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Eric M. Suuberg, Chairman
Division of Engineering
Brown University
Providence, RI 02912

Michael A. Serio, Program Chairman
Advanced Fuel Research, Inc.
P.O. Box 18343
E. Hartford, CT 06118



ANALYZED

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CHARACTERIZATION OF INSOLUBLE ORGANIC MATTER ASSOCIATED WITH CLAY MINERALS FROM SYNCRUDE SLUDGE POND TAILINGS*

Abdul Majid, Bryan D. Sparks and John A. Ripmeester
National Research Council of Canada
Institute for Environmental Chemistry
Ottawa, Ontario, K1A 6R9, CANADA

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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 sand slimes. In previous investigations we had attempted to enrich the insoluble organic matter by dissolving the minerals in concentrated HCl/HF. As a result of this treatment the inorganic material is decomposed, but the organic constituents are also likely to undergo significant changes. In the present work we have attempted 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.

INTRODUCTION

Hot water extraction of bitumen from Alberta oil sands generates large quantities of tailings slurry.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).⁵⁻¹⁰ This IOM is believed to be partly responsible for the intractability of the sludge and could therefore play an important role in determining the nature of slime stability.^{1,5} 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.

In previous work, IOM from a number of oil sands tailing streams as well as oil sand feedstock samples has been isolated and characterized.^{5,7-9,11} IOM was enriched by decomposing the inorganic material with concentrated HCl/HF, which might have resulted in the chemical alterations of the organic constituents. In this investigation we have attempted a milder HCl/HF treatment for mineral dissolution. 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 during the deashing procedure.

EXPERIMENTAL

Sample description and isolation procedure for organic rich solids fraction have been reported previously.⁹

HCl/HF Treatment Procedure. The general procedure for mineral dissolution and IOM enrichment is shown in Figure 1.

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NMR Measurements. The solid state NMR spectra were obtained on a Bruker MSL-300 spectrometer, using a cross polarization technique was used with a magic angle spinning. Each spectrum was the Fourier transform of the FID.

RESULTS AND DISCUSSION

Table I lists the yields for IOM and concentrated acid treatments. The ash content

Table I. Yields

Treatment	IOM Yield
Mild Acid	9.6
Concentrated Acid	
A	24.7
B	2.1

Comparison of the results of mild acid treatment indicates that the organic concentrate when compared to the concentrates produced by a greater possibility of forming insoluble flake treatment. Lower weight loss because of the volatility to the severe acid treatment case is also consistent.

Elemental Analyses. Elemental composition obtained from both mild and severe acid treatments

Table 2. Elemental Analysis

Sample	Treatment Scheme	Element	
		C	H
Solids, 1-6*	Mild Acid	70.3	5.7
Solids, 1-8*	Mild Acid	55.8	4.0
IOM**	Conc. Acid	69.1	6.5
Humic Acid-1	2% NaOH	71.3	6.8

* Figure - 1; ** Previous study ref. 9; *** By difference

NMR Measurements. The solid state ^{13}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 2 ms, and a repetition time of 1 s. Each spectrum was the Fourier transform of 1500-40,000 free induction decay curves.

RESULTS AND DISCUSSION

Table 1 lists the yields for IOM and volatiles obtained during the mild as well as concentrated acid treatments. The ash content of the IOM is also listed.

Table 1. Yields of IOM and Volatiles

Treatment	Yield w/w %		Ash Content of IOM w/w %
	IOM	Volatiles	
Mild Acid	9.6	41	9
Concentrated Acid			
A	24.7	60	35
B	2.1	55	29

Comparison of the results of mild acid treatment with those from the concentrated acid treatment indicates that the organic concentrate obtained from the former exhibited lower ash levels when compared to the concentrates produced by the latter treatment. This observation could result from a greater possibility of forming insoluble fluorosilicates during severe rather than mild acid treatment. Lower weight loss because of the volatiles in the mild acid treatment case as compared to the severe acid treatment case is also consistent with this interpretation.

Elemental Analyses. Elemental compositions of a sample of humic acid and IOM fractions obtained from both mild and severe acid treatments are compared in Table 2.

Table 2. Elemental Analyses (dry, ash free basis)

Sample	Treatment Scheme	Elemental Analyses					Atomic Ratios	
		C	H	N	S	O***	H:C	O:C
Solids, 1-6*	Mild Acid	70.3	5.7	1.3	3.8	18.9	0.97	0.20
Solids, 1-8*	Mild Acid	55.8	4.0	1.0	5.1	34.1	0.86	0.46
IOM**	Conc. Acid	69.1	6.5	0.7	5.6	18.1	1.12	0.20
Humic Acid-1	2% NaOH	71.3	6.8	1.2	2.8	17.9	1.14	0.19

* Figure - 1; ** Previous study ref. 9; *** By difference

The two IOM fractions 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 obtained previously⁹ using severe acid treatment. The average elemental composition of these fractions (humic acid-1, solids 1-6 and IOM from severe acid treatment) are identical to those of the solvent extractable humic acids from Australian brown coal and benzene/methanol extracts from oil phase solids reported previously.^{5,12} Elemental composition of the organic concentrate 1-8, obtained from fraction 1-4, appears to be similar to those reported for peat and soil humic matter.^{13,14} Unlike the findings for the samples subjected to severe acid treatment^{5,9} the present samples showed no trace of halogens.

Figure 2 is a van Krevelen 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. Organic matter of type III kerogens is usually derived from plants of terrestrial origin and is rich in polyaromatic nuclei and heteroatomic ketone and carboxylic acid groups.¹⁵ This type of organic matter is not considered to have any potential for hydrocarbon generation and usually matures to give coal. It is comparable in maturity to humic acids from lignite or subbituminous coals and is relatively immature when considered in light of its oil generation potential.⁷

¹³C NMR Spectra. The CP/MAS ¹³C NMR spectra for a number of samples are shown on Figure 3. 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 aromaticity (f_a) values for fractions 1-6 and 1-8 obtained using mild acid treatment are comparable to those for the IOM obtained from severe acid treatment (0.4 and 0.47 respectively Vs 0.44). These values are considerably higher than those reported for soil and aquatic humic acids and are comparable to those reported for humic acids from subbituminous coal and Victorian brown coal lithotypes.^{5,12} As higher aromaticity is characteristic of a contribution from vascular plants¹⁶, it is likely that the humic matter associated with oil sands is largely derived from terrestrial sources.

CONCLUSIONS

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.

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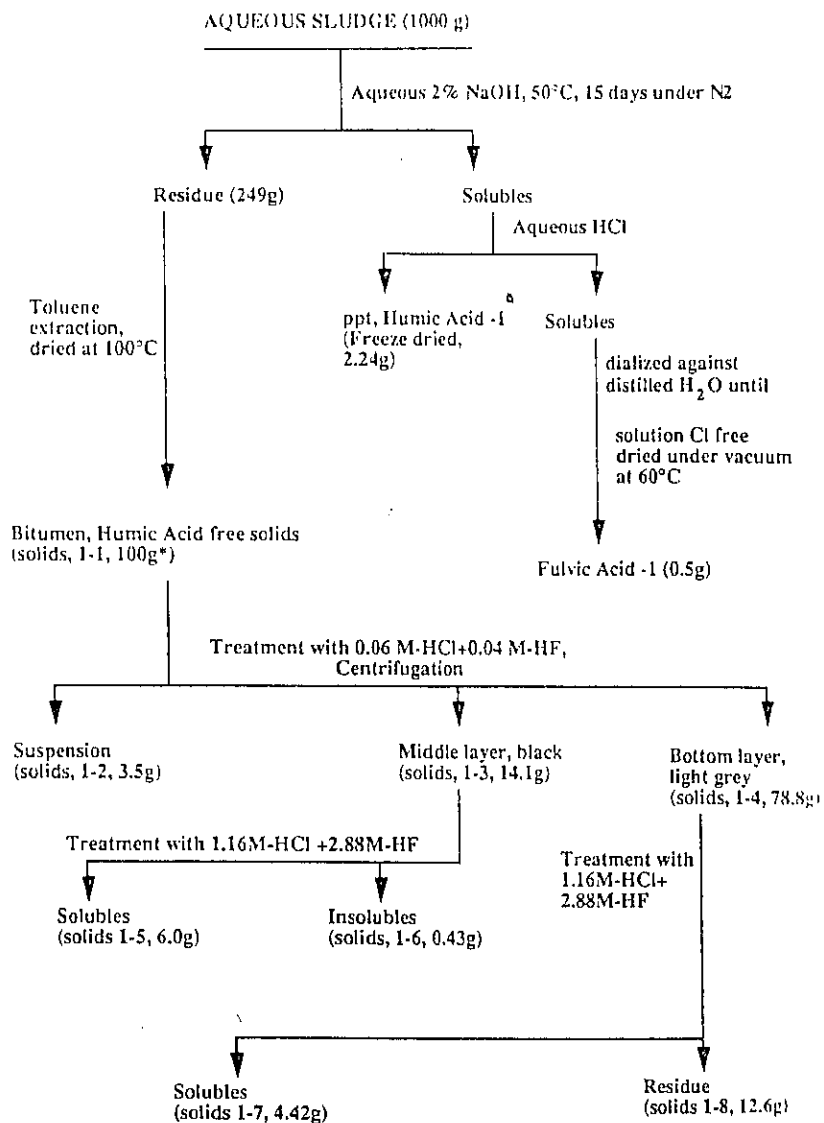


Figure 1. Separation and mild HCl/HF acid treatment scheme
 * Represents amount taken for further treatment and not actual yield.

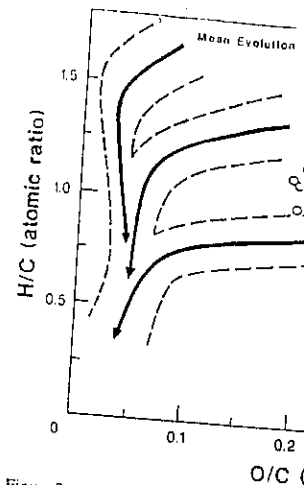


Figure 2. van Krevelen diagram showing the matter concentrate fractions

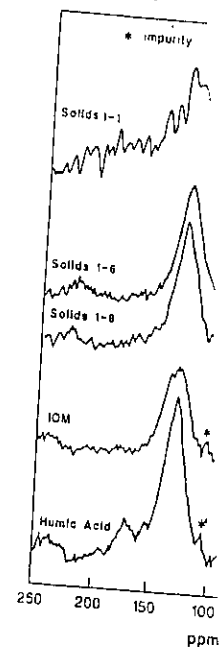


Figure 3. CP/MAS - ¹³C NMR spectra of various fr. shown in Table 2

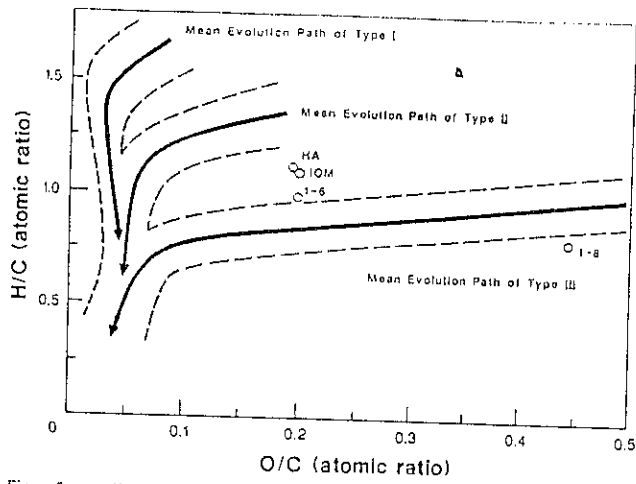


Figure 2. van Krevelen diagram showing the elemental composition of humic acid and organic matter concentrate fractions

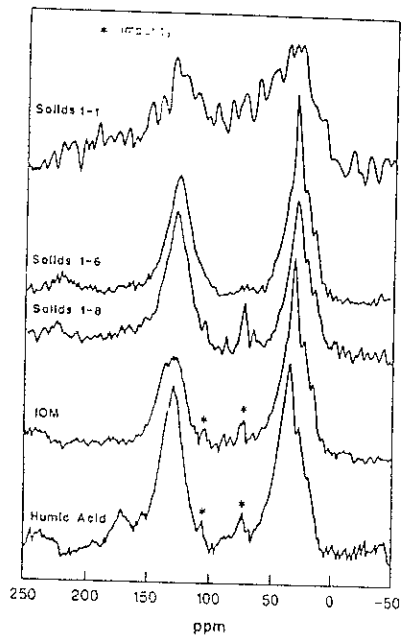


Figure 3. CP/MAS - ^{13}C NMR spectra of various fractions from synecude sludge pond tailings shown in Table 2