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CHARACTERIZATION OF SOLVENT-INSOLUBLE ORGANIC MATTER  
ASSOCIATED WITH MINERAL MATTER FROM OIL SANDS\*

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ABSTRACT

Considerable quantities of insoluble organic matter (IOM) are known to be associated with certain solid fractions found in oil sands. This organic matter is believed to be partly responsible for the intractability of the sludge generated by the hot water process used for the extraction of bitumen from Alberta oil sands. In previous investigations we had attempted to enrich the insoluble organic matter by dissolving the minerals in concentrated HCl/HF mixtures. As a result of this severe acid treatment the inorganic material is decomposed, but the organic constituents are also likely to undergo significant changes. In the present work we have used a milder HCl/HF treatment for mineral dissolution. The results from the current investigation are compared with the results of the previous study to assess the chemical alterations of the organic matter resulting from the two treatments.

The fractions obtained from the mild acid treatment were analyzed using solid state  $^{13}\text{C}$  NMR spectroscopy and elemental analysis. Latter results have been discussed in terms of a van Krevelen diagram which is derived by plotting the atomic H/C ratios against O/C. The NMR data were used to calculate the aromaticities of the various organic fractions. Based on the elemental compositions and the NMR data, it is suggested that the IOM associated with the sludge solids is derived from terrestrial sources.

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## INTRODUCTION

The application of  $^{13}\text{C}$  cross polarization magic-angle spinning nuclear magnetic resonance (CPMAS-NMR) for characterization of the organic material associated with mineral matter has been limited because low C content and relatively high amounts of paramagnetic minerals degrade spectral quality, Preston et al. (1989). Several approaches have been used in attempts to enhance the quality of CP/MAS spectra of organic matter associated with soils. Wilson et al (1987) found that dithionite treatment to remove Fe resulted in some improvement in the  $^{29}\text{Si}$ ,  $^{27}\text{Al}$  and  $^{13}\text{C}$  solid state spectra of the  $<0.2\mu\text{m}$  fraction of mineral soil. Oades et al (1987) also found that dithionite enhanced S/N and resolution of  $^{13}\text{C}$  spectra of particle-sized and density fractions. Arshad et al.(1988) used magnetic separation and organic matter concentration by floatation/sedimentation to obtain fractions with more informative spectra; treatments with Na dithionite or stannous chloride were less successful for their samples.

Dilute aqueous HCl/HF at room temperature has been routinely used to purify humic matter, Preston et al. (1989), Calderoni et al. (1984), Goh (1970) and Almendros (1987). Recently, we used a mixture of HCl/HF for the de-ashing of the insoluble organics associated with certain minerals found in oil sands, Majid et al. (1986, 1990, 1991). ~~The acid concentration and the temperature used in this~~ study were much higher than normally used for the purification of humic matter, Calderoni et al. (1984), Goh (1970) and Almendros (1987). The objective of the current study was to investigate whether the milder de-ashing conditions, reported recently for the purification of humin, Preston et al. (1989), could be applied to concentrate the organic matter associated with oil sands solids. The results from the studies using mild or severe extraction conditions have been compared in order to assess any chemical alterations that might have occurred to the organics during de-ashing procedure.

## EXPERIMENTAL

### Sample Description and Isolation of Organic Rich Solids Fraction by Oil Phase Agglomeration

The sample of sludge used in this work was supplied by Syncrude Research Ltd.; it had been pumped from the seventeen metre level of their tailings pond into

200 L plastic drums, Danielson (1989). Each drum was subsequently mixed, subdivided into 5L plastic jugs and stored in a cooler at 10°C. Before further subdivision, each jug was shaken vigorously by hand. A mineral matter fraction containing insoluble organic matter (IOM) was separated from this sub-sample of Syncrude Sludge Pond tailings by an oil agglomeration procedure reported previously, Majid et al. (1990).

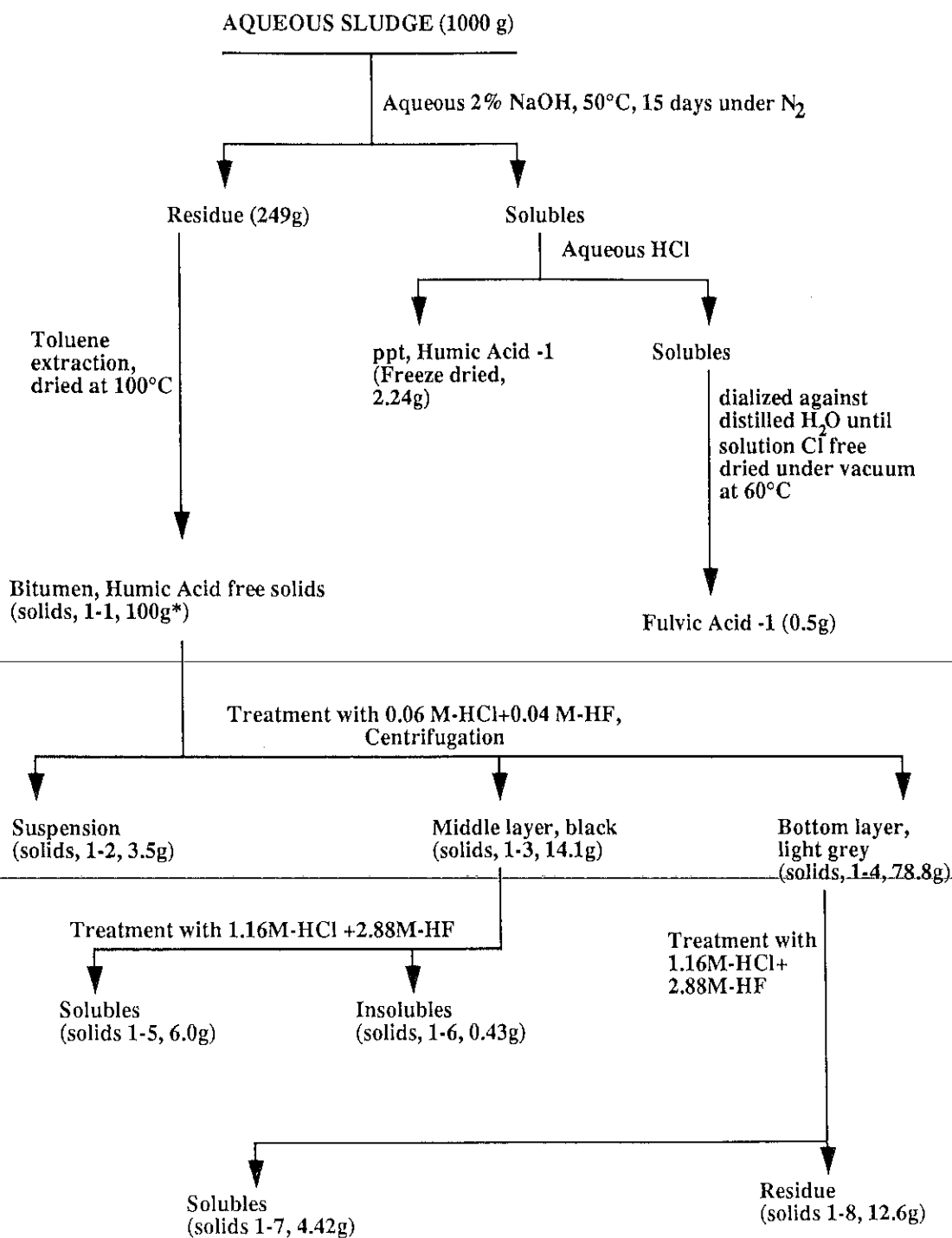
#### HCl/HF Treatment Procedure

The general procedure for mineral dissolution and IOM enrichment is shown in Figure 1. A sample (100g) of bitumen and humic acid free solids separated from Syncrude sludge (solids 1-1), was added to dilute HCl/HF (250 mls of 0.06 M HCl and 0.14 M HF) in a screw capped teflon bottle. The bottle and contents were agitated on a reciprocal shaker at slow speed for two hours. At the end of this time the contents of the bottle were centrifuged at ~200xG for 6 hours. Three layers separated: a top layer of dark brown suspension, followed by a layer of black solids and a bottom layer of light grey solids. The suspension was decanted into a teflon beaker and evaporated to dryness on a hot plate at the lowest setting. The dried residue was washed with distilled water until the pH of the slurry was neutral. The residue slurry was then redried to constant weight under vacuum at 80°C to give solids 1-2.

The solid residue layers from the original treatment with HCl/HF were subjected to two more extractions with dilute HCl/HF. The colorless supernatants obtained after centrifuging the suspensions from the second and third acid treatments were discarded. The two differentiated solid layers obtained after centrifuging the third acid treatment were separated using a spoon spatula to give solids 1-3 and 1-4. These fractions were contacted separately with more concentrated HCl/HF solution (1.16 M HCl and 2.88 M HF) at room temperature for 90 days. The residual end products from this treatment were washed with distilled water until the pH of the filtrates were neutral. The solids were then dried to constant weight under vacuum at 80°C. The final extracted dried layers were designated as solids 1-6 and 1-8 respectively.

#### Elemental Analysis

Carbon, hydrogen and nitrogen analysis were performed using a Perkin-Elmer model 240 CHN analyzer. Carbonate carbon was measured titrimetrically



\* Represents amount taken for further treatment and not actual yield.

Figure 1. Flow sheet for the fractionation of aqueous sludge and mild HCl/HF acid treatment scheme for solids.

after acid digestion. Organic carbon was then determined by subtracting carbonate carbon from total carbon. Sulphur was analyzed as total sulphur using x-ray fluorescence spectroscopy. Oxygen was determined by difference. The inorganic content was determined by prolonged low temperature ashing at  $400\pm 10^{\circ}\text{C}$ . Heavy metals were determined using quantitative inductively coupled plasma atomic emission spectroscopic analysis (ICP-AES), Fassel (1979).

#### NMR Measurements

The solid state  $^{13}\text{C}$  NMR spectra were obtained at 75.47 MHz on a Bruker MSL-300 spectrometer, using a magic angle spinning (MAS) probe. For all samples a cross polarization technique was used with a contact time of 2ms, and a repetition time of 1S. Chemical shifts were determined by substitution relative to tetramethylsilane (TMS). Each spectrum was the Fourier transform of 1500-40,000 free induction decay curves.

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### RESULTS AND DISCUSSION

The flow sheet in Figure 1 describes the general procedure for the fractionation of sludge and the acid demineralization scheme used for the enrichment of organic matter. In the concentrated acid treatment, Majid et al. (1986,1991), only one solid fraction had been separated compared to the three fractions of organic concentrate obtained in the present investigation. The separation into layers was based on density separation as a result of the centrifugation of the slurry after dilute HCl/HF treatment.

Table I lists mass balance data and ash content of the various fractions. The data for organic concentrates, obtained from the concentrated acid treatment scheme reported previously, Majid et al. (1986, 1990), is also included for comparison. Consideration of these data leads to the following conclusions:

1. Dilute acid treatment (0.06 M HCl and 0.14 M HF) results in a 3.6% weight loss, as indicated from the sum of the weights of the fractions after extraction. Although the degree of ash rejection in this step was poor it did prevent vigorous reactions as a result of the hydrolysis of carbonate minerals during subsequent treatment steps with more concentrated acids.

TABLE I  
Material Balance Data

Samples *	Ash w/w %	Starting wt. (g)	Mass balance (w/w %)			Ash Content of Insoluble fraction (w/w %)
			Solubles	Insolubles	Loss	
Solids 1-1 **	92.5	100	?	96.4	3.6	88.3±2.8
Solids 1-3 ***	85.5	14.1	42.6	3.1	54.3	5.7
Solids 1-4 ***	91.1	78.8	56.1	16.1	27.8	12.4
OPS (Majid 1986)****	79.7	100	15.6	24.7	59.7	35.2
Non-Settling Clay (Majid et al. 1990)****	83.7	13	43.2	2.1	54.7	28.6

\* Key to sample No. found in Figure 1, unless stated otherwise.

\*\* Dilute acid treatment (0.06 M HCl and 0.14 M HF).

\*\*\* Mild acid treatment (1.16 M HCl and 2.88 M HF).

\*\*\*\* Concentrated acid treatment (10.2 M HCl and 24 M HF).

2. A slightly more concentrated HCl/HF (1.6 M HCl and 2.88 M HF) dissolved an additional significant amount of mineral matter from both solids 1-3 and solids 1-4. However, the amount of organic concentrate obtained from solids 1-4 was almost five times more than from solids 1-3. The weight loss for solids 1-3 due to the evolution of gaseous products such as SiF<sub>4</sub>, CO<sub>2</sub>, and CO, resulting from the reaction of silicious matter and carboxylates with acids, was twice that obtained from solids 1-4. Also, the organic concentrate from solids 1-4 had a higher ash content than the organic concentrate from solids 1-3. These results can be explained on the basis of higher organic matter content of solids 1-4 as compared to solids 1-3. The higher organic matter coating on solids 1-4 will make the acid penetration more difficult for these solids. As a result the reaction between acids and mineral matter in solids 1-4 will be much slower than the corresponding reactions of solids 1-3.
3. Comparison of the results of this investigation with those from the previous work indicates that the organic concentrates obtained using mild acid treatment

TABLE II  
Elemental Analysis (Dry, ash free basis)

Sample ID*	Yield % of wet sludge	Ash (% of total solids)	Elemental Analysis					Atomic Ratios	
			C	H	N	S	O***	H:C	O:C
Humic Acid -1	0.22	8.9	71.3	6.8	1.2	2.8	17.9	1.14	0.19
Fulvic Acid -1	0.05	87.4	16.7	12.5	1.9	2.6	66.3	8.98	2.98
Solids 1-1	24.9	92.5	26.8	11.7	2.4	3.5	55.6	5.2	1.56
Solids 1-2	0.87	76.2	19.3	4.4	0.2	2.6	73.5	2.74	2.85
Solids 1-3	3.5	85.5	20.3	7.9	1.2	1.8	68.8	4.67	2.54
Solids 1-4	11.0	91.1	19.1	9.6	---	2.9	68.4	6.0	2.69
Solids 1-6	0.1	5.7	70.3	5.7	1.3	3.8	18.9	0.97	0.20
Solids 1-8	3.1	12.4	55.8	4.0	1.0	5.1	34.1	0.86	0.46
Solids from Conc. Acid treatment **	0.27	28.6	69.1	6.5	0.7	5.6	18.1	1.12	0.20

\* Key to sample ID found in Figure 1; \*\* From previous study Majid et al. (1990); \*\*\* By difference.

(present study) exhibited lower ash levels when compared to the concentrates produced by severe acid treatment (previous study), Majid et al. (1986, 1990).

This observation could result from a greater possibility of forming insoluble fluorosilicates during severe rather than mild acid treatment.

### Elemental Analysis

Elemental compositions of the various fractions shown in Figure 1 and a sample of organic concentrate obtained using severe acid treatment are compared in Table II. Elemental analyses were obtained using standard methods. Carbon analysis were corrected for carbonate carbon to determine true organic carbon. No corrections were applied for hydrogen, nitrogen and sulphur analysis. The analysis 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.



The analysis of fulvic acid and the organic matter associated with solids 1-1 to 1-4 appears to be the least reliable, as seen from the exceptionally high H:C ratios for these samples. These results suggest an inorganic hydrogen contribution to the total hydrogen content of these fractions. However, after further acid demineralization H:C ratios for the different fractions were within the range usually associated with humic materials, Schnitzer et al. (1972)..

The two organic matter concentrates obtained after mild acid treatment (solids 1-6 and 1-8) had significantly different elemental compositions. Solids 1-6, the organic concentrate obtained from fraction 1-3, had an elemental composition resembling humic acid -1 and organic concentrate 1-9, obtained previously using severe acid treatment. The average elemental composition of these fractions (Humic Acid -1, solids 1-6 and 1-9) are identical to those of the solvent extractable humic acids from Australian brown coal and benzene/methanol extracts from oil phase solids reported previously, Majid et al. (1986), Verheyen et al. (1982). The elemental composition of the organic concentrate 1-8, obtained from the fraction 1-4, appears to be similar to those reported for peat and soil humic matter, Schnitzer et al. (1972), Hartenstein (1981). Unlike the findings for the samples subjected to severe acid treatment the present samples showed no trace of halogen, Majid et al (1986, 1990).

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, Tissot et al. (1984), Van Krevelen (1961). Figure 2 is such a diagram showing the humic acid and IOM fractions from both mild and severe acid treatments. All samples fall in the region of type III kerogen. 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, van Krevelen (1961). 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.

### <sup>13</sup>C NMR Spectra

The CP/MAS <sup>13</sup>C NMR spectra for a number of samples are shown on Figure 3. The interpretation of these spectra was carried out as reported previously,

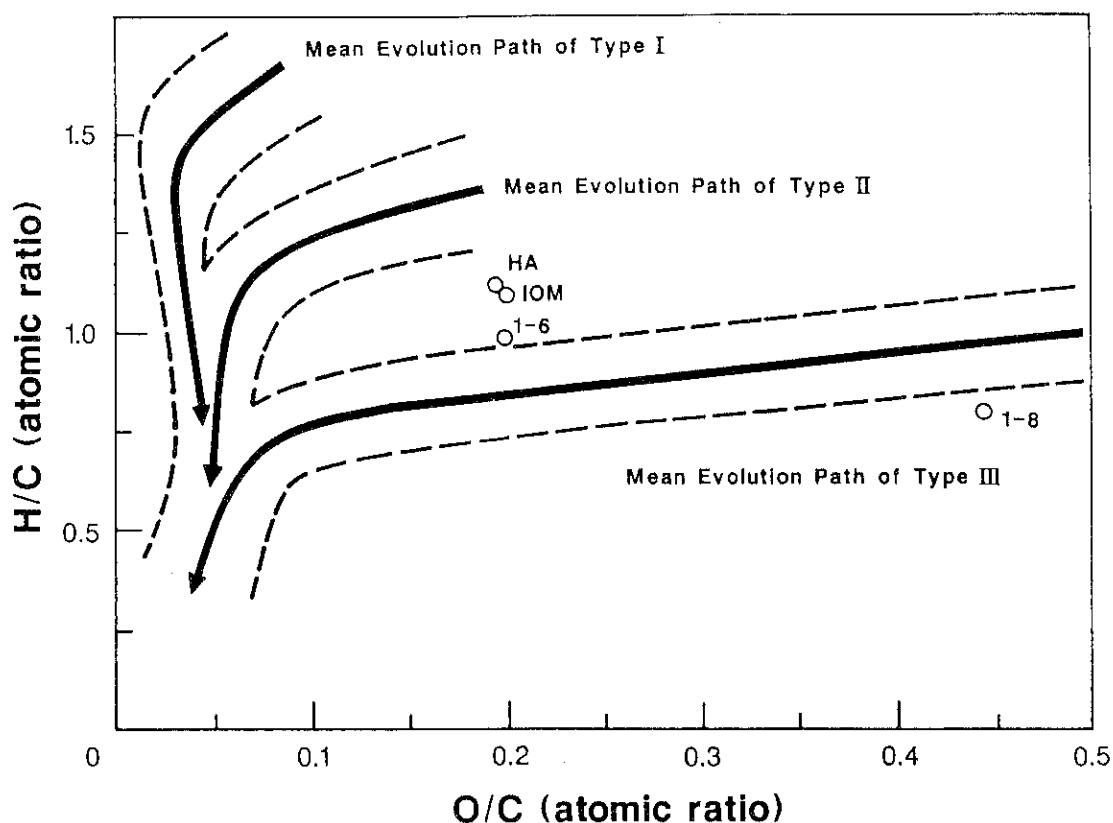


Figure 2. van Krevelen diagram showing the elemental composition of humic acid and organic matter concentrate fractions.

Majid et al. (1986, 1991). A comparison of these spectra indicates that resolution is equally improved for all samples, regardless of the carbon concentration. However, the spectral resolution in the carbohydrate region (50-100 ppm) is much better for solids 1-8 as compared with that for IOM, obtained using concentrated HCl/HF. This suggests that carbohydrates are less susceptible to attack by mild HCl/HF. Also, the peaks for aromatic carbons were sharper for solids 1-6 and 1-8 than in the spectrum for IOM obtained from concentrated acid treatment.

The presence of a broad range of aliphatic compounds is indicated by the resonance in the 10-50 ppm range. The large peak at  $\approx 30$  ppm is due to the presence of a number of repeating polymethylene units in humic macromolecules. The presence of two sharp shoulders at  $\approx 14$  and 20 ppm in all spectra (except that

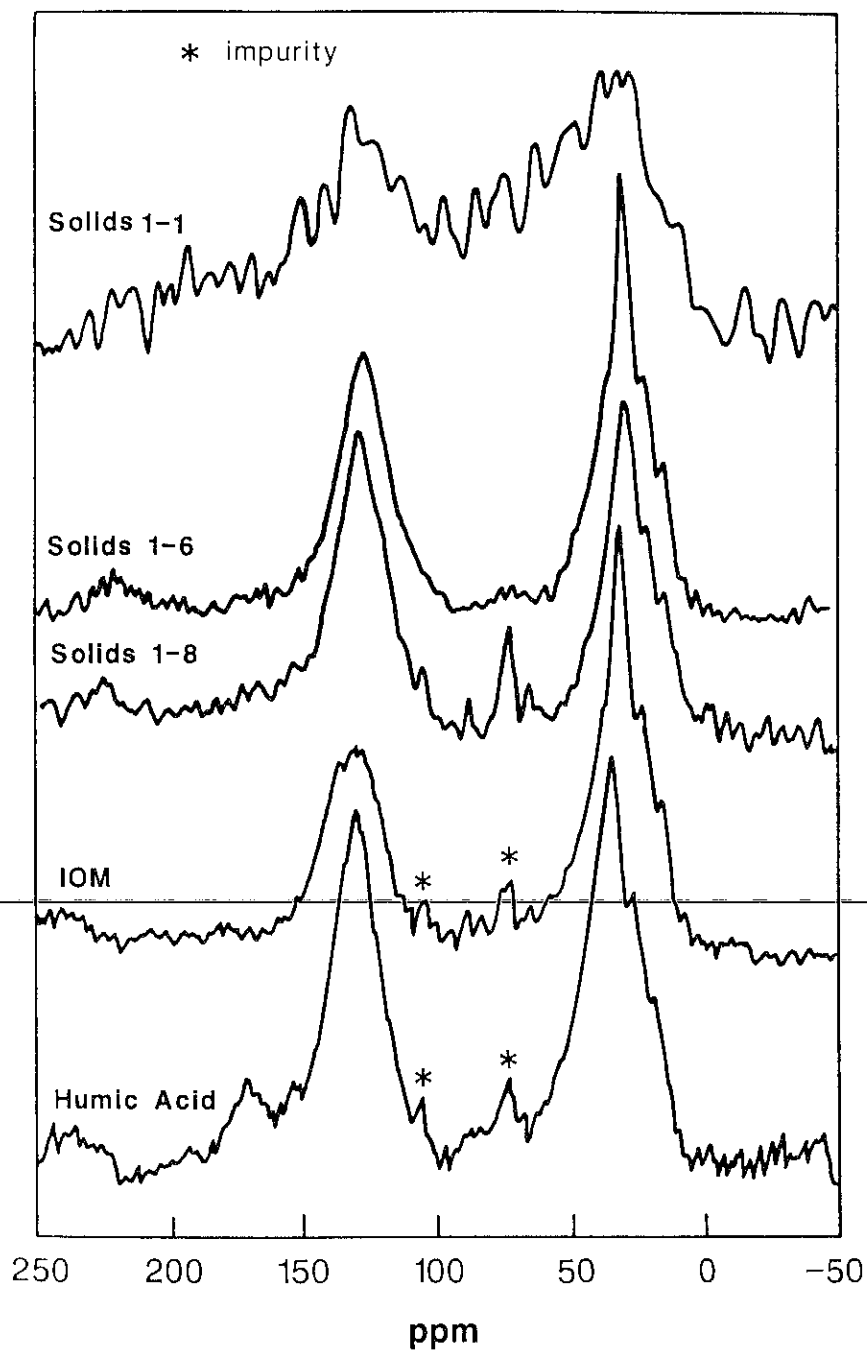


Figure 3. CP/MAS  $^{13}\text{C}$  NMR spectra of various fractions from Syncrude sludge pond tailings shown in Table II.

TABLE III  
Assignment of  $^{13}\text{C}$  Chemical Shift Ranges

Region	Chemical Shift range (ppm)	Carbon type
A <sub>1</sub>	0-50	Aliphatic
A <sub>2</sub>	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 <sub>1</sub>	160-190	Acid, ester, COOH, COOR
D <sub>2</sub>	190-230	Aldehyde, ketone

of solid 1-1) indicates the presence of long chain terminating methyl groups. A number of sharp peaks in the 50-100 ppm region of the spectrum of solid 1-8 and the broad absorption in this region for solid 1-6 could be assigned to oxygen and nitrogen substituted carbons as in carbohydrates, ethers, alcohols or amines. The spectrum of solid 1-8 has a distinguishable sharp resonance around 75 ppm which is due to carbohydrate carbons as in polysaccharides, Poutanen (1986). The presence of carbohydrates in this sample and no other could be the result of ~~resistance of this class of compounds to mild acid treatment; another possibility is~~ that the sample was contaminated at some point in the extraction procedure.

The aromatic region extends from 110-150 ppm. Olefinic carbons also resonate in this region, however, their contributions to the structure of humic substances remains unknown. All spectra show a strong peak in this region. The phenolic carbons in these samples are not resolvable as distinct peaks.

Only the humic acid sample has a distinct signal around 175 ppm due to carboxylic, amide or ester carbons. It is possible that the carbohydrates have been destroyed even by mild HCl/HF treatment, thus explaining the absence of the carboxylic peak in the spectra of IOM fractions (solids 1-6 and 1-8).

The integration of each spectrum was carried out by division into regions and subsequent determination of the individual areas, Majid (1986). The limits

TABLE IV

Quantitative  $^{13}\text{C}$  NMR Data for Various Fractions Listed in Table I

Sample *	Area of total spectrum %					$f_a$
	$A_1 + A_2$	B	C	$D_1$	$D_2$	
Solids 1-1	68	23	9	---	---	0.32
Solids 1-6	58	35	4	3	---	0.40
Solids 1-8	50	39	5	6	---	0.47
Solids 1-9	56	42	2	---	---	0.44
Humic Acid	44	44	4	8	---	0.52

\* Key to sample No. shown in Figure 1.

were chosen according to Verheyen et al., (1982), the four regions are listed in Table III. In Table IV is listed the quantitative area distribution by region. 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 carboxylic carbons, are also listed in Table IV.

The very poor spectral resolution of the NMR parameters calculated from the spectrum for solid 1-1 made these results less reliable than those calculated from the other spectra. A comparison of the data for solids 1-6 and 1-8 with the corresponding data for IOM from severe acid treatment, indicates a considerable variation both for the aromaticity values and the area distribution of various regions. It is likely that most of this difference is due to the fact that during mild acid treatment the composite organic matter subdivided into two fractions of different elemental composition whereas for severe acid treatment only a single fraction was obtained.

The aromaticity values for organic concentrates and the sample of humic acid are considerably higher than those reported for soil and aquatic humic acids. Such higher values are closer to those reported for humic acids from subbituminous coal and Victorian brown coal lithotypes, Majid et al. (1986), Verheyen et al. (1982). As higher aromaticity is characteristic of a contribution from vascular

plants, Christman et al. (1983), it is likely that the humic matter associated with oil sands is largely derived from terrestrial sources.

### CONCLUSIONS

1. The use of a severe HCl/HF extraction scheme for concentrating insoluble organic matter (IOM) from oil sands has many disadvantages compared to the mild acid treatment scheme used in the present investigation. These disadvantages include; higher ash levels in the organic concentrate, owing to the formation of insoluble fluorosilicates, destruction of carbohydrates and also the incorporation of halogens into the organic structure.
2. Enrichment of the organic matter by use of a mild HC/HF treatment resulted in significant improvement of the elemental analysis results and better resolution in the NMR spectra.
3. The results of this investigation are indicative of the presence of at least two different types of organic matter associated with oil sands solids. The two organic types had significantly different elemental compositions with one fraction being almost identical to coal humic acids while the other was similar to peat and soil humic matter. Carbon aromaticities of the two fractions were also different.
4. Humic acid and acid extracted organic matter fractions, obtained from Syncrude sludge pond tailings, fall in the region of type III kerogen, when plotted on a van Krevelan diagram.

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REFERENCES

- Almendros, G. and Gonzalez-Vila, F.J. 1987. Soil Biol. Biochem. **19**:513.
- Arshad, M.A., Ripmeester, J.A. and Schnitzer, M. 1988. Can. J. Soil Sci. **68**:593.
- Calderoni, G. and Schnitzer, M. 1984. Geochim. Cosmochim. Acta. **48**:2045.
- Christman, R.F. and Gjessing, E.T. 1983, "Equatic and Terrestrial Humic Materials", Ann Arbor Sci. Pub. Ann Arbor
- Danielson, L.J. Syncrude Canada Ltd. Internal Report, 1989.
- Fassel, V.A. 1979. Anal. Chem. **51**:1290A
- Goh, K.M. 1970. N.Z.J. Sci. **13**:669.
- Hartenstein, R. 1981. Science **212**:743
- Majid, A. and Ripmeester, J.A. 1986. Fuel **65**:1714
- Majid, A., Sparks, B.D. and Ripmeester, J.A. 1990. Fuel **69**:145
- Majid, A., Sparks, B.D. and Ripmeester, J.A. 1991. Fuel **70**:78
- Oades, J.M., Vassalo, A.M., Waters, A.G. and Wilson, M.A. 1987. Aust. J. Soil Res. **25**:71
- 
- Poutanen, E.L. 1986. Org. Geochem. **9**:163
- Preston, C.M., Schnitzer, M. and Ripmeester, J.A. 1989. Soil Sci. Soc. Am. J. **53**:1442
- Schnitzer, M. and Khan, S.U. 1972. "Humic Substances in the Environment", Marcell Dekker, New York
- Tissot, B.P. and Welte, D.H. 1984. in "Petroleum Formation and Occurrence", Springer Verlag, New York, USA.
- van Krevelen, D.W. 1961. in "Coal", Elsevier, Amsterdam, The Netherlands.
- Verheyen, T.V., Johns, R.B. and Blackburn, D.T. 1982. Geochim. Cosmochim. Acta. **46**:269
- Wilson, M.A., Vassalo, A.M., Perdue, E.M. and Reuter, J.H. 1987. Anal. Chem. **59**:551

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