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Characterization of insoluble organic matter associated with non-settling clay minerals from Syncrude sludge pond tailings*

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Hot water extraction of bitumen from Alberta oil sands generates large quantities of tailings slurry. The fine grained sludge component of this waste is the most troublesome because of its stability and poor compaction potential. Dispersed bitumen, and organic matter that is insoluble in common solvents (IOM), are 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 behavioural characteristics of oil sands slimes. In this investigation the settling behaviour of the sludge was studied after removal of emulsified bitumen by an oil phase agglomeration technique. After partial removal of bitumen the sludge was fractionated into settling and non-settling fractions. The insoluble organic matter associated with the clay fines present in the non-settling portion of sludge was concentrated by dissolving the mineral matter in HCl/HF. These fractions were analysed using elemental analysis and solid state ^{13}C n.m.r. spectroscopy. The elemental analyses were discussed in terms of a van Krevelen diagram by plotting H/C atomic ratios against O/C atomic ratios. N.m.r. data were used to calculate the aromaticities of the various organic fractions. Based on the n.m.r. data, it is suggested that the IOM associated with sludge solids is derived from the parent oil sand feed.

The hot water process used by Suncor and Syncrude to extract bitumen from Athabasca oil sands produces large volumes of tailings[1-4]. These tailings consist mainly of sand and an aqueous dispersion of various clay minerals, some of which are associated with significant amounts of insoluble organic matter (IOM)[1,5-8]. The sand setttles rapidly from the tailings and presents no real disposal problem; in fact it is used to build the containment dykes for the clay sludge fraction, which shows limited tendency to dewater and consolidate, even when subjected to mechanical dewatering procedures[2]. The inevitable buildup of these partially settled clay sludges presents not only an environmental problem but also a significant repository for non-recycleable water.

The reason for the intractability of the clay slimes has been the subject of considerable study[7-13]. Based on the results of published work, it is generally believed that the interaction of organics with clay minerals is important in determining the nature of oil sand slimes[1,5,7]. It is known[14] that IOM can impose a hydrophobic character on clay surfaces allowing interparticle bridging by residual bitumen to set up a weak gel structure. A greater part of this IOM has been shown to consist of humic matter[7,8].

Relatively little information is currently available concerning the association between organic matter and the solids phase in oil sands. In previous work[5] a heavy metal mineral fraction was selectively recovered from Suncor tailings sludge using an oil phase agglomeration technique. The IOM associated with this fraction was then concentrated by mineral dissolution with HCl/HF.

These fractions were characterized using elemental analysis and solid state ^{13}C n.m.r. spectroscopy. In this investigation, Syncrude tailings pond sludge was treated in the same way. The data are discussed in terms of the chemical structure of the IOM and its geochemical significance. This study should provide insight into the contribution of IOM to the intractable nature of oil sand slimes in existing tailings ponds.

EXPERIMENTAL

Description of sample

Aqueous sludge from the 17 m level of the Syncrude tailings pond was pumped into 200 l plastic drums[15]; each drum was inverted five times (with a barrel tipper) before being divided among a number of 20 l pails, which were then stored in a cooler at $\approx 10°C$. Sub-samples were removed from the pails after thorough mixing with a wooden broom handle, and placed in 1 l plastic bottles. The results presented in this report were obtained on these sub-samples. Before further sub-sampling, each sample was thoroughly mixed on a roller mill, then stirred with a spatula. The physicochemical properties[16] of sludge are presented in *Table 1*.

Recovery of bitumen

A counter-rotating stirring device (grease kettle) was used to separate free and emulsified bitumen from the sludge[17]. Suncor coker feed bitumen, obtained from the Alberta Research Council sample bank, was applied to the stirring vanes of the grease kettle to act as the collector phase. The weight of the bitumen used for this purpose was determined by difference. Sodium silicate solution

Table 1 Physicochemical properties of Syncrude sludge

Property	Value
pH at 17.8±0.5°C	7.83±0.03
Conductivity (mS cm^{-1})	1.6 ±0.01
Total solids [GRAV] (wt%)	26.6 ±0.1
Bitumen [OWS] (wt%)	0.9 ±0.05
Solids [OWS] (wt%)	25.61±0.14
Density (calculated) (g ml^{-1})	1.19
Solids <44 μm (%)	99.2 ±1.0
Solids <22 μm (%)	94.9 ±1.9
Solids <11 μm (%)	83.7 ±2.1

was used to bring the sludge to a pH of about 10. Stirring was started to allow the oleaginous phase to collect on the stirring vanes. During the kneading process, the 'oil' was washed several times with fresh water at pH 10 to remove occluded, water-dispersible, finely divided mineral particles. After ≈12 h, the organic phase was separated from the aqueous phase. The organic phase was extracted with toluene, leaving a residue in the form of a hydrophobic, dark powder or 'oil phase solid', amounting to 0.1 wt% of the original sludge.

Fractionation of aqueous phase

The general procedure for the fractionation of Syncrude sludge is shown in *Figure 1*. The aqueous phase from this separation was transferred into a 500 ml beaker, and the contents were allowed to settle for one week. The suspension was then decanted off to leave the settled solids. Water was evaporated at 100°C to obtain the mineral solids from the supernatant liquor. The dried solids fraction from the suspension was demineralized using HCl and HF to concentrate the organic matter associated with the mineral fines[5]. The residual organic matter fraction, after further toluene extraction, was leached with 0.5 M NaOH under nitrogen at 60°C for one week to extract humic acids. The NaOH insoluble fraction was assumed to be humin.

Elemental analysis

C, H and N analyses were performed; sulphur was analysed as total sulphur using X-ray fluorescence spectroscopy, and oxygen was determined by difference. Inorganic content was determined by low temperature ashing at 400±10°C.

N.m.r. measurements

The solid state ^{13}C n.m.r. spectra were obtained either at 45.28 MHz or at 75.47 MHz, using a magic angle spinning (MAS) probe. For all samples a cross polarization technique was used with a contact time of 2–3 ms, and a repetition time of 1 s. Chemical shifts were determined by substitution relative to tetramethylsilane (TMS). Each spectrum was the Fourier transform of 1500–40000 free induction decay curves.

RESULTS AND DISCUSSION

The flow sheet in *Figure 1* describes the general procedure and gives yields for the recovery of the bitumen fraction and the amount of insoluble organic matter (IOM) associated with the non-settling portion of the clay minerals from Syncrude sludge pond tailings. About half of the bitumen present in the sludge was recovered by

absorption into Suncor coker feed bitumen in a grease kettle mixer. This compares with over 90% bitumen removal achieved in previous work with Suncor sludge and other tailings streams[18,19]. In previous investigations more viscous oils, such as reduced still bottoms, were used as collectors; it is therefore possible that the poor recovery of bitumen in this case was owing to the lower viscosity of bitumen compared with reduced still bottoms. The quality (in terms of organic content and yield) of the oil phase solids obtained from Syncrude pond sludge was also poor compared with those obtained from other tailings streams.

Partial removal of the residual free bitumen improved the settling behaviour of the sludge to the extent that about 50% of the solids gravity settled in just one week. The sediment obtained had a pulp consistency of ≈50% compared with 29% for the untreated sludge. However, no further improvement in the settling behaviour of the suspended solids was observed even after an additional three weeks of standing. This is contrary to previous results for various tailings streams from oil sands plants, in which complete solids settling was observed in a relatively short time. Incomplete removal of the organic matter, especially the insoluble organic matter associated with the mineral fines, could be one reason for this difference. Some compositional differences between Syncrude sludge and the other tailings streams studied previously could also be responsible for the different settling behaviours after removal of organic mineral complexes.

The organic matter associated with the mineral fraction of the non-settling portion of treated sludge was concentrated using an acid dissolution scheme reported previously[5]. A major portion of the mineral matter could be dissolved in HF, as indicated by the low ash content of the resulting organic residue. Elemental compositions of humic matter fractions, as well as of the total organic matter associated with mineral fines, are given in *Table 2*. Elemental analyses were obtained using standard methods. Carbon analyses were corrected for carbonate
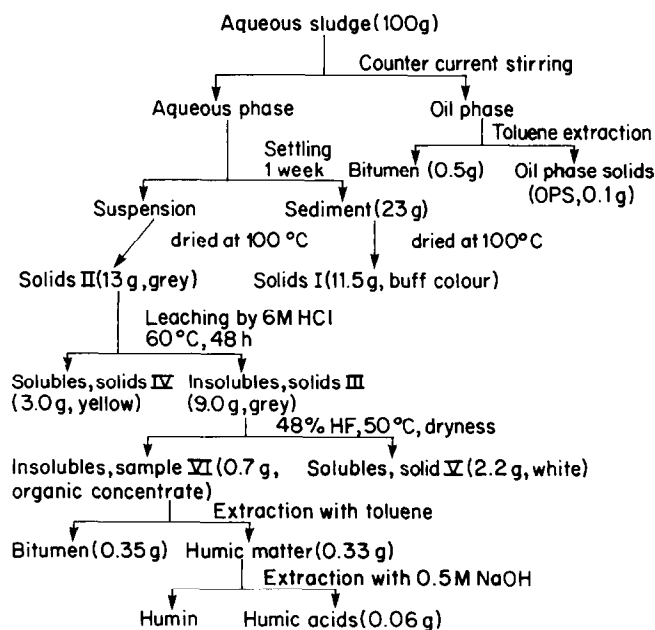

Figure 1 Flowsheet for the fractionation of aqueous sludge

Table 2 Elemental analyses (dry, ash free basis)

Sample[a]	Wt%							Atomic ratios	
	Ash	C	H	N	S	F	O[b]	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 (sediment)	87.4	31.8	7.5	–	6.8	–	53.9	2.83	1.27
Solids II (suspension)	83.7	35.3	8.7	1.5	5.8	–	48.7	2.95	1.03
Solids III (HCl treated solids II)	83.0	52.9	8.06	0.65	ND	–	38.4	2.03	0.54
Solids VI (HF treated solids III)	11.8	75.9	7.2	1.0	4.1	0.5	11.3	1.14	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

[a] Key to sample no. shown in *Figure 1*
[b] By difference
ND = not determined

carbon to determine true organic carbon. No corrections were applied for hydrogen, nitrogen and sulphur analyses, so these analyses reflect total elemental content rather than that associated solely with the organic phase. Oxygen was determined using a standard difference method. The accuracy of the oxygen results was limited, owing to the possibility of large errors resulting from the high mineral content of these samples.

Assuming that acid treatment dissolves only mineral matter without affecting the organic matter, then the elemental composition of the remaining organic matter (on an ash free basis) from the various fractions (*Figure 1*) should be the same. However, considerable variations in the elemental composition of the organic matter associated with various mineral fractions were observed in both the H/C and O/C ratios. Organic matter associated with the untreated dried sludge, OPS, and solids I, II and III had a considerably lower carbon content and higher oxygen content compared with the organic matter associated with solids VI, humic matter, humic acid and humin fractions. Treatment of solids II (suspension solids) with HCl resulted in a ⩾20% decrease in the oxygen content of the organic matter. This change is also reflected in a 50% increase in the carbon content of the organic matter of solids III relative to that of solids II. Oxygen content of the organic matter of solids VI, obtained after treatment of solids III with HF, was only about 23% of the total oxygen content of the organic matter of solids III (feed material). This resulted in a further increase (of ≈43%) in carbon content of the organic matter of solids VI relative to that of solids III.

The elemental compositions (ash free basis) of humic matter, humic acid and humin fractions were different from that of the organic matter of solids VI. The organic matter of solids VI had a higher carbon and hydrogen content and lower oxygen content compared with humic matter, humic acid and humin fractions. The organic matter of solids VI also had a much lower ash content than humic matter and humin fractions. However, these differences could be explained on the basis that this fraction contained the unrecovered free bitumen. On the other hand, humic matter, humic acid and humin fractions contained no free bitumen and consist only of insoluble organic matter.

The elemental composition of composite humic matter, humic acid and humin fractions was essentially the same

except for the nitrogen and sulphur contents. Humic acid had a higher nitrogen content and a lower sulphur content than the humin fraction. Carbon and hydrogen contents of humic acid were slightly higher than those of the humic acids extracted directly from oil sands[7], while the nitrogen and sulphur contents of humic acid were in the same range as reported for oil sands humic acid. The oxygen content of all three humic matter fractions appeared to be the lowest published in the literature to date[5,7,20].

Small amounts of fluorine were detected in the solids VI and the humic matter fraction, but all other fractions were free of halogens. The presence of fluorine in the humic matter fraction, and its absence in the humic acid and humin fractions, suggests that halogens were not incorporated into the organic matter during acid dissolution of mineral matter. The small amounts detected were probably present as strongly adsorbed fluoride that was washed away during extraction with NaOH.

The average elemental compositions of the organic matter associated with humic matter, humic acid and humin fractions, had a greater similarity to those of the solvent extractable humic acids from Australian brown coal[21] and benzene/methanol extracts from oil phase solids[5], than to the alkali extractable humic acids. However, the elemental compositions of the untreated organic matter associated with dried sludge, sediment (solids I) and suspension (solids II) were more like those of fulvic acid and carbohydrate-like materials[20,22].

Although the oxygen content was determined by difference and contained all accumulated errors, the magnitude of the difference in the oxygen contents of various fractions suggests that a substantial amount of oxygen was lost during acid treatment. This was supported by the calculated mass balances, listed in *Table 3*. Treatment of solids II with HCl resulted in almost complete recovery of carbon, but over 40% loss of oxygen. This suggested that some oxygen containing species (such as carbohydrates), were decomposed on HCl treatment, releasing oxygen in forms other than carbon oxides, most probably in the form of water. Treatment of solids III with HF resulted in ≈37% loss of carbon, ≈80% loss of hydrogen, nitrogen and sulphur, and ≈94% loss of oxygen (compared with solids II). This reflects the severity of reaction with HF compared with HCl. The reaction with HF appeared to decompose

Table 3 Total elemental concentrations[a]

Sample	Yield[b]	C	H	N	S	O[c]
Untreated dried sludge	26.6	1.48	0.35	0.013	0.29	1.85
Solids I (sediment)	11.5	0.46	0.11	–	0.10	0.79
Solids II (suspension)	13	0.75	0.18	0.032	0.12	1.16
Solids III (HCl treated solids II)	9	0.73	0.12	0.01	ND	0.67
Solids VI (HF treated solids III)	0.7	0.47	0.04	0.006	0.025	0.07

[a] Calculated as: (percentage of element in the sample × yield)/100
[b] Based on 100 g of sludge, *Figure 1*
[c] By difference
ND = not determined
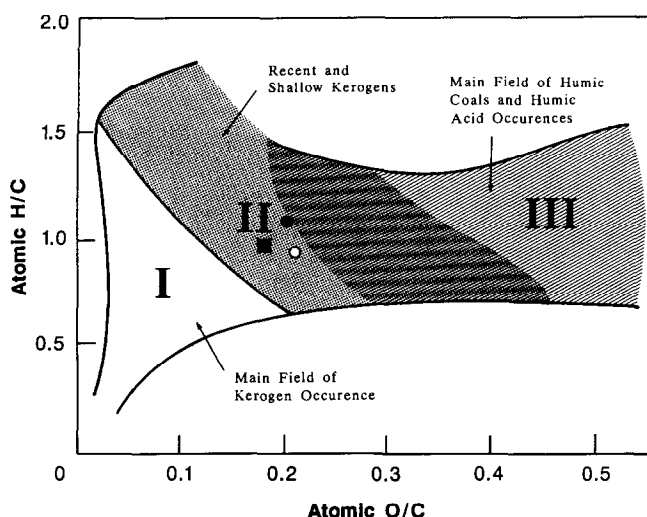
Figure 2 van Krevelen diagram showing the elemental composition of bitumen free, acid treated organic matter fractions: ■, humic matter; ○, humic acid; ●, humin

most of the remaining oxygen containing species. Oxygen was probably lost in the form of a number of volatile species, such as hydrogen, carbon, nitrogen and sulphur oxides. Almost quantitative recovery of carbon after HCl treatment and the lower recovery of carbon after HF treatment suggested that the lower carbon content of the organic matter in dried sludge, OPS and solids I, II and III could not be due to the incomplete combustion of carbon in the presence of mineral matter.

The van Krevelen diagram, which is a graph of atomic H/C versus O/C ratios, provides a useful approach for the characterization of coals, kerogens and humic matter[23,24]. *Figure 2* is a van Krevelen diagram for the bitumen free organic matter fractions (humic matter, humic acid and humin fractions). The evolution paths of kerogens and humic coals are also shown for comparison. It is obvious from *Figure 2* that the data obtained in this work fall in the region of the recent and shallow kerogens. This type of organic matter is usually derived from plants of terrestrial origin, and is rich in polyaromatic nuclei and heteroatomic ketone and carboxylic acid groups[24]. It is not considered to have potential for hydrocarbon generation and usually matures to give coal. It appears to be of comparable maturity to humic coals and is relatively immature when considered in light of its oil generation potential. This organic material has undergone acid treatment and has possibly been decomposed.

[13]C n.m.r. spectra

The CP/MAS [13]C n.m.r. 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 3*. The spectra show only bands rather than sharp peaks. However, the resolution was much better than for the spectra of adsorbed organic matter associated with the heavy metal minerals reported previously[5]. Treatment of solids II with 6M HCl dissolved the major portion of the iron and manganese minerals, resulting in carbon enrichment. Consequently, resolution in the n.m.r. spectra improved, as demonstrated by comparison with the spectra of solids III and solids II. The signals in the 70-100 ppm region in the spectra of humic acid and humin are believed to be an anomaly resulting from contamination of the sample by paper fibres[25] as a result of the samples being dried on filter paper. Interpretation of the [13]C n.m.r. spectra is based on published data on humic substances and coal related materials[5,21,25,26].

The presence of a broad range of aliphatic compounds is indicated in all the spectra by the resonance in the 10-50 ppm range. The large peak at ≈ 30 ppm is due to the presence of a number of repeating polymethylene units in 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. Because of the poor spectral resolution, the presence of carbohydrates in the 50-100 ppm region can neither be confirmed nor ruled
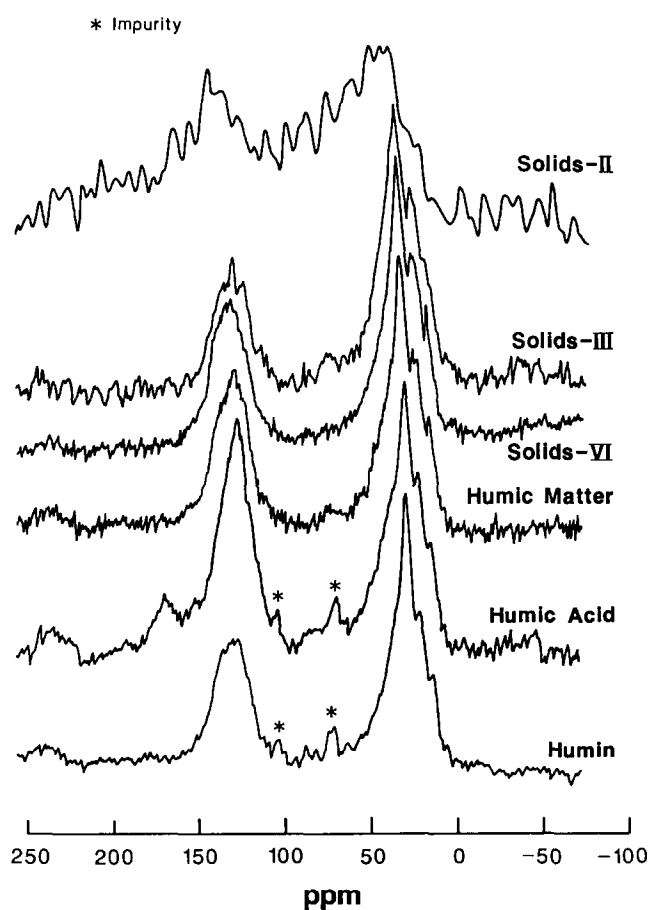

Figure 3 CP/MAS-[13]C n.m.r. spectra of various fractions from Syncrude sludge pond tailings shown in *Figure 1*

Table 4 Assignment of ^{13}C chemical shift ranges

Region	Chemical shift range	Carbon type
A_1	0–50	Aliphatic
A_2	50–110	Aliphatic C—OH, C—OR, carbohydrate
B	110–145	Aromatic C—H, aromatic C—C, alkyl substituted aromatic carbon
C	145–160	Aromatic C—OH, C—OR
D_1	160–190	Acid, ester, COOH, COOR
D_2	190–230	Aldehyde, ketone

out in the n.m.r. spectrum of solids II. However, no noticeable resonance in this region was observed in the n.m.r. spectra of the other fractions. As carbohydrates have been identified as major components of some sedimentary humic acids[5,27] it is probable that these were removed during acid treatment to dissolve inorganic material. This explanation is consistent with the elemental analysis results.

All spectra show a strong resonance in the 110–160 ppm region, characteristic of aromatic carbons, olefinic carbons and phenolic carbons. However, only the humic acid sample has a distinct signal around 175 ppm, due 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[26]. The absence of carbonyl 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 the humic matter fractions is puzzling, because these fractions contain composite organic matter including humic acid.

The integration of each spectrum was carried out by division into regions and subsequent determination of their individual areas[5]. The limits were chosen according to Verheyen et al.[21] and the four regions are listed in *Table 4*. *Table 5* lists the quantitative distribution of these regions. The aromaticities (f_a), calculated by integrating peak areas assigned to aromatic carbons (100–160 ppm) and normalizing to total area less the area of carboxyl carbons, are also listed in *Table 5*.

The n.m.r. parameters calculated from the spectra of various fractions should be comparable if the acid treatment used for the dissolution of mineral matter does not affect the composite organic matter associated with these fractions. However, a comparison of the data in *Table 5* indicates a considerable variation, especially in the aromaticity values. The aromaticity of the composite organic matter associated with solids II, III, VI and humic matter is lower than that of the humic acid and humin fractions. Aromaticity values for the organic matter associated with solids II and III are comparable, but are the lowest of all the fractions. In spite of the significant improvement in spectral resolution after treatment with dilute HCl, the aromaticity values remain unchanged. However, treatment with HF resulted in a significant increase in the aromatic content of the material. This suggests that the organic material is attacked by HF, resulting in the conversion of a portion of aliphatics to aromatics, and/or that organic carbon is underestimated because of the interference from the mineral matter associated with the organic matter.

The aromaticity of the humin fraction was the highest

of all other fractions except humic acid. This fraction was obtained by extracting NaOH soluble material (humic acid) from the humic matter fraction. The mineral matter associated with these fractions (humin and humic matter) is expected to be essentially similar. This makes the explanation of the underestimation of aromaticity even more difficult. Because of these limitations, a certain amount of caution must be exercised in the interpretation of aromaticity and related n.m.r. data.

The aromaticity of the humic acid fraction is comparable with previously reported[7] values for various humic matter fractions from oil sands. This suggests that the maturity was comparable with that of subbituminous coal. The similarity between the two humic materials (oil sands and sludge pond tailings) suggests that in terms of aromaticity the sludge-derived material might have come from the parent oil sand feed rather than being formed during oil sands processing or storage of the sludge.

The humic matter and humin spectra were very similar, and resemble those obtained for asphaltenes, whereas the humic acid spectrum was similar to spectra published elsewhere for humic materials[7]. Given the very similar chemical analyses for humic matter, humin and humic acid, it should be considered that the [13]C n.m.r. spectra may not be represenative 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 $\approx 50\%$ of the solids gravity settled in one week. However, there was no further settling of the remaining solids even after one month.

2. Insoluble organic matter associated with the minerals from the non-settling portion of the sludge was concentrated by dissolving the minerals in HCl/HF. This resulted in significant improvements in the n.m.r. spectra for the insoluble organic matter.

3. Acid treatment decomposed most of the oxygen containing species associated with the organic matter of the various fractions investigated. This resulted in a considerably lower oxygen content of the acid treated materials relative to untreated material. However, there was no indication of halogen incorporation into the organic matter.

4. The average elemental composition of the organic matter fractions associated with acid treated solids, was closer to those of the solvent extractable humic acids from Australian brown coal and benzene/

Table 5 Quantitative [13]C n.m.r. data for humic acid and related materials

Sample[a]	Area of total spectrum (%)					f_a
	$A_1 + A_2$	B	C	D_1	D_2	
Solids II	68	23	9.0	–	–	0.32
Solids III	73.2	26.4	0.4	–	–	0.30
Solids VI	60.3	37.2	2.5	–	–	0.40
Humic matter	60.8	36.8	2.4	–	–	0.40
Humic acid	44.3	44.4	3.9	7.4	–	0.52
Humin	55.7	42.1	2.2	–	–	0.44

[a] Key to sample no. shown in *Figure 1*

methanol extracts from oil phase solids than to that of the alkali extractable humic acids. However, the elemental composition of the untreated organic matter fractions resembled those of fulvic acids and carbohydrate-like materials.

5. Acid treated organic matter fractions fell in the region of recent and shallow kerogens when plotted on a van Krevelen diagram.

6. CP/MAS ^{13}C n.m.r. results indicated that organic carbon in certain samples was underestimated, possibly because of the interference from the mineral matter present.

ACKNOWLEDGEMENTS

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