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Characterization of organic-rich solids fractions isolated from Athabasca oil sand using a cold water agitation test

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Using a cold water agitation test (CWAT), different grades of oil-sand solids were separated into three fractions with respect to their insoluble organic carbon content (IOCC). Solids enriched with humic matter (IOCC ~36%) were present in association with bitumen, whereas solids with an IOCC of about 5% occurred suspended in the aqueous phase. The IOCC of the remaining solids was very low (<0.3%). Comparison of H/C and O/C atomic ratios of the different solid fractions rich in organic matter with corresponding results for different types of kerogen indicated that oil-sand organic matter has the same origin as kerogen type III. On the basis of ^{13}C n.m.r. data the oil-sand humic matter was found to be of similar maturity as subbituminous coal. It has been shown that solids associated with bitumen have high concentrations of Ti, Zr and Fe. Solids occurring in the form of an aqueous suspension were enriched with alumina.

(Keywords: oil sand; kerogen; chemical characterization)

It has long been known that the ease of bitumen recovery from oil sand by hot or cold water separation techniques depends upon the surface properties of the components, especially the water wet character of the clay and sand particles¹⁻⁵. Oil wetting of some of the oil-sand solids is believed to be caused by the presence of strongly held organic matter which cannot be removed by extraction with good solvents for bitumen, such as toluene or dichloromethane. Relatively little information is currently available concerning characterization of this strongly held organic matter^{4,6-9}. It is believed that the greater part of this material is composed of humic substances⁴ which are considered to be a complex mixture of organic matter of plant and microbial origin. In order to improve bitumen separation, a better understanding of the chemical nature and the origin of the tightly bound organic matter (humic matter) is needed. To this end it is necessary to liberate organic-rich material from the rest of the solids to be able to analyse it further. In addition, the interaction between oil and humic matter (wettability) could be studied and compared with that of the clean mineral matter. In an earlier report¹⁰ insoluble organic matter complexed with non-crystalline inorganic material was separated from the bulk of different grades of toluene-extracted oil sand. In this work, using the cold water agitation test (CWAT), the solids fractions enriched with insoluble organic matter have been isolated from the original oil-sand feeds. The distribution and the chemical nature of organic matter present in different CWAT fractions have been analysed. For comparison, humic coals of different ranks have also been studied.

EXPERIMENTAL

The work presented here was carried out on oil sand of estuarine origin obtained from the Syncrude quarry, Fort McMurray, Alberta. The oil sands were ground using a Comomil†, mixed to prepare homogenized samples and then stored in sealed containers. The compositions of the oil-sand samples studied were determined using Soxhlet extractors in conjunction with Dean and Stark separators¹¹. The series of treatments given to each sample of oil sand is shown schematically in *Figure 1*.

Samples of humic coals were obtained through the courtesy of R. M. Bustin, and originated from the Eureka Sound Formation, Ellesmere Island¹².

Cold water agitation test (CWAT)

The cold water agitation test was used in this work to separate oil-sand solids into three fractions on the basis of the amount of insoluble organic matter associated with the inorganic solids. The procedure described in detail elsewhere¹⁰ is briefly as follows: to ~40 g of unextracted oil-sand feedstock in a 100 ml jar was added a known amount of 0.1% $\text{Na}_4\text{P}_2\text{O}_7$ solution. The oil sand: $\text{Na}_4\text{P}_2\text{O}_7$ solution ratio was kept approximately equal to unity (weight basis) for all samples. Samples were agitated using a high-intensity Spex mixer. After gravity separation for about an hour the following layers (from the top to bottom) were formed: a bitumen layer (B) which was easily skimmed off, a solids suspension layer (A) which was separated by decantation, and a residue layer containing the bulk of the solids (RS). Toluene was added to each layer to dissolve bitumen. Solids, separated from the toluene solution of the B layer by centrifugation (1 h at 428g), will be referred to as bitumen layer solids

† Quadro Engineering Inc., Waterloo, Ontario

Figure 1 Treatment scheme for oil sands

(BS). The BS as well as A and RS fractions were repeatedly washed with aliquots of fresh toluene until the supernatant toluene solution was colourless. The solids of bitumen-free A which will be referred to as AS, were flocculated with acetone. Bitumen-free RS samples were separated according to particle size by wet sieving.

Acid treatment

In order to concentrate organic matter, CWAT fractions were leached with acids. The procedure was as follows. To acetone-wetted BS, AS and RS, 6N HCl was added; suspensions were stirred for 24 h at 60°C under nitrogen. The remaining solids were then extracted with concentrated HF for 24 h at room temperature. Insoluble fluoride salts were converted to more soluble forms by stirring oil-sand solids residues with warm saturated boric acid for 6 h (Ref. 13).

Solid-state CP/MAS ¹³C n.m.r.

¹³C N.m.r. spectra were recorded on a Bruker CXP 180/90 n.m.r. spectrometer operating at either 45.2 or 22.6 MHz. Single cross polarization contacts of 1 ms were used with rf field amplitudes of 40 kHz at 22.6 MHz and 60 kHz at 45.2 MHz. Magic angle spinning rates were 3 kHz using an Andrew-Beams type spinner at the lower frequency, and 5.2 kHz in a Doty Scientific probe at the higher frequency.

Analysis

The elemental analysis (C, H, N) was performed using a Perkin-Elmer model 240 CHN analyser. Sulphur was analysed by a titrimetric oxygen flask combustion method, using a Schöniger type combustion apparatus¹⁴. Oxygen was estimated by difference. The insoluble organic carbon content (IOCC) of all solid fractions was obtained by subtracting carbonate carbon from the total

carbon. Carbonate carbon was analysed titrimetrically after acid digestion using a Carbon Dioxide Coulometer Model 5010¹⁵. Mass balance calculations for the IOCC of bitumen-free BS, AS and RS gave satisfactory agreement ($\pm 7\%$) with the amount measured in the initial bitumen-free (Soxhlet-extracted) solids. Metals were analysed semiquantitatively by DC arc emission spectrometry.

RESULTS AND DISCUSSION

IOCC of oil-sand solids fractions separated by CWAT

The compositions and the fines content of the oil-sand samples studied are presented in Table 1. With respect to bitumen concentration, oil sands were arbitrarily divided into high (I-1, I-2, I-3), medium (II-1, II-2) and low (III, IV) grades. Different grades of oil sands were selected because not only does the bitumen concentration vary in these grades but the particle-size distribution varies and it was desirable to investigate the IOCC with respect to these differences.

As a result of the CWAT treatment all three grades of oil sands gave three distinct layers: bitumen layer (B), solids suspension layer (A) and residual solids layer (RS). The solids distribution in the layers and the IOCC of BS, AS and RS are given in Table 2. The solids collected from layer B represent only 0.2–0.3% of the total oil sand solids. The amount of solids in layer A ranged from 1% to 2.5%, whereas the majority of the solids was concentrated in RS. The bitumen-free solids derived from the layers were different in appearance: BS and AS were dark whereas the residual solids (RS) had the appearance of clean sand. It can be seen from Table 2 that for all oil sands the IOCC differed markedly in the solids of the different layers. The BS fractions had the highest IOCC, 34.6–

Table 1 Compositions of oil sands

Sample	Oil sand composition (wt %)			Fines ^b (wt %)
	Bitumen ^a	Water	Solids	
I-1	15.9	0.5	83.6	3.4
I-2	15.4	0.3	84.3	3.8
I-3	15.8	1.4	82.8	3.8
II-1	12.0	1.3	86.7	8.0
II-2	12.1	3.5	84.4	19.0
III	8.7	5.2	86.1	25.8
IV	7.0	4.1	88.9	29.4

^a The toluene extract is reported as bitumen

^b Based on bitumen-free dry oil-sand solids

Table 2 The solids distribution and IOCC in CWAT layers

Sample	Solids distribution by layer (wt % related to the total solids ^a in initial sample)			IOCC (wt % of dry bitumen-free solids of various types)		
	BS	AS	RS	BS	AS	RS
I-1	0.2	2.4	97.4	34.75	5.40	0.03
I-2	0.2	1.0	98.8	37.11	5.48	0.10
I-3	0.2	1.2	98.6	34.58	5.65	0.09
II-1	0.2	1.9	97.9	35.22	5.90	0.20
II-2	0.2	2.0	97.8	36.69	5.12	0.19
III	0.2	2.0	97.7	37.10	5.47	0.13
IV	0.3	2.5	97.2	36.41	5.55	0.22

^a Includes the inorganic and insoluble organic solids

Table 3 Capacity of BS, AS and RS fractions to hold humic mater

Sample	Insoluble organic carbon, retained by different layer solids (wt % of IOCC in initial oil-sand solids)		
	BS	AS	RS
I-1	30	57	13
I-2	33	24	43
I-3	31	30	39
II-1	19	29	52
II-2	20	28	52
III	24	35	41
IV	24	30	46

37.1 %, followed by the AS fractions with IOCC of 5.1–5.9 % and the RS fractions with IOCC of less than 0.3 % of the dry bitumen-free solids. It should be pointed out that IOCC as a percentage of the various solids (BS, AS and RS) is remarkably independent of the grade of the oil sand, although there appears to be a trend towards higher values for the IOCC in the RS for low-grade compared with high-grade oil sand.

The following reasons are thought to account for the separation of oil-sands solids into three fractions by the CWAT: (1) the severe agitation frees the organic matter from the mineral matter and induces the mineral matter to become water wet; (2) as a result of the gravity separation the lower density and finer material tends to concentrate at the top; (3) within the water-wet minerals the separation takes place on the basis of the sedimentation rate. It is also believed that BS appears in the bitumen phase not only because of the density of the particles but that it is also a matter of the proportion of the surface that is oil wet or water wet after agitation treatment. The bitumen-layer solids (BS) occur as 'free' organic matter (discrete particles of coals and carbonized wood) and as inorganic particles coated with insoluble organic matter. These solids are dark in colour and are readily oil wetted and thus appear in the bitumen phase, even though the particle densities and IOCC of this fraction cover a wide range; these are discussed more fully in a subsequent paper¹⁶.

The AS particles are considered to be only partially coated with insoluble organic matter and to have more exposed water-wet mineral matter. This would seem to be in agreement with the fact that these particles have an average of 5.4 % IOCC based on AS. The presence of organic matter in the AS particles will reduce the average particle density by virtue of the relatively low density of organic matter itself and by virtue of the fact that this organic matter may interact with bitumen. The effect of both these factors would be to reduce the sedimentation velocity relative to the RS particles sufficiently to allow the formation of a distinctly separate layer of AS on top of the RS.

Knowing the IOCC of BS, AS and RS, as well as the solids distribution by layers, the capacity of the solids in the different layers to hold humic matter was estimated (Table 3). This Table shows that 19–33 wt % of insoluble organic carbon, initially present in the oil sands, occurred in association with BS. AS accounted for 24–57 wt % of oil sands IOCC. Although the RS appears to be relatively free of humic matter it still contains up to 52 % of the total IOCC. Thus the results indicate that, first, based on IOCC, three different fractions of solids can be

distinguished in all the grades of oil sand studied; second, the CWAT can be used to isolate the organic-rich fractions (BS and AS) from the bulk of the solids represented by the RS fraction with a low IOCC.

Elemental analyses of demineralized CWAT fractions

In order to compare types of organic matter present in different CWAT fractions, demineralized BS, AS and RS derived from oil sands representing high (I-1), medium (II-1) and low (IV) grades were subjected to elemental analysis. The results showing elemental composition on a dry ash-free basis and atomic H/C and O/C ratios of the acid-treated solids are given in Table 4. It can be seen from Table 4 that variations in C, H and N of the insoluble organic matter in the different layers were small, indicating the similarity of the material in each of the samples studied. Relatively high sulphur and nitrogen contents of these fractions could be an integral part of humic matter or, alternatively, could arise from the extremely polar matter present in the bitumen and adsorbed on the humic matter and clay⁴. From Table 4 it can also be seen that all the samples studied have generally low H/C and high O/C atomic ratios. In order to get some information about the nature of this material, H/C and O/C atomic ratios were plotted on the van Krevelen diagram (Figure 2). The van Krevelen diagram was first used¹⁷ to characterize coals and their coalification paths. This diagram was also found to be useful for classifying kerogens. In general, three main types of kerogen should be distinguishable¹⁸. Type-I kerogen contains many aliphatic chains, and few aromatic nuclei; the H/C ratio is originally high, and there is good potential for oil generation. This type of kerogen is mainly derived either from algal lipids or from organic matter enriched in lipids by microbial activity. Type-II kerogen contains more aromatic and naphthenic rings; the H/C ratio and the oil-generation potential are lower than that for type-I kerogen, but it is still very important. This type of kerogen is usually related to marine organic matter deposited in a reducing environment. Type-III kerogen contains mostly condensed polyaromatics and oxygenated functional groups; both the H/C ratio and the oil-generation potential are low. This organic matter is mostly derived from terrestrial higher plants. Changes in composition of

Table 4 Elemental composition of demineralized CWAT fractions

Sample	D.a.f. ^a (%)					Ash (%)	H/C	O/C
	C	H	N	O ^b	S			
I-1								
BS	66.70	4.64	1.10	26.0	1.60	6.7	0.84	0.29
AS	64.22	4.88	1.24	25.2	4.50	10.3	0.91	0.29
RS	63.25	5.26	1.50	26.2	3.78	12.1	0.99	0.31
II-1								
BS	65.55	4.70	1.10	25.7	3.00	8.3	0.86	0.29
AS	67.36	5.32	1.11	23.6	2.64	9.4	0.95	0.26
RS	66.10	5.34	1.05	23.9	3.57	8.5	0.97	0.27
IV								
BS	66.15	4.67	1.00	24.4	3.80	7.8	0.85	0.28
AS	67.00	4.80	1.11	21.0	6.07	16.0	0.86	0.24
RS	65.16	4.90	1.43	23.8	4.70	15.5	0.90	0.27

^a Dry ash-free basis

^b By difference

Figure 2 Position of the elemental analysis of acid-leached oil-sand solids (BA, AS, RS) in the van Krevelen diagram

various kerogen types can be compared with the chemical changes in coal during its evolution, as it is known¹⁸ that coals and type-III kerogen have the same evolution paths. When comparing our experimental results with those for different types of kerogen, it can be seen that our data fall in the area of the evolution path of kerogen-III (Figure 2) and, consequently, of coal. This suggests that, first, as with kerogen-III and coals, terrestrial higher plants are the main precursors for insoluble organic matter present in Syncrude oil sand; second, as in the case of kerogen-III, the generally low H/C ratios obtained point to condensed aromatic ring structures similar to those found in coals of low to moderate maturity. The high O/C ratios indicate the high degree of oxygen substitution in these structures.

¹³C N.m.r. of demineralized CWAT fractions and humic coals

In this work ¹³C n.m.r. has been used, first, to determine structural parameters of insoluble organic matter present in different CWAT fractions, and second, to compare the n.m.r. characteristics of oil-sands insoluble organic matter with those of humic coals of different maturity. The maturity of the coals used increased in rank from brown coal to lignite to subbituminous coal (vitrinite reflectances are 0.18, 0.27 and 0.5, respectively). Typical solid-state ¹³C n.m.r. spectra of selected acid-leached CWAT fractions (oil sand I-1), together with the results for humic coals are given in Figure 3.

Interpretation of the ¹³C n.m.r. spectra is based on the reported data for coal-like materials¹⁹⁻²⁷. The integration of each spectrum was performed by division into six regions and subsequent determination of their individual areas. The position of regional boundaries is a matter of definition, as no representative model compounds for these materials are available. Assignments for chemical shifts in these regions are given in Table 5.

The spectrum of brown coal has peaks indicating that this coal is of ligno-cellulosic origin. One main

component is holocellulose with peaks at 65, 72, 85, 90 and 106 ppm. The spectrum also shows prominent peaks (55 and 132, 150 ppm) related to lignin structure. The carbon peak at 55 ppm corresponds to methoxyl carbon. The peak at 150 ppm is that of oxygen-substituted (phenol and alkyl aryl ether) aromatic structures. The 125-135 ppm region is attributable to unsubstituted aromatic carbon and carbon in condensed aromatic rings. The 110-120 ppm region is typical of aromatic carbon *ortho* or *para* to oxygen-substituted aromatic carbon.

On going from brown coal to lignite, the spectrum shows major losses of the holocellulose peaks (72, 85, 90, 106 ppm). Some lignin structure is still present, as suggested by the existence of methoxyl carbons (peak at 55 ppm and shoulder at 150 ppm).

In the same fashion as previously reported results^{21,22}, the trend for n.m.r. spectra to become simpler with increase in coal rank can be seen from Figure 3. The spectrum for subbituminous coal shows the complete loss of peaks for holocellulose. Distinct lignin features have also changed significantly with loss of the peak at 55 in

Figure 3 Solid-state CPMAS ¹³C n.m.r. spectra for acid-leached bitumen-layer solids (BS), aqueous suspension-layer solids (AS) and residual solids (RS) in comparison with humic coals

Table 5 ^{13}C n.m.r. chemical shift regions for various types of carbon present in coal-like substances

Region I (0–50 ppm)	Region II (50–110 ppm)	Region III (110–145 ppm)	Region IV (145–160 ppm)	Region IV (160–190 ppm)	Region V (190–220 ppm)
Paraffinic C:C–C–C $\begin{array}{c} \text{C} \\ \diagup \quad \diagdown \\ \text{C}-\text{C}-\text{C} \\ \diagdown \quad \diagup \\ \text{C} \end{array}$ $\begin{array}{c} \text{C} \\ \\ \text{C}-\text{C}-\text{C} \\ \\ \text{C} \end{array}$ C–CH ₃	Alcohols C–OH Amines (C–NH ₂ CNHR.C–NR ₂) Carbohydrates Ethers (C–O–C) Methoxyl (OCH ₃) Acetals $\begin{array}{c} \text{O} \\ \\ \text{C}-\text{O} \end{array}$	Aromatic C–H Aromatic C–C Alkyl- substituted aromatic	Aromatic C–OH Aromatic C–OR	Carboxyls $\begin{array}{c} \text{O} \\ \parallel \\ \text{C}-\text{OH} \end{array}$ Ester $\begin{array}{c} \text{O} \\ \parallel \\ \text{C}-\text{OR} \end{array}$ Amide $\begin{array}{c} \text{O} \\ \parallel \\ \text{C}-\text{N} \end{array}$	Aldehyde $\begin{array}{c} \text{O} \\ \parallel \\ \text{C}-\text{H} \end{array}$ Ketone $\begin{array}{c} \text{O} \\ \parallel \\ \text{C} \end{array}$

Table 6 Aromatic fraction (f_a) and fraction associated with oxygen (f_{ox})

Sample	f_a	f_{ox}
Brown coal	31	56
Lignite	40	39
Subbit. coal	44	32
BS	44	27
AS	42	26
RS	51	34

the n.m.r. spectrum. This spectrum is characterized by two major broad peaks, one centred at 130 ppm and the other at 37 ppm. Such a broad unresolved spectrum very often characterizes coals with a rank higher than that of lignite²¹.

The spectra of demineralized BS, AS and RS fractions resemble each other and are similar to that of subbituminous coal. As in the case of subbituminous coal, spectra for CWAT fractions are characterized by two major broad peaks centred at 130 and 37 ppm. Peaks related to methoxyl carbon (55 ppm), oxygen-substituted aromatic carbon (150 ppm) and aromatic carbons *ortho* or *para* to an oxygen-substituted aromatic carbon (120 ppm) are clearly absent in the spectrum. All spectra show a small peak at 175 ppm which is an indication of carboxyl carbon.

For comparison, two quantitative parameters were extracted from the n.m.r. spectra: the aromatic fraction (f_a) and the fraction of carbon associated with oxygen (f_{ox}). The fraction f_{ox} should be used only as a rough indication, as sometimes one, and at other times two, carbons might be associated with each oxygen. Using the division given in Table 5:

$$f_a = f_{III} + f_{IV}; \quad f_{ox} = f_{II} + f_{IV} + f_V + f_{VI}$$

Results of such an assignment are given in Table 6. It can be seen that in accordance with the data reported in the literature^{21,28,29}, the aromaticity of coals increases and the fraction of carbon associated with oxygen decreases with the degree of coalification. These results are the reflection of a gradual decrease in the concentration of cellulose and other oxygen-substituted carbons relative to the backbone aromatic structures as coalification

Table 7 Metals analysis of CWAT fractions (no acid treatment)

Oil sand	CWAT fraction	Percentage						
		Fe	Al	Ti	Zr ^a	Ca	Mg	Mn ^a
I-1	BS	4.3	1.0	0.71	610	0.67	0.20	1700
	AS	3.1	11.7	0.32	270	1.30	0.98	1620
	RS	2.9	7.9	0.55	210	0.27	0.23	1030
	(fines)							
II-1	BS	6.9	3.7	2.80	630	0.40	0.20	3710
	AS	2.5	12.7	0.34	340	0.11	0.68	780
	RS	1.6	6.2	0.74	200	0.13	0.26	260
	(fines)							
IV	BS	3.2	3.6	3.80	3500	0.33	0.40	2300
	AS	1.9	8.4	0.31	680	n.d.	n.d.	750
	RS	0.8	5.5	0.71	230	0.10	0.24	160
	(fines)							

^a ppm

n.d., not determined

progresses. The aromaticity and fraction of carbon associated with oxygen of the CWAT solids are close to those of subbituminous coal, suggesting that this coal and coal-like material present in oil sands were exposed to similar levels of maturation during the course of their history.

Metals analysis of CWAT fractions

Results showing metals contents of BS, AS and the fines fraction (<38 μm) derived from RS (prior to acids treatment) are given in Table 7. According to Table 7, in the case of all the grades of oil sands studied, the solids associated with bitumen (BS) have a relatively high concentration of Ti, Zr and Mn, compared with that in AS and RS. The results showing a high Ti content of the BS are in accord with the observation that Ti often concentrates in low-density float–sink fractions of coal³⁰. This phenomenon has been related³⁰ to the strong tendency of titanium to form highly dispersed colloidal precipitates of anatase in the coal-precursor environment. In addition to Ti occurring as colloidal precipitate, many coal deposits are expected to contain detrital Ti minerals. A significant amount of Ti in coals could be associated with the clay minerals. It is not clear whether Ti plays a role in mineral–organic complexation. There is a point of view that in the case of coals a substantial fraction of the Ti is

'organically associated', although no organic Ti compounds have been identified³⁰. Table 7 shows that solids associated with bitumen (BS) are also enriched in iron, which is known for its ability to be directly involved in interaction with humic matter^{31,32}; therefore it is to be expected that at least some of the Fe in BS is organically associated. The iron participating in association with organic matter may be in the form of exchangeable cations or as an integral part of the clay structure. It can also be seen from Table 7 that the solids separated in the form of an aqueous suspension (AS) are enriched in alumina. It was also observed that Fe, Zr and Mn are present in the AS fraction in higher concentration than in the fines (<38 µm) fraction derived from RS. It has been suggested previously¹⁰ that most of the Al and Fe present in AS are in the form of amorphous metal oxides which are known to have a high capacity for binding humic matter^{31,33}.

CONCLUSIONS

Using the CWAT procedure, different grades of oil sands solids were separated into three fractions based on their IOCC. In all cases, solids enriched with humic matter (IOCC ~36%) were separated with bitumen and solids with intermediate IOCC (~5%) remaining suspended in the aqueous phase. The IOCC of the majority of the solids was very low (<0.3%). It was found that H/C and O/C atomic ratios of insoluble organic matter present in all CWAT fractions were close to those of kerogen type-III and humic coals. These results indicated that, as with kerogen-III, the main precursors for oil-sand humic matter were terrestrial higher plants. ¹³C N.m.r. data gave evidence that the coalification rank of the coal-like material derived from oil sand was similar to that of subbituminous coal. It has also been shown that solids associated with bitumen were enriched in Ti, Zr and Fe. The concentration of Al was highest in the AS fractions.

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