Synergetic Role of Polymer Flocculant in Low-Temperature Bitumen Extraction and Tailings Treatment

H. Li, J. Long, Z. Xu, and J. H. Masliyah*

Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta, Canada T6G 2G6

This paper presents a preliminary study on the synergetic effect of a polymer flocculant, derived from hydrolyzed polyacrylamide (HPAM), on both bitumen extraction and tailings treatment as applied to oil sands. Bitumen extraction experiments and tailings settling tests were carried out with the addition of HPAM directly in the bitumen extraction process. To understand how the polymer affects bitumen recovery and tailings treatment, the long-range interaction and adhesion forces between bitumen and solids (clay and silica) and between clay and silica were measured using an atomic force microscope (AFM). Our study clearly demonstrated a synergetic role of HPAM in processing poor oil sand ores, which are characterized by high clay fines content. The addition of HPAM at an appropriate dosage not only improved bitumen liberation and recovery but also increased the tailings settling rate. Such improvements were attributed to the selective flocculation of clay fines by HPAM, which was supported by the AFM data. On the basis of the results of the present study, it is suggested to directly add HPAM into the bitumen extraction process, rather than to tailings, to facilitate both bitumen recovery and tailings treatment in production operations.

1. Introduction

In the Clark Hot Water Extraction (CHWE) process for bitumen extraction from oil sand ores,[1] water is added to oil sands to form a slurry from which bitumen is separated from the solids (clay fines, mostly kaolinite and illite, and silica sand). The remaining slurry in the primary separation vessel (PSV) and flotation cells is discharged as tailings into tailings ponds. Since the fine solids in the tailings are too small ($<10~\mu$m) to settle quickly or may not settle at all,[2] chemicals such as calcium sulfate (gypsum) are often added to accelerate their settling. The process with gypsum addition is normally referred to as consolidated tailings, CT. The action of gypsum is explained by the fact that a high calcium concentration produced by gypsum addition leads to fines aggregation due to the collapse of the electric double layer and reduced surface charge on the fines. The clear supernatant water, called process water, from tailings ponds is reused in the bitumen extraction process. Test results showed that high concentrations of divalent ions in the process water, including calcium and magnesium, enhance the heterocoagulation of bitumen and clay fines, leading to poor bitumen−air bubble attachment.[3−5]

A new process of tailings disposal called "Beach and Paste" was proposed,[6] in which anionic polymers are added into a tailings thickener where the fines are flocculated and thickened into a paste. According to the results of Cymerman et al.,[6] high-molecular-weight, medium-charge-density anionic copolymers of acrylamide and acrylates can lead to the flocculation of the fines. At a slurry pH above 8.5, for example, Percol 727 (Ciba Specialty Chemicals) was found to be very effective in flocculating the fines. In particular, this polymer was much more efficient in the presence of divalent cations when used for the flocculation of Syncrude fine tailings.[7] However, the effect of this type of polymer on the bitumen extraction (bitumen liberation from sand grains, bitumen−air bubble attachment, and subsequent recovery of aerated bitumen by flotation) remains unknown. Particularly, for low-grade oil sands ores with relatively high fines content, there are some concerns as to whether this type of polymer is harmful to bitumen recovery when present as residual in the process water.

Ideally, for good bitumen recovery, one would like to have (1) ease of bitumen recession and liberation from sand grains, (2) good attachment of bitumen−air bubble, and (3) flotation of the aerated bitumen. Bitumen

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* Author to whom correspondence should be addressed. E-mail: Jacob.Masliyah@ualberta.ca.

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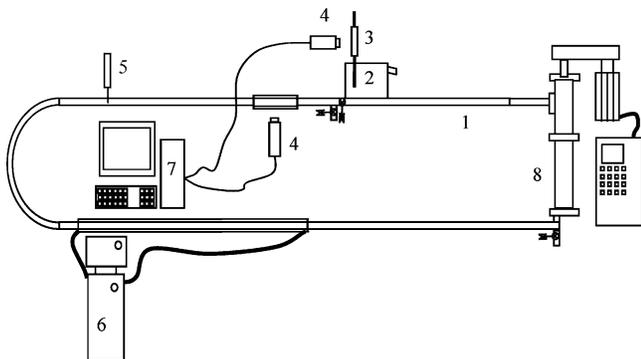(7) Sworska, A.; Laskowski, J. S.; Cymerman, G. *Int. J. Miner. Process.* **2000**, *60*, 143−152.

Figure 1. Laboratory hydrotransport extraction system (LHES). System parts: 1. Hydrotransport loop. 2. Froth collector. 3. Sample visualization tube. 4. CCD camera. 5. Air injection. 6. Circulating bath. 7. Computer. 8. Pump.
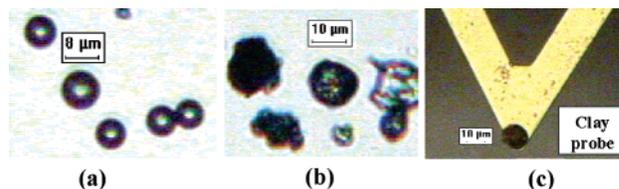

Figure 2. Images obtained with a light microscope showing (a) model silica spheres, (b) solid particles from tailings slurry, and (c) a prepared clay particle probe.

recession from sand grains is much affected by the interfacial properties of the bitumen and the sand grains, as manifested at the three-phase contact point (bitumen−sand−water). Any factors, such as polymer addition or presence of cations, that would hinder bitumen recession from the sand grain or bitumen liberation would lower bitumen recovery. It has been found that for certain type of low-grade ores, poor processibility is mainly related to the high content of clay fines in the ores.[5] That is because the surface of bitumen and air bubbles is covered by the fines, thereby reducing the probability of bitumen−air bubble attachment and resulting in poor bitumen recovery and/or poor froth quality. The presence of divalent ions further aggravates this situation, as demonstrated by bitumen flotation results of Kasongo et al.[4]

To achieve good bitumen−air bubble attachment, it is desirable that both bitumen and air bubble surfaces are not covered by fine solids. In other words, a low adhesion force between bitumen and fine solids is desirable. Once the bitumen is aerated, it is essential for the aerated bitumen to float so that it is recovered. Ideally, a good flotation environment is present when the fine solids are fully dispersed, as the dispersed fines lead to low slurry viscosity. Strong coagulation of the fines would lead to floc formation and an increase in the slurry viscosity with subsequent negative impact on bitumen recovery. However, fines−fines coagulation is beneficial to avoid slime coating during bitumen extraction, quick settling of fines, and fast water recycle in tailings treatment. It becomes clear that a "good" chemical additive would be able to improve bitumen recovery and at the same time to act as a good flocculant for the fines. This is the focus of the current study. In this paper, we will demonstrate that at an optimal concentration, hydrolyzed polyacrylamide can improve both bitumen recovery from oil sands and fines settling.

2. Experimental Methodology and Materials

2.1. Methodology. This study involves three interrelated aspects: bitumen extraction, tailings settling, and colloidal force measurements.

2.1.1. Bitumen Extraction. Bitumen extraction experiments were conducted using a laboratory hydrotransport extraction system (LHES) (Figure 1),[8] which is capable of simulating the commercial bitumen production conditions in hydrotransport slurry pipelines and PSV. To evaluate the effect of chemical addition on bitumen liberation from sand grains, a high-speed black and white CCD camera was mounted in front of a specially designed square section of the glass pipeline. Images of flowing oil sands slurry were captured on-line and analyzed by an interfaced computer using an interactive image analysis technique[9] which utilizes the variation of reflected light intensities caused by the varied amount of bitumen on the solid surface. The digitized images are recorded as an array of numbers that represent the light intensities (grey level) for each picture element (pixel). Each pixel has a numeral value related to light intensity. The image analysis was accomplished by a commercial software, Sigma Scan Pro, which assigns a value of zero to the lowest intensity (black) pixels and a maximum numerical value of 256 to the highest intensity (white) pixels whereas intermediate values represent a continuum of gray levels from black to white. By analyzing the variations in gray scale intensities, the degree of "darkness" of the images was taken as an inverse measure of the degree of bitumen liberation from the sand grains.

For each bitumen extraction experiment, 3 L of Aurora process water preheated to 35 °C along with desired hydrolyzed polyacrylamide (HPAM) addition was added in the LHES (Figure 1). One kilogram of oil sands sample was then fed. Unless otherwise stated, all bitumen extraction experiments were carried out at a slurry temperature of 35 °C. Bitumen recovery in the LHES involves two main steps, bitumen liberation and bitumen flotation. Bitumen liberation takes place while initially recirculating the slurry containing the oil sands and process water for 5 min prior to air addition. When air is introduced into the slurry at 195 mL/min through a stainless steel needle with a blunt end, bitumen starts to float and flotation time is recorded. Six froth samples are collected at different time intervals. Slurry pH values are not controlled, and they are measured by a pH meter. The slurry temperature is measured by a digital thermometer.

After an extraction experiment, the froth samples were assayed using Syncrude standard procedure to determine bitumen, solids, and water content while the tailings slurry was used for tailings settling tests. Bitumen recovery was calculated on the basis of the ratio of bitumen weight in the froth to that in the feed. This procedure allows us to investigate the kinetics of bitumen flotation.

2.1.2. Tailings Settling Tests. Tailings slurry samples, including coarse and fine solids, taken directly from the bitumen extraction experiments were used to conduct settling tests in closed graduated cylinders. The descent of the solids−liquid interface (mud line) was recorded as a function of time. The supernatant layer height against time was used to determine the initial settling rate.

2.1.3. Colloidal Force Measurements. A Nanoscope E atomic force microscope (AFM) with a vendor-supplied fluid cell (Digital Instruments, Santa Barbara, CA) was used for the surface force measurement. Gold-coated silicon nitride cantilevers also from Digital Instruments were chosen. Model silica spheres as shown in Figure 2a (Purchased from Silica Duke Scientific Co. USA) or clay particles with a pseudospherical

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shape such as the one at the center of Figure 2b were used as the probe for the force measurements by attaching them onto the apex of a cantilever (lever type 100 μm wide) with a spring constant of 0.58 N/m. The clay particles were chosen under an optical microscope from a great number of particles, which were directly obtained from the tailings slurry of a bitumen extraction experiment without chemical addition. Prior to each set of force measurements, the prepared probes (Figure 2c) were thoroughly rinsed with deionized water and ethanol followed by blow-drying with ultrapure-grade nitrogen. The probes were then exposed to an ultraviolet light for more than 5 h to remove any possible organic contaminants. The details of preparing such colloid probes and using AFM for force measurements are provided elsewhere.[10,11] Briefly, in AFM force mode, a triangular waveform is applied to the AFM Z piezo tube. As a result, the sample surface attached to the piezo tube moves toward and away from the cantilever tip (the colloid probe) by the extension and retraction of the piezo tube, respectively. The force acting between the probe and the surface is determined from the deflection of the cantilever by using Hooke's law. Each force plot represents a complete extension−retraction cycle of the piezo. When a sample surface approaches a probe, the long-range interaction force between the two surfaces is measured while the adhesion (or pull-off) force can be obtained during the retraction process. For quantitative comparison, the measured long-range interaction force (F) and adhesion force (pull-off force) were normalized by probe radius (R).

Force measurements were performed in a fluid cell where clay (or silica) probes interacted with bitumen or silica surface in aqueous solutions that were directly taken from the supernatant of tailing slurry of bitumen extraction. The bitumen surface was prepared by coating a thin layer (∼100 nm) of bitumen onto 10 × 10 mm^2 silica wafers (NANOFAB, University of Alberta, Canada) using a spin-coater. The silica wafers had an oxidized surface layer of ∼0.6 μm. A detailed description on the preparation of the bitumen surface and the characteristics of the prepared bitumen surface can be found elsewhere.[11] All force measurements were conducted after an incubation time of 30 min. Preliminary experiments showed that 30 min was sufficient for the two surfaces immersed in the aqueous medium to equilibrate. As the surface of the clay probes was quite irregular, each force measurement was performed several times with different clay probes to obtain representative results. All force measurements were conducted at a room temperature of 22 ± 1 °C.

2.2. Materials. The oil sands ore used was a poor processing ore, called transition ore, provided by Syncrude Canada Ltd. The ore consists of 9.2 wt% bitumen, 7.3 wt% connate water, and 83.5 wt% solids. The solids contain 33% fine solids (less than 44 μm in size). The bulk oil sands ore was homogenized, packed in 600-g plastic bags and stored in a freezer at −29 °C to prevent aging. The water used for the bitumen extraction experiments was the Aurora recycle process water from the commercial plant of Syncrude Canada Ltd. Atomic absorption spectrometer (AAS) analysis showed that this water contained 47.0 ppm calcium and 15.0 ppm magnesium. The water has a pH of 8.2.

The polymer flocculant, Percol 727, was purchased from Ciba Specialty Chemicals. It is a high-molecular-weight HPAM (average MW of 17.5 × 10^6) with 22% anionicity.[7] A stock polymer solution was prepared at 0.04 wt% with deionized water and was slowly added with a 20 mL syringe to the flowing process water inside the laboratory hydrotransport extraction system. All polymer dosages (ppm) refer to the volume of the slurry.
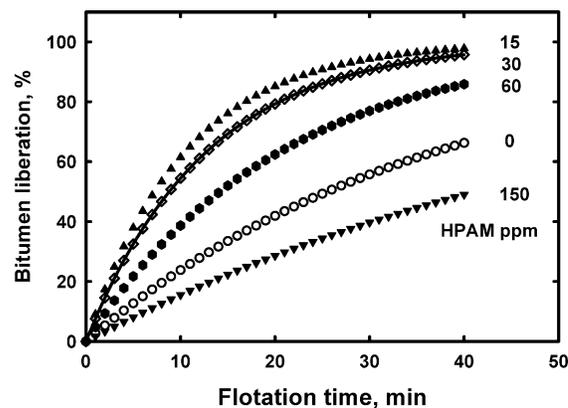

Figure 3. Measured bitumen liberation at various HPAM dosages. Symbols are experimental data and solid line is the curve fit using eq 1.

3. Experimental Results

Water-soluble polymers have been widely used in the mineral processing industry to aid solid−liquid or solid−solid separation. Among these, the most commonly used products are from the polyacrylamide family.[12] It has been found that the properties of polyacrylamide, such as solubility, nature of charge and charge density of the copolymerized acrylamide (cationic, nonionic, anionic), and molecular weight, affect the polymer performance. Among these properties, the optimal charge density (e.g., anionicity) for a given polyacrylamide is determined by the level of dissolved solids in the liquor, pH value, and the properties of the slurry. In this study, Percol 727 was used.

3.1. Bitumen Extraction Experiments with HPAM. The effect of HPAM on bitumen extraction was evaluated on the basis of its effects on the two subprocesses: bitumen liberation from sand grains and bitumen flotation where air−bitumen aggregates in the form of froth are formed and recovered. During the extraction process, the bitumen froth product was collected with a small spatula from the froth−slurry interface inside the froth collector. Solids can enter the bitumen froth either via bitumen−solids attachment, bubble−solids attachment, and/or entrainment. To achieve satisfactory bitumen content in the froth, it is especially important to eliminate or minimize as much as possible the amount of clay fines in the froth.

Bitumen liberation plays an important role in bitumen extraction. Generally, bitumen liberation is controlled by the interactions between bitumen and sand grains.[13] Therefore, the effect of HPAM on bitumen extraction will be first reflected in its effect on bitumen liberation. Figure 3 shows bitumen liberation results against flotation time at various HPAM dosages. The bitumen liberation is clearly affected by the HPAM dosage. To quantify the HPAM effect on bitumen liberation, the liberation rate constant is calculated using a first-order equation:

$$L_{Bt} = L_{B\infty} (1 - e^{-kt}) \qquad (1)$$

where L_{Bt} is the bitumen liberation at time t, $L_{B\infty}$ is the

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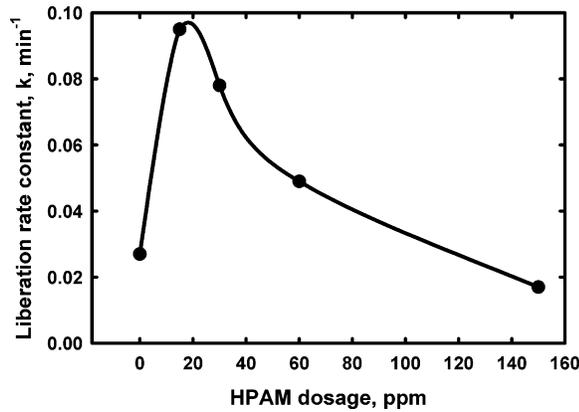
Figure 4. Bitumen liberation rate constant at various HPAM dosages.
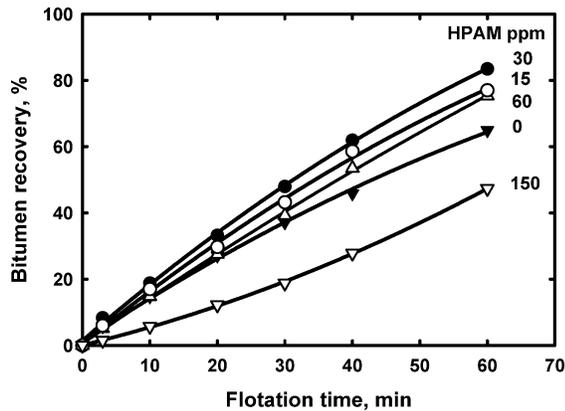

Figure 5. Bitumen recovery at various HPAM dosages.

maximum bitumen liberation at time infinity, and k is the liberation rate constant. By fitting the collected data for a given experiment to eq 1, the maximum bitumen liberation and liberation rate constant for the test can be obtained. One fitting example at 30 ppm HPAM is shown by the solid line in Figure 3. Figure 4 shows the liberation rate constants against the HPAM dosage. Compared to the case without polymer addition, the addition of 15 ppm HPAM significantly increased the liberation rate constant from 0.03 to 0.1 min^{-1}. Beyond this dosage, the rate constant deteriorated. At 150 ppm HPAM, for example, the rate constant of bitumen liberation was sharply reduced to 0.02 min^{-1}. An optimal HPAM dosage for bitumen extraction is limited to about 15 ppm from the standpoint of bitumen liberation. A direct benefit obtained from improved bitumen liberation is the increased bitumen recovery as shown in Figure 5 that will be discussed in more detail at a later stage.

When air is introduced and dispersed into the slurry in the form of air bubbles after the bitumen liberation stage, bitumen droplets and air bubbles begin to attach to each other and bitumen flotation takes place with the formation of bitumen−air bubble aggregates. Therefore, to a large degree, flotation is affected by bitumen liberation. It is expected that the improved bitumen liberation due to HPAM addition would result in a better bitumen recovery. This was confirmed by the experimental results shown in Figure 5, which gives bitumen recovery versus flotation time. Bitumen recovery is defined by percent total bitumen collected in the froth to that in the feed. Similar to bitumen liberation,
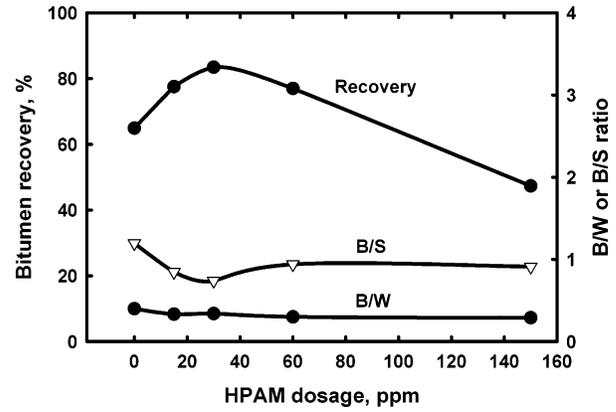

Figure 6. Bitumen flotation results at different HPAM dosages.

the extent of increased bitumen recovery depends on the HPAM dosage. It is noted that bitumen recovery increased when the HPAM dosage was in the range of 15−60 ppm. Figure 6 shows bitumen recovery together with froth quality at various HPAM dosage after 1 h of extraction. The froth quality is given by the ratio of the weight of bitumen to solids, B/S, and ratio of the weight of bitumen to water in the collected froth, B/W.

On the recovery curve, the cumulative bitumen recovery was found to increase with the addition of HPAM at a low dosage, and a peak value of 84% recovery appears at 30 ppm. This represents an increase of about 20% in bitumen recovery as compared to that (64%) without polymer addition. As HPAM dosage was further increased, the recovery began to decrease and dropped below 50% at 150 ppm HPAM addition. With respect to the froth quality, no significant improvement in B/S or B/W ratio was observed with polymer addition.

Clearly, the addition of HPAM to the oil sands slurry provided a favorable condition for bitumen liberation and flotation. This finding suggests that HPAM can be considered as a process aid for bitumen extraction. From the present experimental conditions, the optimal HPAM dosage is at about 30 ppm.

3.2. Interactions between Bitumen and Solids. To understand the effect of HPAM addition on bitumen extraction, the long-range interaction force and adhesion forces between bitumen and solids (silica sand and clay fines) were measured by AFM. The strength of the measured forces between bitumen and solids would reflect on bitumen liberation from the sand grains and on bitumen−fines heterocoagulation that is harmful to bitumen−air bubble attachment.

For each AFM measurement, one of the selected solid particles was glued to the AFM cantilever and then immersed into a solution with given chemistry conditions. Here, tailings water taken from the tailings of bitumen extraction experiments at various polymer dosages was used in order to provide the same chemistry conditions for the AFM measurements as used in bitumen extraction experiments. The clear water samples are the supernatants of tailings slurries after settling for 48 h. Figure 7 shows the measured forces between bitumen and silica. The long-range interaction force between bitumen and silica, shown in Figure 7a, was purely repulsive when the silica particle and bitumen surface approached each other. HPAM addition at a lower dosage (15, 30 ppm) shows little influence on the
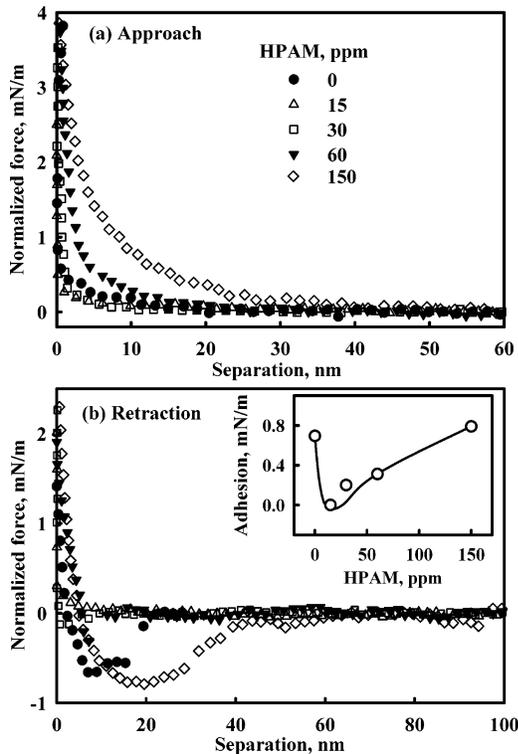
Figure 7. Long-range interaction (a) and adhesion (b) forces between model silica spheres and bitumen measured in tailings water.

Figure 8. Long-range interaction (a) and adhesion (b) forces between selected clay particles and bitumen measured in tailings water.

long-range force. However, when the dosage was increased to 60 ppm or higher, the repulsive force becomes stronger.

Figure 7b shows the retraction branch of the force profiles from which the adhesion forces between bitumen and model silica were obtained. The normalized adhesion force is shown in the inset of Figure 7b. In the absence of HPAM, an adhesion force was measured at about 0.7 mN/m. When HPAM was added at a dosage of 15 ppm, the adhesion force became nearly zero. Beyond 15 ppm, the adhesion force became stronger with the increased HPAM additions. To liberate bitumen from the sand grains, the adhesion force between bitumen and sand must be overcome. As indicated by the results of measured adhesion force, HPAM addition at the appropriate dosage, e.g., 15 ppm, can reduce the adhesion force and consequently should facilitate liberation of bitumen from the sand grains.

Figure 8 shows the measured forces between bitumen and selected clay particles obtained from the tailings solids. Different from the case between bitumen and model silica spheres (Figure 7a), the long-range force between bitumen and clay shows attraction, as seen in Figure 8a. The maximum attraction for each HPAM dosage was plotted in the inset of Figure 8a. The degree of attraction decreases with increasing HPAM addition from 0 to 30 ppm but increases with further increasing HPAM addition from 30 to 150 ppm. The long-range interaction force became purely repulsive only at 30 ppm HPAM addition. Figure 8b shows the retraction branch of the force profiles between bitumen and clay. The adhesion forces obtained from the force profiles are shown in the inset of Figure 8b. An adhesion force exists (about 2 mN/m) between bitumen and clay in the absence of HPAM. The adhesion force was depressed
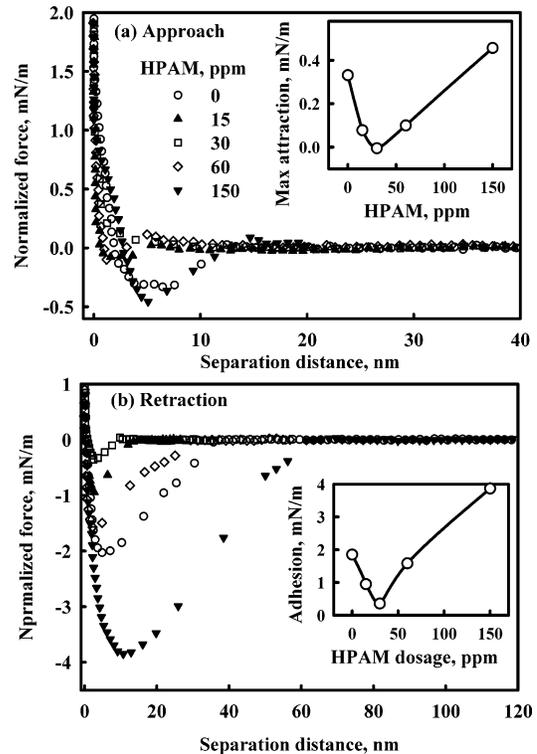
to 0.2 mN/m by HPAM addition at a lower dosage, e.g., from 15 to 30 ppm. However, the adhesion force was restored and became stronger with increasing HPAM addition, e.g., from 60 to 150 ppm. The results presented in Figure 8 indicate that, in the absence of HPAM, a strong heterocoagulation between bitumen and clay could occur because the long-range interaction force is attractive and an adhesion force exists. Such a heterocoagulation can reduce or even prevent the attachment of air bubbles to bitumen droplets, thus resulting in a poor bitumen flotation and recovery. With HPAM addition at an appropriate dosage, e.g., 30 ppm, the results in Figure 8 show that the long-range interaction force was changed from attractive to repulsive while the adhesion force significantly decreased. This indicates that HPAM addition at a proper dosage can reduce or even prevent heterocoagulation between bitumen and clay fines. As a result, bitumen recovery can be improved.

The results of Figures 7b and 8b clearly demonstrate that the adhesion force between bitumen and silica (0.7 mN/m) is much weaker than that between bitumen and clay (2 mN/M) in the absence of HPAM, thereby implying that the challenge for improving bitumen recovery from poor processing oil sands resides mainly on bitumen−clay heterocoagulation. In that case, a higher dosage of HPAM (30 ppm) is needed to eliminate clay−bitumen heterocoagulation than that used to increase bitumen liberation (15 ppm). These findings explain well the results of bitumen liberation and recovery as summarized in Figure 9, where test results of bitumen extraction experiments and bitumen−solids (silica and clay) adhesion forces at various HPAM dosages are shown. Generally, it is evident that bitumen liberation and recovery have a very similar response to
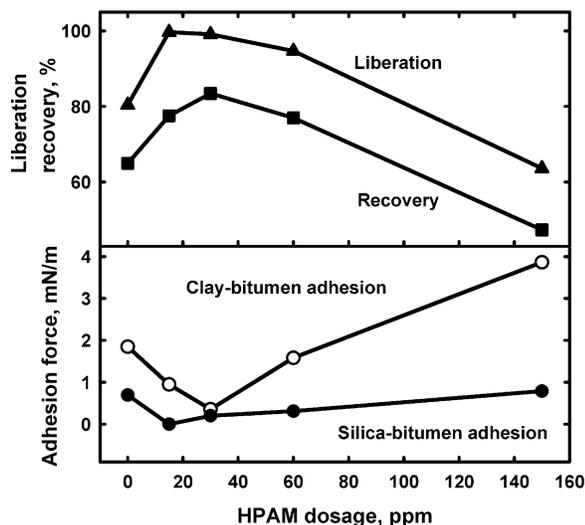
Figure 9. Bitumen liberation, recovery, and solids−bitumen adhesion force at different HPAM dosages.

Figure 10. Normalized supernatant height as a function of time at different HPAM dosages.

Figure 11. A photo showing tailings settling at different HPAM dosages.

HPAM addition but the trends are just the opposite for bitumen−solids adhesion forces. Without HPAM addition, both adhesion forces of bitumen−silica and bitumen−clay are relatively high, indicating a natural attachment or heterocoagulation state of bitumen−silica and bitumen−clay. In this case, bitumen liberation (80%) and recovery (65%) are poor. However, HPAM addition can reduce the adhesion forces. At a HPAM dosage of 15 ppm, the bitumen−silica adhesion force becomes nearly zero. Thus, bitumen liberation is increased to a maximum value ($\sim$95%). At a HPAM dosage of 30 ppm, the bitumen−clay adhesion force becomes nearly zero. This would lead to a less coverage on the bitumen surface by the fine solids, and thus, the bitumen surface becomes more amenable for air bubbles attachment. In this case, a high bitumen recovery (85%) was obtained. With further increasing HPAM addition (60 and 150 ppm), the adhesion forces begin to increase, thus resulting in a decrease in bitumen liberation and recovery. These results indicate that a polymer overdosage would deteriorate bitumen extraction performance.

3.3. Tailings Settling Tests with HPAM. The results of the above bitumen extraction experiments and AFM force measurements show that controlled HPAM addition is beneficial to bitumen recovery. We now concern ourselves on its effect on tailings treatment. Tailings treatment refers to a process that would increase the fine particle settling rate and consequently make solid−liquid separation more efficient. Although a large number of studies have been reported on HPAM applications in clay flocculation,[14−17] whether flocs of clay fines can be formed by adding the HPAM in bitumen extraction process and whether this flocculation process can help bitumen recovery remain to be explored. Therefore, tailings settling tests were conducted following bitumen extraction experiments. The

initial slurry solids concentration is about 25 wt% and the particle size, d_{80}, of the suspension is 4.3 μm.

Figure 10 shows the normalized supernatant height (supernatant height divided by the total initial slurry height) as a function of settling time. The HPAM flocculating action on fines is clear: the normalized supernatant height after 60 min of settling is only 33% at 0 ppm HPAM, and it increased to 71% at 15 ppm and reached its maximum (around 77%) at 30 ppm, thereby implying the formation of denser flocs. Further addition of the polymer deteriorated solids settling as the normalized supernatant height is reduced back to 69% at 60 ppm HPAM. At 150 ppm, there was nearly no clear supernatant liquid, thereby indicating a possible dispersed state of solids at this high HPAM dosage. The photograph of Figure 11 shows a distinct layer of clear supernatant at HPAM dosages of 15 and 30 ppm, but such clear supernatant was not obtained at 0 and 150 ppm (not shown in this figure) at the end of a settling time of 150 min.

The significance of the settling test results is that they reveal the effectiveness of HPAM on tailings treatment when the polymer was initially added in bitumen extraction stage.

3.4. Interactions between Clay Fines and Silica Wafer. To explain the finding that direct HPAM addition to the bitumen extraction stage improves tailings treatment, the interaction and adhesion forces between clay particle and silica wafer (representing sand grains in oil sands) were measured in tailings water by AFM. Figure 12a shows that, in all cases, the measured long-range interaction forces are purely repulsive. Increasing

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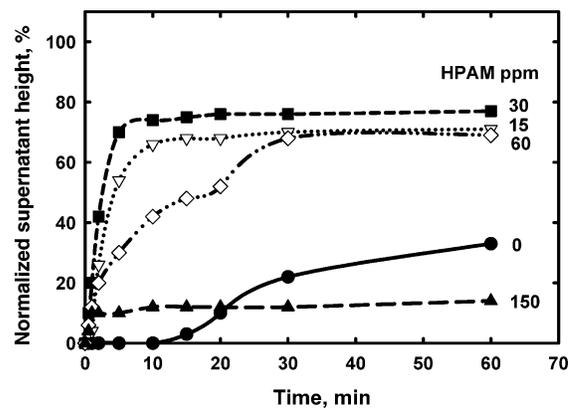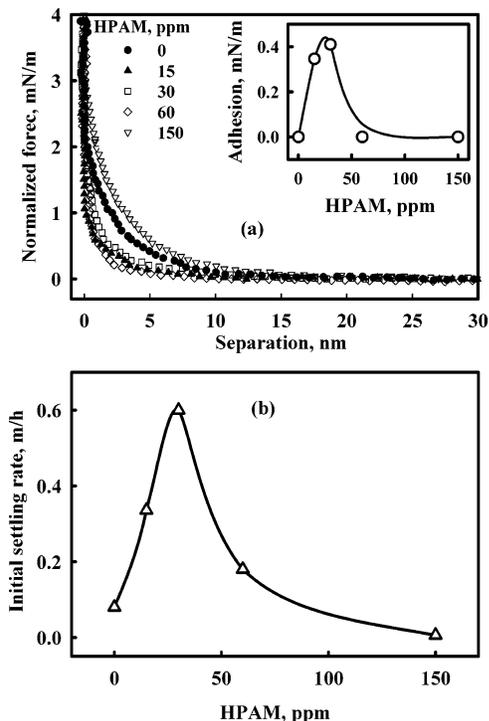(17) Yoon, S.-Y.; Deng, Y. *J. Colloid Interface Sci.* **2005**, *278*, 139−145.

Figure 12. (a) Measured force between clay and silica in tailings water. (b) Effect of HPAM dosage on the initial tailings settling rate.

the HPAM addition from 15 to 60 has little effect on the long-range interaction. As the dosage was further increased, e.g., up to 150 ppm, the repulsive force became stronger. The results of the adhesion force between clay and silica are shown in the inset of Figure 12a. In the absence of HPAM, there is no adhesion between clay and silica, indicating an initial dispersed state of fine solids in the tailings. However, in the presence of HPAM at 15 and 30 ppm, an adhesion force of about 0.4 mN/m was measured. This is because HPAM can adsorb onto both silica and clay surfaces and the dangling tails of the polymer on one surface can contact and adsorb onto other surfaces, thus resulting in the formation of polymer bridging across the two surfaces. This indicates that HPAM addition at these dosages can induce fine particle flocculation and result in quick tailings settling. However, when the HPAM dosage was increased to 150 ppm, the particles surface was fully covered by HPAM. As a result, a strong repulsive long-range force and a zero adhesion force were measured. In this case, the particles would be stabilized.

Figure 12b shows the results of the initial settling rate as a function of HPAM dosage. The initial settling rate was calculated from the results of settling tests in Figure 10. This rate is the slope of the initial portion of the settling curve. The adhesion force between clay and silica as shown in the inset of Figure 12a correlates well with the initial settling rate shown in Figure 12b. Without HPAM addition, the clay fines are in a naturally dispersed state and the initial settling rate is very small. No adhesion was measured in this case. By adding HPAM at a lower dosage (15, 30 ppm), the initial settling rate increased as the adhesion force between fine particles became stronger. With HPAM addition at 30 ppm, which is the optimal dosage for bitumen

extraction, the initial settling rate reaches its highest value. This implies the formation of large size, dense flocs. Consistently, the strongest silica−clay adhesion force was measured at this dosage. When the polymer dosage was increased to 60 ppm, a zero adhesion force was measured and the tailings settling rate was low. At a further increase of HPAM dosage to 150 ppm, the tailings slurry was in a dispersed state (Figure 11) and thus settling was extremely slow. This is consistent with the results of the measured forces.

4. Discussion

Through this study, the advantage of adding HPAM directly in the bitumen extraction circuit has been found to be 2-fold: improving bitumen extraction and enhancing tailings treatment. To illustrate this synergetic role of HPAM, adhesion forces of both bitumen−clay and silica−clay were compared at various HPAM dosage, and how the HPAM addition affects bitumen−fines interactions at various dosage is schematically shown in Figure 13.

On the basis of the results shown in Figures 9 and 12, it can be found that silica−clay adhesion force was very weak without HPAM addition, indicating that clay fines were in a dispersed state and bitumen−clay heterocoagulation took place (Figure 13A). However, HPAM addition changed the interactions of bitumen−clay and silica−clay. The weakest bitumen−clay adhesion force and the strongest silica−clay adhesion force were obtained at 30 ppm HPAM dosage. This finding would indicate that using the polymer at a proper dosage reduced bitumen−clay attachment and made a selective flocculation, i.e., only the fine solids but no bitumen were flocculated from a bitumen−solids mixture (Figure 13B). The reason is that electrostatic repulsive force plays an important role in the HPAM selective flocculation. It has been known that HPAM is a negatively charged polyelectrolyte, as shown by its molecular structure (Figure 14), and in the oil sands slurry, the surface charges of both clay fines and bitumen were found to be negative.[11,14] The ζ potential values are around -20 mV for clay fines and -60 mV for bitumen in Aurora process water at pH 8.5. Bitumen carries a much more negative surface charge than clay fines. As a result, a stronger electrostatic repulsive force exists between bitumen and HPAM than that between clay fines and HPAM. Thus, the fines are first flocculated by HPAM at low dosages.

During the flocculation process, the divalent ions, such as calcium and magnesium, are found to have a notable effect on the flocculation of fine particles by HPAM.[7,18] Cation bridging (HPAM−Ca−clay) was identified to be the main factor in promoting HPAM molecular−clay fines attachment.[18] As an evidence of cation bridging, the consumption of cations by HPAM in Aurora process water was determined. Figure 15 presents the measured ion concentrations by an atomic absorption spectrometer (model Spectr AA 220FS) at pH 8.5. This plot clearly shows a decrease in calcium and magnesium concentrations with increasing HPAM dosage. In the absence of HPAM, the calcium and magnesium concentrations were 39 and 13 ppm, respec-

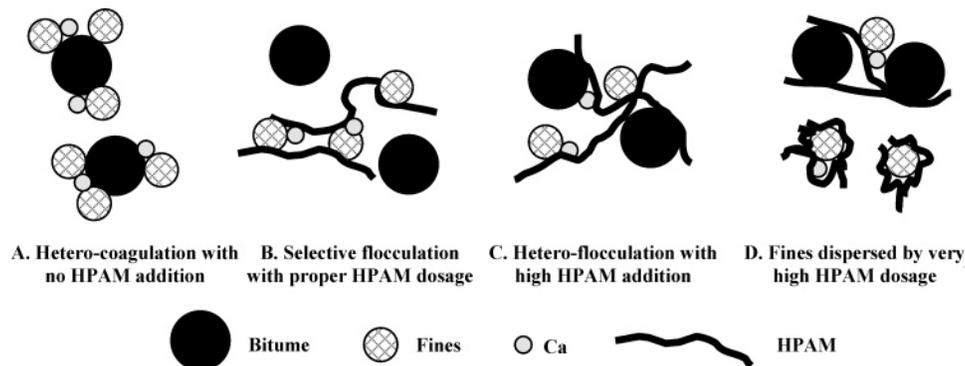(18) Laird, D. A. *Soil Sci.* **1997**, *162*, 826−832.

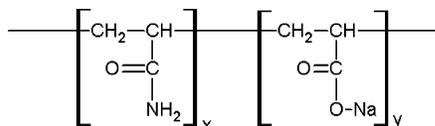**Figure 13.** Schematic presentation of the effect of HPAM on bitumen−clay fines interaction.

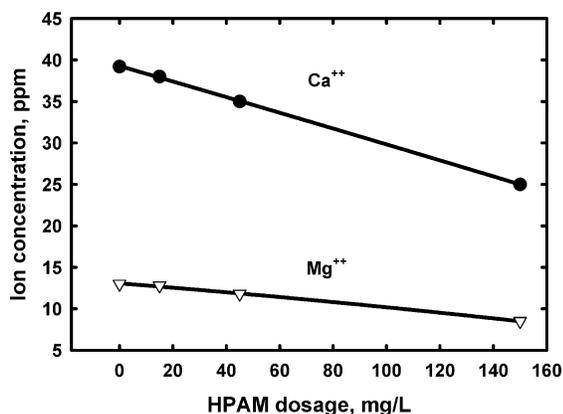**Figure 14.** Molecular structure of anionic polyacrylamide.

Figure 15. Effect of HPAM dosage on calcium and magnesium concentrations in process water measured by atomic absorption spectrometer at pH 8.5.

tively. At a dosage of 150 ppm HPAM, the calcium and magnesium concentrations were reduced to 25 and 8.5 ppm, respectively, indicating ion absorption by HPAM. Thus, with the promotion of cation bridging, a stronger adsorption of HPAM on the negatively charged edge surface of clay particles takes place.[19] Under such circumstance, HPAM has less chance to attach onto bitumen surface due to electrostatic repulsion. Another benefit of using HPAM in bitumen extraction deriving from this mechanism is that the undesired cation-promoting heterocoagulation of bitumen and fines can be reduced due to the reduction of these cation concentrations in the process water.

At higher dosages, HPAM can bond the bitumen and solid fines together (heteroflocculation) (Figure 13C). An increase in chemical potential of HPAM at high con-

centration enhances the hydrogen bonding and hydrophobic bonding between the bitumen and HPAM to overcome the electrostatic repulsive force and to promote fines−bitumen attachment. The flocculation of bitumen with solid fines impedes bitumen−air bubble attachment.[18] At excessive high dosages of HPAM, some of the solid fines are stabilized by being fully covered by the HPAM (Figure 13D).

From the results obtained in this study, it can be concluded that controlling HPAM dosage is identified to be a key factor in achieving the best efficiency for bitumen extraction and tailings treatment. Our study demonstrates an effective use of HPAM as a process aid for bitumen extraction from a poor processing oil sand ore. With selective flocculation of solid fines by HPAM addition, both bitumen recovery and tailing treatment can be improved.

5. Conclusions

1. An anionic HPAM can be beneficial to bitumen liberation and recovery, as well as to tailings settling.

2. The role of HPAM addition has been identified to be selective flocculation of solid fines. The highest bitumen liberation and recovery were obtained at a HPAM dosage of about 15−30 ppm, at which the adhesion forces between the bitumen and solid fines are the weakest. At the same dosage, the highest fines flocculation induced by HPAM occurred, which coincided with the strongest clay−silica adhesion.

3. The addition of HPAM is also found to consume cations such as calcium and magnesium that are harmful to bitumen extraction. The binding of divalent cations (M) with HPAM to form HPAM−M bridging promotes adhesion between HPAM and clay fines that enhances clay fine flocculation.

(19) Pefferkorn, E.; Nabzar, L.; Carroy, A. *J. Colloid Interface Sci.* **1985**, *106*, 94−103.