

FRACTIONATION AND CHARACTERIZATION OF SYNCRUDE SLUDGE POND TAILINGS

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Two commercial oil sand extraction plants in Alberta generate vast quantities of tailings slurry as a result of the hot water extraction of bitumen from tar sands. The fine grained sludge component of this waste is the most troublesome because of its stability and poor compaction potential. Considerable quantities of organic matter are strongly associated with the fines contained in these clay slimes. This organic matter is believed to be partly responsible for the intractability of the sludge and it could therefore play an important role in determining the nature of slime stability. In this investigation we have isolated organic matter from the mineral fines present in the Syncrude sludge pond tailings. The sludge was first fractionated into recoverable bitumen, sediment and suspension using an oil phase agglomeration technique. The organic matter, associated with the clay fines present in the suspension, was then concentrated by dissolving the mineral matter in HCl/HF. These fractions have been characterized using elemental analysis and solid state ^{13}C NMR spectroscopy.

INTRODUCTION

Considerable quantities of organic material, insoluble in common organic solvents, are known to be associated with the clay slimes generated as a result of the hot water extraction of bitumen from tar sands (1-4). Most of this insoluble organic matter (IOM) is strongly associated with the mineral fines (5). The IOM appears to play an important role in the stability and incompressibility of the oil sand slimes (1,3). It is believed that the IOM causes the clay particle surfaces to develop a hydrophobic character, allowing particle bridging, by means of residual bitumen, thereby setting up a weak gel structure. A greater part of the IOM has been reported to consist of humic matter (6,7).

In our previous work we have isolated and characterized this insoluble organic matter from a number of oil sands tailings streams obtained from both Suncor and Syncrude plants (3,6). In this investigation we have attempted to fractionate sludge pond tailings from the Syncrude Canada Ltd. plant in Alberta. The clay fraction containing most of the humic matter was separated from the sludge after removing residual bitumen by means of an oil phase agglomeration technique. The IOM associated with the clay fraction was then concentrated by dissolving the mineral matter in acids (3). These fractions have been characterized using elemental analysis and solid state ^{13}C NMR spectroscopy.

EXPERIMENTAL

Residual bitumen from aqueous sludge was recovered as reported in our previous publications (2,4). The general procedure for the fractionation of Syncrude sludge is shown in Figure 1. After removing bitumen from the sludge the aqueous phase was transferred into a 500 ml beaker and the contents were allowed to settle by gravity for one week. The suspension was decanted off and the water evaporated to obtain dry solids. The organic matter associated with the latter solids was concentrated using an acid dissolution scheme reported previously (3). The organic concentrate thus obtained was extracted with 0.5M-NaOH in order to obtain the humic acid fraction.

The procedures for elemental analyses and NMR measurements have been reported previously (3,6).

RESULTS AND DISCUSSION

About half of the emulsified bitumen present in the sludge was recovered, using Suncor coker feed bitumen as the collector in a grease kettle. This result compares with recoveries of over 90% achieved in our previous work with Suncor sludge and other tailings streams (2,8). In our previous investigations we had used more viscous oils, such as reduced still bottoms, as collectors. It is therefore possible that the poor recovery of bitumen in the present investigation was caused by the lower viscosity of the bitumen compared to reduced still bottoms. The quality and yield of the oil phase solids was also poor compared with our previous investigations.

Partial removal of residual bitumen improved the settling behaviour of the sludge to the extent that about 50% of the solids gravity settled during one week. However, no further improvement in the settling behaviour of the suspension was observed even after an additional month of observation. In previous tests on various tailings streams from tar sands processing (2) complete settling of the solids had been observed after similar treatment. Incomplete removal of organic matter, especially the humic matter associated with the mineral fines could be one reason for this difference. Some compositional differences in the Syncrude Sludge and other tailings streams studied previously could also be responsible. Further work is in progress in order to elucidate this difference; the findings will be reported at a later date.

The organic matter associated with the mineral fraction of the non-settling portion of sludge was concentrated using an acid dissolution scheme reported previously, (3). A major portion of the mineral matter dissolved in HF, as indicated by the low ash content of the resulting organic concentrate.

The elemental compositions of humic matter fractions as well as of the total organic matter associated with the mineral fines are given in the Table I. Elemental analyses were obtained using standard methods. The elemental compositions of a typical sludge pond bitumen and asphaltenes sample are included for comparison (3). Carbon analyses were corrected for carbonate carbon to determine the true organic carbon content. No corrections were applied for hydrogen, nitrogen and sulfur analyses. These analyses thus reflect total rather than solely organic content. Oxygen was determined using the standard difference method. The accuracy of these oxygen results is limited owing to the possibility of large errors because of the high mineral content of these samples.

Total organic matter associated with untreated dried sludge, OPS, Solids-I and II, should be similar to the organic matter associated with solids-VI except that the former has a considerably higher ash content than the latter. The elemental compositions of these fractions should therefore be comparable. However, the elemental composition of the organic matter associated with solids-

VI was significantly different to the elemental composition of the total organic matter associated with the other fractions, with the major differences lying in the carbon and oxygen contents of these fractions. The carbon content of the organic matter associated with Solids-VI is approximately double that of the other fractions. This suggests incomplete combustion, and hence underestimation of carbon, in the presence of large amounts of mineral matter. As oxygen was determined by difference underestimation of carbon results in the overestimation of oxygen in these samples. Unusually high H:C ratios for dried sludge, Solids-I and Solids-II indicates a significant contribution from inorganic hydrogen such as of water of hydration of clay minerals associated with these samples. These results demonstrate the importance of ash reduction for the accurate determination of elemental compositions of the organic materials associated with inorganic or mineral matter.

The elemental composition of the organic matter associated with Solids-VI is also different from that of the humic matter fractions. The former has a higher carbon and hydrogen content and lower oxygen content compared to the latter. Organic matter associated with Solid-VI also has a lower ash content than the humic matter and humin fractions. These differences result from the presence of significant (~ 50%) quantities of free bitumen remaining with the organic matter associated with Solids-VI.

The elemental compositions of the humic matter, humic acid and humin fractions was essentially the same except for the nitrogen and sulfur content. Humic acid has a higher nitrogen level compared with the humin fraction, which in turn, has a higher sulfur content than humic acid. Carbon and hydrogen contents of the humic acid were slightly higher than that of the humic acids extracted from oil sands (6). Nitrogen and sulfur contents of humic acid were in the same range as those reported for oil sands humic acid. The oxygen content of all three humic matter fractions appear to be lower than any values published in the literature to date (3,6,9). Small amounts of fluoride were detected only in the Solids-VI and humic matter fractions. The presence of these small amounts of fluoride in the humic matter fractions and its absence in the humic acid and humin fractions, obtained by extraction with NaOH, suggests that the halogen might not have been incorporated into the organic matter during acid dissolution of mineral matter. A more likely scenario is that strongly adsorbed fluoride was washed away during extraction with NaOH.

The average elemental compositions of humic matter fractions from Syncrude sludge have a greater similarity to that of the solvent extractable humic acids from Australian brown coal (10) and benzene/methanol extracts from oil phase solids reported previously (3), than to alkali extractable humic acids. This suggests that a significant portion of the organic matter associated with the mineral solids in Syncrude sludge pond tailings might be of a non-humic nature. Although it is difficult to predict the exact origin of this organic matter, oxidized bitumen or asphaltene complexed to the clay minerals could be one possibility.

¹³C NMR Spectra. The CP/MAS-¹³C NMR spectra of the strongly bound organic matter associated with the mineral fines fraction of Syncrude sludge pond tailings, and a sample of humic acid extracted from these fractions, are shown in Figure 2. The spectra show only bands rather than sharp peaks. However, the resolution is much better than for the spectra of adsorbed organic matter associated with heavy metal minerals reported previously (3). Treatment of Solids-II with 6N HCl dissolved a greater portion of iron and manganese causing carbon enrichment. This resulted in a considerable improvement in resolution, as demonstrated by the spectrum of solids-III compared to the spectrum of Solids-II. The samples of humic acid and humin were dried on a filter paper. While removing the samples with a spatula, fine fragments of filter paper inevitably

contaminated the sample. The signals in the 70-100 ppm region in the spectra of humic acid and humin result from the cellulose-related resonance of this filter paper impurity (11). The interpretation of the ^{13}C NMR spectra is based on published data on humic substances and coal related materials (3,10-12).

The presence of a broad range of aliphatic compounds in all the spectra is indicated by the resonance in the 10-50 ppm range. The large peak at ~30 ppm results from the presence of a number of repeating polymethylene units in the humic macromolecules. The presence of two sharp shoulders at ~14 and 20 ppm in all spectra except that of Solid-II, indicates the presence of long-chain-terminating methyl groups.

Although carbohydrates have been identified as major components of some sedimentary humic acids (3,13), no noticeable resonances were observed in the 50-100 ppm region. It may be implied that the carbohydrates have been removed during acid treatment.

All spectra show strong resonance in the 110-160 ppm region, characteristic of aromatic carbons and olefinic carbons. However, only the humic acid sample has a distinct signal around 175 ppm which could be assigned to carboxylic, amide or ester carbons. It has been suggested that humic acids are structural equivalents of humin that have been oxidized, resulting in the introduction of carboxyl groups. The absence of carboxyl carbon resonance in the spectrum of the humin fraction is thus understandable. However, the absence of this resonance in the spectra of Solid-II, Solid-III, Solid-VI and humic matter fractions is puzzling, because these fractions contain composite organic matter including humic acid. As humic acid had the lowest ash content of all the fractions, it is possible that the mineral matter associated with the fractions interferes with the detection of carboxyl carbons.

The humic matter and humin spectra were very similar and resemble those obtained for asphaltenes, whereas the humic acid spectrum is similar to spectra published elsewhere for humic materials. Given the very similar nature of the chemical analyses for humic matter, humin and humic acid, it should be considered that the ^{13}C NMR spectrum may not be representative of all the organic matter present, especially for high ash samples. This could be due to specific interactions of humic fractions with mineral components.

CONCLUSIONS

1. Partial removal of residual bitumen from Syncrude sludge pond tailings improved its settling behaviour to the extent that about 50% of the solids gravity settled in one week. However, there was no further improvement in the settling of the remaining solids.
2. Insoluble organic matter associated with the mineral matter from the non-settling portion of the sludge was concentrated by dissolving the mineral matter in HCl/HF. This resulted in significant improvements in the elemental analysis results for the insoluble organic matter.
3. The elemental composition of the insoluble organic matter is different from that of oil sands humic acids. Elemental analysis results indicate a similarity of this organic matter to the solvent extractable humic acids from Australian brown coals and benzene/methanol extracts from oil phase solids reported previously. These results suggest that a significant portion of the organic matter associated with clay minerals from Syncrude sludge may be non-humic, possibly oxidized bitumen or asphaltenes.

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Figure Captions

Figure 1. Flowsheet for the fractionation of aqueous sludge.

Figure 2. CP/MAS-¹³C NMR spectra of various fractions from Syncrude sludge pond tailings shown in Figure 1.

Table 1. Elemental Analyses (in percentage of dry, ash free basis)

Sample*	Wt. %							Atomic Ratios	
	Ash	C	H	N	S	F	O**	H:C	O:C
Untreated dried Sludge	85.0	37	8.7	0.3	7.3	-	46.7	2.82	0.95
OPS	70.0	45	3.3	-	-	-	51.7	0.88	0.86
Solids-I	87.4	31.8	7.5	-	6.8	-	53.9	2.83	1.27
Solids-II	83.7	35.3	8.7	1.5	5.8	-	48.7	2.95	1.03
Solids-VI	11.8	75.9	7.2	1.0	4.1	0.5	11.3	1.4	0.11
Humic Matter	24.2	71	5.8	1.1	4.8	0.5	16.8	0.99	0.18
Humic Acid	7.6	70.4	5.7	1.4	2.8	-	19.7	0.97	0.21
Humin	28.6	69.1	6.5	0.7	5.6	-	18.1	1.12	0.20
Sludge Pond Bitumen ***	1.0	81.1	8.9	0.6	6.0	-	3.4	1.32	0.03
Asphaltenes from Sludge Pond Bitumen***	5.3	80.2	8.0	1.2	7.9	-	2.7	1.20	0.03

* Key to sample No. found in Figure 1

** By Difference

*** Ref. 3

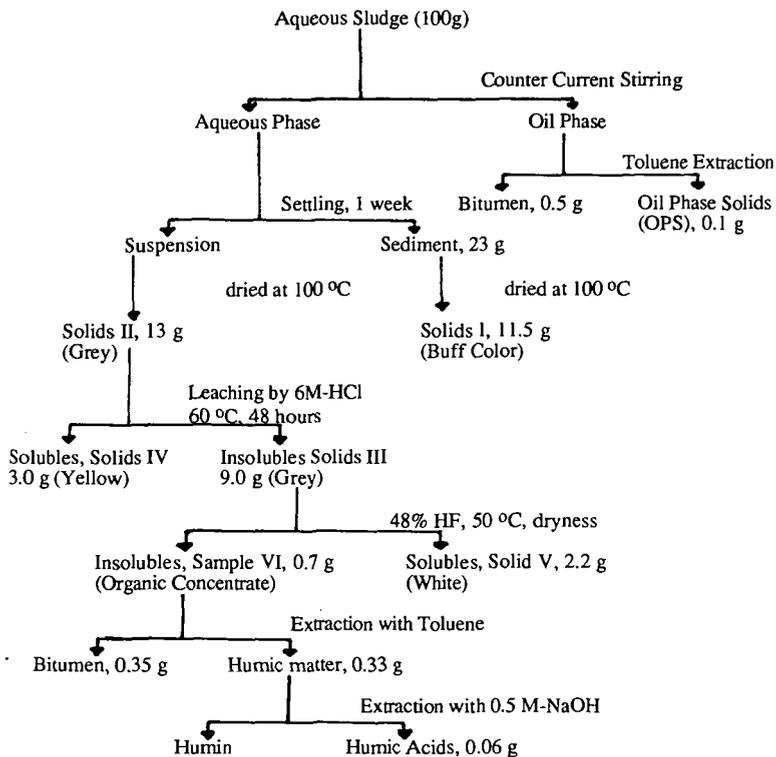


Figure 1. Flow sheet for the fractionation of aqueous sludge.

