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Characterization of solvent-insoluble organic matter isolated from Alberta oil sands*

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Considerable quantities of organic material, insoluble in common organic solvents, are known to be associated with the inorganic minerals present in oil sands. This insoluble organic matter (IOM) consists of both humic and non-humic components containing numerous oxygen functions. In this investigation IOM was beneficiated from a number of feedstocks using HCl/HF mineral dissolution techniques normally used for the isolation of kerogen concentrate from oil shales. The feedstocks included two different grades of Athabasca oil sand, three tailings stream fractions from oil sand plants in Alberta, and a sample of New Brunswick oil shale. The various fractions were analysed for elemental composition and then characterized by infrared and CP/MAS ^{13}C n.m.r. methods. The elemental analyses have been discussed in terms of a van Krevelen diagram by plotting H/C atomic ratios against O/C atomic ratios. N.m.r. data have been used to calculate the aromaticities of various fractions.

(Keywords: oil sand; sedimentology; organic matter)

Considerable quantities of organic material, insoluble in common organic solvents, are known to be associated with the inorganic minerals present in oil sands[1–6]. Most of this insoluble organic matter (IOM) is strongly associated with the fines fractions of the solids[3]. This organic matter is known to consist of humic and non-humic components containing numerous oxygen functions[4–7]. In previous work, IOM from a number of oil sands tailings streams has been isolated and characterized[2–6]. Based on the comparison of IOM with peat, coal, humic acids, and asphaltenes from oil sand bitumen, it was concluded that the maturity of this material was comparable with that of the humic acids from lignite or subbituminous coals, and that it was relatively immature when considered in light of its oil generation potential.

In an attempt to assess the geochemical relevance of IOM to oil sands, material was isolated from various samples of oil sands and tailings streams. The IOM fractions were then studied using elemental analyses and spectroscopic techniques. It is hoped that this study will be helpful in understanding the origins of oil sands as well as providing insight into the intractable nature of oil sand slimes during the sludge formation process in existing tailings ponds.

EXPERIMENTAL

Materials

Table 1 describes the various feedstocks that were treated to extract the insoluble organic matter (IOM) components. Oil sand samples were obtained from the Alberta Research Council sample bank. The samples of Syncrude centrifuge tailings and sludge pond tailings were provided by Syncrude Canada Ltd. Oil phase solids (OPS), the heavy metal minerals fraction containing unextractable organic matter, were isolated from Suncor sludge using an oil phase agglomeration technique reported elsewhere[4,5]. A sample of New Brunswick oil shale, for the isolation of kerogen, was obtained from D. Abbott of the New Brunswick Research and Productivity Council. Non-settling solids from Syncrude sludge pond tailings were obtained according to the scheme shown in *Figure 1a*.

Isolation of insoluble organic matter (IOM)

To isolate IOM from various feedstocks, the inorganic matrix was selectively dissolved in HCl/HF. The general procedure for mineral dissolution and isolation of the IOM is shown in *Figure 1b*.

Elemental analysis

C, H and N analyses were performed, and sulphur was analysed as total sulphur, using X-ray fluorescence spectroscopy. Oxygen was determined either by difference or directly[8]. Chlorine was analysed using the Volhard technique and fluorine by the Alzarine fluorine blue method[9,10]. Heavy metals were determined by a quantitative, inductively coupled plasma atomic emission spectroscopic method (ICP-AES)[11]. The ash content of the humic matter fractions was determined[12] at 400 ± 10°C.

Instrumental analysis

Solid state ^{13}C n.m.r. spectra were obtained at 22.6 MHz using the cross-polarization (CP) technique with magic angle spinning (MAS). A contact time of 1 ms and a repetition time of 2 s were used at MAS speeds of 3.0–3.4 kHz. Chemical shifts were determined by substitution relative to tetramethylsilane (TMS). Each spectrum was the Fourier transform of 3000–10 000

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Table 1 Sample description and analysis of feed materials

Sample no.	Feedstock	Description	Analyses (wt% dry basis)			
			Fines (<38 μm)	Bitumen	Loss on ignition at 400°C[a]	Organic carbon[a]
1	OS-1	Low grade oil sands sample 1[b]	32	3.5	1.30	1.0
2	OS-2	Low grade oil sands sample 2[b]	22	8.3	1.20	0.9
3	SCT	Syncrude centrifuge tailings	15	5.5	18.0	11.1
4	NSSSS	Non-settling solids from Syncrude sludge[c]	100	2.9	16.3	5.75
5	OPS[d]	Oil phase solids	0	–	32.5	19.3
6	NBOS	New Brunswick oil shaes	66	1.1[e]	10.5	5.4

[a] Of toluene extracted dry feed
[b] Samples were from Suncor Mine sites; Section 23, Township 92, range 10, west of Fort Meridian. Sample 1 was 5% overburden bench while sample 2 was 7% mining bench
[c] See *Figure 1*
[d] Oil phase solids, *Figure 1* (Refs. 4 and 5)
[e] Although most of the organic matter associated with NBOS is kerogen, a small part dissolves in benzene

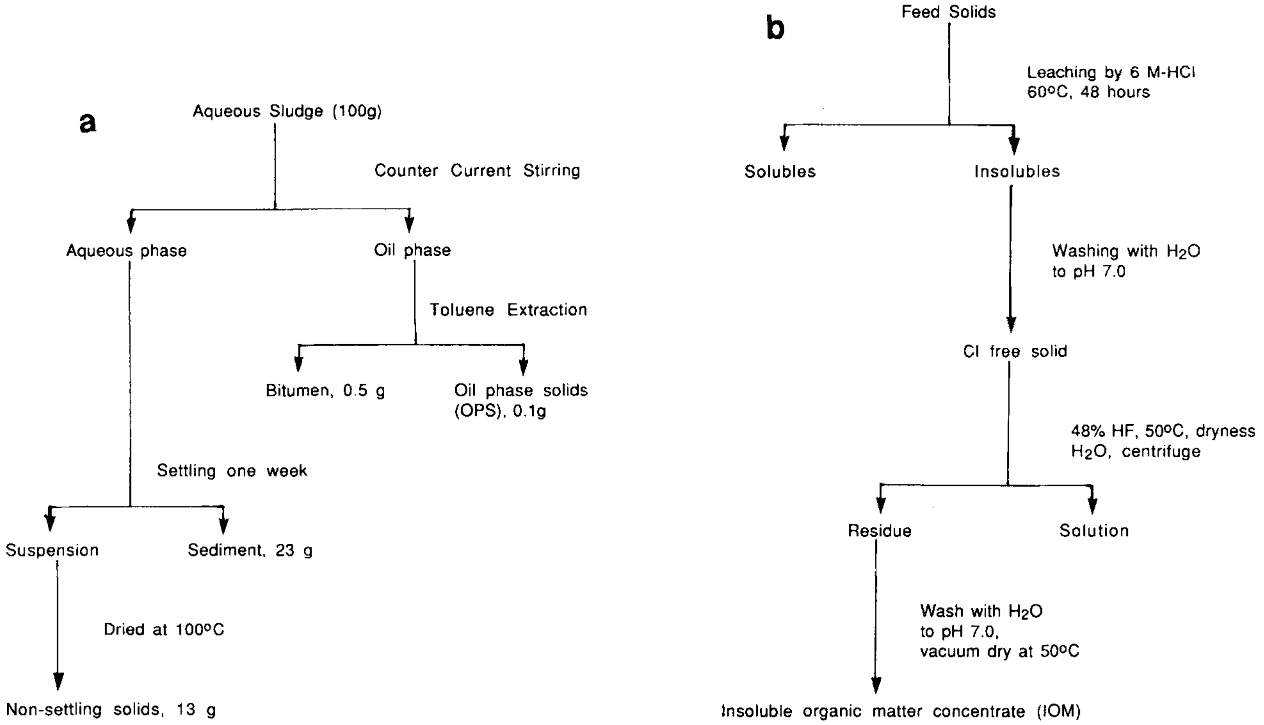

Figure 1 a, Flow sheet for the fractionation of aqueous sludge; b, mineral dissolution scheme for the concentration of IOM by successive acid leaching

free-induction decay curves. For a few samples, a dipolar dephasing technique[13] was also used to distinguish the non-protonated carbons (except groups in motion, e.g. CH_3) from those attached to hydrogens. Infrared spectra were recorded with samples run as KBr pellets. These spectra were used only qualitatively for quick identification of general features and the presence or absence of functional groups.

RESULTS AND DISCUSSION

Recently, an HCl/HF mineral dissolution scheme, commonly used for the isolation of kerogen concentrates from oil shales, has been applied to the beneficiation of insoluble organic matter (IOM) from oil sands[4]. A major portion of the mineral matter in most samples was dissolved by HF, as indicated by the low ash content of the resulting organic residues OS-2, SCT, NSSS and OPS. However, the extent of mineral dissolution varied considerably for the different starting materials. In general, non-settling solids from Syncrude sludge and OPS samples gave organic residues with low ash. The mineral matter associated with oil sand samples, Syncrude centrifuge tailings, and oil shale were the most resistant to acid treatment.

Table 2 lists the elemental compositions of IOM from the various samples. There was considerable variation in the elemental composition of the concentrated IOM fractions. However, a few trends were obvious from examination of the data.

1. IOM obtained from the demineralization of the three oil sand samples and OPS had the lowest carbon content.

Table 2 Elemental analyses and atomic ratios of IOM from various feedstocks

Sample no.	Feedstock	Analysis (wt%, dry ash-free basis) C	H	N	S	O[a]	Atomic ratios H:C	O:C	Ash (% w/w)	Halogen (% w/w)
1	OS-1	61.6	5.6	0.9	8.9	23.0	1.09	0.28	55.6	ND
2	OS-2	60.7	6.0	0.7	10.0	13.7	1.19	0.17	30.1	8.4
3	SCT	70.8	5.3	0.9	5.2	17.8	0.90	0.19	27.3	ND
4	NSSSS	71.0	5.8	1.1	4.8	16.8	0.99	0.18	11.8	ND
5	OPS	61.2	5.2	2.4	4.5	26.7	1.02	0.33	9.5	ND
6	NBOS	67.5	7.4	1.8	4.0	19.3	1.32	0.21	44.9	0.5

[a] By difference
ND = Not determined

2. Demineralized oil shale samples had the highest hydrogen contents.
3. Demineralized sample OS-2 had the lowest nitrogen content, followed by OS-1, CT, and non-settlng solids. The IOM from OPS and NBOS had the highest nitrogen contents. These differences might be due to the presence of nitrogen functionalities having different resistances to acid hydrolysis.
4. Sulphur contents of IOM from oil sands were almost double the sulphur contents of all other samples.
5. There was also considerable variation in the oxygen content of IOM fractions from different feedstocks. Although the oxygen content was determined by difference and contained all accumulated errors, the magnitude of the difference between the various IOM fractions suggests that a substantial amount of oxygen might have been lost from some of the fractions during acid treatment. This is consistent with published reports that suggest the loss of oxygen by acid catalysed decarboxylation reactions during the isolation of sedimentary humic acid fractions using HF[14].
6. Considerable quantities of halogens were also detected in some IOM fractions. This suggests that the organic matter associated with these feedstocks might have undergone chemical interaction with HCl/HF. It is well established that certain organic compounds react readily with both hydrochloric and hydrofluoric acids, resulting in alteration of their chemical/physical properties. For example, esters, amides, olefins, quinones and alcohols undergo various hydrolysis, addition, and alkyl halide formation reactions in the presence of HCl[15,16]. In the case of HF, condensation reactions involving olefins and aromatic compounds occur readily[16]. The high halogen concentrations in the IOM fractions could also be the result of contamination by neoformed fluorides, formed during the demineralization process[17].

van Krevelen diagrams, which are plots of atomic H/C versus O/C ratios, provide a useful approach for the characterization of coals, kerogens and humic matter[18,19]. *Figure 2* is the van Krevelen diagram for the IOM fractions derived from the various samples. IOM from oil sands and tailings streams all fall in the region of type III kerogen, while the sample from New Brunswick oil shale is in the type II kerogen region on this diagram. 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[18]. This type of organic matter is not considered to have any potential for hydrocarbon generation and usually matures to give coal[18]. 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[6].

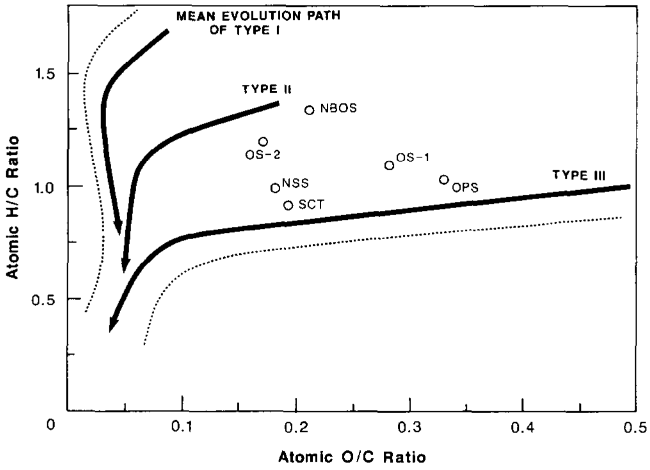

Figure 2 van Krevelen diagram

The van Krevelen diagram provides a practical interpretation for elemental analysis data; however, it must be emphasized that the IOM analysed was obtained by the destruction of the mineral phase through acid hydrolysis. This treatment might have changed the elemental composition of the IOM to the extent that it is no longer representative of the original organic matter. Also, the IOM is a mixture of humic and non-humic matter such as kerogen[4]. This is supported by the fact that there were considerable variations in the elemental compositions of the IOM from the different samples. As a result of these limitations, the elemental analysis results should be interpreted with caution. It appears that, in addition to the humic matter, part of the organic matter may have been incorporated into the sediment through a different pathway not involving the fulvic or humic acid stage.

^{13}C n.m.r. spectra

^{13}C CP/MAS n.m.r. spectra of IOM fractions from various feedstocks are shown in *Figure 3*. All spectra show a broad resonance in the aromatic region (110–150 ppm), but a considerable amount of fine

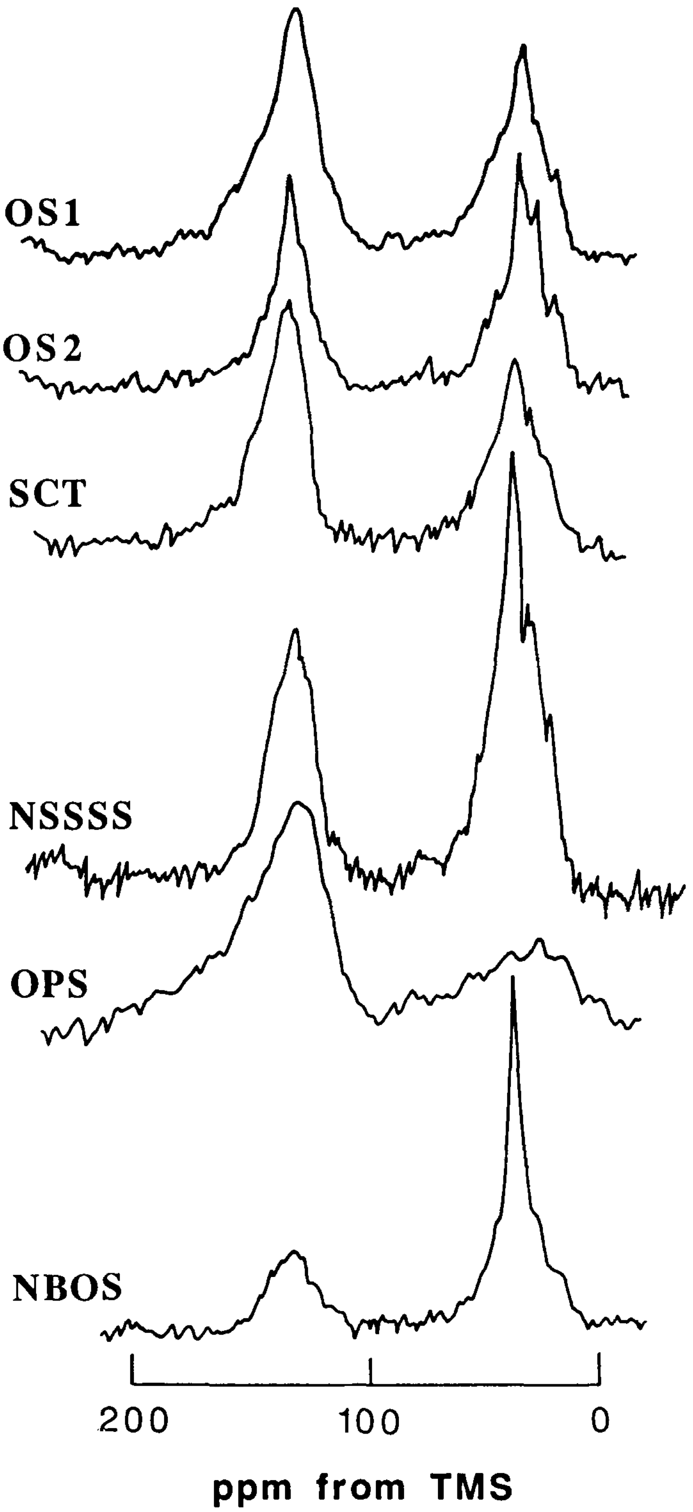

Figure 3 ^{13}C MAS n.m.r. spectra of IOM fractions from various feedstocks shown in *Table 1*

structure can be seen in the aliphatic regions of all spectra (except those for demineralized oil shale samples). Distinguishable peaks for carbohydrates (= 75 ppm) are only present in the spectrum of the sample from oil sand-2. Non-settling solids from Syncrude sludge, oil sands sample-1, and OPS samples show a broad resonance in this region.

All spectra show a relatively intense and broad signal for aromatic carbons (110–150 ppm). The relative intensity of this signal indicates that a large proportion of the aromatic rings are not substituted by strong electron-donating substituents such as oxygen and nitrogen. The chemical shift region for aromatic carbons substituted by O and N functions groups (e.g. $-OCH_3$, —OH, -OR, $-NH_2$) lies between 150–165 ppm. None of the samples shows a well defined peak in this region, although OS-1, SCT and OPS samples show some broad resonance.

Carboxylic, amide and ester carbons did not appear to be important components of these samples as none of the spectra showed any distinct, resolved peak between 169 and 190 ppm. However, the spectrum for OPS did show a weak, broad resonance in this region. *Table 3* gives the ^{13}C chemical shift range assignments. *Table 4* lists the percentage compositions of the various regions shown in *Table 3*. It is obvious from these data that there is a wide variation in the distribution of various carbon types for acid demineralized feedstocks. The paraffinic and aromatic carbons contributed 37–61% and 36–52% respectively of the total carbons in these samples. The amounts of carbohydrate, phenolic and carboxylic carbons were 3–11%, 2–5% and 0–9%, respectively.

The O/C ratios calculated from ^{13}C n.m.r. were smaller than those calculated from the elemental analyses. This suggested that the IOM associated with these samples contained ether or alcoholic oxygen groups rather than carboxyl and phenolic. The total contribution of these aliphatic oxygen functions to the IOM structures could not be estimated because of the possibility of errors in the elemental analysis[4]. Also the high ash content of these samples could result in a large contribution from the inorganic or mineral components[20]. Oxygen in most of these samples has been determined by difference so that all analytical errors accumulated in the result for this element.

The aromaticities (f_a) calculated from the integrated areas of the ^{13}C n.m.r. spectra are listed in *Table 5*. The aromaticity values for bitumen, asphaltenes and humic acid samples from coal, soil and oil sands are also included for comparison. It is obvious from comparison of these data that the oil sand and tailings samples have aromaticity values greater than the values for soil humic acids and oil shale kerogens (acid demineralized New Brunswick oil shale). Two oil sand samples, and OPS and SCT samples, have aromaticity values comparable to the values for humic acids from oil sands and subbituminous coal. The non-settling solids from Syncrude sludge have a much lower aromaticity, which is comparable to the value for asphaltenes from oil sands bitumen. This suggests that the organic matter associated with the non-settling solids from Syncrude sludge could be structurally different from the IOM associated with the bulk of the solids from oil sands.

Table 3 Assignment of ^{13}C chemical shift ranges

Region	Chemical shift range (ppm)	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

Table 4 Relative intensities for various regions of the ^{13}C n.m.r. spectra of acid-demineralized feedstocks

		Total intensity (%)					
Sample no.	Feedstock	A_1+A_2 (0–110 ppm)	B (110–145 ppm)	C (145–160 ppm)	D_1+D_2 (160–220 ppm)	Atomic O/C[a]	Δ[b]
1	OS-1	42.0	52.0	2.6	3.4	0.09	−0.19
2	OS-2	54.3	36.5	4.8	4.4	0.14	−0.03
3	BS	83.2	23.7	3.1	–	0.03	−0.20
4	OB-1	53.6	28.2	5.3	12.9	0.03	−0.20
5	OB-2	57.7	34.2	3.6	4.5	0.13	0.0
6	SCT	44.6	49.1	4.4	1.9	0.08	−0.11
7	NSSSS	60.8	36.8	2.4	–	0.18	−0.16
8	OPS	46.6	38.8	5.4	9.2	0.24	−0.12

[a] $O/C=(C+2D_1)/100$
[b] $\Delta=(O/C\ ^{13}C\ n.m.r.)-(O/C\ elemental\ analysis)$

Table 5 Aromaticites of insoluble organic matter fractions

Sample no.	Feedstock	f_a
1	OS-1	0.57
2	OS-2	0.51
3	SCT	0.55
4	NSSSS	0.40
5	OPS	0.53
6	NBOS	0.28
7	Oil sands humic acids[a]	0.51
8	Humic acids from subbituminous coal	0.59
9	Soil humic acids	0.35
10	Oil sands bitumen	0.30
11	Ashpaltenes from oil sands bitumen	0.42

[a] Data from Ref. 4

The aromaticity has been plotted against H/C and O/C atomic ratios in *Figure 4*. Considering the limitations of n.m.r. measurements and elemental analysis, a fairly good correlation between increased aromaticity and increased O/C and decreased H/C ratios is obvious when the data point for New Brunswick oil shale is excluded. Similar correlations have been reported for coals[21].

Infrared spectra

The infrared spectra of IOM fractions from the various samples are shown in *Figure 5*. The assignment of the various bands in the infrared spectra is based on published work for coal, asphaltenes and humic materials[22–30]. The main zones of interest are as follows:

1. a broad absorption band around 3200–3400 cm^{-1} is related to H-bonded OH groups (phenolic, alcoholic, carboxylic OH), while small contributions from N–H groups are also possible;
2. weak to strong absorptions in the ≈2900 cm^{-1} region are attributed to CH_2 and CH_3 aliphatic groups;
3. a medium to strong intensity band around 1700–1730 cm^{-1} is related to various C=O groups (ketones, acids, esters);
4. a weak to medium-intensity band, centred at 1600 cm^{-1}, is attributed partly to conjugated C=C bonds and partly to the carbonyl groups of ketones and/or quinones;
5. varying intensity bands at 1450 and 1380 cm^{-1} are due to bending frequencies of asymmetric C—CH_3 bonds and/or methylene and symmetric C—CH_3 bonds, respectively;

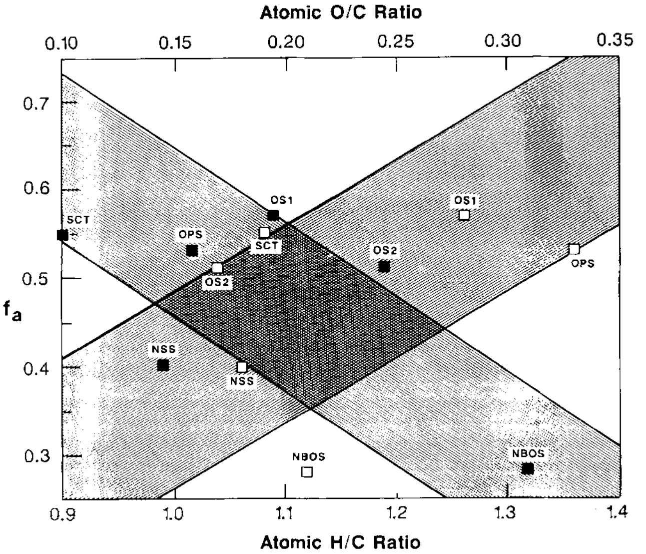

Figure 4 Aromaticity versus H/C and O/C ratios for acid demineralized feedstocks: □, H/C; ■, O/C

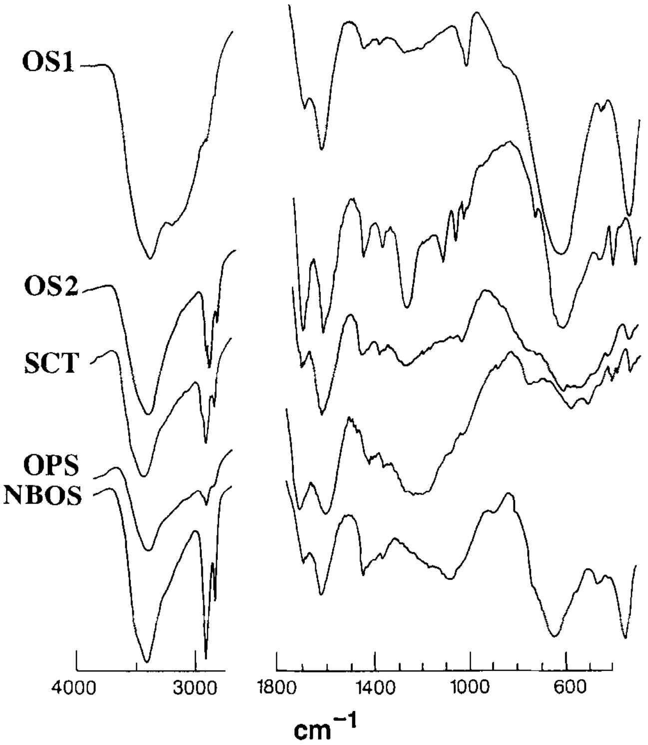

Figure 5 Infrared spectra of acid-demineralized feedstocks

6. a group of bands located in the 1300–900 cm^{-1} region is assigned to C—O stretch in aromatic oxygenated compounds such as aromatic ethers, sulphoxides and polysaccharides: some of the strong absorptions in this region could be due to retained mineral matter or insoluble fluorides formed with retained calcium during demineralization.

The basic features of the infrared spectra were similar; however, for various samples, the relative intensities of infrared bands varied considerably. The most striking differences can be summarized as follows. The intensities of the bands at 2850–2930, 1460 and 1380 cm^{-1} suggest a considerable variation in the content of aliphatic CH components in the IOM fractions from different samples. Oil sands sample-2 and NBOS samples had the highest aliphatic CH components, which is consistent with the higher H/C elemental ratios for these samples.

The intensity of the absorption band around 1700 cm^{-1} also varied considerably. Strong absorptions in this region were only observed for OS-1 and the OPS sample. All other samples had weak absorptions in this region. The differences in intensity of the absorption in this region could reflect the different degrees of decarboxylation of IOM fractions as a result of HCl/HF treatment. Some data in the literature indicate that a weaker absorption around 1700 cm^{-1} might be caused not only by a lower number of carboxyl groups but by the presence of carboxylate ions[29]. Another striking difference in these spectra is the relatively sharper absorptions in the 1000–1500 cm^{-1} region for the OS-2 sample compared with the much broader absorptions for all other samples.

CONCLUSIONS

The effectiveness of the acid demineralization technique for the beneficiation of IOM from different reservoir matrices varies considerably. Elemental analysis results for demineralized feedstocks suggested that HCl/HF reacts with IOM, possibly via decarboxylation. A plot of the H/C versus O/C atomic ratios for IOM fractions from various feedstocks suggests that most of the data fall in the type III kerogen region. Based on the values of carbon aromaticities, the IOM associated with the various samples investigated appears to be comparable in maturity to the subbituminous coals. Considering the limitations of n.m.r. measurements and elemental analysis results, there is a fairly good correlation between increased aromaticity and increased O/C and decreased H/C ratios. Although the basic features of the infrared spectra of IOM from different feedstocks were similar, the relative intensities of infrared bands varied considerably for the different samples. These variations could reflect different degrees of attack by HCl/HF. In establishing the relationship between the different types of IOM, the limitations of the isolation techniques in conjunction with uncertainties in elemental and spectroscopic analyses in the presence of mineral matter should be realized.

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