Application of Compound Flocculant for Oil Sand Mature Fine Tailings Two-Stage Treatment

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Abstract. The flocculation method had a good effect in treating oil sands tailings, and polyacrylamide (PAM) was commonly used as an effective flocculant. In this paper, polydiallyl dimethyl ammonium chloride (PDADMAC) combined with PAM and several supplementary materials into three compound flocculants were used to treat oil-sand tailings for the first time. The compound flocculants were applied for two-stage treatment to compare their performance with that of PAM. The first stage flocculation results showed that mature fine tailings (MFT) treated by compound flocculants had faster initial settling rate, higher clarity of supernatant and higher solid content of sediment than PAM, especially Flocculant A. The second stage dewatering of the mud layer indicated that the water release ability of sediment treated with compound flocculants was better than that of PAM, the yield stress was more appropriate and the capillary suction time (CST) was shorter. The deposits treated with the same flocculant for the two stages had great strength gain so reclamation became much easier, which provided a new and efficient flocculation solution for the treatment of oil sands mature fine tailings.

1. Introduction

Oil sands are a naturally occurring mixture of thick, heavy oil, water and sand. Certain areas of the oil sands of northern Alberta in Canada are mined and processed for the production of bitumen. After extraction, huge amount of tailings contain water, clay, sand and residual bitumen are produced, and then transported and stored within surface tailings ponds. The fast-settling sand particles segregate from the slurry upon deposition at the edge of the tailings ponds while the fine fraction accumulates in the center of the pond and settles to become mature fine tailings (MFT). Although most of the water is released and recycled back into the process, 86% of the volume of MFT consists of water[1]. MFT only settles to about 30% to 35% solids content after a few years of placement[2]. Settling occurs much more slowly after this point and tailings remain fluid-like for decades or centuries. As of 2014, about one billion cubic meters of MFT exist within the tailings ponds. If there is no change in tailings management, the inventory of fluid tailings is forecast to reach two billion in 2034[3-4].

Mature fine tailings (MFT), as a mixture of residual bitumen, sand, silt, fine clay particles and water, are a byproduct of oil sands extraction. The large volume, and poor consolidation and water release ability of MFT have been causing significant economic and environmental concerns. One of the major operational and environmental challenges oil sands mining facing is the separation of water from the fine tailings to strengthen the deposits so they can be reclaimed. Therefore, a large amount of work[5-14] has been implemented on finding innovative dewatering/disposal techniques. One of these techniques is tailings flocculation. Flocculation is used to describe the action of polymeric materials which form bridges between individual particles. Bridging occurs when segments of a polymer chain
adsorb different particles thus help particles aggregate\cite{15-17}. And it is a technique in which discrete, colloidal-sized particles were agglomerated by an appropriate reagent and, as a result, settle out of suspension. Polyacrylamide (PAM) is generally used as an effective flocculant in tailings treatment. However, MFT is rather difficult to be flocculated due to its small particle size when only PAM is applied.

This paper proposed to apply compound flocculant contained PAM, poly diallyl dimethyl ammonium chloride (PDADMAC) and some supplementary materials to treat MFT. In this paper, three compound flocculants of the aforesaid components in varying proportions were applied for two-stage MFT flocculation to test their performance comparing with the results when only PAM was applied. The purpose of the two-stage treatment was as follows, flocculating the tailings to realize rapid solid-liquid separation for the first stage, and dewatering the underflow solids from the first stage to strengthen the deposits for the second stage.

2. Experimental

2.1. Materials and reagents

Mature fine tailings (MFT) sample was collected from a Canada oil company.

Polyacrylamide (PAM) of 30\% ionic degree with 10,000,000 molecular weight.

Poly diallyl dimethyl ammonium chloride (PDADMAC) with 500,000 molecular weight.

Mixtures of PAM, PDADMAC and some supplementary materials in varying proportions were combined to form three compound flocculants, Flocculant A, Flocculant B and Flocculant C.

2.2. Instrumentation

Laser diffraction SEISHIN LMS-30 was used to test the particle size distribution. The viscosity was carried out by Brookfield RV DV-3T with vane spindle at 6rpm, and test temperature was 25\degree C. The density was measured at 25\degree C by Pear-shaped pycnometer. MBI was measured by Methylene Blue Clay Analyzer to obtain clay content. The underflow (U/F) and overflow (O/F) were dried at 120\degree C for 3 hours to obtain their solid contents. The yield stress was tested by Brookfield RV DV-3T with vane spindle at 0.5rpm, and test temperature was 25\degree C. The Capillary Suction Time (CST) of the flocculated tailings was measured using a TRITON ELECTRONICS LIMITED Type 304M Capillary Suction Timer.

2.3. Sample preparation and two-stage flocculation method

2.3.1. Preparation of flocculant solution.

Powder flocculant sample (0.500g) was weighed accurately, and was dissolved in 100mL of water respectively. The solution was stirred for about 1 hour. This solution was regarded as mother flocculant solution at concentration of 0.5\%. The mother solution was then diluted to 0.05\% with water for the first stage flocculation and 0.2\% for Stage 2.

2.3.2. Two-stage flocculation.

The first stage: The MFT sample was shaked well and was weighed 1000g in a 2L beaker. The sample was stirred with a speed of 350rpm for 3 minutes, and then was adjusted down to 160rpm with adding 0.05\% flocculant solution into the beaker. Begin timing when the flocculant was injected. The duration of flocculant injection and mixing was 1min with additional 1min post-floculate shear. Shut down the agitator and the flocculated tailings was transferred to a 1-L volumetric cylinder.

The second Stage: After the first stage flocculation for 2 hours, O/F was decanted and mud layer was taken out for second stage. The mud layer was stirred with a speed of 200rpm for 1 minute, and then 0.2\% flocculant solution was added into the beaker. Begin timing when the flocculant was injected. The duration of flocculant injection and mixing was usually 1min with additional 1min post-floculate shear. Shut down the agitator and the flocculated tailings was transferred to a 1-L volumetric cylinder.
3. Results and discussion

3.1. Properties of MFT

3.1.1. Basic properties. The thickener feed of MFT was analyzed using the distillation method[18] to determine the contents of bitumen and water. All the properties of MFT sample were tested as mentioned in Section 2.2 and detailed results were shown in Table 1.

Table 1. Basic properties of MFT

| Sample | Solids (%) | Bitumen (%) | Water (%) | MBI (g/100g) | Viscosity (cp) | Density (g/cm³) |
|--------|------------|-------------|-----------|-------------|--------------|----------------|
| MFT    | 35.66      | 4.59        | 64.34     | 0.92        | 3050.0       | 1.23           |

Table 2. Parameter for Particle Size Distribution of MFT

| ITEM                | ITEM                |
|---------------------|---------------------|
| Dispersion-medium   | Water               |
|                     | Specific area       |
|                     | 2.129m²/cm³         |
| Dispersing agent    | Water               |
| RR-N                | RR-B                |
| 1.330-0.00i         | 0.03669             |
| Tortuosity ratio    | Normal distribution,50% |
| 1.000               | 4.916μm             |
| Shape factor        | Normal distribution, σg |
| X10                 | 1.518μm             |
| X50                 | 4.654μm             |
| X90                 | 16.980μm            |

3.1.2. Particle Size Distribution of the Test Sample. Laser diffraction was applied to find out the particle size distribution of this MFT sample. According to the distribution drawing (Figure 1), the particle size of MFT distributed homogeneously, and the mean particle size was between 5μm and 10μm, the percent of the particle diameter below 44μm was up to 90%.

3.2. Flocculation

Polyacrylamide (PAM) has been widely used as process aids in the oil sand industries to enhance solid-solid or solid-liquid separation. Their performance strongly depends on their physicochemical properties such as integrated functional groups, charge density and molecular weight (MW). Previous studies have indicated that a hydrolyzed polyacrylamide (HPAM) polymer of 30% anionicity with a high MW was functional in the flocculation of oil sands tailings. However, MFT was rather difficult to be flocculated due to its small particle size when only PAM was applied. So this paper proposed to apply compound flocculant contained PAM, PDADMAC and some supplementary materials to treat...
MFT. In this paper, three compound flocculants containing different contents of the aforesaid components were applied for two-stage MFT flocculation to test their performance comparing with the results when only PAM was applied. The entire chemical screening with PAM, Flocculant A, B and C for both the first Stage and the second Stage has been performed. The detailed results will be shown in this section.

3.2.1. The First Stage.

3.2.1.1. Flocculation Performance. The effectiveness of a flocculant for the first stage was quantified in terms of (i) initial settling rate; (ii) turbidity of supernatant, and (iii) solid content in the sediment after settling. In view of this, settling curves, solid contents of underflow (U/F) and overflow (O/F) were carried out to optimize the operating conditions and to maximize the solid density and dewatering rate with minimized polymer dosage. The dosage was designed as 100/200/300/400g/ton to confirm the most appropriate dosage. The concentration of flocculant was 0.05%. In this paper, flocculant dosages were expressed with reference to total suspension mass, unless other stated.

Settling of the solids for the tailings was marginal without flocculant addition. With the addition of flocculant, quick formation of large, dense flocs with high mechanical strength led to rapid settling and a clear supernatant, which was highly desirable and hence, represented the best performance of a polymer as a flocculant. Settling tests (Figure 2) were therefore used as a method to evaluate flocculation performance of flocculants for tailings. Meanwhile, solid contents of U/F and O/F were tested and Net Water Release (NWR) was calculated to determine the optimum dosage (Figure 3). The U/F solids and O/F solids were acquired after settling for 2 hours.

It was incredible that settling was nearly finished within 2s when flocculated with Flocculant A at 300g/ton dosage, and its settling rate was up to 8.7m/min, which performed significantly better than PAM alone. Besides, the compound flocculant with PDADMAC addition was able to not only improve the clarity of supernatant after settling but also achieve a high settling efficiency. It was probably because PDADMAC had features of low molecular weight and good water solubility.
Figure 2. Settling Curve for Different Samples
(a) Flocculant A, (b) Flocculant B, (c) Flocculant C, (d) PAM

Figure 3. Flocculation performance with 4 flocculants at 4 dosages for the first Stage
(a) U/F solids, (b) O/F solids, (c) Settling rate, (d) NWR
Table 3. Results under optimum operating condition

| Flocculant  | Dosage (g/ton) | Density (g/cm³) | U/F Solid (%) | O/F Solid (%) | Settling rate (m/min) | NWR (%) |
|------------|----------------|----------------|---------------|---------------|-----------------------|---------|
| PAM        | 300            | 1.15           | 30.78         | 0.50          | 0.84                  | 23.09   |
| Flocculant A | 200           | 1.07           | 49.87         | 0.42          | 1.68                  | 44.30   |
| Flocculant B | 300           | 1.10           | 40.29         | 0.44          | 2.88                  | 33.66   |
| Flocculant C | 300           | 1.13           | 38.68         | 0.49          | 2.88                  | 31.87   |

3.2.1.2. Optimum Operating Condition. Taken solid contents, settling rate and economy principle together, dose of 200g/ton which performed the best was selected as the optimum dosage for Flocculant A, and that of 300g/ton for other flocculants. Results of each flocculant for the first stage flocculation were list in Table 3.

3.2.2. The second Stage. The goal in second Stage treatment is to re-flocculate the underflow solids to minimize fines as the mud layer is pumped to the tailing pond. The mud layer coming from the first stage flocculation is selected as the experiment object. It’s worth mentioning that the following test objects were mud layers from the first Stage with their own optimum dosages for each tailings sample, i.e. 200g/ton for Flocculant A, and 300g/ton for others. If the thickener underflow is above 45%, dilute it to 45% using water, if thickener underflow is under 45%, use the sample as is. Therefore, mud layer after flocculated with Flocculant A was diluted to 45% with water before the second stage flocculation test, and mud layers after flocculated with Flocculant B, C and PAM were used for the second stage flocculation directly.

3.2.2.1 Character of Thickened U/F and Mixing Energy for the second stage. Feedstock should be sheared to an yield strength of 0-20 Pa, because this was useful for the second stage flocculation and makes sure that the underflow can be pumped through the pipeline. Series of experiments verified that all the thickened U/F could be sheared to an yield strength of 0-20 Pa at 350rpm for 8min. Table 4 showed the yield stress of the samples before and after agitation.

Table 4. Characterize the Thickened U/F

| Sample                              | Viscosity (cp) | Density (g/cm³) | YG Stress (Pa) | Before agitation | After agitation |
|-------------------------------------|----------------|-----------------|----------------|------------------|----------------|
| U/F after flocculated with PAM      | 14890.0        | 1.11            | 40.70          | 5.52             |
| U/F after flocculated with Flocculant A | 35150.0        | 1.08            | 310.8          | 12.48            |
| U/F after flocculated with Flocculant B | 21220.0        | 1.10            | 72.00          | 9.04             |
| U/F after flocculated with Flocculant C | 18890.0        | 1.12            | 61.10          | 7.56             |

3.2.2.2 Dewatering Performance. The dewaterability of a flocculant for the second stage was quantified in terms of (i) dewatering rate; (ii) yield stress, to reflect the stress required before the flocculated material started to yield,and (iii) Capillary Suction Time (CST), to reflect the dewatering ability of the flocculated tailings. Dewaterability was thus measured as a function of how long it took for water to be suctioned through a filter and low values indicated rapid dewatering whereas high values indicated slow dewatering ability. In other words, a low CST number indicated good
dewatering. All above were generally used to determine the performance of the flocculant and also the optimum dosage. The concentration of flocculant was 0.2%.

As can be seen in Figure 4, the solid content data indicated the effect of different dosages. For each flocculant sample, dosage of 200g/ton clearly reflected good performance except Flocculant A. As the yield stress increased more fines were captured in the reflocculated underflow. Similarly, it can be seen that as the dewatering improved (i.e., the CST decreased), more fine were captured in the underflow. Based on the above tests, the preferred dosage of flocculant was determined to be 70 g/ton for Flocculant A, 200g/ton for the other flocculants. By all indications, the dewaterability of the compound flocculants, especially A, was obviously better than that of PAM alone.

3.2.2.3 Strength Gain vs. Time. Strength gain after two stage flocculation was monitored for 10 days. After 7 days, strength gain can up to 1000Pa for each sample (Figure 5).

3.2.2.4 Total Water Recovery vs. Time. Tailings’ solid contents were also monitored for 10 days, which indicated that dewatering rate increases over time (Figure 6). After 7 days, % solids can get satisfied values of 70.00%, 78.00%, 74.50% and 71.20% respectively.
3.2.2.5 Optimum condition. Taken NWR, yield stress, CST and economy principle together, dose of 70g/ton which performed the best was selected as the optimum dosage for Flocculant A, and that of 200g/ton for other flocculants. Results of each flocculant for the first stage flocculation were listed in Table 5.

Table 5. Results under Optimum Operating Condition

| Flocculant | Dosage (g/ton) | Solid Content (%) | NWR (%) | Yield Stress (Pa) | CST (s) |
|------------|----------------|------------------|---------|------------------|---------|
| PAM        | 200            | 42.60            | 36.22   | 24.60            | 99.6    |
| A          | 70             | 52.88            | 47.64   | 91.00            | 27.3    |
| B          | 200            | 50.40            | 44.89   | 71.80            | 37.9    |
| C          | 200            | 47.95            | 42.17   | 101.2            | 52.5    |

4. Conclusions
This study showed that compound flocculants, which consisted of PAM, PDADMAC and several supplementary materials in varying proportions, performed much better in oil sands mature fine tailings two-stage treatment than a single PAM.

In the first stage, MFT sample was respectively flocculated with the four flocculants to realize solid-liquid separation. Initial settling rate, turbidity of supernatant, and solid content in the sediment after settling were measured to compare the flocculation ability of the four flocculants, and 200g/ton Flocculant A was then recommended for its best settling performance due to the very thick underflow of 49.87% solid content and the very clear supernatant of 0.42% solid content.

In the second stage, the mud layer coming from the first stage flocculation was respectively dewatered with the four flocculants to strengthen the deposits. Dewatering rate, yield stress and CST were measured to compare the dewaterability of the four flocculants, and 70g/ton Flocculant A was recommended for its best dewatering performance due to its high solid content, a relatively high yield stress and a relatively low CST.

After two stage flocculation, the test showed that the solid content of re-flocculated U/F can reach 66.70% for Flocculant A, while exhibiting a strength gain of greater than 1KPa after 5 days consolidation. More importantly, compound flocculant A can work in both two stages, so that only one chemical will be prepared in the future field operation, and only one set of dissolving equipment will be needed, which provided a new and efficient flocculation solution for the treatment of oil sands tailings.
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