Breakage and Reformation of Flocs in Oil Sands Tailings Slurries

Philip Watson, Ph.D., Thomas Fenderson, Amir Mahmoudkhani, Ph.D., Mohan Nair, Ph.D., Aditya Patel, Gayla Roberts

Kemira, Atlanta, USA

Abstract

Tailings management presents a key challenge in effectively exploiting oil sands resources, since every barrel of bitumen recovered generates two to three barrels of tailings waste. With the recent adoption of Canadian Energy Resources Conservation Board Directive 74, however, this waste can no longer be discharged as-is, but must be dewatered and rendered trafficable within five years of generation. Not only are process tailings targeted for remediation, but also the approximately 700 million m^3 of mature fine tailings that have been accumulated over decades of processing and lie in large containment ponds.

Chemical strategies for dewatering tailings involve treatment with additives that bind the tailings particles together into larger flocs, with floc size and shape influencing settling rates and compaction. Mechanical operations such as centrifugation or even pipeline transport, however, can break apart flocs, altering their sedimentation and packing behavior. In this research, mature fine tailings were treated with a range of organic flocculants and coagulants to induce floc formation. Floc breakage and reformation were assessed rheologically and by dynamic measurements of particle size distributions.

Introduction

Solid-liquid separation can be accomplished through chemical means, physical means, or a combination of both. Chemical strategies for solid-liquid separation strive to overcome steric and electrostatic forces that keep particles apart, and instead bring them together. As Stokes' Law dictates, sedimentation velocity increases with particle size and density, so creating large aggregates from small particles can cause solids to fall from suspension. Destabilization can occur through many mechanisms: Salts can collapse the electrostatic double layer surrounding solids, and coagulants can neutralize repulsive ionic surface charges and allow van der Waals forces to form flocs. Coagulants and flocculants can also bind to a surface and form a patch containing an opposite charge, a sticky site that can capture another particle. Finally, ultra-high molecular weight flocculants can bind to a particle surface and then reach into the suspension jellyfish-like, grabbing neighboring particles by bridging flocculation (Fuerstenau, 1976). Figure 1, below, illustrates these different flocculation schemes.

The simplest physical separation methods rely on gravitational sedimentation, but other methods can be employed to accelerate this process. Thickeners use rakes to cut drainage channels in flocculated beds, creating avenues that allow water trapped between compacting solids to escape (Nilufer, 2006; Xu, 2003). Centrifuges and hydrocyclones spin out particles (Chalaturnyk, 2002), while filters trap solids in a membrane (Xu, 2008). Strategies combining chemical and physical separation can further improve performance – for example, using chemicals to floc small particles that would otherwise pass through a centrifuge or filter. But the aggregates must also be strong enough to survive the mechanical separation process; if they cannot, separation efficiency can be compromised.
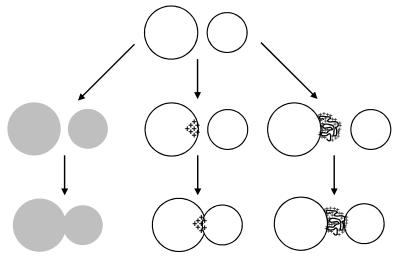
Figure 1: **Flocculation of two anionic particles by charge neutralization (left), cationic charge patch formation (middle), and bridging by a cationic flocculant (right).**

Even after the separation process, mechanical factors are still of importance. Solids must be transported from the separation location to their final destination, and pumping them may break apart flocs that were so challenging to form in the first place. Furthermore, when Directive 74 fully comes into effect in 2012, tailings waste can still contain up to 50% solids, meaning that additional dewatering will have to occur in order for the tailings to become fully trafficable within 5 years. While studies have shown that some shear can rearrange flocculated tailings to dewater more efficiently, too much shear can ruin dewaterability. (McFarlane, 2008; Demoz, 2010)

Two chief ways exist to engineer a shear-resistant floc. The first method is to create a floc with very strong particle-particle and particle-flocculant interactions. As long as any applied forces are lower than the aggregation forces, the floc will hold together. The other method is to create a floc that can reform after it is broken apart. These two methods are not mutually exclusive, and can be combined to tailor solutions for different solid-liquid separation challenges.

Experimental Methods

Materials

Samples of mature fine tailings (MFT) were obtained from a major oil sand producer in Alberta, Canada, and treated with the following organic polymers:

- Cationic coagulants
    - A 1 wt% solution of linear poly(diallyldimethylammonium chloride) [Linear pDADMAC]
    - A 1 wt% solution of branched epi-polyamine [Branched Epi]
- Anionic flocculants
    - An 0.5 wt% solution of linear 30 mol% acrylic acid/70 mol% acrylamide [Linear 30/70 AA/AMD]
    - An 0.5 wt% solution of branched 30 mol% acrylic acid/70 mol% acrylamide [Branched 30/70 AA/AMD]

o   An 0.5 wt% solution of linear 60 mol% acrylic acid/40 mol% acrylamide [Linear 60/40 AA/AMD]

Sample Preparation

The mature fine tailings (MFT) were diluted to 20 wt% solids, homogenized, and then a 1-kg aliquot was placed in a Kemira-designed glass beaker that contained 3 vertical baffles evenly spaced along its circumference. The slurry was agitated at 600 rpm with an overhead stirrer equipped with 2 Lightnin A310 3-bladed impellers, and then polymer solutions were added via syringes. The slurry was stirred for an additional 15 s at 600 rpm, and then the speed was reduced to 100 rpm for 30 s before mixing was stopped.

Particle Size Measurements

Particle size distributions (PSD) were measured with a Malvern Mastersizer S, which measures the angular dependence of scattered light. Flocculated samples were diluted with Milli-Q water, and then added to the impeller-driven flow loop of the Mastersizer. Particle size distributions were computed as equivalent-sphere size distributions based on Mie scattering and Fraunhofer diffraction formalisms applied to the scattering data. The optical constants ($\lambda = 432.8$ nm) used for these computations were a complex refractive index of 1.5295, 0.100i for the solids and a real refractive index of 1.3300 for the continuous phase. Measurements were taken during each test at 30, 60, 120, and 180 seconds after addition to the flow loop at a single impeller speed. Typically, the size distributions after 30 s of mixing were used for comparisons in order to minimize any effects from shear on aggregate size.

Rheological Measurements

Rheological measurements were performed at 25 °C on an Anton Paar MCR 300 rheometer equipped with either a 12.5 mm roughened parallel plate or a 50 mm smooth parallel plate geometry. Flocculated solids were placed on the lower plate, and then the upper plate was lowered to a gap of 1.050 mm for trimming. Finally, the gap was narrowed to 1.000 mm and the sample was equilibrated for 60 s before measurements began.

The linear viscoelastic (LVE) regions of the samples were measured by sinusoidally oscillating the upper plate logarithmically from an initial strain of 0.1 to a final strain of 100 Pa at a constant frequency of 10 rad/s. The upper boundary of each LVE region was determined by fitting a plot of the storage modulus (G') versus shear stress (τ) to the rational function shown in Equation 1, and then solving for the point where the first derivative of the rational function was equal to -0.1.

$$G' = \frac{a + b\tau}{1 + c\tau + d\tau^2} \qquad (1)$$

Next, floc recovery was assessed with a three-interval thixotropy test. First, the upper plate was oscillated for 5 minutes at a frequency of 10 rad/s and at a shear stress less than the sample's LVE boundary. In the second interval, the sample was rotationally sheared for 10 minutes at 500 s^{-1} to break all floc structure. Finally, the conditions from the first interval were restored, and the sample was oscillated for 10 minutes. Recovery was calculated by expressing the storage modulus from the end of the third interval as a percentage of the storage modulus from the end of the first interval, according to Equation 2. A recovery of 100% meant the sample completely recovered, while lower values indicate the sample was unable to match its initial rheology.

$$\text{Recovery (\%)} = 100 \times G'/G'_0 \quad (2)$$

Results and Discussion

Several methods exist for measuring a fluid's yield stress, which is the point at which a fluid begins to flow. One of the gentlest methods, determination of the linear viscoelastic (LVE) boundary, was chosen for this study as a proxy for the average floc shear strength. At shears below the LVE boundary, the slurry acts as an elastic solid and deforms reversibly, but the application of greater shears causes irreversible deformation by breaking flocs and moving flocs past each other (Larson, 1999). Figure 2 shows an example of the test procedure, while Figure 3 illustrates the results.

Figure 2: **A typical amplitude sweep procedure. An oscillatory strain or shear stress is applied to a fluid, the amplitude of which increases over time (left). Meanwhile, the storage modulus of the fluid is measured as a function of the applied shear (right), and the boundary of the LVE region is identified (circle).**
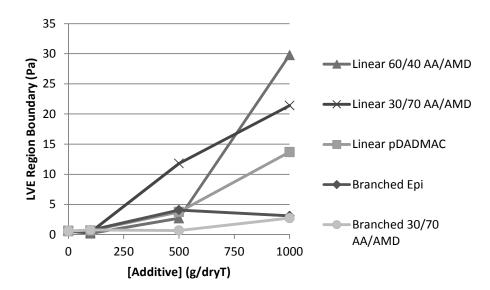

Figure 3: **Effect of additive and additive concentration on the shear strength of flocs.**

In this system, floc strength depends on the strength of the interaction between a polymer and different surfaces, as well as the number of polymer/surface interactions. In mature fine tailings the clay surfaces have both anionic and cationic sites, allowing strong ionic interactions to occur with both anionic and cationic polymers. The second factor, polymer size, depends on molecular weight and structure. The flocculants are approximately two orders of magnitude higher in molecular weight than the coagulants. However, branching in the 30/70 AA/AMD flocculant and the epi-polyamine coagulant reduce the size of the polymer particle in solution by packing monomeric units into a smaller and denser particle. In these measurements, the linear flocculants cause the biggest increase in floc strength, followed by the linear coagulant. Finally, the branched flocculant and coagulant result in only a slight improvement in floc strength (Mortimer, 1991).

Next, slurries where coagulants and then flocculants were added were measured. Figure 4 shows one set of results for the branched epi-polyamine coagulant and the linear 60/40 AA/AMD flocculant. Treating with a coagulant before flocculation provides a moderate boost to aggregate strength, although the effect of the flocculant is more pronounced. Again, the size disparity between the two additives is primarily responsible for this behavior.
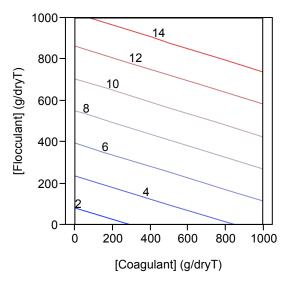

Figure 4: **Effect of the branched epi-polyamine coagulant and linear 60/40 AA/AMD flocculant concentrations on MFT floc strength. Contour values represent shear strength in Pascals.**

The particle size distributions (PSD) in Figure 5 tell a similar story. Again, larger polymer molecules tend to tie MFT solids together better, allowing them to form larger flocs. Of interest is the lack of a clear trend in size for tailings treated with the coagulants. One possible explanation is that at some concentrations the coagulants may increase ionic repulsive forces, causing dispersion instead of aggregation.
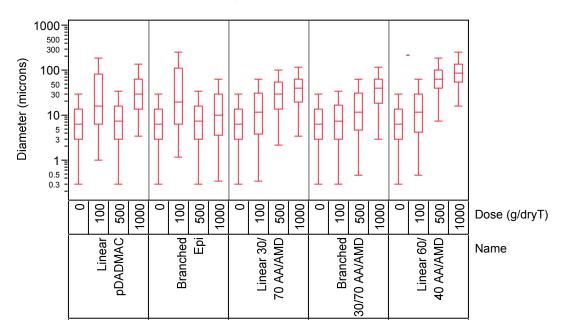
Figure 5: **Effects of additive and additive concentration on MFT particle size distributions.**

Figure 6 shows contour plots of the D10 (10th percentile), D50 (median), and D90 (90th percentile) sizes after treatment with different levels of the branched epi-polyamine and linear 60/40 AA/AMPS flocculant. All sizes respond well to the flocculant, while the D90 and D50 are influenced more by the coagulant than the D10.
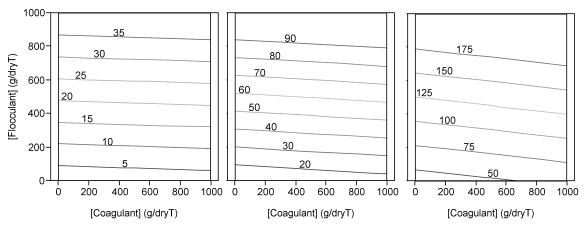

Figure 6: **Effect of the linear 60/40 AA/AMD flocculant and branched epi-polyamine coagulant concentrations the D10 (10th percentile), D50 (median), and D90 (90th percentile) diameters of MFT particles. Contour values represent diameters in microns.**

Thixotropy tests are a method of separating time-independent and time-dependent rheological behavior. Time-independent rheological behavior includes shear thinning and shear thickening, reversible processes that are functions of only the amount of shear applied. These processes can be likened to traffic flow on highways: shear thinning occurs when particles orient themselves to move in a flow field with the least amount of resistance, while shear thickening stems from what are effectively particulate traffic jams. In both cases, however, once the shear ceases, the fluid returns to its original rheological state (Macosko, 1994).

Thixotropy is a different beast, however. Under no-shear or low-shear conditions, many particles form aggregates over time, and these aggregates are broken up by shear. When the shear ceases, the fluid will not immediately return to its original rheological state, because the aggregates require time – seconds, minutes, hours, days, or even longer – to reform. Several techniques for measuring thixotropy exist, from simple hysteresis curves (Macosko, 1994) to advanced modelling (Dullaert, 2005).

For this research, a three-interval thixotropy test was chosen, following the scheme in Figure 7. In the first interval, a fluid is subjected to a very low shear in order to establish a baseline rheology. Then, the shear is suddenly increased in the second interval to break apart any aggregates. Finally, the fluid is returned to the original low-shear conditions to observe how quickly the aggregates reform. For the floc samples in this study, intervals 1 and 3 applied an oscillatory shear that was less than the LVE boundary established by prior testing, so the storage modulus of the fluid before and after high-shear were compared instead of the shear stress.
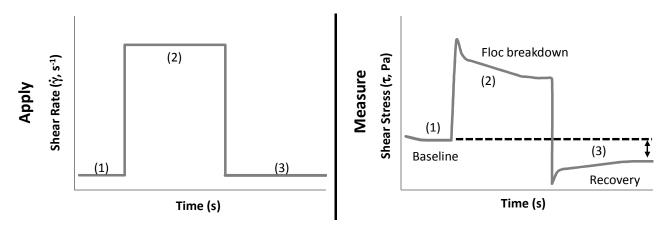

Figure 7:   An example three-interval thixotropy test diagram. The first interval measures a baseline rheology, the second interval breaks up aggregates, and the third interval measures re-aggregation.

Figure 8 shows the results of the thixotropy tests, which almost follow an inverse relationship to the floc strength measurements. The cationic coagulants recover the most, the linear flocculants the least, and the branched flocculant in-between. The contour plot in Figure 9 illustrates that a combination of a coagulant and a flocculant can give a higher recovery than a flocculant by itself would by itself, but lower than treatment by a single coagulant.
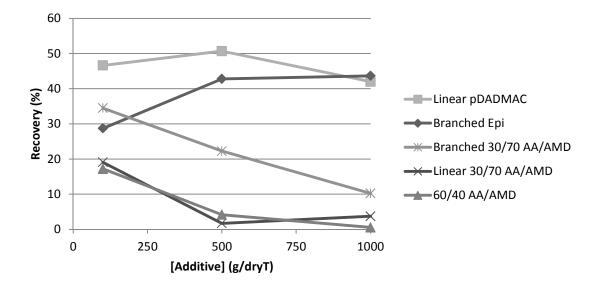
Figure 8: Post-shear recovery of MFT slurries treated with different additives. Higher recoveries indicate a higher degree of re-flocculation.
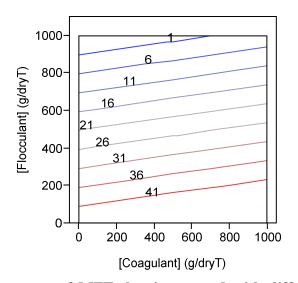

Figure 9: Post-shear recovery of MFT slurries treated with different concentrations of the linear 60/40 AA/AMD flocculant and branched epi-polyamine coagulant. Contour values correspond to recovery percentages, with higher values indicating higher recoveries.

The effect of high shear on the particle size distributions of MFT treated with the branched epi-polyamine coagulant and linear 60/40 AA/AMD flocculant can be seen in Figure 10. Flocs treated with only the coagulant are fairly shear-insensitive, while PSD of flocculant-treated tailings show the most degradation. Figure 11 shows specific effects on the D10, D50, and D90 particle sizes after shear.
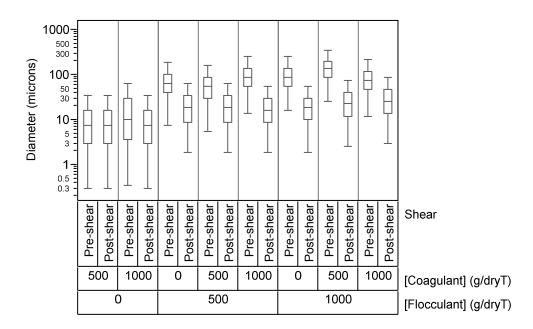
Figure 10: **Effect of different concentrations of the branched epi-polyamine coagulant and linear 60/40 AA/AMD flocculant on MFT particle size distributions before and after high shear.**
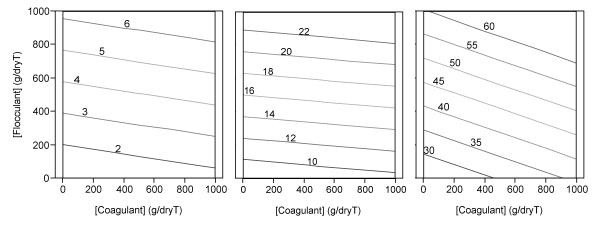

Figure 11: **Effect of the linear 60/40 AA/AMD flocculant and branched epi-polyamine coagulant concentrations the D10 (10th percentile), D50 (median), and D90 (90th percentile) post-shear diameters of MFT particles. Contour values represent diameters in microns.**

Conclusions

Floc strength is an important underlying factor for establishing compliance with ERCB Directive 74, since MFT dewatering can be adversely affected by aggregates being sheared apart during processing. One method for engineering shear-resistant flocs is to make the forces aggregating the particles as strong as possible. As long as shear forces are less than the interparticle forces, the flocs will remain whole – but when the flocs break, floc size suffers greatly. Aggregates formed by treating solids with high molecular weight linear polymeric flocculants tend to follow this behavior. The other method for engineering shear-resistant flocs is to make flocs that have weaker interparticle forces, but quickly reform after being sheared apart. Flocs formed from coagulants or branched polymeric flocculants tend to follow this behavior.

However, different types of additives can be combined to create flocs that fall somewhere in-between – sacrificing a little floc strength for increased recovery, or sacrificing a little recovery for better floc strength. And it is conceivable that the proper combination of additives could even result in performance that exceeded that of the individual components.

Acknowledgements

References

Chalaturnyk, R.J., Scott, J.D. and Ozum, B., 2002. Management of Oil Sand Tailings. *Petroleum Science Technology*, 20 (9), 1025-1046.

Demoz, A., Munoz, V. and Mikula R. Optimizing MFT Dewatering by Controlling Polymer Mixing. *Second International Oil Sands Tailings Conference*, 107-121.

Dullaert, K. and Mewis, J., 2005. Thixotropy: Build-up and breakdown curves during flow. *Journal of Rheology*, 49 (6), 1213-1231.

Fuerstenau, D.W. and Raghavan, S., 1995. Some Aspects of the Thermodynamics of Flotation. *In:* M.C. Fuerstenau, ed. *Flotation - A. M. Gaudin Memorial Volume*. New York, NY: AIME, 21-65.

Larson, R.G., 1999. *The Structure and Rheology of Complex Fluids*. Oxford: Oxford University Press.

Macosko, C.W., 1994. *Rheology: Principles, Measurements, and Applications*. New York: Wiley-VCH.

McFarlane, A. J., Addai-Mensah, J. and Bremmell, K., 2008. Rheology of flocculated kaolinite dispersions. *The Korean Society of Rheology*, 17 (4), 181-190.

Mortimer, D.A. Synthetic polyelectrolytes—A review. *Polymer International*, 25 (1), 29-41.

Nilufer, K., 2006. *A Study of Channelling Behaviour in Batch Sedimentation*. Thesis (PhD). Royal Melbourne Institute of Technology.

Xu, Y. and Hamza, H., 2003. Thickening and disposal of oil sand tailings. *2002 SME Annual Meeting*, 55, 1-7.

Xu, Y., Dabros, T. and Kan., J. Filterability of oil sands tailings. *Process Safety and Environmental Protection*, 86, 268-276.