Role of Colloidal Interactions in Oil Sand Tailings Treatment

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To provide fundamental insights into the treatment of oil sand tailings, the forces between a clay fine or silica particle and a silica wafer in aqueous solutions were measured using an atomic force microscope. A high molecular weight, partially hydrolyzed polyacrylamide (HPAM) was used as the flocculant. The effect of polymer dosage, solution pH, and addition of calcium and magnesium ions on the interaction and adhesion forces was studied. Tailings settling tests were carried out to link the measured forces with tailings treatment. The results showed that the addition of the polymer at low dosages or divalent ions at low concentrations resulted in adhesion interactions. The adhesion force increased with increasing polymer dosage or cation concentration until an optimum dosage or concentration was reached. Higher polymer dosage and ion concentration resulted in a weaker adhesion or even purely repulsive force profiles. The synergy of the polymer and divalent ions significantly enhanced the adhesion between fine solids. The measured adhesion forces correlated well with settling characteristics: the stronger the adhesion, the higher the initial settling rate. This study suggests a potential new technology for oil sand tailings treatment using the synergic effect of polymers and divalent cations. © 2005 American Institute of Chemical Engineers *AIChE J,* 52: 371–383, 2006
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Introduction

Colloid forces play a crucial role in a variety of disciplines, ranging from biological systems to industrial processes. Taking the treatment of oil sand tailings as an example, the settling of clay fines in tailings is largely determined by the long-range interactions and adhesion forces between the fine clay particles. Presently, water-based processes are widely used to extract bitumen from oil sands ores.[1-3] In these processes, water is added to oil sands to form a slurry from which bitumen is liberated and recovered by flotation after aeration. The remainder of the slurry (the tailings) is a mixture, containing water, sand, silt, clay, and a small amount of unrecovered bitumen. Traditionally, the tailings are discharged into tailings ponds, in which coarse sand settles quickly while the fine clay solids settle slowly. After several years, a stable suspension containing 30 wt % fine solids, often referred to as mature fine tailings (MFT), is formed. If the existing tailings management practices are continued, the accumulated volume of MFT is estimated to increase to over one billion cubic meters by the year 2020.[4] Long-term storage of large volumes of MFT is costly and poses an environmental liability. In addition, about 2–3 m^3 of water are needed to produce one barrel of bitumen, and thus the water demand of these processes is massive. Because of a limitation in fresh water supply, 75% of the required water has to come from recycled process water. Therefore, the fine solids in the tailing ponds are required to settle fairly quickly to allow for immediate reuse of warm processing water. As a result, a sustainable development of the Canadian oil sands industry relies largely on the development of solutions for tailings management and water recycling.

Over the last 20 years, significant research efforts have been devoted to improving the consolidation and water release characteristics of oil sand tailings.[4-9] These efforts have led to the

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development of several processes for the treatment of the tailings, including the composite or consolidated tailings (CT) process[5-7] and paste technology.[10-12] In the CT process, gypsum is added along with coarse sands to consolidate the MFT, whereas in the paste technology polyelectrolytes are used to flocculate the fine clays. These two technologies have been tested to be satisfactory for the tailings treatment at both laboratory and pilot scale. Although successful, the clarification time by these two technologies remains relatively long and a relatively large amount of ultrafine solids is retained in the process water. Furthermore, a negative impact of the chemical additives remaining in the process (recycled) water from the CT process on bitumen extraction has been observed in pilot tests[6] and confirmed in a laboratory bitumen extraction test by Kasongo et al.[13] The negative impact has been a hurdle for sustainable implementation of the CT technology. For the paste technology, the impact of residual flocculant in the recycled water on bitumen extraction, on the other hand, is largely unknown. Therefore, it is highly desirable to develop new processes that can minimize the accumulation of chemical additives while improving water clarification and solid consolidation.

Although the role of polyelectrolytes as flocculant in the paste technology[12] and gypsum as coagulant in the CT process[7] is known, direct evidences on how the chemical additives affect the interaction forces responsible for holding particles together during coagulation and flocculation remain to be determined. Fundamental understanding of surface forces in flocculation/coagulation and subsequent consolidation of fine tailings with chemical addition is the key for the development of any new process for oil sand tailings treatment and perhaps for any other industrial tailing management. In recent years, equipment for directly measuring the interaction forces between colloidal particles has been developed. The surface force apparatus (SFA)[14,15] and the atomic force microscope (AFM)[16] allow the effects of chemical addition to a colloid system on the colloid forces to be investigated.[17-19] Direct force measurements between mica/silica/glass surfaces in various well-prepared polyelectrolyte solutions have been carried out in numerous studies.[20-33]

To provide fundamental insight into the treatment of oil sand tailings, the present study focuses on direct measurement of interaction and adhesion forces between fine particles in aqueous solutions using an atomic force microscope (AFM). The polyelectrolyte used was a high molecular weight, partially hydrolyzed polyacrylamide (HPAM, commercially known as Percol 727). For oil sand tailings treatment, a variety of commercially available polyelectrolytes have been tested.[10-12] It has been found that high molecular weight polymers with medium charge densities, such as Percol 727, performed the best.[12] To better simulate the interactions between clay fines in tailings, the interactions between a clay fine particle obtained directly from dry tailings and a silica plate in the supernatant of a tailing slurry were measured. The effect of polymer dosage and divalent ion addition on the interaction/adhesion forces was studied. Particularly, the synergic effect of polyelectrolyte and divalent cations was investigated to explore the potential for developing new technologies for treating oil sand tailings. The measured adhesion forces were correlated with tailings settling rate. To our best knowledge, such a study has not been reported in the open literature.

Experimental

Materials

HPAM was obtained from Ciba Specialty Chemicals (Tarrytown, NY). It is a copolymer of sodium acrylate ($CH_2CHCOONa$) and acrylamide ($CH_2CHCONH_2$) with a molecular weight of 17,500,000 and 22% anionicity.[34] Silica microspheres ($\sim$8 μm in diameter), used as a model probe to represent sand grains in the tailings for colloidal force measurements, were purchased from Duke Scientific Co. (Palo Alto, CA). Silicon wafers with an oxidized surface layer of about 0.6 μm were obtained from NANOFAB (University of Alberta, Canada). Reagent-grade HCl and NaOH (Fisher Scientific, Pittsburgh, PA) were used as pH modifiers. Ultrahigh-purity KCl (>99.999%, Aldrich, Milwaukee, WI) was used as the supporting electrolyte. Reagent-grade $CaCl_2$ and $MgCl_2$ (Fisher Scientific) were used as the source of calcium and magnesium ions, respectively. Deionized water with a resistivity of 18.2 MΩ·cm, prepared with an Elix 5 followed by a Millipore-UV Plus water purification system (Millipore Corp., Mississauga, Canada), was used where applicable throughout this study.

Colloid probe preparation

To measure the colloidal forces, gold-coated silicon nitride probes from Digital Instruments (Santa Barbara, CA) were used. Lever-type cantilevers with a width of 100 μm and a spring constant of 0.58 N/m were chosen for the force measurements. A colloidal probe, silica sphere or clay fine particle, was attached to the apex of the cantilever using an extremely small quantity of epoxy resin.[35] To be used as a probe, fine particles with a nearly spherical shape were chosen under an optical microscope from a great number of clay fine particles, directly taken from the tailings of a bitumen extraction test. The bitumen extraction test was carried out using a transitional oil sand ore and the Aurora commercial plant recycle process water without any chemical addition. The Aurora plant recycle process water is the recycled pond water from the Aurora plant of Syncrude Canada Ltd. and some relevant properties of this water are given in Table 1. The ore was from the Aurora region of Syncrude Canada Ltd. and its composition is also given in Table 1. The details for the bitumen extraction tests can be found elsewhere.[36] Before each set of force measurements, the prepared probes 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 exact size of the silica spheres or fine particles was determined with an optical microscope before the force measurement.

Surface force measurement

A Nanoscope E atomic force microscope (AFM) with a vendor-supplied fluid cell (Digital Instruments) was used for the colloidal force measurement. A detailed description of using AFM to measure colloid and molecular forces is provided elsewhere.[35,37] Briefly, a surface under investigation approaches a colloid probe. The deflection of the cantilever of known spring constant under the influence of colloidal forces is measured using a laser beam reflected off the cantilever onto a

Table 1. Properties of Various Waters and Oil Sand Ores Used

	HPAM ppm*	Mg^{2+} ppm	Ca^{2+} ppm	pH	Comments
Aurora plant water	N/A	15.0	47.0	8.2	Recycle pond water from the Aurora plant of Syncrude Canada Ltd.
Supernatant I	0	13	39.2	8.2	Obtained from the tailings of bitumen extraction using an Aurora transition ore.[36]
Supernatant II	15	12.8	38	8.2	
Supernatant III	30	11.8	35	8.2	
Supernatant IV	60	11.0	32	8.0	
Supernatant V	150	8.5	25	8.1	
Aurora transition ore	One of the problem ores from the Aurora area of Syncrude Canada Ltd. with 9.2 wt % bitumen, 7.3% water, and 83.5% solids. The solids contains 33% of fines ($<44\ \mu$m in size)				

*HPAM was directly added in the bitumen extraction step. The polymer dosage, ppm, refers to the volume of oil sands slurry, not the polymer concentration in the supernatants.

position-sensitive split photodiode. The onset of the constant compliance region is defined as zero separation distance, where the deflection of the cantilever varies linearly with respect to the displacement of the approaching surface. Separation between the two interacting surfaces is then estimated from the displacement of the lower surface relative to this constant compliance region. Although there may have been polymers sandwiched between the two surfaces, the layer thickness under this condition does not change, so that the separation can be considered constant. With AFM, there is no possible way to determine the absolute separation (and thus the layer thickness) or the contact area. However, this does not alter the form of the interaction. The force acting between the probe and the surface is simply determined from the deflection of the cantilever using Hooke's law, $F = kx$, where x represents the deflection, k is the spring constant of the cantilever, and F is the force. For quantitative comparison, the measured interaction force (F) and adhesion force (pull-off force) were normalized by probe radius (R).

To simulate the interactions between fine particles in tailings, two systems were investigated in this study: a silica–silica system and a fine–silica system. Because the major solids in oil sands are sand grains and clay fines, model silica spheres were chosen to represent the sand grains. The interactions between a silica sphere and a silica plate were measured in 20 mM KCl solutions, in which the KCl served as a background electrolyte. This system was well defined in terms of the shape of the probe and the composition of the solution, facilitating the investigation on the effect of various factors such as polymer dosage, solution pH, and addition of divalent ions. To study the interactions between clay fines and sand grains, forces between a fine clay particle and a silica plate were measured. In this system, fine particles selected from the dry tailings of a bitumen extraction test served as the probe. The aqueous solution used in this system was the supernatant of the tailing slurry obtained from the bitumen extraction tests.[36] The concentrations of calcium and magnesium ions and the pH values of the supernatants are summarized in Table 1. In this table, supernatants I–V refer to the supernatants obtained with HPAM being directly added to the bitumen extraction tests at dosages of 0, 15, 30, 60, to 150 ppm, respectively. The polymer dosage in ppm refers to the original volume of oil sands slurry, not the polymer concentration in the supernatants. Table 1 shows that the concentration of calcium (and magnesium) ions in supernatants I–V decreases with increasing polymer dosage. The purpose for the direct addition of the polymer in the extraction process is to investigate how the polymer affects bitumen liberation, recovery, and tailings settling.[36] Because the direct measurement of the interactions between two fine particles is not operative with AFM, the interactions between a fine particle and a silica surface in a supernatant are used in the present study as the best approximation to the interactions between fine particles in tailings.

Force measurements were performed in a fluid cell filled with testing liquids in which a colloidal probe (a silica sphere or a clay fine) interacts with a flat silica plate. The silica plates were washed with chloroform to remove adsorbed organic contaminants, rinsed with deionized water followed by ethanol, and then blow-dried with ultrapure-grade nitrogen. Before the use in force measurement, the fluid cell and the silica plates were exposed to an ultraviolet light for more than 5 h to remove any possible organic contaminants. All force measurements were conducted after an incubation time of 30 min at room temperature of 23 ± 1°C. Preliminary experiments showed that a 30-min incubation was sufficient for the two surfaces immersed in the solution to reach equilibrium. For silica probes, the measurement under each test condition was performed at a number of different locations on a silica surface. For clay fine probes, because the surface of the probes was quite irregular, force measurement under each condition was performed several times with different probes for consistency. The conditions along with the probe, flat substrate, and solutions used in the force measurements in the present study are listed in Table 2.

Tailings settling and floccules formation

Tailings from the laboratory bitumen extraction process using the Aurora transition ore[36] were collected. In the extraction process, HPAM was added at dosages of 0, 15, 30, 60, and 150 ppm, respectively, into an oil sand slurry containing 1 kg of the oil sand ore and 3 L of Aurora plant recycled process water. The polymer dosage in ppm refers to the oil sands slurry volume. Settling tests were conducted in 50-mL graduated cylinders at room temperature (23 ± 1°C). The descent of the solid/solution interface (mud line) was recorded as a function of time. Plot of the supernatant layer height vs. time was used to determine the initial settling rate (m/h) from the slope of the initial linear portion of the plot.

To directly observe formation of floccules, two suspensions containing 2 wt % of fine kaolinite (Wards Natural Science

Table 2. List of Force Measurements

Set	Probe–Substrate	Solutions	Results Shown in	Comments
1	Silica–silica	20 mM KCl solution with 0, 0.5, 5, 10, and 50 ppm of HPAM, respectively, at pH 8.2	Figure 1	Effect of HPAM concentration
2	Silica–silica	20 mM KCl solutions with 0.5 mM calcium or 2 mM magnesium at pH 8.2	Figure 3	Effect of calcium or magnesium without HPAM
3	Silica–silica	20 mM KCl and 5 ppm HPAM solution with 0, 0.1, 0.5, 2, 8, and 20 mM of calcium, respectively, at pH 8.2	Figure 4	Effect of calcium at the presence of HPAM
4	Silica–silica	20 mM KCl and 5 ppm HPAM solution with 0, 0.1, 0.5, 2, 8, and 20 mM of magnesium, respectively, at pH 8.2	Figure 5	Effect of magnesium at the presence of HPAM
5	Silica–silica	Supernatants I–V (Table 1)	Figure 7	Effect of process water and polymer dosage
6	Fine–silica	Supernatants I–V (Table 1)	Figure 8	

Ltd., Ontario, Canada) were prepared using the Aurora plant water (see Table 1 for some properties of this water). HPAM was then added into one suspension at 30 ppm in terms of suspension volume. Both suspensions were imaged by a progressive B&W camera (model STC-1100).

Results and Analysis

Effect of HPAM concentration

The measured interaction forces between a silica sphere and a silica plate in a 20 mM KCl solution at pH ~ 8.2, containing 0, 0.5, 5, 10, and 50 ppm HPAM (force measurement set 1 of Table 2) are shown in Figure 1. The long-range force profiles obtained during the approach process of the two surfaces are shown in Figure 1a, whereas the corresponding force profiles on retraction are shown in Figure 1b. Figure 1a shows that the long-range force profiles are purely repulsive. Without polymer addition, the repulsive force (inverted triangles) starts from a separation distance around 10 nm and the force profile can be well fitted with the classical DLVO (Derjaguin–Landau–Verwey–Overbeek) theory.[38] The close fit indicates that the long-range repulsive force is dominated by the electrostatic double-layer forces. When the polymer was added at a low concentration (such as 0.5 ppm), the force profile obtained is nearly the same as that without polymer addition. As the polymer concentration was increased from 0.5 to 5, 10, and 50 ppm, the repulsive force becomes stronger and extends to a larger separation distance. A further increase in the polymer concentration > 50 ppm caused little further change in the force profiles. This finding indicates that the solid surface was likely saturated by the polymer at 50 ppm dosage.

On retraction (Figure 1b), the force profile for the case without polymer addition is identical to that on approach. The identical force profiles on approaching and retracting indicate the absence of adhesion. When 0.5 to 5 ppm HPAM was added, adhesion forces were observed (circles and triangles). The presence of adhesion upon polymer addition suggests that the polymer was adsorbed onto both silica surfaces with partial surface coverage. Figure 2 provides a schematic showing the approaching and retracting processes in a cycle of force measurement with HPAM addition. The partial surface coverage is shown in Figure 2a(i). Although there could be a layer of polymer on the two surfaces, some free surface was still available for polymer adsorption [Figures 2a(ii) and 2(iii)]. Under this condition, the dangling tails and/or loops of the polymer on one surface can contact and be adsorbed onto the other surface, exhibiting a bridging adhesion [Figures 2a(iii) and 2(iv)]. The polymer bridging is justified by observed stretching of two surfaces, presumably polymer chains, before detaching on retraction profiles. The presence of the adhesion

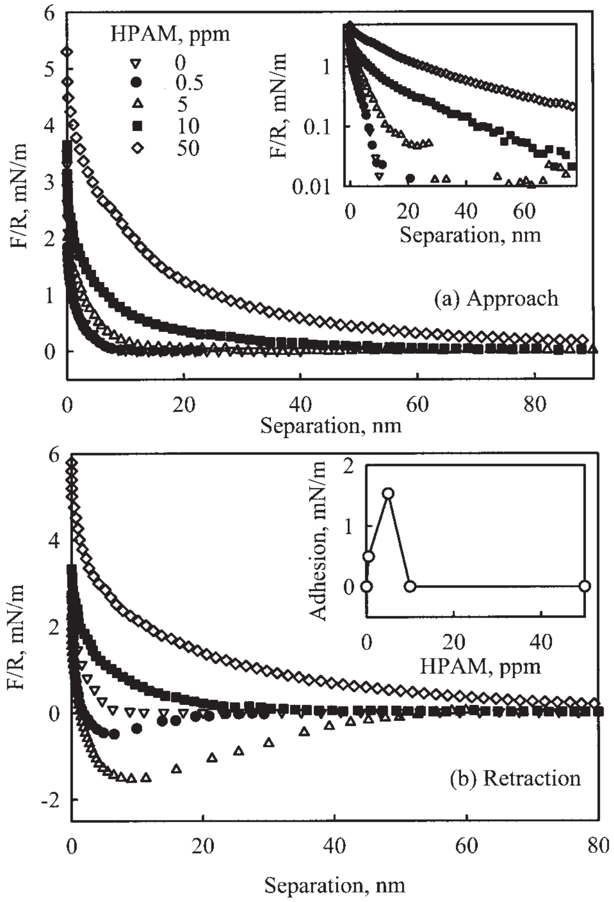
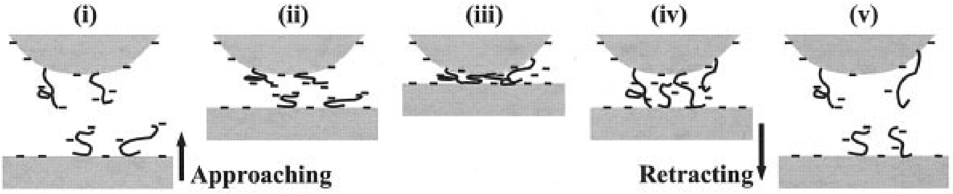
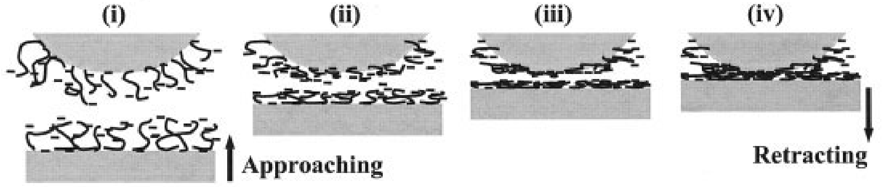


Figure 1. Measured forces between two silica surfaces in 20 mM KCl solutions at pH 8.2 as a function of separation distance with (a) on approach and (b) on retraction—effect of polymer concentration.

F/*R* represents the normalized force, where *F* is the measured force and *R* is the radius of the probe. Inset in (a) shows force profiles on semilog plot. Inset in (b) shows the dependency of adhesion on polymer concentration. Keys: (▽) 0, (●) 0.5, (△) 5, (■) 10, and (◇) 50 ppm HPAM added.



(a) Low HPAM concentration



(b) High HPAM concentration

Figure 2. Approaching and retracting processes in a cycle of force measurement.

At a low HPAM concentration (a), both surfaces are partially covered by the adsorbed HPAM molecules (i). When the two surfaces approach each other, a repulsive force can be detected and the stretched HPAM chains shrink (ii) until the two surfaces are in contact (iii). Single molecules can adsorb on both surfaces (iii). Then the substrate surface pulls off the upper surface. The molecules adsorbed on both surfaces cause a bridging adhesion (iv) until both surfaces separate from each other (v). At a high concentration (b), both surfaces are possibly saturated by adsorbed HPAM molecules (i). As the lower surface approaches the upper one, a strong repulsion can be measured (ii). As a result of further approaching, both surfaces are fully covered by a layer of adsorbed HPAM molecules (iii) until they are in contact (iv). The retracting process then goes reversibly from (iv) and (iii) to (ii) and (i).

force would indicate that the addition of HPAM at low concentrations can induce the flocculation of the fine particles in tailings and thus increase solids settling. When the polymer concentration was increased to 10 ppm and above, the adhesion force disappeared. The force profiles on retraction become identical to those on approach. Figure 2b shows the reversible approaching and retracting processes. In these cases, both silica surfaces are fully covered by the adsorbed polymers [Figure 2b(i)]. The larger long-range repulsion is attributed to electrosteric repulsion between adsorbed polymer layers [Figures 2b(ii), 2(iii), and 2(iv)]. For the system studied, 5 ppm is close to the optimum concentration for maximum adhesion.

Effect of calcium and magnesium

It has been known that divalent cations, such as calcium and magnesium, can lead to fines coagulation as a result of the collapse of the electric double layer and the decrease of surface charge. For the treatment of oil sand tailings, gypsum along with coarse sands are added to the mature fine tailings (MFTs) in the composite or consolidated tailings (CT) process.[5-7] A fast consolidation of the CT slurry has been achieved in commercial operations. To clearly understand the role of these divalent ions in tuning surface forces between fine particles, direct force measurements with calcium or magnesium added in prepared KCl solutions were carried out. In particular, given that HPAM and the divalent ions are both helpful in tailings treatment, it is of interest to determine whether there is any synergetic effect between the polymer and these divalent ions.

Figure 3 shows the effect of calcium and magnesium on the silica–silica interaction in 20 mM KCl solutions without HPAM addition (force measurement set 2 of Table 2). Figure 3a shows that the long-range force is purely repulsive. The addition of calcium at 2 mM or magnesium at 0.5 mM decreases the repulsive force. The three force profiles in this figure can be well fitted with the DLVO theory,[38] as shown by the solid curves (see the semilogarithmic plot in the inset for more details). The excellent fit shown in this figure suggests that the long-range repulsive force is predominantly from the electrostatic double-layer interactions. The fitted surface potentials of silica are -28, -24, and -20 mV for the cases without addition of divalent ions and with 0.5 mM of magnesium and 2 mM of calcium addition, respectively. Figure 3a also shows that the measured repulsive force at a separation distance $<$ 2–3 nm is inconsistent with an attractive force regime that would be predicted by the DLVO theory, suggesting the presence of non-DLVO repulsive forces.

Figure 3b shows the effect of calcium and magnesium on the adhesion (pull-off) force. Without divalent ion addition, the force profile (squares in Figure 3b) is identical to that on approach (squares in Figure 3a). This finding indicates no adhesion between the two silica surfaces. However, with calcium or magnesium addition, an adhesion force between the two silica surfaces was measured at the level of 0.32 and 0.12 mN/m for 2 mM calcium and 0.5 mM magnesium, respectively. A very interesting finding is that the force measurement on approach does not give an attraction force and consequently would indicate no coagulation. However, there is an adhesion force in the presence of calcium or magnesium. Such a finding would indicate the necessity of an additional force, such as a hydrodynamic force, to induce coagulation.

Synergy of HPAM with calcium

The above discussion shows that both HPAM and the divalent ions can result in adhesion interactions between two silica surfaces. It becomes of interest to see how the adhesion force will be affected if the polymer and divalent ions coexist in the solution. The interaction forces between two silica surfaces in a 5 ppm HPAM and 20 mM KCl solution with calcium or

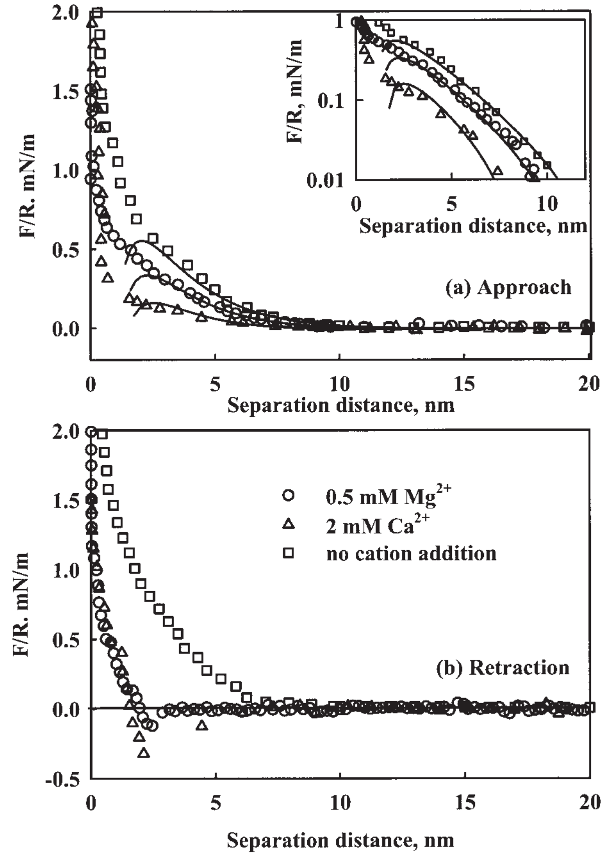


Figure 3. Measured forces (*F/R*) between two silica surfaces in 20 mM KCl solutions as a function of separation distance with (a) on approach and (b) on retraction—effect of calcium and magnesium ions.

Inset in (a) shows force profiles on semilog plot. Curves: DLVO fitting with Hamker constant $A = 8 \times 10^{-21}$ and surface potential $\Psi = -28$ mV for no divalent ion addition, -24 mV for magnesium added, and -20 mV for calcium added. Keys: (□) no calcium and magnesium, (○) 0.5 mM magnesium added, and (△) 2 mM calcium added.

magnesium addition at various concentrations were measured. As was shown in Figure 1b, the addition of HPAM at 5 ppm produced the strongest adhesion. This HPAM concentration was thus chosen to study the synergic effect of the polymer with calcium or magnesium. Figure 4 shows the synergic effect of the polymer and calcium on the interactions between two silica surfaces (force measurement set 3 of Table 2). At a low calcium concentration of 0.1 mM, the long-range force profile (inverted triangles in Figure 4a) is repulsive and very close to the force profile without the addition of divalent ions (crosses). With increasing calcium concentration to 0.5 mM, the long-range force changes progressively from repulsive to attractive, which indicates the dramatic effect of calcium addition on the long-range interaction. A further increase in calcium concentration to 2 mM produces an even stronger attraction. This attraction appears at a separation distance of 30 nm. At a calcium concentration of ≥8 mM, the long-range force becomes purely repulsive and shows little change.

The effect of calcium on the adhesion force is evident (Figure 4b). The dependency of the measured adhesion on the calcium concentration is shown in the inset of Figure 4b. This inset shows that, at low concentrations, the adhesion force increases with increasing calcium concentration until a maximum adhesion is reached at a calcium concentration of 2 mM. The maximum adhesion force is 5.5 mN/m. Without calcium addition (0 ppm of calcium, crosses in Figure 4b), the adhesion force is 1.5 mN/m. The synergic effect of HPAM with calcium causes a nearly fourfold increase in the adhesion force. Compared with the adhesion force with 2 mM calcium but no HPAM addition (triangles in Figure 3b), 0.3 mN/m, the synergic effect provides an increase of at least one order in the adhesion force. The results suggest that the synergy of HPAM and calcium significantly enhances the adhesion. Clearly, this synergy is favorable to solids settling in tailings treatment.

Synergy of HPAM with magnesium

The measured forces between two silica surfaces in a 5 ppm HPAM and 20 mM KCl solution with magnesium addition at various concentrations (force measurement set 4 of Table 2) are

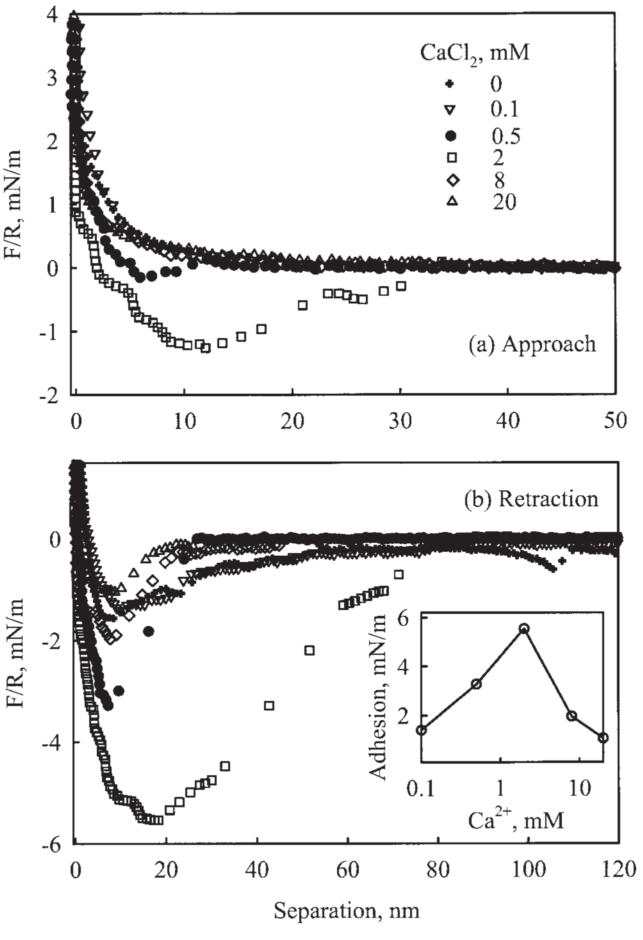


Figure 4. Measured forces (*F/R*) between two silica surfaces in a 20 mM KCl and 5 ppm HPAM solution as a function of separation distance with (a) on approach and (b) on retraction—synergic effect of the polymer and calcium.

Inset in (b) shows the dependency of adhesion on the concentration of calcium ions. Keys: (✚) 0, (▽) 0.1, (●) 0.5, (□) 2, (◇) 8, and (△) 2 mM CaCl$_2$ added.

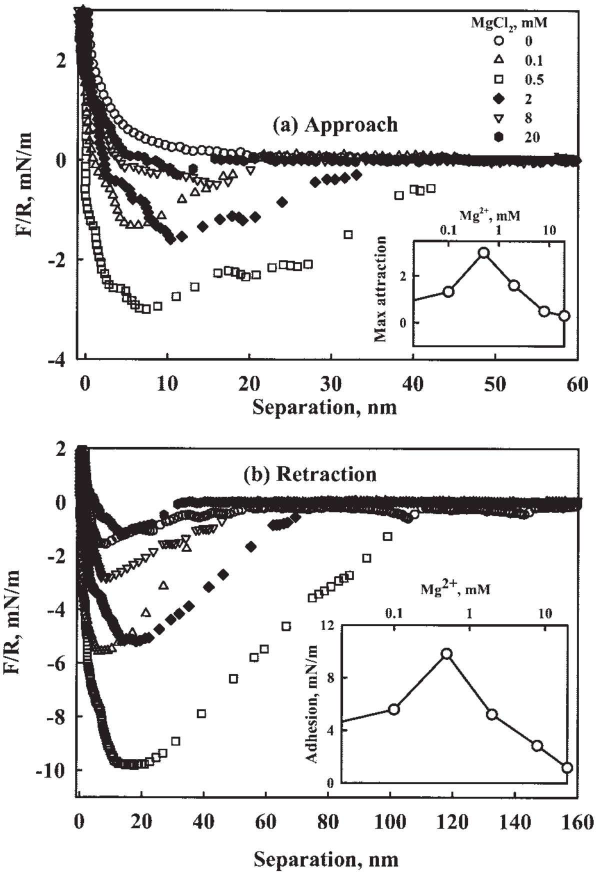


Figure 5. Measured forces (*F/R*) between two silica surfaces in a 20 mM KCl and 5 ppm HPAM solution as a function of separation distance with (a) on approach and (b) on retraction—synergic effect of the polymer and magnesium.

Insets in (a) and (b) show the dependency of the maximum attraction and the adhesion force on the concentration of magnesium ions, respectively. Keys: (○) 0, (△) 0.1, (□) 0.5, (◆) 2, (▽) 8, and (●) 20 mM MgCl$_2$ added.

presented in Figure 5. The force profiles on approach (Figure 5a) show an attractive long-range interaction, starting from 20 nm (triangles), with magnesium addition at a low concentration of 0.1 mM. The attraction progressively increased with increasing magnesium concentration. At 0.5 mM, the attraction starts at a separation distance of 50 nm and has a maximum of 3.0 mN/m. The attraction then decreases with a further increase in magnesium concentration. The long-range interaction is still attractive at a high magnesium concentration of 20 mM. The inset of Figure 5a shows the relationship between the attraction and the magnesium concentration. In this inset, the maximum attraction from each force profile is plotted against the corresponding magnesium concentration.

The force profiles on retraction are shown in Figure 5b and its inset shows the dependency of the adhesion force on the magnesium concentration. The adhesion force increases sharply with increasing magnesium concentration from 0 to 0.5 mM and then decreases with a further increase in magnesium concentration. With 0.5 mM magnesium addition, a maximum adhesion is obtained. This maximum adhesion force, 9.8 mN/m, is nearly sixfold higher than that with HPAM addition alone (1.5 mN/m, circles in Figure 5b) and 80-fold higher than that with magnesium addition alone (0.12 mN/m, circles in Figure 3b). These values indicate that the synergic effect of HPAM and magnesium results in a very strong adhesion. This synergy effect is even stronger than that of HPAM with calcium. The maximum adhesion force, 9.8 mN/m, obtained with 0.5 mM magnesium addition in a 5 ppm polymer solution is nearly twice the maximum adhesion force obtained with 2 mM calcium addition in a 5 ppm polymer solution, 5.5 mN/m (Figure 4b). In addition, to achieve a maximum adhesion, the required concentration of calcium (2 mM) is much higher than that of magnesium (0.5 mM). These comparisons show that the synergy of HPAM with either calcium or magnesium can significantly enhance the adhesion and that magnesium is more effective than calcium.

The effect of calcium and magnesium cations on the HPAM–assisted settling of oil sand tailings was studied by Sworska et al.[8] In their tests, calcium or magnesium ions were added to the tailing slurry before the addition of HPAM. Three of their settling results are chosen and shown as a bar graph in Figure 6. With HPAM addition alone at a dosage of 20 ppm, referring to the solids in the tailings slurry[9] at pH ~ 8.6, the initial settling rate is about 4 m/h. With 8 mM of calcium and 20 ppm of HPAM addition, the initial settling rate increased to about 11 m/h. A further increase to about 13 m/h was measured with 8 mM of magnesium and 20 ppm of HPAM addition in the tailings slurry. These results show that polymer-assisted settling of oil sand tailings is much more efficient in the presence of divalent cations. To determine the correlation between their settling results and the adhesion forces, the maximum adhesion forces between two silica surfaces in 5 ppm HPAM solutions with and without the addition of calcium and magnesium are also plotted in Figure 6. Comparing the settling rates with the adhesion forces, it is clear that the initial settling rate increases with increasing adhesion force. In addition, Sworska et al.[8]

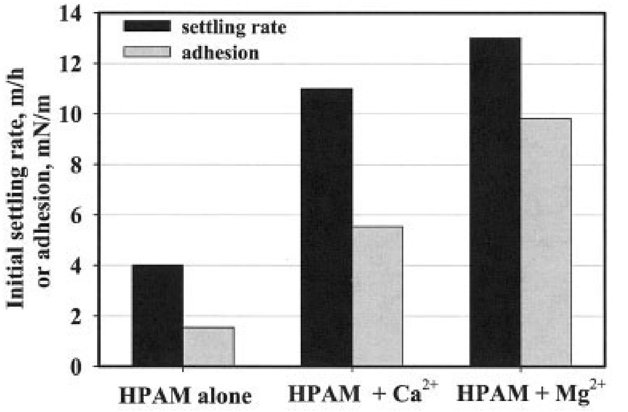


Figure 6. Comparison of the initial settling rates and the adhesion forces—synergic effect of HPAM and calcium/magnesium.

The black bars are the settling results of Sworska et al.[8] at HPAM dosage of 20 ppm (pH ~ 8.6). The concentrations of both calcium and magnesium ions they used were 8 mM. The gray bars are the measured adhesion forces between two silica surfaces in a 20 mM KCl and 5 ppm HPAM solution. The concentrations of added calcium and magnesium ions were 2 and 0.5 mM, respectively.

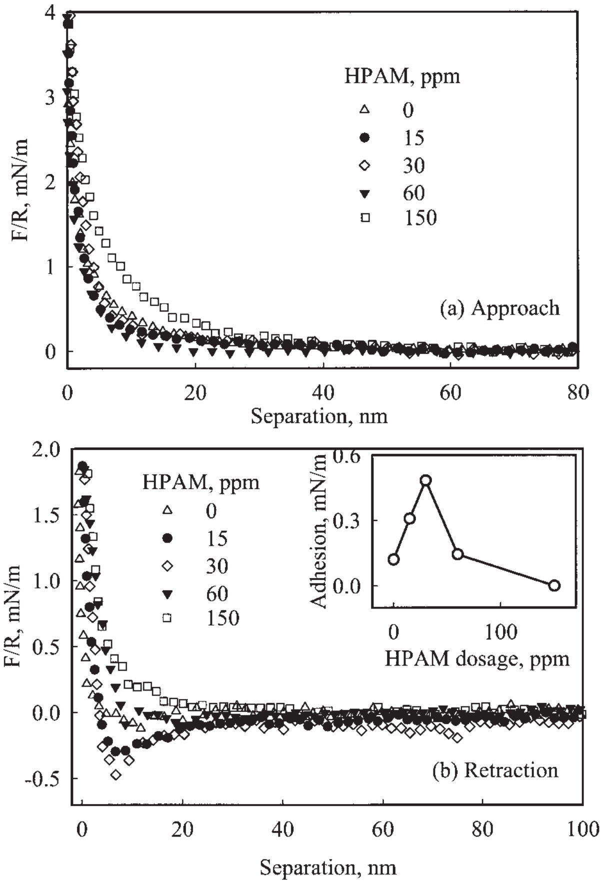


Figure 7. Measured forces (*F*/*R*) between two silica surfaces in the supernatants of tailings as a function of separation distance with (a) on approach and (b) on retraction—effect of polymer dosage.

The supernatants were directly taken from the tailings after the bitumen extraction (Table 1). Inset in (b) shows the dependency of adhesion on polymer dosage. Keys: (△) 0, (●) 15, (◇) 30, (▼) 60, and (□) 150 ppm HPAM added in the extraction process.

reported that in a set of preliminary experiments an optimum dosage of the divalent cations, calcium or magnesium, was established to be 8 mM. From our force measurements, we also found that there was an optimal concentration for calcium and magnesium at which the strongest adhesion force was obtained.

Silica–silica interactions in tailing supernatants

The results presented in Figures 1 and 3–5 were obtained in prepared KCl solutions, which could be quite different from process water in tailings in terms of chemical composition and other properties. To study the effect of water chemistry, the interaction forces between two silica surfaces in the supernatants of the collected tailings (force measurement set 5 of Table 2) were measured. The concentrations of calcium and magnesium, pH of the supernatant solutions, and the initial polymer dosages used in the bitumen extraction process are listed in Table 1. Because of the polymer adsorption on solid surfaces during the extraction, the actual HPAM concentration in these supernatants is not known. Figure 7 shows the results of the measured forces. From Figure 7a, it can be observed that the force profiles on approach do not change substantially with polymer addition from 0 to 60 ppm. This finding indicates that the amount of HPAM remained in the supernatants is significantly less than the initial dosages and thus has little influence on the long-range repulsive force. Only when the polymer dosage was increased to 150 ppm does the repulsive force become slightly stronger, indicating the presence of a substantial level of residual polymer in the supernatant.

On retraction (Figure 7b), adhesion forces are observed for polymer dosages from 0 to 60 ppm. The adhesion force increases with increasing polymer dosage until a maximum adhesion is obtained at the dosage of 30 ppm. A further increase in polymer dosage results in a decrease in adhesion. When the polymer concentration was increased up to 150 ppm, the adhesion disappeared. The change of adhesion force with polymer dosage is shown in the inset of Figure 7b. Without HPAM addition in the extraction process, the supernatant obtained (supernatant I of Table 1) contained 39.2 ppm of calcium and 13.0 ppm of magnesium. The presence of these divalent ions contributes to the observed adhesion force. When a certain amount of HPAM (that is, 15 and 30 ppm) was added in bitumen extraction, the residual polymer in the process water was adsorbed onto both silica surfaces. Thus, the polymer chains, connected to both silica surfaces, would produce a bridging adhesion force (see Figure 2a). When the polymer concentration was sufficiently high (that is, up to 150 ppm), a full coverage of the surfaces resulted in pure repulsive forces (see Figure 2b).

From Figure 7, one finds that the strongest adhesion was obtained at the polymer dosage of 30 ppm, which is much higher than the optimal polymer concentration in the prepared KCl solution (5 ppm, Figure 1). Such a difference could be accounted for by the following considerations. First, only part of the 30 ppm HPAM added in the extraction process would remain in the tailing supernatant where the true concentration of HPAM in the supernatant would be much lower than 30 ppm. This is reflected in the slight influence of polymer addition of this level on the approaching force profiles. Second, it is believed that oleate- as well as naphthenate-type surfactants released during the extraction process are present in the supernatant.[39] These surfactants serve as dispersants in the supernatant solutions[40] and may interfere with polymer adsorption.

Fine–silica interactions in supernatants of tailings

The results presented above were obtained with a spherical silica probe. To better approximate the interactions between fine particles in tailings, fine particles directly obtained from the tailings were used as the probe to measure the interactions in the supernatants (force measurement set 6 of Table 2). Figure 8 presents the results of measured forces between fine and silica. From the interaction forces shown in Figure 8a, one can observe that there is little or no change in the force profile for polymer dosages from 0 to 60 ppm added in the bitumen extraction process. Purely repulsive forces starting from a separation distance of 10 nm are observed and the forces are quite small. As the polymer dosage was further increased to 150 ppm, the repulsive force becomes slightly stronger. On retraction (Figure 8b), adhesion forces are observed at the HPAM dosages of 15 and 30 ppm. This finding suggests that at

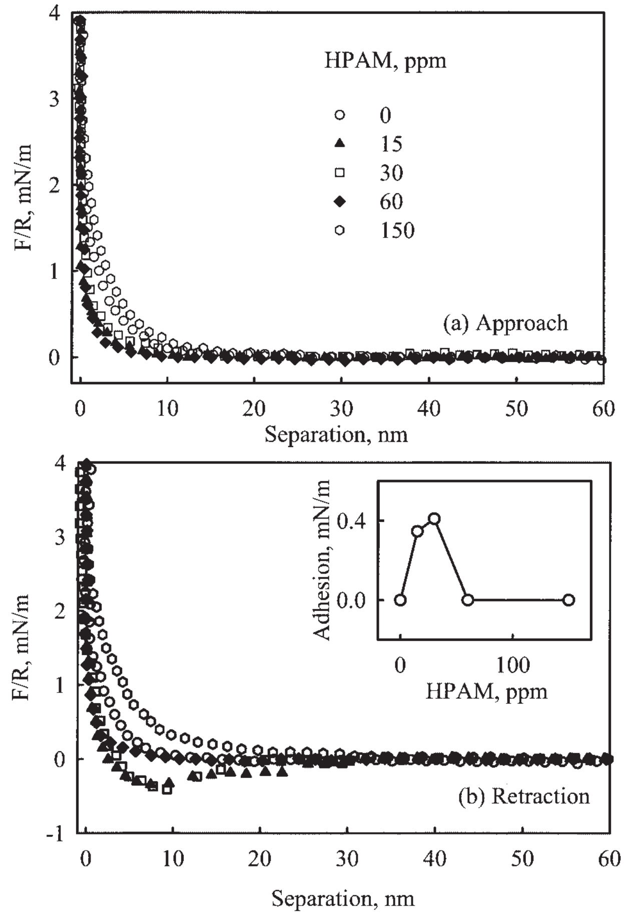


Figure 8. Measured forces (*F/R*) between a fine particle and a silica surface in various process waters as a function of separation distance with (a) on approach and (b) on retraction— effect of polymer dosage.

Inset in (b) shows the dependency of adhesion on polymer dosage. Keys: (○) 0, (▲) 15, (□) 30, (◆) 60, and (◦) 150 ppm HPAM added in the extraction process.

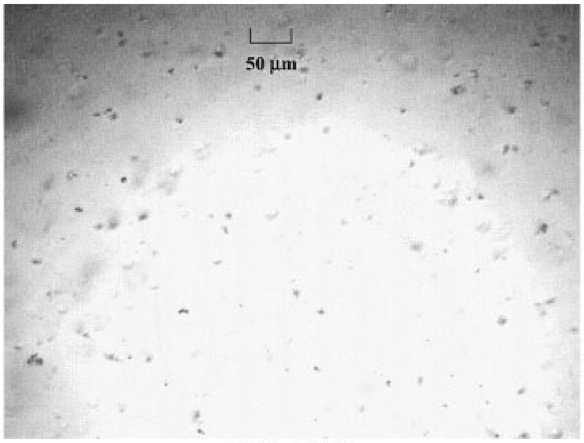
these dosages the surfaces of the fine particle and the silica plate are partially covered by the adsorbed polymer and thus polymer bridges can form across the surfaces. When the polymer dosage was increased to 60 ppm and above, no adhesion is observed. These results show that at high dosages, both the fine particle and the silica surface are saturated with adsorbed polymer. The dependency of fine–silica adhesion in the supernatants on polymer dosage added in the extraction is shown in the inset of Figure 8b. The adhesion curve in this inset is very similar to the silica–silica adhesion curve shown in the inset of Figure 7b.

Flocculation of clays

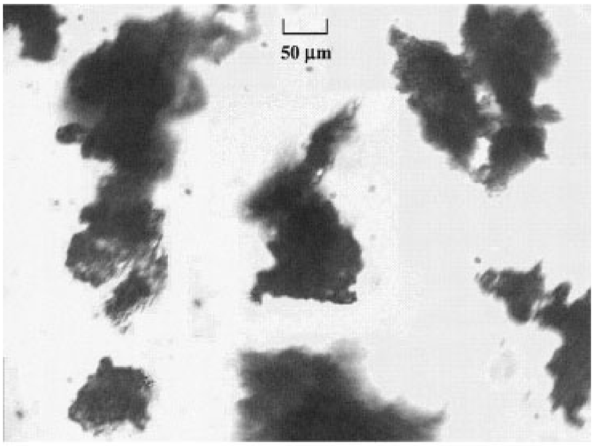
The above discussion demonstrates that HPAM can significantly alter the interaction force between fine particles. When low polymer dosages (~30 ppm) are used, adsorption of HPAM on fine particles causes a strong adhesion between the particles through polymer bridges. This adhesion force tends to hold the particles together and thus results in the formation of large floccules, which is favorable to quick settling. To verify the effect of HPAM on the flocculation of fine particles, images of two suspensions of fine kaolinite in the Aurora plant water with and without HPAM addition were taken. The top image in Figure 9 shows that without HPAM addition, the clay fines are in a well-dispersed state. In contrast, the addition of 30 ppm HPAM causes effective flocculation as shown by the large size floccules in the bottom image of Figure 9. Such large floccules can settle much more quickly than dispersed fines can.

Tailings settling

Figure 10a shows a typical settling curve of bitumen extraction tailings with 30 ppm HPAM addition in the extraction process. The supernatant layer height *h*, as defined in the inset, is plotted as a function of settling time. From the slope of the initial linear portion of the curve, as shown by the dash line, the initial settling rate of 0.6 m/h was obtained. In the same way, the initial settling rates of bitumen extraction tailings with varying HPAM dosages were also obtained and are shown in Figure 10b. The results in Figure 10b show that the initial settling rate increases with increasing HPAM dosage from 0 to 15 ppm, reaching a maximum at 30 ppm. A further increase in



(a) No HPAM



(b) 30 ppm HPAM added

Figure 9. Images of 0.6 wt % kaolinite in process water (23°C) with (a) no HPAM and (b) HPAM added at a dosage of 30 ppm.

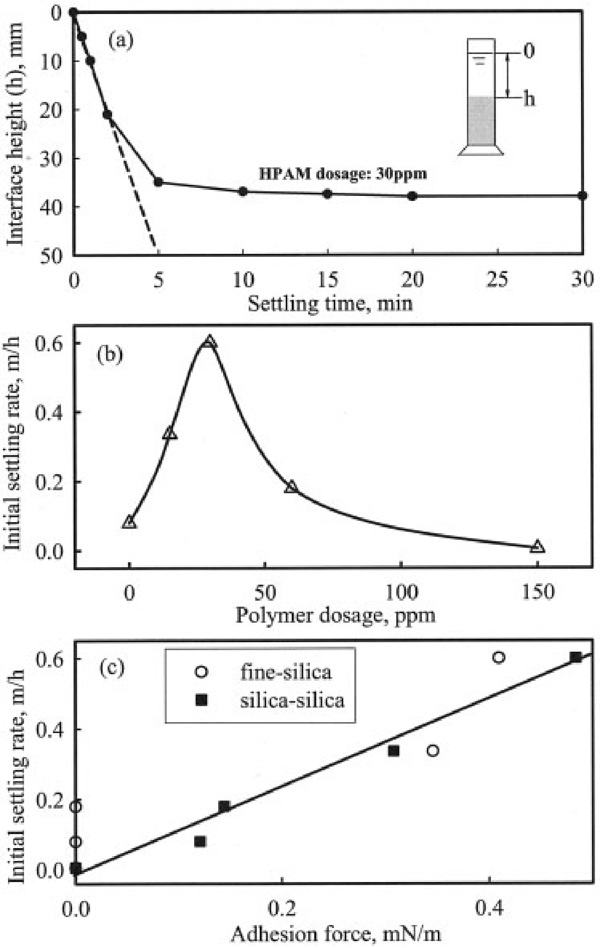


Figure 10. (a) A typical settling curve for the case with 30 ppm HPAM added in the bitumen extraction process; the inset shows the definition of the interface height; (b) effect of polymer dosage on the initial settling rate; (c) dependency of the initial settling rate on the adhesion force.

HPAM dosage results in a decrease in the initial settling rate. The settling rate with 150 ppm HPAM addition is even lower than that without HPAM addition. A similar trend of initial settling rate for oil sand tailings as a function of HPAM dosage was reported by Xu and Cymerman.[10] The adhesion forces between two silica surfaces and between a fine clay particle and a silica surface, as shown in the insets of Figure 7b and Figure 8b, respectively, also increases with increasing HPAM dosage from 0 to 15 ppm and reaches a maximum at about 30 ppm and then decreases with a further increase in HPAM dosage. The relationship between the initial settling rate and the adhesion force is shown in Figure 10c. From this plot, it can be observed that the initial settling rate increases with increasing adhesion force. The trend would be expected because a strong adhesion force would more likely lead to large/dense floccules.

In the settling tests, a clear layer of supernatant was observed after several minutes of settling in the graduated cylinder for the tailings with 15 and 30 ppm HPAM addition in the extraction process. At the HPAM dosage of 150 ppm or above, the supernatant of tailings was not clear even after a very long period of settling. These phenomena correlated well with the measured force profiles and adhesion forces. At low HPAM dosages of 15 and 30 ppm, the attraction and adhesion force held the fine particles together to form large aggregates, thereby resulting in a high setting rate and clear supernatant. At high HPAM dosage of 150 ppm, the strong repulsive force without adhesion stabilized the fine particles and, consequently, the settling rate is extremely low with supernatant containing a substantial amount of ultrafines.

Discussion on the Adsorption Mechanism of HPAM

The results discussed above show that the dosage of HPAM and the addition of divalent ions all have a significant impact on the interaction forces between silica (or fine particle) and silica, and consequently on the settling of oil sand tailings. Because the interaction forces are directly related to (or even controlled by) the adsorption of HPAM on the fine particles or silica surfaces, it becomes essential to discuss the adsorption mechanism to have a better understanding of the effects of these factors.

The molecular structure of HPAM is shown in Figure 11a. It has a long hydrocarbon chain, as its main structure. With some amide groups, $-CONH_2$, being replaced by carboxylic groups, $-COO^-$, in an aqueous solution, an electrostatic repulsion exists between the negatively charged carboxylic groups. This induces the extendability of the long hydrocarbon chain, which is advantageous for HPAM to be an effective flocculant. Given that silica surfaces or clay fines are normally negatively charged in a neutral or alkaline solution, there is also an electrostatic repulsive force between HPAM molecules and

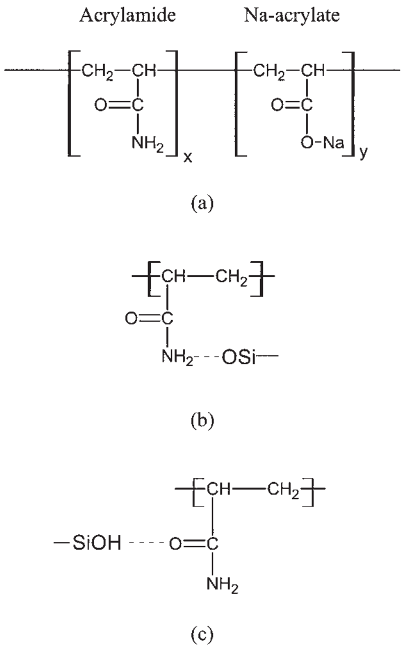


Figure 11. Adsorption mechanism of HPAM on silica.

(a) Molecular structure of the HPAM. (b) Hydrogen bonding between the hydrogen atoms of amide groups of HPAM and oxygenic surfaces of silica. (c) Hydrogen bonding between the oxygen atoms of amide groups of HPAM and hydroxylic surfaces of silica.

silica (or clay) surfaces. Thus, electrostatic interaction can be excluded as the driving force for HPAM to be adsorbed onto these surfaces. However, several investigators suggested that an electrostatic attraction can still arise locally if the charge distribution on the surfaces is inhomogeneous, that is, both negative and positive sites are present.[41-43] The adsorption can be caused by the spatial inhomogeneity of the surface charges, which creates attractive regions with charge sites different from the net charges of the surface. Other adsorption mechanisms have also been suggested. For example, Holmberg et al.[44] considered that the driving force of the adsorption originates from attractive van der Waals forces between the polymer and the surface. Others[45-48] suggested the formation of hydrogen bonding as a possible adsorption mechanism. The hydrogen bonding can occur between (1) the hydrogen atoms of amide groups of HPAM and the oxygenic surface of silica as shown in Figure 11b, and/or (2) the oxygen atoms of amide groups and the hydroxylic surface of silica (Figure 11c). The formation of hydrogen bonding between HPAM and silica surface has been experimentally verified by the infrared spectroscopic analysis of Peng and Di[48] and the XPS analysis of Yang and Li.[49]

Effect of calcium or magnesium ions

As was shown in Figures 4 and 5, the addition of calcium or magnesium ions in a 5 ppm polymer and 20 mM KCl solution leads to a significant promotion in the adhesion force between two silica surfaces. The influence of calcium on the adsorption of HPAM on silica surfaces has been studied.[48,50-52] Three mechanisms contribute to the increase in polyacrylamide adsorption upon the addition of calcium[50]: (1) reduction in electrostatic repulsion by charge screening; (2) specific interaction of calcium with polymer in the solution, thereby decreasing its charge and affinity for solvent; and (3) fixation of calcium on the silica surface, thereby reducing surface charge and creating new adsorption sites for the polymer.

If a sufficient amount of surface active groups is present calcium complexes such as $\equiv$SiOCa$^+$ or even ($\equiv$SiO)$_2$Ca can be found, reducing the negative surface charge of silica ($\equiv$SiO$^-$ groups present). The activating cation may act as a bridge for joining the carboxylic group (–COO$^-$) to active sites on the silica surface as shown in Figure 12a. In addition, calcium ions can also be adsorbed on the –COO$^-$ functional group of HPAM to form –(COO)$_2$Ca. Calcium ions may exist as CaOH$^+$ in the solution. CaOH$^+$ may also interact with the –COO$^-$ functional group to form –COOCa(OH).[48] As the concentration of calcium ion increases, more calcium ions are available to be combined with HPAM. Thus crosslinking between these polymer molecules may occur.[53-56] Figure 12b shows a possible adsorption mechanism with such crosslinked polymers. When the concentration of calcium ion is too high, the anionicity loss of HPAM and the charge reversal of silica surface may result in electrostatic repulsion, leading to lower adsorption. This may explain the presence of an optimal concentration for the divalent ions. The effect of magnesium on the adsorption of HPAM is similar to that of calcium. However, magnesium is more efficient than calcium in promoting adhesion and consequently in improving settling. This is because when solution pH is high, the amount of magnesium adsorbed on silica is much higher than that of calcium. Wang et al.[57] studied the adsorption of both calcium and magnesium on silica. The distribution coefficients (the ratio of the adsorbed amount of cation per unit mass of solids to the concentration in aqueous solution, mL/g) at pH 9 are 5.7×10^3 for magnesium and 1.5×10^3 for calcium. A nearly fourfold increase in distribution coefficient shows that much more magnesium ions can be adsorbed onto the silica surface. Zevenhoven-Onderwater et al.[58] also found that in the pH range of 6–8, $\equiv$SiOCa$^+$ and $\equiv$SiOMg$^+$ complexes were formed and that the magnesium complexes were stronger than the calcium complexes. This is consistent with our adhesion measurements: magnesium can induce much stronger bridging adsorption and thus adhesion than calcium.

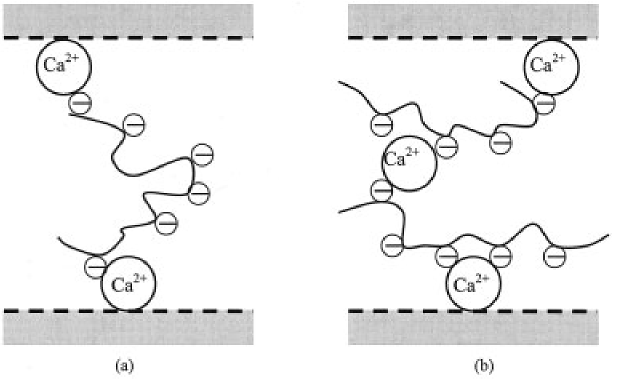


Figure 12. Calcium bridge formed between two negatively charged surfaces.

(a) A single chain connected to two surfaces. (b) Possible ionic crosslink between polymer molecules.

From the above analysis, it can be concluded that the adsorption mechanism of HPAM on silica (or fine particles) with the addition of the divalent ions is different from that without the addition of these ions. The complexation of calcium (or magnesium) with HPAM and silica induces a much stronger bridging adhesion compared with the adhesion originated from the hydrogen bonding. This may explain the synergic effect of HPAM with the divalent ions.

Conclusions

The effects of HPAM, calcium, and magnesium ions on surface interactions between fine particles were investigated by direct force measurements with an atomic force microscope. The following conclusions can be drawn from this study:

(1) At low polymer dosages, a partial surface coverage by the adsorbed polymer causes a bridging attraction between fine particles. The adhesion force increased as the polymer dosage was increased up to an optimum dosage at which the strongest adhesion was measured. A further increase in polymer dosage is not helpful for tailings treatment because it results in a weaker adhesion or even purely repulsive force profile between fine particles.

(2) Both calcium and magnesium ions induce adhesion between fine particles. In particular, the synergic effect of the polymer and the divalent ions can significantly enhance the adhesion between fine particles.

(3) The measured adhesion forces are correlated with the

results of tailings settling tests: the stronger the adhesion force, the higher the initial settling rate.

(4) This study indicates a potential to develop new technologies for oil sand tailings treatment based on the synergy of the polymer and the divalent ions.

Acknowledgments

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