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Biwetted ultrafine solids and structure formation in oil sands fine tailings

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A high water holding capacity of oil sands fine tailing has been attributed to the presence of ultrafine ($<0.2\ \mu\text{m}$) clay fractions. On the basis of hydrophobic character two major types of ultrafines are recognized: biwetted, associated with a significant coverage of organic matter and preferentially hydrophilic solids. The effect of biwetted solids on the colloidal stability of ultrafine clays in aqueous suspensions has been studied by dynamic light scattering and ^2H n.m.r. methods. The organic matter associates with the surfaces of the biwetted solids is believed to be responsible for their accelerating effect on aggregation. The results indicate that prevention, or reduction, of the amount of biwetted solids entering the tailings pond could be beneficial.

(Keywords: oil sand tailings; biwetted solids; gel formation)

The hot water extraction process is currently used to extract bitumen from Athabasca oil sands. The tailings remaining after bitumen extraction are a slurry of sand, silt, clay and a minor amount of bitumen, all suspended in water. This slurry is transported to tailings or sedimentation ponds, where the coarse solids settle rapidly. Fine solids and almost all the bitumen remain in suspension and flow to the centre of the pond to form fine tailings, containing substantial amounts of the process water. Toxicity and the loss of bitumen and process water are among the most serious problems associated with the buildup of these clay tailings¹.

In previous work^{2,3} the intractable behaviour and high water-holding capacity of these tailings have been attributed to the presence of ultra fine ($<0.2\ \mu\text{m}$) aluminosilicate clays (kaolinite and mica). These components readily flocculate to form gels, within which coarse particles may be embedded. For gel formation to occur, an appropriate combination of ultrafine solids (amount and particle size) and water chemistry (salt type and concentration) is needed⁴. In terms of degree of hydrophobicity, two major types of ultrafine solids have been recognized in both oil sand ores and fine tailings; these are the biwetted ultrafine solids (BUS), which are associated with various amounts of so-called 'strongly bound' organic matter², and preferentially hydrophilic solids (AS). The presence of the organic matter on the surfaces of the biwetted solids is an important factor affecting the degree of flocculation and gelation^{2,5,6}. This factor ultimately controls the amount of water lost to the tailings and hence their final volume.

In this work, photon correlation spectroscopy (PCS) has been used to monitor the aggregation kinetics of ultrafines in the presence of model tailings-pond water

containing NaCl or NaHCO_3 . The effect of biwetted solids on the gel-forming propensity of ultrafines has also been evaluated by a ^2H n.m.r. technique⁷. Knowledge gained from this work is of importance with respect to the mechanism of aggregation. Understanding of this mechanism makes it possible to propose technical strategies for reducing the volume of fine tailings.

EXPERIMENTAL

Raw material

Fine tailings samples were supplied by Suncor Inc., containing on average 31.2 wt% solids and 3.5 wt% bitumen, with the balance water.

Separation

The treatment scheme for sample preparation is outlined in *Figure 1*. Ultrafine solids were separated from the bulk fine tailings as an aqueous colloidal suspension, using mechanical agitation followed by mild centrifugation (200g for 1 h)⁸. Separated suspensions were then fractionated into hydrophilic and biwetted components by emulsification with toluene using a procedure involving agitation, followed by flotation. This approach makes use of the characteristic of biwetted solids that allows them to stabilize emulsions by forming a cohesive film at the oil–water interface. Biwetted ultrafines were washed with toluene to remove any associated bitumen and then prepared for surface analysis by X-ray photoelectron spectroscopy (XPS). The hydrophilic ultrafines were deflocculated by replacing salty pond water with distilled water⁴. Centrifugation at 1500g was then used to sediment particles $>100\ \text{nm}$. The supernatant was concentrated by high-speed centrifugation to give a stock suspension containing 6.7 wt% of the smallest ($<100\ \text{nm}$) ultrafine particles. Samples in which the biwetted solids were retained were also

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Figure 1 Treatment scheme for sample preparation

prepared using a similar treatment scheme, except that the step involving flotation with toluene was omitted.

Analysis

The colloidal suspensions to be studied by PCS were prepared by dilution of the stock suspension to 0.3 wt% solids with different electrolyte solutions. Dynamic light scattering experiments were performed using a Malvern ZetaSizer 3 PCS system, with a 5 mW, 633 nm He–Ne laser. Photon correlation measurements of scattered light intensity were made at a scattering angle of 90° using a 64-channel autocorrelator; the method of cumulants⁹ was used to analyse the autocorrelation functions. The first cumulant Γ_1 of the correlation function was used to obtain the translational diffusion coefficient $D = \Gamma_1/q^2$, where q is a scattering vector. From D and the Stokes–Einstein relation the mean hydrodynamic radius R was calculated:

$$D = 6\pi\eta R/k_bT \tag{1}$$

where η is the viscosity of the suspension liquid, T the absolute temperature and k_b Boltzmann’s constant.

X-ray photoelectron spectroscopy (XPS) measurements were carried out using a PHI 5500 instrument with an Al $K\alpha$ source of X-rays. The pressure inside the instrument during analysis was always <1 μ Pa. An electron flood gun was used to neutralize any charge developed at the surface of the sample while the spectra were being recorded. High-resolution spectra were obtained at a pass energy of 29.6 eV, and survey spectra at a pass energy of 156 eV. Several repetitions were made to ensure accuracy of the results.

Samples for ²H n.m.r. study were prepared by replacing the distilled water in the stock suspension with pond water. A series of dilutions was prepared for use in a gelation study. Deuterium n.m.r. spectra were recorded with a Bruker MSL 300 spectrometer (magnetic field 7.1 T) at a frequency of 46.07 MHz. In typical experiments, 16 transients were acquired in 8 K points, with a spectral width of 1000 Hz.

RESULTS AND DISCUSSION

The high water-holding capacity of oil sands fine tailings can be attributed to the presence of a porous, three-dimensional gel network structure, formed by

ultrafine solids. Such a network is capable of entrapping other sludge components such as coarser solids and free or emulsified bitumen. It has been observed previously⁸ that the structure of fine tailings is not resistant to mechanical agitation. This characteristic can be used to disrupt the organization of the particles, allowing the coarse, high-density solids to settle and form a dense bottom layer. Bitumen and its associated low-density, hydrophobic solids form a distinct top layer. An aqueous suspension of ultrafines separates between these two layers. These ultrafines are capable of rapid gelation, a behaviour typical of parent fine tailings themselves. The implication of this observation is that the ultrafines in the middlings layer exist as flocs rather than discrete particles¹⁰. Each floc is associated with a certain amount of immobilized water phase.

Nature of ultrafines

X-ray diffractometry of powder specimens in random mounts (for whole mineral composition) and in preferred orientation (for characterization of phyllosilicates) showed that mica and kaolinite are the main inorganic components³. Transmission electron microscopy showed that the particles of ultrafines are very thin (down to a few layers), anisotropic and of both hexagonal and irregular morphology (ref. 3 and Y. LePage, personal communication, 1993). Particle sizes are in the range 20–200 nm. About 30% of the total ultrafines exhibit biwetted surface characteristics which make them prone to separation from the hydrophilic fraction in any process step involving interfacial interaction, such as flotation. This behaviour is in accord with the results of XPS analysis, which shows that the surfaces of the biwetted solids are dominated by up to 40 at.% carbon, as opposed to the hydrophilic ultrafines, which are associated with <4 at.% carbon: see Table 1.

Aggregation kinetics

To examine the effect of biwetted solids on the aggregation of ultrafines, the mean hydrodynamic radius R of growing aggregates with and without biwetted solids in the presence of model tailings-pond water containing NaCl or NaHCO₃ was monitored as a function of time by photon correlation spectroscopy. Typical results for 20 mM NaCl solutions at pH 6.7 and 11 are given in Figure 2. It is apparent that aggregation progresses faster at lower pH; suspensions containing both types of particles coagulated spontaneously at pH < 3.5. This observation is not surprising, considering that in anisotropic clays the platelet faces carry a fairly constant negative charge over the entire pH range whereas the edges are positive in acidic and neutral or negative in basic media¹¹. Also, at low pH the net charge on the particles is low and edge-to-face association is possible, even before the addition of electrolyte. It was observed that the ultrafines suspensions aggregated much faster when biwetted solids were present.

Table 1 XPS analyses of ultrafine solids (at.%)

Fraction	C	O	Si	Al
Hydrophilic	3.8	68.5	15.5	9.9
Biwetted	39.7	42.9	10.2	6.3

Figure 2 Effect of biwetted solids on stability of ultrafines to aggregation in the presence of NaCl

Figure 3 Stability of ultrafines suspensions to aggregation in the presence of sodium bicarbonate solution

When 20 mM NaHCO_3 ($\text{pH} = 8.4$) was used instead of NaCl, no growth in particle size was observed for either of the suspensions studied. This could be due to the peptizing or deflocculating action of bicarbonate anion. At present, the effect is attributed to the specific reactivity of bicarbonate anions with the exposed octahedral cations at the edges of clays, with which they can form either complex anions or insoluble salts¹¹. A more concentrated solution of sodium bicarbonate, 80 mM, was required to initiate aggregation, Figure 3. At the higher concentration of NaHCO_3 , the aggregation is driven by the increased concentration of sodium ions. Samples with biwetted solids again aggregated faster than those with hydrophilic particles alone.

Effect of biwetted solids on gelation

The gelation of ultrafines, both with and without biwetted solids, was followed by using ^2H n.m.r. as a probe⁷. The ^2H n.m.r. method relies on the slitting (Δ) of the deuterium peak owing to the rapid exchange of deuterium molecules between the bulk water and particle surface environments. As the gel structure forms, this exchange process is inhibited and the splitting gradually disappears. The normalized change in splitting, I (gelation index), was calculated as

$$I = 100(\Delta_0 - \Delta_t) / \Delta_0 \tag{2}$$

where Δ_0 is the ^2H n.m.r. splitting at zero time and Δ_t , the corresponding splitting at time t . The gelation index reflects a change in mobility caused by cluster formation

and is related to degree of gelation. Values of I range from 0 for a sol or a stable colloidal suspension to 100% for a stiff gel. Systems with $I \sim 35\text{--}40\%$ generally display thickening behaviour, that is, they exhibit a noticeable increase in viscosity. The growth of gel networks was monitored for samples having solids concentrations ranging from 0.5 to 6.7 wt% over periods ranging from 0 to 2 weeks. Three-dimensional plots showing concentration and time dependence of gelation index for both hydrophilic and biwetted ultrafine mixtures and hydrophilic ultrafines only, suspended in tailings-pond water, are presented in Figures 4 and 5. For both samples, I remained close to zero for the first 4 h, indicating a limited degree of aggregation. With further increase in time, the gelation of suspensions containing biwetted solids proceeded very rapidly, so that for the most concentrated suspensions (6.7 wt%), I reached 100% after only 48 h. A suspension containing 2 wt% ultrafines required 216 h for I to reach 100%, that is to approach the state at which a large cluster spanning the container had formed. For the sample without biwetted solids, the sol-gel transition was obviously much slower. During the observation period no stiff gel was formed by the 2 wt% suspension, and it took 216 h for a suspension of 6.7 wt% solids to gel completely.

To summarize, the results show that the presence of biwetted solids accelerates aggregation in both model pond water and natural pond water. This points to an important role played by biwetted solids in fine-tailings structure formation and stability. At present the mechanism of this phenomenon is far from well understood. Several possibilities may be considered:

Figure 4 Time and concentration dependence of gelation index (I) for a mixture of hydrophilic and biwetted ultrafine particles in pond water

Figure 5 Time and concentration dependence of gelation index (I) for hydrophilic ultrafines in pond water

flocculation by 'physical bridging' or electrical charge neutralization, as in the presence of salts, or both. The 'bridging model' is favoured when the adsorbed polymers (possibly humic matter in this case) have long chain segments extended into the dispersed phase, and when the amount adsorbed is below saturation coverage⁵.

CONCLUSIONS

Oil sands fine tailings contain a fraction of ultrafine solids which displays biwetted characteristics. This behaviour is attributed to the presence of an organic coating on the particulate surfaces. Biwetted particles accelerate aggregation of dilute suspensions of ultrafines in electrolyte solutions. Enhancement of the gel-forming propensity also occurs in concentrated systems, possibly through interaction between organic surface layers. This effect could have major implications for the role played by the biwetted solids in fine tailings behaviour. At present neither the distribution, as a uniform thin layer completely covering the particle surfaces or as discontinuous patches, nor the nature of the organics is understood. These important factors are currently under investigation.

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