

## COMPLEX ACIDS AND THEIR ROLE IN THE STABILITY OF CLAY SLUDGES FROM OIL SANDS

**Key Words**—Bitumen, Carboxyl, Clay Sludge, Illite, Infrared Spectroscopy, Kaolinite, Oil Sands.

The production of large quantities of intractable clay sludges during the hot-water extraction of bitumen from Athabasca oil sand represents a significant problem for this industry, both from a water-demand and an environmental point of view. Several articles (e.g., Camp, 1976; Kessick, 1978) have discussed the implications of this clay-sludge production and have outlined the research currently being undertaken to curtail it.

A previous communication from this laboratory (Kessick, 1979) couches reasons for the poor dewaterability of the settled clay sludges from oil sands in terms of structuring caused by the interaction of residual bitumen and clays (kaolinite and illite). The organic phase that is closely bound to clay particles may be a key link between the essentially hydrophilic clay particles and the bituminous material. This closely bound organic material consists of water-insoluble, carboxylic-type compounds that are complexed with Fe(III). The iron had been previously noticed as a buff-red discoloration on ignition of clay which still contained this closely bound material. The presence of iron was confirmed by examination under an electron microscope with an energy dispersive attachment.

Approximately 0.1 to 0.2 g of bitumen per gram of dried clay sludge can be extracted in a Soxhlet apparatus with methylene chloride. About 40% of this material is present as discrete droplets in the liquid sludge and can be removed by filtering through glass wool. The infrared (IR) pattern (Figure 1a) of this bitumen shows absorption maxima which are generally attributed to aliphatic stretching and deformation vibrations. Iron was not detected. Further extraction with acidified methyl ethyl ketone (1.4% of 2.5 M HCl in MEK), however, removed an additional 0.02 g of organic material per gram of dry, unextracted sludge. This closely bound organic fraction contains about 1.8 mg of ferric iron per gram of dry, unextracted sludge and is amenable to chromatographic fractionation.

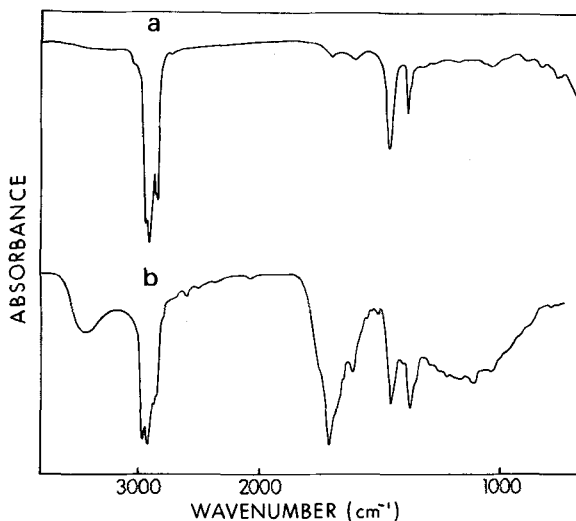


Figure 1. IR spectra of (a) residual bitumen, and (b) low iron-content fraction of closely bound organic material (Fraction 1).

The acid/MEK extract was evaporated down, redissolved in methylene chloride, and placed on a basic alumina (W200, ICN Pharmaceuticals, GmbH) column packed in methylene chloride. Subsequent elution with acid/MEK yielded five distinct fractions. The first fraction was eluted with the solvent front and contained less than 0.5% iron (Table 1). In addition to aliphatic functionality, the IR spectrum of the first fraction (Figure 1b) indicates the presence of hydrogen-bonded hydroxyl ( $3450\text{ cm}^{-1}$ ) and carbonyl ( $1710\text{ cm}^{-1}$ ,  $1620\text{ cm}^{-1}$ ) groups. The  $1710\text{-cm}^{-1}$  absorption most likely corresponds to a ketonic or carboxylic acid carbonyl, whereas that at  $1620\text{ cm}^{-1}$  may indicate a carbonyl group conjugated with a carbon-carbon double bond, hydrogen bonded, or associated with a carboxylate anion or a diketonic structure. The second fraction also contained negligible iron ( $\sim 0.5\%$ ) and had an IR spectrum similar to that of the first. In both spectra the  $1620\text{-cm}^{-1}$  peak is small in comparison to the  $1710\text{-cm}^{-1}$  peak.

The remaining three fractions contained from 5.23 to 9.78% iron. The order of iron content (fraction  $4 > 3 > 5$ ; Table 1) was paralleled by a change in the relative intensity of the carbonyl IR absorptions at  $1580\text{ cm}^{-1}$  and  $1710\text{ cm}^{-1}$ , with the lower frequency band being relatively more intense the greater the iron content (Figure 2a, b, c). This indicates that the iron is held in a chelate structure involving carbonyl oxygens which were originally part of carboxylate or diketonic groups. The absorption of such carbonyl groups would be expected to shift to lower frequencies on chelation.

The IR spectra of fractions 1 and 2 (Figure 1b) are similar to that of the water-soluble constituents of Athabasca bitumen, described by Moschopedis *et al.* (1977) as asphaltic acids. The spectra of fractions 3, 4, and 5 (Figure 2a, b, c) resemble that reported by Schnitzer (1971) for fulvic acid. Schnitzer and Kodama (1972) have shown that this substance is held extremely tightly to internal and external clay (montmorillonite) surfaces containing  $\text{Cu}^{2+}$ , as well as other multivalent cations, including  $\text{Fe}^{3+}$ . It is likely that the same interactions are operative in this case, with the closely bound organic material being held strongly to kaolinite and illite surfaces containing  $\text{Fe}^{3+}$ . This would constitute a form of cross-complexation through metal ions which is also believed to be

Table 1. Chromatographic fractions of clay-bound organic material.

Fraction no.	Wt. residue recovered (g)	Wt. % Fe in residue
1	0.0095	0.19
2	0.0043	0.38
3	0.0045	5.48
4	0.0034	9.78
5	0.0482	5.23

The total residue before chromatography amounted to 0.2244 g. The difference between this weight and the sum of the above represents material eluted from the column between bands and material that remained on the column. It is likely that some decomposition of the complexes occurred during chromatography.

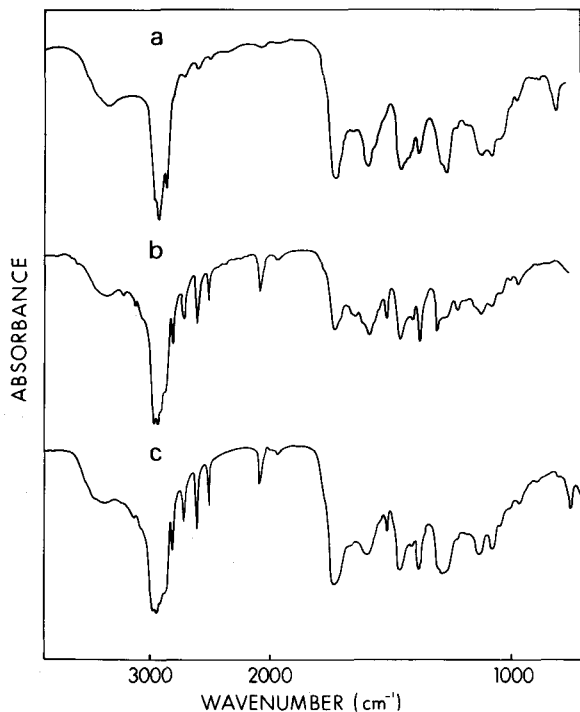


Figure 2. IR spectra of iron-containing fractions of closely bound organic material. (a) Fraction 3, (b) Fraction 4, (c) Fraction 5.

important in binding biological material to surfaces of various kinds (Kessick and Wagner, 1978). In the context of clay slimes from oil sands, the iron appears to be another link in the chain of interactions that promotes structure formation and consequent poor dewaterability.

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