation was achieved in a 600 mL non-baffled glass Pyrex beaker featuring a 2 mm wide vertical imaging slit carved in its wall where a thin microscopy grade glass was placed. The high speed (27.5 frames/s) 2D-time imaging was achieved by combining the capabilities of the built-in resonant scanner and a piezo scanner (Piezo System Jena, MIPOS 250/500) mounted on a periscope arm together with the 20x oil immersion objective. The images were acquired in a 256 × 256 format and a resulting image size of 465 × 465 μm which was sufficient for capturing dynamics of the floc formation and localization of clay and bitumen. The flocs structure and component localization were imaged by a combination of fluorescence and reflectance mode embedded in the LSCM system (Fig. 1). As a complex mixture of organic molecules, bitumen's fluorescent properties have been reported in the UV and blue visible light region, depending on the component of interest (as received bitumen or different bitumen components, e.g. asphaltenes and naphthenic acid). In this work, bitumen fluorescence detection in MFT was achieved in the region of 500–550 nm (the peak of the 500–750 nm fluorescence band) upon excitation with the 488 nm laser light (Fig. 1). The hybrid detector was gated to collect emission light in the time window of 0.25–6.0 milliseconds following excitation, preventing any detection of glass or clay reflection. On the other hand, the MFT clays are not intrinsically fluorescent, hence their localization was achieved by the detection of the 633 nm laser incident light reflected off of their surface in a narrow region of 630–635 nm. This region was chosen as it offered good signal-to-noise ratio of the clay channel.

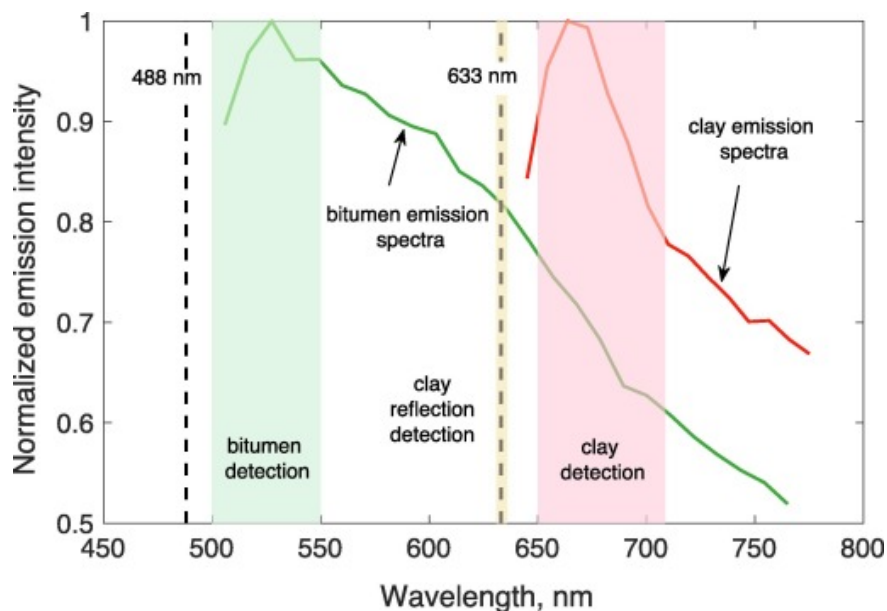


Figure 1. Bitumen and kaolinite clay fluorescence emission spectra with appropriate lasers used for their excitation and their fluorescence detection range marked with green and red shaded regions. The clay reflection was achieved by the incident 633 nm

3.3 LSCM image data reconstruction protocol

The stacks of 2D images were pre-processed using MATLAB software followed by the 3D surface reconstruction using Avizo® software version 9.1. The separate image channels of clay and bitumen required different image processing techniques to elucidate their morphological features. The complete pre-processing procedure is shown step-by-step on a selected 2D image in separate clay and bitumen channels in Fig. 2. Starting from the overlaid raw bitumen and clay image, the objective was to obtain accurate binary image data for separate clay and bitumen channels with clay or bitumen (the only labeled material) being a part of the foreground object (having the intensity value 1) and all unlabeled material (surrounding non-fluorescent water and polymer with the intensity of 0) as a part of the background. For proper differentiation between the foreground and the background in a binary image, a series of image enhancement techniques were required before applying any thresholding method.

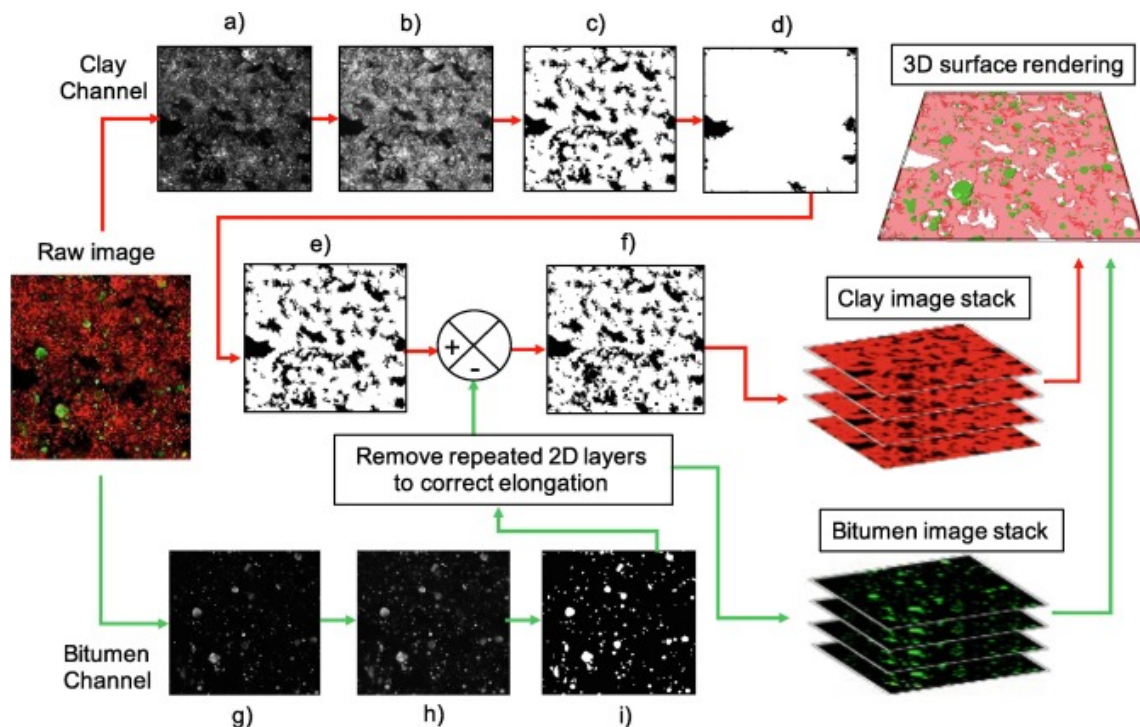


Figure 2. 3D image reconstruction protocol. Clay channel: a) raw clay channel transformation to gray scale; b) contrast enhancement using CLAHE method, noise reduction and smoothing with mean filter; c) Voids reconstruction by opening and closing-by-reconstruction methods followed by thresholding using Otsu's method; d) edge reconstruction by Sobel operator; e) binary image combining the preceding two steps; f) final clay binary image with bitumen regions removed using arithmetic operation. Bitumen channel: g) gray scale transformation of the raw bitumen channel image; h) contrast enhancement and mean filtering; i) image segmentation using Otsu's thresholding method. Same procedure was repeated for all images within a 3D stack, followed by the 3D surface reconstruction to give final 3D structure of the sediment.

4 RESULTS AND DISCUSSION

The first set of experiments were performed with Flopamfloculant to establish the imaging protocols, as well as the link of structural parameters to the rheological signature of flocculated tailings systems. Note that we did not present results of all of the polymers tested here for the sake of conciseness of the report.

4.1 Validation of the imaging protocol

In order to confirm that bitumen can be imaged through its autofluorescence and clay through reflectance microscopy, we imaged the same flocculated real tailings sample with cryo-SEM and LSCM (Fig. 3). Through EDX analysis, clay, bitumen and water regions can be easily identified within the SEM image due to the fact that aluminium is detected only in clay, strong carbon signal belongs to bitumen, while oxygen signal comes from the frozen water regions. Even though the structure is slightly altered during the sample transfer to the LSCM stage due to defrosting of the cryogenically frozen sample at room temperature, the two images confirm validity of the proposed imaging approach. Both images reveal a nested water droplet within the bitumen droplet, which eliminates the possibility of imaging artifacts with the LSCM technique. The occurrence of the water emulsions within the oil phase is common given that the oil extraction from the oil sands is a water based, high temperature process that employs surfactants and diluents which can lead to water dispersion within the oil phase. The nested emulsions are not desirable and hard to deal with in the demulsification step, which is why the volume fraction estimation can be of interest for the improvements of the extraction process.

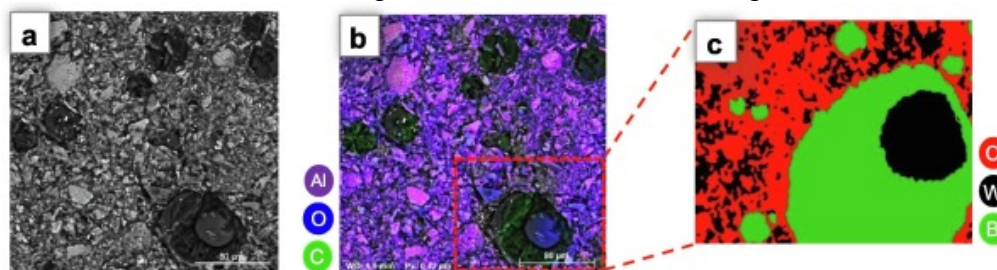


Figure 3. Comparison of the cryo-SEM and LSCM imaging of the particular region within the flocculated sediment: a) raw cryo-SEM image; b) EDX mapping and cryo-SEM overlay; c) LSCM image of the same region within the sample. The bitumen and clay colocalize within

4.2 In-situ monitoring of the floc formation process

Fig. 4 represents time lapse of the flocculation process captured by *in-situ* imaging. By analyzing time-series images, we can examine micro- and meso-structural features of the flocculation process. Following the initial mixing period where clay and bitumen are uniformly dispersed within the sample at a high mixing rate ($t=0\text{sec}$), the polymer solution is added over a short period of time to the tailings mixture at $t=25\text{sec}$. The onset of the flocculation is evident immediately whereby the formation of small, not fully formed flocs is seen throughout the sample. The floc formation continues through orthokinetic aggregation of the smaller flocs into bigger flocs ($t=32\text{sec}$) which continue to densify ($t=41\text{sec}$) even upon reduced rate of mixing ($t=49\text{sec}$). The spanning network of flocs formed at $t=49\text{sec}$ is broken under prolonged mixing into smaller flocs ($t=155\text{sec}$), more uniform in shape than the ones formed earlier at $t=41\text{sec}$. Direct imaging depicts the complexity of the flocculation process itself. The aggregation and breakage of flocs occur simultaneously and the nonuniformity of the structure at different mixing

rates indicates a heterogeneous distribution of stress propagating through the network. The ability to capture these spatio-temporal changes dynamically opens new possibilities for probing factors influencing flocculation efficiency.

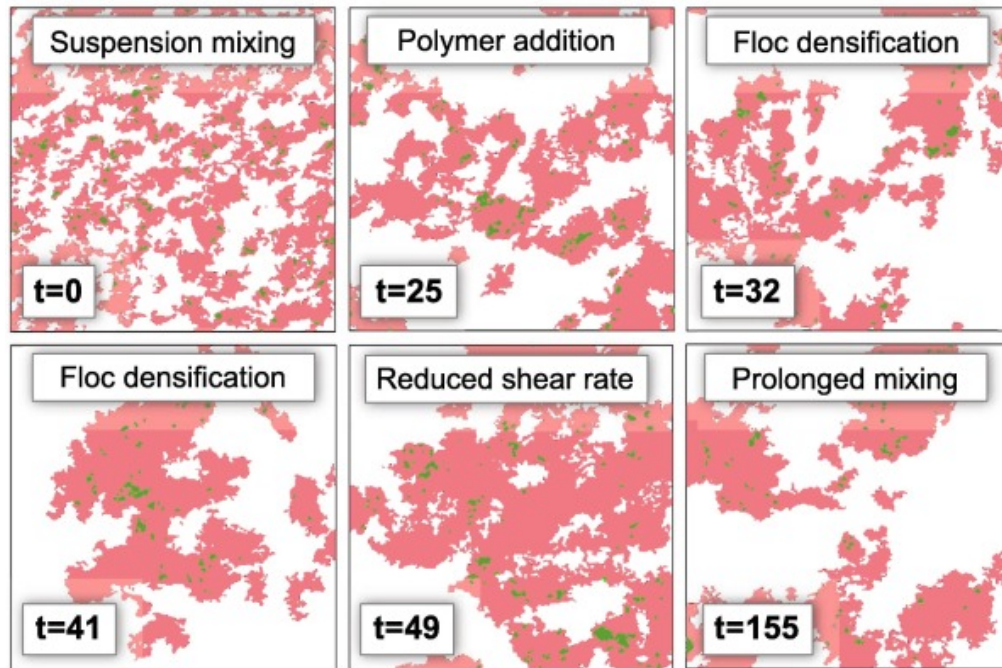


Figure 4. 2D captions of the polymer flocculation at various time points. The time stamps on the images are in seconds.

4.3 3D Visualisation and structural characterization of the polymer flocculated tailings sediment

Following the flocculation procedure, the MFT sediments formed with different dosages of polymer flocculant (i.e. 750, 1000 and 5000 ppm) were allowed to densify over the course of 24 h before their structure was visualized and assessed through the 3D imaging using the same fluorescence/reflectance technique described previously. The representative 3D images of the flocculated bed with overlaid clay (red) and bitumen (green) channels are shown in Fig. 5. Due to the complex composition and high solids content within the imaged sediment, the maximum imaged thickness of 4.5 μm may be limiting for capturing the 3D character of the flocculated sediment.

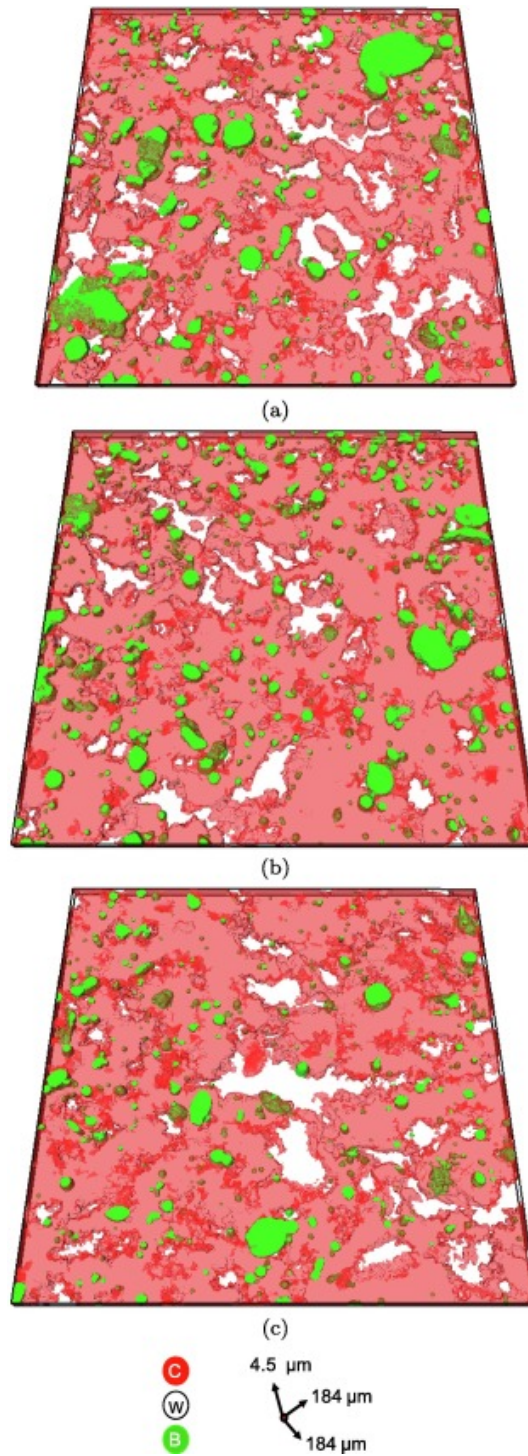


Figure 5. 3D structure of the flocculated real MFT sediments at different dosages of polymer flocculant showing the localization of clay (red) and bitumen (green) components within the porous sediment network: a) 750 ppm; b) 1000 ppm; c) 5000 ppm.

4.4 Strength of the flocculated MFT sediment

The oscillatory stress sweeps were performed on the 5-day old sediments for each of the polymer dosages and the results are shown in Fig. 6. Therefore, the network formed with smaller and

more irregular but compacted flocs at 750 ppm polymer dosage (Fig. 5a) is stronger than the network formed at higher polymer dosages. The decrease of rheological characteristics has been observed before for overdosed sludges. This brings out the importance of the permeability of the sediment and how this property is affected by the interfloc and intrafloc porosity in the sediment, as well as the water holding capacity of flocs containing hydrophilic polymer flocculant. During sediment formation, the flocs formed with 750 ppm dosage constrict their interfloc space more efficiently establishing the stronger network. At higher polymer dosages, lower water release, evident from the reduced solids content, induces weaker network formation in the sediment. This is an important addition to the existing body of work on polymer flocculation of mineral suspensions which indicates that the flocs formed by anionic polyacrylamide polymers are more compressible and therefore show better consolidation properties. However, not many studies discuss the distribution between bound intrafloc vs. free interfloc water in the sediment. Here we show the route to gain understanding of intrafloc and interfloc channel connectivity, which is crucial for consolidation process but has not been probed in depth before.

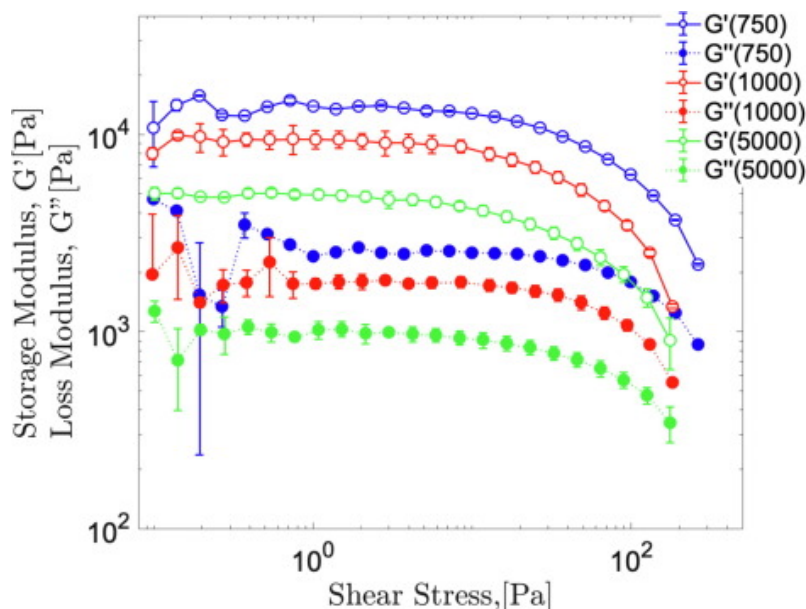


Figure 6. Oscillatory shear sweep results for flocculated MFT sediments at three dosages of polymer flocculant. The sediment network is the strongest for the lowest polymer loading

4.5 Flocculation with Hydrophobic Polymers

The first part of this task was to study the structure of polymer by varying the amount of functional groups while keeping the polymer backbone the same. Soares's group synthesized ethylene propylene diene terpolymer grafted with poly(methyl acrylate) (EPDM-g-PMA) in which EPDM backbone is kept the same, while the percent of PMA grafting efficiency is varied from 30, 40 to 50%. The interesting part of these polymers is that their hydrophobic backbone could aid water repelling while hydrophilic PMA groups can aid bridging clay particles. Therefore, the mechanism of their flocculation is very different from typically water-soluble flocculants such as polyacrylamide (PAM) and polyethylene oxide (PEO).

Figure 7 shows the effect of grafting efficiency on the polymer flocculation of MFT. The MFT was flocculated with each of the three polymers at 2000 ppm dosage and was allowed to settle in

order to get compacted. Their 3D structures are visualized through imaging in a fluorescence confocal spectroscopy over a span of 2 weeks at day 1, 7 and 14 respectively.

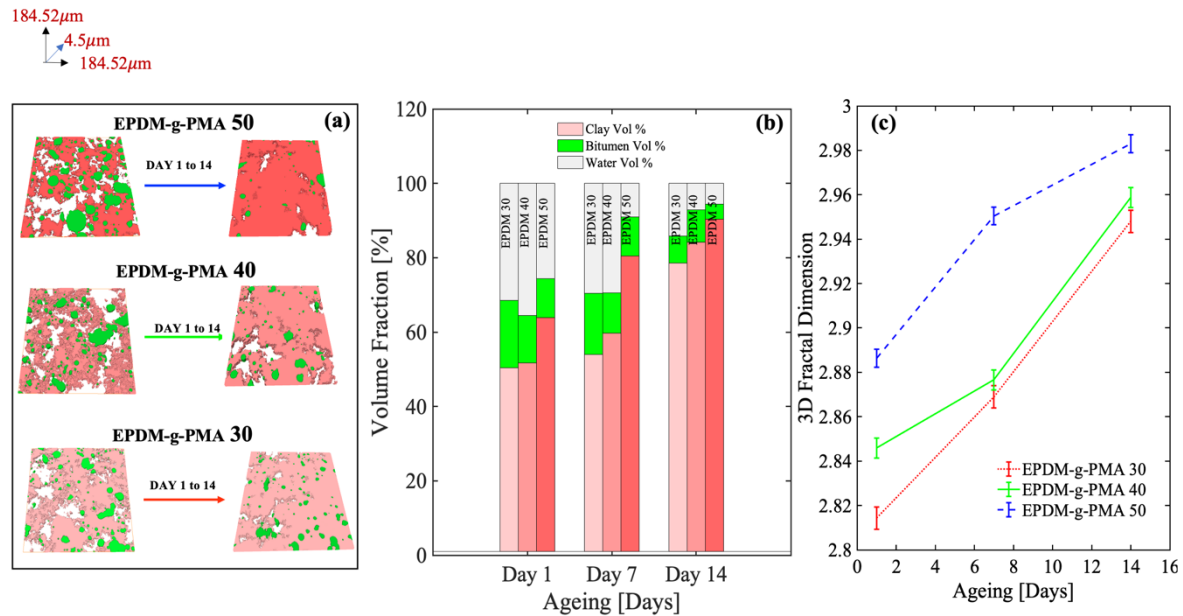


Figure 7. Microstructure Quantification post MFT flocculation. (a) 3D structure of the flocculated MFT sediment each at 2000ppm dosage of polymer flocculant showing the presence of clay (red) and bitumen (green) components within the porous sediment system. (b, c) The average structural parameters (Volume Fraction and 3D fractal Dimension) each of which are quantified from 3 different 3D images for each of the polymer treated MFT over a period of 14 days were displayed

The 3D illustrative of the flocculated sediment with superimposed layers of clay, bitumen and water are represented as red, green and white respectively in the Figure (a, b). The colour code of light, medium and dark red corresponds to the polymers EPDM-g-PMA with 30%, 40% and 50% grafting efficiency, respectively. The visual inspection of the packed sediments in the Figure (a) shows that more compact structure is evolved as the aging progresses, but that the polymer with the highest grafting efficiency of PMA (EPDM-g-PMA 50) results in the most compacted structures. This is also confirmed by the clay and bitumen volume fractions as well as fractal dimension (higher values indicate more compact structures).

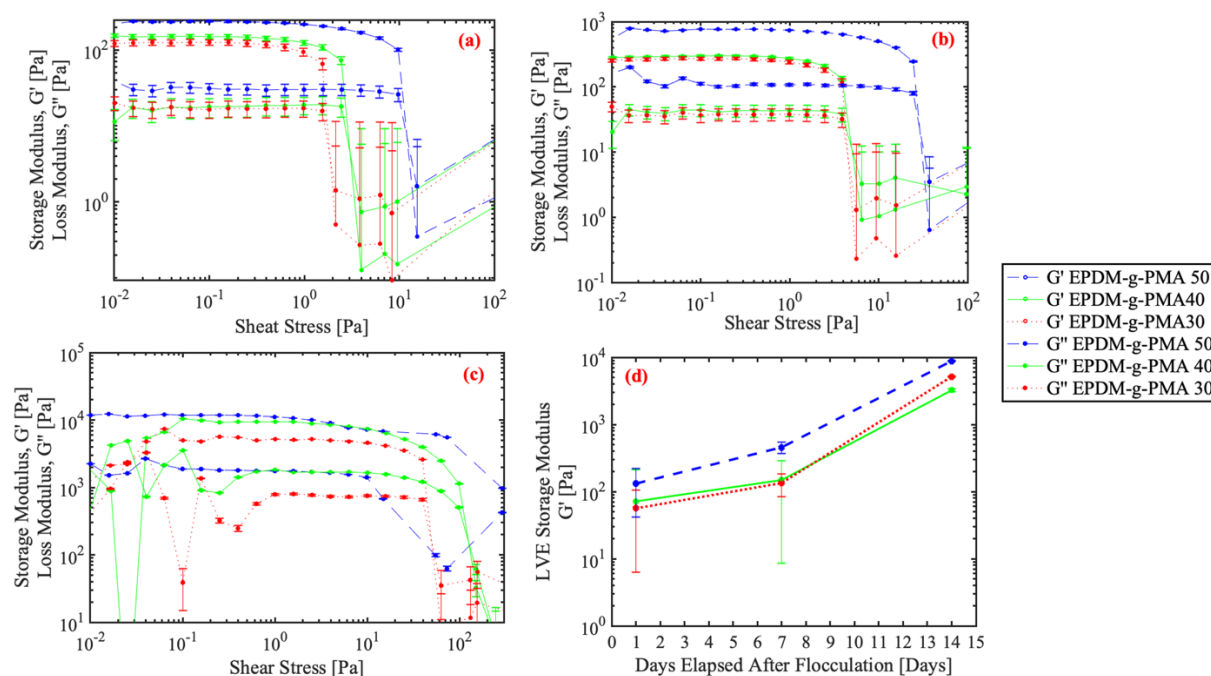


Figure 8. Shear sweep results for the flocculated MFT sediments with each of the three grafted polymers at 2000ppm over a period of 2 weeks is shown. (a),(b),(c) corresponds to day 1, day 7 and day 14 of the stress sweep results from rheology. (d) LVE storage modulus for flocculated MFT sediments at different ageing times. The strongest network is obtained for the sediment treated with EPDM-g-PMA 50 on all the four cases.

Rheological signature of each of these sediments agrees with their microstructural parameters. Plots of storage (G') and loss (G'') moduli against the stress were observed from the rheology during day 1, 7 and 14. From the above experiments, the average storage modulus in the linear visco-elastic region (G'_{LVE}) are determined and they show an increase in the solid-like behaviour of the sediment with ageing. This is because, as the sediment age, it becomes more compact due to the release of the interfloc water. The storage modulus of the treated sediments follow the same trend as the solids content at applied shear (EPDM-g-PMA 50 > 40 > 30). The G'_{LVE} was higher for EPDM-g-PMA 50, followed by EPDM-g-PMA 40 and 30 for same MFT.

Flocculation with Fluorescent Polymers

In order to understand the distribution of polymer within a floc, Soares's group synthesized Poly(vinyl benzyl trimethyl ammonium-co-aminopropylacrylamide) which is tagged with a fluorophore shown below. The polymer is cationic in nature, which was interesting to study as cationic polymers inherently behave differently than anionic polymers in their mechanism of flocculation.

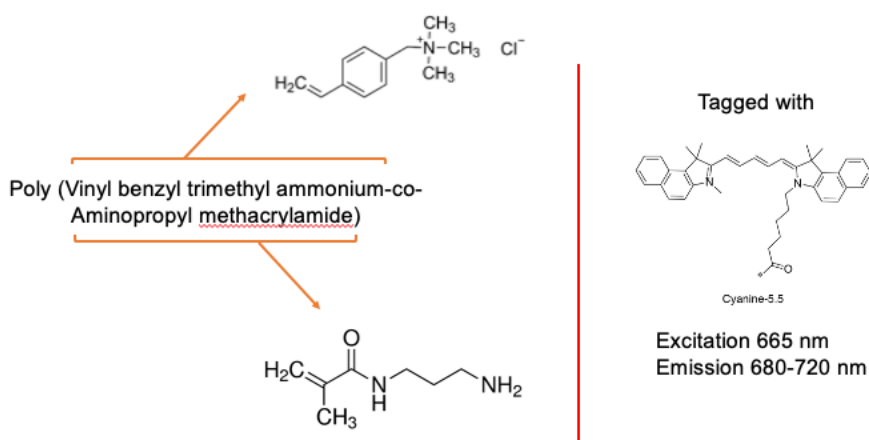


Figure 9 shows the 3D images of the sediment generated by flocculation with this fluorescently tagged polymer. To the best of our knowledge, this is the first representation of polymer distribution within the floc. As seen from the 2D image (on the left) the floc is present within the floc, but the 3D structure shows that it is mainly on the surface, which can be explained by its affinity for the negatively charged clay surface. Therefore, any excess of polymer will coat the flocs which can result in locking the additional water within the floc and slow down the consolidation process.

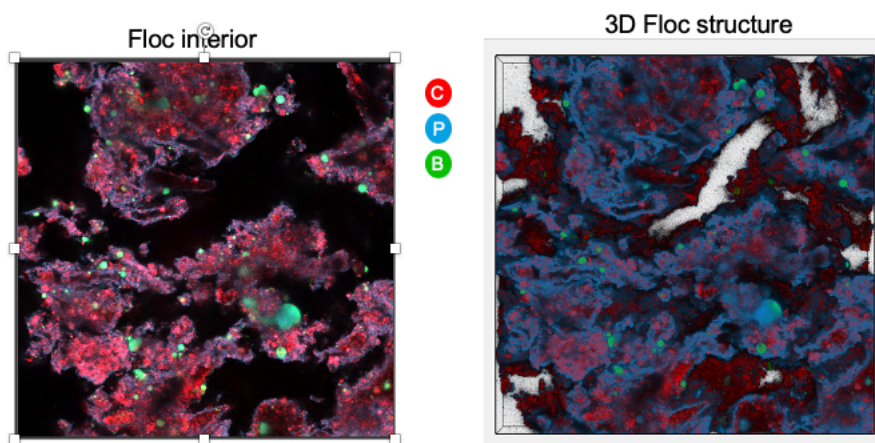


Figure 9. 2D image (left) and 3D image of sediment structure. Blue denotes polymer, red represents clay and green represents bitumen in the image.

The ongoing study investigates the effect of dosage on polymer distribution and synthesis of fluorescently labeled anionic polymer to study the effect of charge on the polymer distribution.

5 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In this work, we have developed a novel dual-mode fluorescence/reflectance confocal imaging method for *in-situ* monitoring of the oil sand tailings flocculation process and the consequent sediment formation. The novelty of the method is the ability to capture the flocculation in real time and the consequent quantification of the acquired image data. The qualitative investigation of the microstructural development during floc formation revealed that larger flocs were broken into more compacted ones with prolonged mixing. This observation is in agreement with the previous studies stressing the importance of mixing protocol for the efficient polymer flocculation. Previous studies have employed fluorescent confocal imaging technique for the visualization of the internal floc structure using fluorescent polymer flocculant in 2D. Our work expands the scope to the tridimensional confocal imaging which enables capturing the interactions of different components (fluorescent organics and reflective mineral particles) within the flocculated sediment. We show that bitumen and clay components within the system form fractal structures where bitumen is embedded into the 3D clay network. The image reconstruction protocol enabled further quantification of the sediment structural characteristics through calculation of the pseudo fractal dimension and volume fractions of the clay, bitumen, and water.

These structural parameters together with the bulk sediment properties (strength and solids content) show that we can find the optimal polymer dosage based on the lower extent of intrafloc water channels which results in the strongest sediment network. Increasing the polymer dosage increases the regularity of the sediment network and reduces the sediment interflocporosity, but prevents formation of the strong sediment network as flocs have the ability to hold more water with higher dosages of hydrophilic polymer present in their interior structure. We also studied a range of polymers with different polymer structure and hydrophobicity extent. We show that EPDM-g-PMA polymers have a promise to be utilized for tailings flocculation and their efficiency can be tuned by tailoring the grafting efficiency of hydrophilic groups. The approach presented in this work can help bridge the gap in understanding the link between the polymer-particle interactions leading to the favorable sediment structure that would ensure efficient dewatering and consequent sediment strength development.

5.2 Recommendations for Future Work

We propose to apply the developed techniques for the further in-depth quantitative study of the flocculation process where the fine details of the polymer-particle interactions in dense tailings systems will be connected to the polymer structure, the underlying flocculation mechanism, and the resulting strength of the sediment network upon consolidation.

When MFT is flocculated with an anionic hydrophilic polymer, retaining more water within the floc structure with increasing polymer dosage is expected. The significance of the favorable intrafloc structure for the overall sediment dewatering has been emphasized before for overdosed flocculated kaolinite suspensions and suspensions with high initial solids volume fraction. Even though we cannot resolve the microchannels within a floc with LSCM, estimates of the pseudo

fractal dimension along with the volume fractions of individual components enable deeper understanding of the sediment's structure. In particular, the proposed method technique allows us to gain understanding of how water is distributed within the sediment, which is of extreme importance for the efficiency of the consolidation process. We propose to study the water distribution within the sediment achieved with different types of polymers to understand their effect on consolidation.

6 ACKNOWLEDGEMENTS

We acknowledge the help of IOSI members and their valuable feedback during the annual IOSI meetings.

7 REFERENCES

- [1] A. Govedarica, E. J. Molina Bacca, and M. Trifkovic(2020) Structural investigation of tailings flocculation and consolidation via quantitative 3D dual fluorescence/reflectance confocal microscopy, *J. Colloid Interface Sci.*, vol. 571, pp. 194–204.
- [2] Li, H., Long, J., Xu, Z., & Masliyah, J. H. (2005) “Synergetic role of polymer flocculant in low-temperature bitumen extraction and tailings treatment”, *Energy & Fuels*, 19(3), 936-943.
- [3] Farkish, A., & Fall, M. (2013) “Rapid dewatering of oil sand mature fine tailings using super absorbent polymer (SAP)”, *Minerals Engineering*, 50, 38-47.
- [4] Alamgir, A., Harbottle, D., Masliyah, J., & Xu, Z. (2012) “Al-PAM assisted filtration system for abatement of mature fine tailings”, *Chemical Engineering Science*, 80, 91-99.
- [5] Ruiz-Cabello, F. J. M., Maroni, P., & Borkovec, M. (2013) “Direct measurements of forces between different charged colloidal particles and their prediction by the theory of Derjaguin, Landau, Verwey, and Overbeek (DLVO)”, *The Journal of Chemical Physics*, (23)138, 234705.
- [6] Caughill, D. L., Morgenstern, N. R., & Scott, J. D. (1993) “Geotechnics of nonsegregating oil sand tailings”, *Canadian Geotechnical Journal*, 30(5), 801-811.
- [7] Jeeravipoolvarn, S. (2005) “Compression behaviour of thixotropic oil sands tailings”. (Masters dissertation, University of Alberta).
- [8] Eckert, W. F., Masliyah, J. H., Gray, M. R., & Fedorak, P. M. (1996) “Prediction of sedimentation and consolidation of fine tails”, *AIChE journal*, 42(4), 960-972.

APPENDIX: LIST OF PUBLICATIONS AND PATENT FILING/APPLICATION

Journal Publications:

1. **Effect of Grafting Extent of Hydrophilic Branches on Hydrophobic Polymer Backbone on Microstructure and Rheological Properties of Flocculated Mature Fine Tailings**, G. Kalyanaraman, Z. Rastami, J. Soares, and M. Trifkovic, 2020 – submitted.
2. **Structural investigation of tailings flocculation and consolidation via quantitative 3D dual fluorescence/reflectance confocal microscopy**, A. Govedarica, E. J. Molina Bacca, and M. Trifkovic, *J. Colloid Interface Sci.*, vol. 571, pp. 194–204, 2020.

Note that two more papers are currently being prepared, will be submitted in a few weeks time:

3. **Floc Structure-Consolidation Efficiency Link in Tailings Systems Treated with Polymers of Varying Architectures, Charge Character and Degrees of Hydrophobicity**, A. Govedarica, F. Isufaj, J. Soares, and M. Trifkovic, 2020 – in progress
4. **Fluorescence-Based In-Situ Study of Floc Formation Mechanism and Resulting Sediment Consolidation in a Cationic Polymer-Dosed Tailings System**, A. Govedarica, D. Dixon, J. Soares, M. Trifkovic, 2020 – in progress

Conference Presentations:

1. **Direct Visualization of Shear Dependent Flocculation in Mature Fine Tailings**, A. Govedarica, B. Pilapil and M. Trifkovic, 65th Canadian Chemical Engineering Conference, October 4-7, 2015, Calgary, AB
2. **Towards Improved Understanding of Polymer Flocculation Mechanism: Visualization of Mature Fine Tailings during Shear**, A. Govedarica, B. Pilapil and M. Trifkovic, AIChE Annual Meeting, November 8-13, 2015, Salt Lake City, Utah, USA
3. **Polymer Treatment of Oil Sands Tailings: Confocal Microscopy and Rheological Study of the Consolidation Process**, A. Govedarica, B. Workman and M. Trifkovic, 5th International Oil Sands Tailings Conference, December 4, 2016, Lake Louise, AB
4. **Polymer Treatment of Oil Sands Tailings: Confocal Rheology Study of the Consolidation Process**, A. Govedarica, B. Workman and M. Trifkovic, 54th Annual Clay Minerals Society Conference, June 7, 2017, Edmonton, AB (**won best presentation award**)
5. **Polymer Flocculation of Oil Sands Tailings: Dynamic Rheological and Microstructural Properties of Floc Formation**, A. Govedarica, S. Shrivastava, B. Workman and M. Trifkovic, 67th Canadian Chemical Engineering Conference, October 22-25, 2017, Edmonton, AB.