CHARACTERIZATION OF COLLOIDAL SOLIDS FROM ATHABASCA FINE TAILS[1]

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Abstract—During processing of Athabasca oil sands, the finely divided solids form an aqueous suspension, which ultimately stabilizes as a gel-like structure retaining up to 90% of the process water. This gelling phenomenon is believed to be caused by colloidal inorganic components. Kaolinite and mica are the main crystalline minerals in these colloidal solids; swelling clays are present in only trace amounts. Noncrystalline components are more concentrated in the finer fraction of the solids. Although the surfaces of the colloidal solids are virtually free of Fe, some contamination with polar organic matter is observed.

Key Words—Fine tails, Hydrophilic, Colloidal solids.

INTRODUCTION

The Hot Water Extraction process is presently used in Alberta to extract bitumen from oil sands. In this process the bituminous sand is mixed with steam and hot water to which a small amount of sodium hydroxide has been added. After the separation of bitumen by flotation, the remaining tailings are predominantly an aqueous slurry of sand, silt, clay and a minor amount of bitumen. The slurry is transported to sedimentation ponds where the solid particles are allowed to settle out and clean water is separated for recycling to the extraction process. Some coarse sand and silt are used to form the dykes surrounding the tailings pond, while the remainder of the tailings is discharged to form a beach. About one half of the silt and clay and almost all the bitumen remain in suspension and flow to the centre of the pond to form a gel-like system (fine tails) with very poor settling and compaction rates. Toxicity, loss of bitumen, diluent naphtha and process water are among the problems associated with the buildup of these fine tails (Camp, 1977).

It has been demonstrated (Kotlyar *et al.,* 1991) that the unusual properties of the fine tails could be attributed to the presence of colloidal (≤ 1 μm) inorganic components. These components readily form gels (Ripmeester *et al.,* 1992) within which coarse particles may be embedded. For gel formation to occur, an appropriate combination of colloidal solids (amount and particle size) and water chemistry (salt concentration) are needed (Kotlyar *et al.,* 1992).

The objective of the present study was to determine the chemical and mineralogical characteristics of the colloidal solids that are responsible for the gel forming propensity. This knowledge is of a great importance as it relates to the question of the mechanism of gelation. By understanding the mechanism it will be possible to propose fine tails reduction methods for industrial use.

EXPERIMENTAL METHODS

The fine tails sample was supplied by Suncor Inc. Average samples contained 23.6 wt. % solids and 1.8 wt. % bitumen with the remainder being water containing dissolved organic and inorganic species.

Separation

The colloidal solids were separated from the fine tails sample using the sequence of procedures as illustrated in Figure 1. First, excess water, containing dissolved salts, was removed from the samples by centrifugation at 1500 g for 2 hours. Distilled water was then added to the sediment and the mixture agitated. This caused deflocculation of the colloidal solids and release of any entrapped materials. Mild centrifugation (200 g, 10 min) was then applied to separate a dense sediment of coarse solids from an aqueous layer (A), containing the suspended colloidal solids. Layer A contains bitumen and closely associated solids. These components were removed by floatation with toluene. Sequential centrifugation at progressively higher speeds was used to subdivide the colloidal solids into the following fractions: I (200 g for 1 hour); II (500 g for 2 hours); III (1500 g for 2 hours); and IV (unsettled at 1500 g). The information in parenthesis defines the separation conditions used. Average particle sizes of these fractions were determined by electron microscopy and are given in Table 1.

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Table 1. Solids distribution and properties of colloidal solids fractions.

Sample	Average particle size, nm	Solids distribution,[1] wt %	IOCC, wt %	Weight loss as a result of Tiron treatment,[2] wt %
I	400	35.0	0.5	2.9
II	200	25.0	0.9	10.2
III	100	22.4	1.0	n.a.
IV	50	17.6	2.0	29.0

[1] Wt % of total colloidal solids (bitumen free, dry basis).
[2] The amount of non-crystalline material in the corresponding fraction.
n.a. = not available.

Analysis

Total C was determined using a LECO CR12 C analyzer. The insoluble organic C content (IOCC) was obtained by subtracting carbonate C from the total C.

X-ray diffraction analysis was performed on powder specimens in two ways: in random mounts for the determination of whole sample mineral composition, and with preferred orientation for characterizing phyllosilicates. For the random mount, approximately 100–250 mg of air-dried sample was gently packed by backloading in a Plexiglas® sample holder. For preferred orientation mounts, 30 mg of sample was suspended in 1 ml of water (for samples air-dried and heated at 550°C) and in 1ml of 2% glycerol aqueous solution (for samples solvated with glycerol). Sub-samples were pipetted onto glass slides (30 mm × 25 mm) and allowed to air dry. The samples were analyzed using a Scintag PAD V diffractometer with Co radiation and a graphite monochromator.

The selective chemical dissolution method with alkaline Tiron (1,2-dihydroxybenzene-3,5-disulfonic acid disodium salt; Kodama and Jaakkimainen, 1982) was applied to extract non-crystalline components from the samples. The weight loss during extraction was assumed to represent the amount of these components.

The morphology of the clay particles was investigated by TEM. For these observations, a drop of the suspended sample, after sonication for 1 minute, was deposited on a carbon coated copper grid. After 1 minute, the liquid was blotted to leave only a thin layer which was then allowed to dry. The grid was then examined with a Carl Zeiss Model 902 TEM, operated at 80 kV.

For X-ray photoelectron spectroscopy (XPS) measurements, drops of the suspension were spread over a clean glass slide and allowed to air dry. The dried solids were then scraped off the glass with a razor blade and pressed onto a piece of In foil. XPS spectra were recorded using a PHI 5500 Instrument using Al Kα as the source of X-rays. The pressure inside the instrument during analysis was always below 8×10^{-9} torr. An electron flood gun was used to neutralize the charge
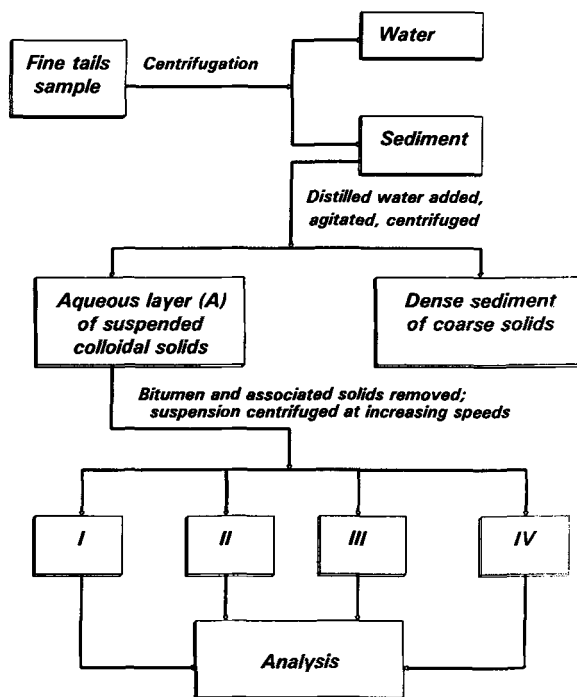

Figure 1. Treatment scheme for fine tails.

developing at the surface of the sample during the recording of the spectra. High resolution spectra were obtained at a pass energy of 29.6 electron-volt (ev). Survey spectra were recorded at a pass energy of 156 ev. Several repetitions were made to assure repeatability of the results. These spectra were used to calculate the atomic fraction of the element i using the software supplied with the equipment, based on the formula

$$C_i = (I_i/S_i)/\Sigma(I_j/S_j)$$

where I is the area under a spectral peak and S is the sensitivity factor (Muilenberg, 1979). Values of 0.296, 0.711, 0.262, 0.870, 0.213 and 1.791, suggested by the instrument manufacturer, were used for the sensitivity factors of C1s, O1s, Si2p, K2p, Al2s and Fe2p3.

^{29}Si MAS NMR spectra (spinning rates 3.5 kHz) were recorded at 59.62 MHz on a Bruker MSL-300 NMR spectrometer (magnetic field 7.1 T). About 8000 free induction decays (FIDs) were accumulated, with the repetition time being 2 s. Chemical shifts are given in ppm with respect to tetramethylsilane (TMS).

RESULTS AND DISCUSSION

The average particle size, wt % solids, insoluble organic C content, and weight loss due to Tiron extraction (IOCCs) of the colloidal solids fractions are shown in Table 1. The IOCCs were relatively low in all cases; some increase with decrease in particle size was observed.
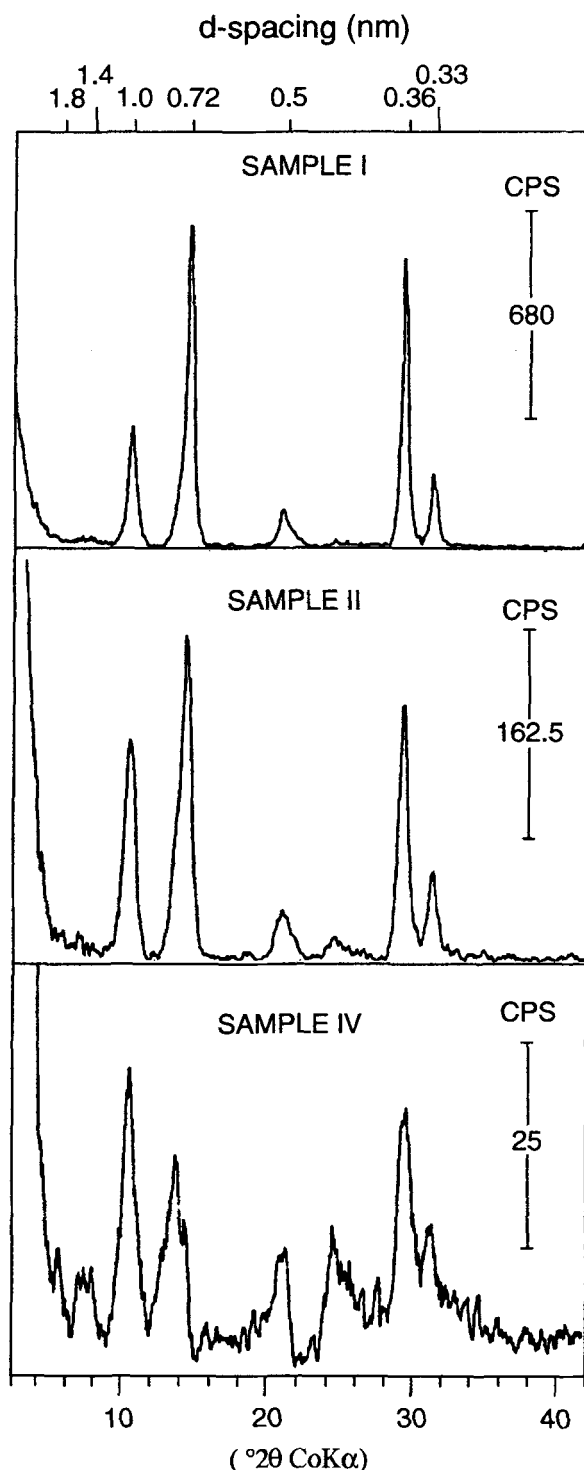
Figure 2. XRD spectra of glycerolated samples I (400 nm fraction), II (200 nm fraction), and IV (50 nm fraction) of the colloidal solids.
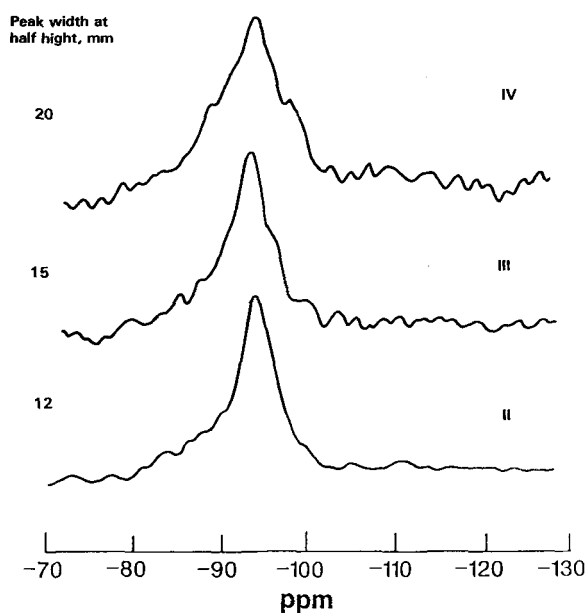

Figure 3. ^{29}Si MAS NMR spectra of the samples II (200 nm fraction), III (100 nm fraction) and IV (50 nm fraction) of colloidal solids.

X-ray diffraction

X-ray diffraction data indicated that for all the fractionated samples analyzed the major crystalline components were kaolinite and mica. In addition, trace amounts of smectite and vermiculitic minerals were detected in sample IV (Figure 2). The intensity of diffraction by crystalline components decreased with decrease in particle size (Figure 2) while the relative intensity of mica appeared to increase. Under the experimental conditions employed, the intensity factor ratio—1 nm mica peak/0.72 nm kaolinite peak—was 1.0/1.4 (unpublished data), so relative quantities of mica to kaolinite were 0.5, 0.9 and 1.8 for samples I, II and IV, respectively. Also, the amount of non-crystalline material increased for the finer particles as evidenced by the XRD patterns of random mounts (not shown) which exhibited high background levels and two humps with very broad maxima near 0.7 and 0.4 nm. The XRD pattern for sample IV was similar to that of kaolinite ground for 144 hours (Kodama *et al.*, 1989). The increase in the amount of non-crystalline components with decrease in particle size was confirmed by the results for the Tiron extraction (Table 1).

^{29}Si NMR

The ^{29}Si NMR patterns are shown on Figure 3. All spectra exhibited resonances in the range from −80 to −110 ppm, which is typical for aluminosilicates (Maciel and Sindorf, 1980). The spectra were centered at about −92 ppm (characteristic for kaolinite) but were obviously broader than expected, indicating a disor-
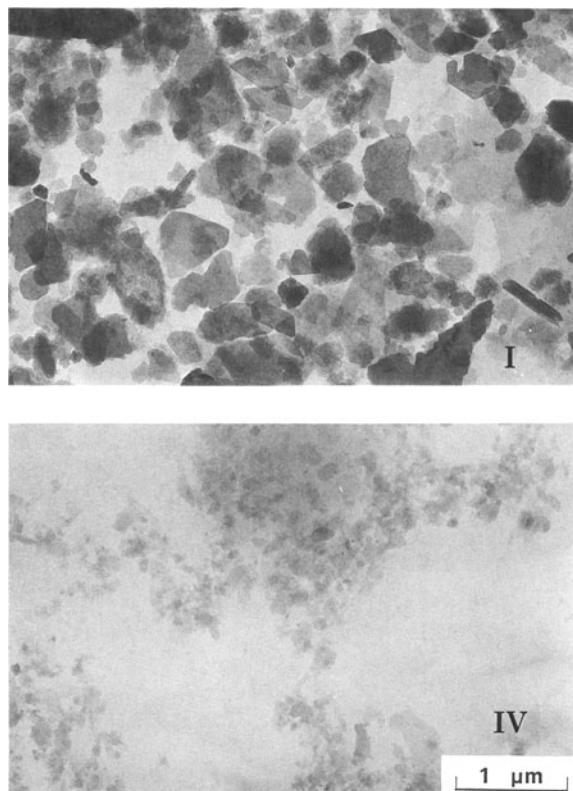
Figure 4. TEM of the samples I (400 nm fraction) and IV (50 nm fraction) of colloidal solids.
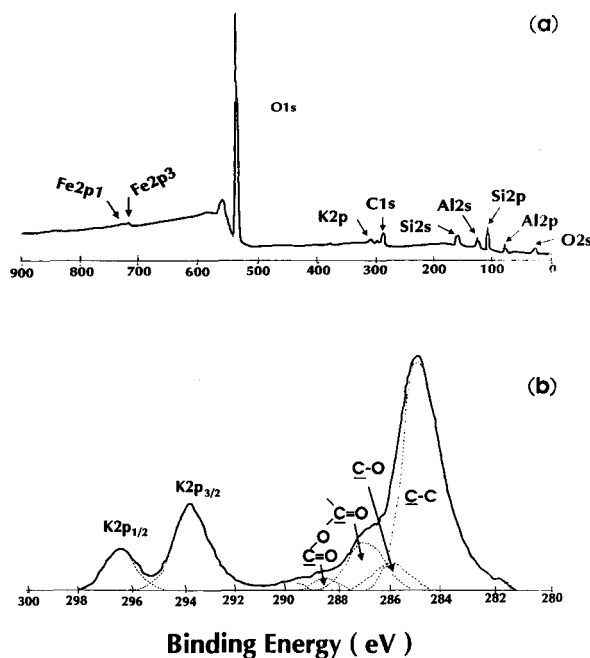

Binding Energy (eV)

Figure 5. Surface characterization of the colloidal solids: a) XPS survey spectrum and b) deconvolution of carbon XPS peak of sample IV (50 nm fraction).

Table 2. Atomic percentages determined by X-ray photoelectron spectroscopy of colloidal solids.

Sample	Atomic %						Si/Al
	C	O	Si	Al	K	Fe	
I	8.7	62.4	16.7	11.1	1.0	0.2	1.5
II	11.1	62.4	14.8	10.7	1.0	0.2	1.4
III	13.7	59.1	15.2	11.1	0.9	0.2	1.4
IV	13.5	60.7	16.1	9.0	0.7	0.3	1.8

dered environment (Kodama, *et al.,* 1989). The peak width at half-height was used as a quantitative parameter to characterize the degree of broadness of the resonances. These measurements also demonstrated an increasing non-crystalline character with decreasing particle size.

Transmission electron microscopy

Typical transmission electron micrographs are shown in Figure 4. The particles were small and platy; a few were hexagonal, although the morphology of most was irregular. The average particle sizes were in the range of 50 nm to 400 nm, Table 1.

Surface characterization of colloidal solids by XPS

A typical XPS survey spectrum of the colloidal solids (results for subfraction IV) is shown in Figure 5a. The spectrum shows a surface dominated by oxygen atoms with a contribution from C, Al and Si atoms. Small quantities of K and Fe were also detected. The atomic concentration (atomic %) of these elements for all four fractions, are tabulated in Table 2. The chemical composition of the surface for each of the fractions was similar. There seemed to be a slight increase in C content as particle size decreased, balanced by a corresponding decrease in O. The Si and Al signals were relatively constant, suggesting that the thickness and morphology of the layer of carbonaceous materials at the surface was similar for all samples. The K and Fe content at the surface was below 1%.

For organic materials, XPS provides information for a surface layer about 7.5 nm thick (Bhatia *et al.,* 1988). Therefore, this technique alone cannot differentiate between organic matter present as either a uniform thin layer completely covering particle surfaces, or discontinuous, patchy coatings of organic matter, where clay minerals are partially exposed. Information about this important aspect of sample characterization may be obtained by secondary ion mass spectrometry (SIMS), and such a study is currently underway.

One interesting result highlighted by the XPS data was the Si/Al ratio of about 1.5, which is higher than the expected ratio for kaolinite and mica (Si/Al ≈ 1). This suggests that the particle surfaces are covered by non-crystalline, silicon rich coatings.

Figure 5b shows an example of the deconvolution of the C1s peak envelope into different functionalities.

Table 3. Carbon distribution results by deconvolution of the C1s peak.

Sample	% of carbon				
	Carbon- carbon	Alcohol, ether	Carbonyl	Carboxyl	Carbonate
I	73.4	5.7	9.6	6.2	5.0
II	76.7	7.6	8.8	3.3	3.6
IV	74.5	7.5	13.2	3.2	1.3

The relative amounts of the C-containing components were calculated and are listed in Table 3. It should be pointed out that, because of the complex chemical nature of the material, the envelope is rather broad. Consequently, the deconvoluted spectra should be considered as semi-quantitative only. However, we believe that the data clearly supports the conclusion that the organic matter is relatively polar because the quantity of C atoms linked to O atoms accounted for 20 to 25% of the total C signal. This information is of interest as nature of organic matter can be an important factor effecting gel formation.

CONCLUSIONS

Kaolinite and mica, with average particle sizes in the range of 50 to 400 nm, are the main crystalline components of the colloidal solids present in oil sand fine tails. The amount of non-crystalline material increases with decrease in particle size. The surfaces of the colloidal solids are contaminated with relatively polar organic matter.

ACKNOWLEDGMENTS

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