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Residual Organic Matter Associated with Toluene-Extracted Oil Sands Solids and Its Potential Role in Bitumen Recovery via Adsorption onto Clay Minerals[†]

Fu Dongbao,[‡] John R. Woods,[‡] Judy Kung,^{*,‡} David M. Kingston,[‡] Luba S. Kotlyar,[‡] Bryan D. Sparks,[§] Patrick H. J. Mercier,[‡] Thomas McCracken,[‡] and Samson Ng^{||}

[‡]Institute for Chemical and Environmental Technology, National Research Council of Canada, 1200 Montreal Road, Ottawa, Ontario K1A 0R6, Canada, [§]V. Bede Technical Associates, 614 La Verendrye Drive, Ottawa, Ontario K1J 7C4, Canada, and ^{||}Edmonton Research Centre, Syncrude Canada Limited, 9421-17 Avenue, Edmonton, Alberta T6N 1H4, Canada

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Adsorption of hydrocarbon components, particularly by clay minerals, has an important influence on the recovery of conventional oil from reservoir rocks. In the same vein, biwetted clay particles have been associated with bitumen losses during processing of surface-mined oil sands. In this work, we examined four oil sands with very different batch-extraction unit (BEU) bitumen recovery profiles. Bitumen-free solids from these ores were subjected to supercritical fluid extraction with methanol to separate quantitatively any toluene-insoluble, residual organic matter. The yield of extract correlated well with the amounts of solids in the fine (<44 μm) and clay (<3 μm) size fractions as well as with the concentrations of kaolinite and illite present in the oil sands ores. It is generally assumed that organic matter adsorbed by reservoir solids is asphaltic in origin; however, in the results discussed here, the compositional and structural analysis of the methanol extracts showed more similarities to the resin component of bitumen. Also, in comparison to other bitumen saturates, aromatics, resins, and asphaltenes (SARA) fractions, the extracts from each oil sands were somewhat enriched with pyridines, sulphoxides, and sulphones. We argue that the physicochemical properties of the residual organic matter separated by supercritical extraction strongly influence the wettability of solids in the ores through adsorption onto clay minerals. We suggest that this mechanism is a prerequisite for the formation of biwetted clay particles capable of stabilizing emulsified bitumen-in-water droplets that are too small to be successfully recovered by flotation.

1. Introduction

Currently, commercial oil sands surface mining operations use an aqueous conditioning process, usually with chemical addition, such as caustic, to liberate bitumen from an unconsolidated, largely quartz matrix. This is followed by a combination of gravity separation of the coarse solids and a secondary flotation step to produce a bituminous froth. The classic Clark hot-water extraction process uses steam and 95 °C hot water to produce oil sands slurry at 80 °C. More recently, several innovative processes have reduced energy input by lowering operating temperatures. Bitumen recovery varies, often unpredictably, depending upon the type of oil sands, process water used, and operating conditions. As a consequence, it is of great interest to understand the mechanisms causing recovery losses during bitumen separation.

Similar to conventional reservoir rocks, Athabasca oil sands contain solids whose surfaces are altered by the

presence of strongly bound, toluene-insoluble organic matter (TIOM).^{1–4} Such organic-rich solids (ORS)⁵ comprise a complex mixture of minerals whose properties represent a continuum with respect to size, density, and surface condition. In water-based, gravity separation processes, coarser, higher density ORS tend to remain with the tailings and any bitumen associated with these solids is lost. Some ORS particles have biwetted characteristics and can be separated by collection at oil–water interfaces.^{6,7} The finest particles of this type, usually clay minerals, are capable of stabilizing small oil droplets⁸ as Pickering emulsions.⁹ In oil sands, the presence of such solids will produce small bitumen droplets

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^{*} To whom correspondence should be addressed. E-mail: judy.kung@nrc.ca.

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(< 1 mm diameter) that will not be floatable; in such cases, bitumen recovery by gravity separation is reduced.^{10,11}

Previously, we separated and characterized a humic matter fraction from toluene-extracted oil sands by a combination of alkaline extraction and ¹³C nuclear magnetic resonance (NMR) measurements.¹² In other work, nonhumic residual organic matter components were recovered by supercritical fluid extraction (SCFE) with methanol.¹³ In the present investigation, we used the latter approach to determine the disposition of residual organic matter from oil sands solids previously extracted with toluene to remove all free bitumen. On the basis of their radically different bitumen recoveries, two each of marine and estuarine oil sands were selected from a group of 10 ores from a previous study to correlate bitumen recovery in standard batch-extraction unit (BEU) tests with the mineralogy and size distribution of clay minerals as determined by a novel X-ray diffraction (XRD) approach.¹⁴

Earlier studies showed that TIOM concentrates selectively with the fines (<44 μm solids), particularly the clay size fraction (<3 μm solids)^{15,16} of oil sands solids. In the oil sands studied here, this latter fraction is represented primarily by illite and kaolinite, with minor amounts (2–6 wt %) of quartz.¹⁴ The illite fraction of some ores was also characterized by a large proportion of clay mineral crystallites, with a thickness of only 1–3 composite layers;¹⁴ electron microscopic examination has shown such ultra-thin clay particles to have major lateral dimensions of 60–300 nm and thicknesses of 1–10 nm.¹⁷

In the present work, SCFE with methanol was used to separate residual organic matter from four toluene-extracted oil sands chosen from a representative set of 10 ores from a previous study.¹⁴ The methanol extracts (MEs) were then characterized by elemental analysis as well as ¹H and ¹³C NMR. These results were compared to similar data for saturates, aromatics, resins, and asphaltenes (SARA) fractions from bitumen separated from the corresponding parent oil sands by solvent extraction with toluene. Through such systematic comparisons, we establish clear correlations between properties of organic matter and mineral solids: (1) yields of MEs from supercritical separation, (2) concentrations of

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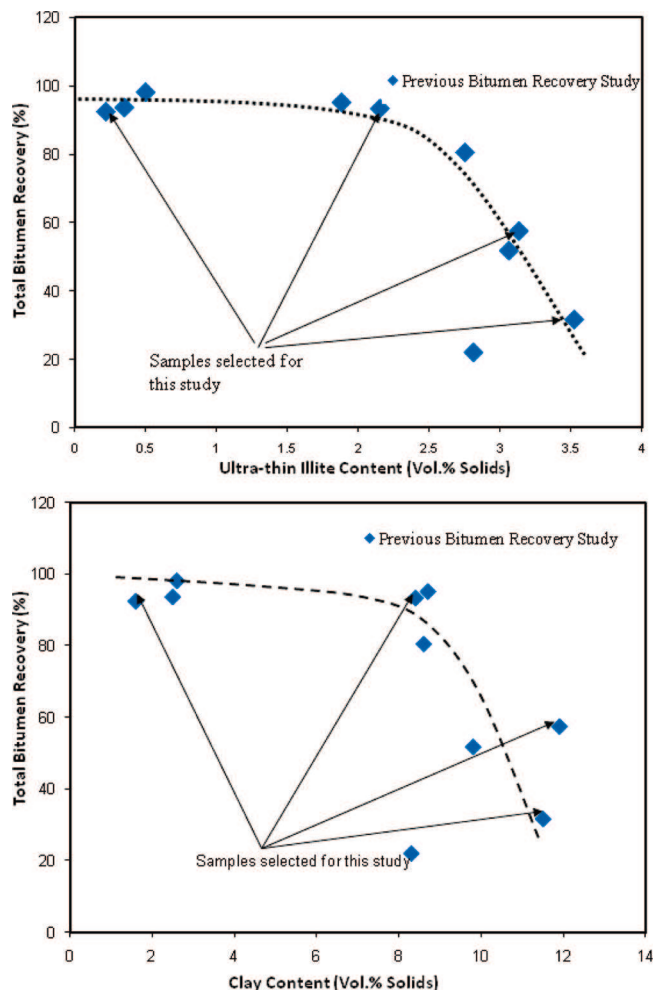


Figure 1. Bitumen recovery as a function of ultra-thin illite and clay contents from a previous study. Arrows identify oil sands used in this work.

fines- and clay-sized particles in the oil sands solids, (3) clay mineral properties, (4) nitrogen contents of MEs and resin subfractions from bitumen, and (5) poor bitumen recoveries measured in BEU tests. We argue that the physicochemical properties of the residual organic matter separated by supercritical extraction strongly influence the wettability of solids in the ores through adsorption onto clay minerals. We suggest that this mechanism is a prerequisite for the formation of biwetted clay particles capable of stabilizing bitumen-in-water emulsion droplets that are too small to be successfully recovered by flotation. Such a mechanism could explain differences in bitumen separation efficiencies between oil sands where all other characteristics are quite similar.

2. Experimental Section

2.1. Samples. Syncrude Canada Ltd. (Edmonton Research Centre) provided a total of 10 oil sands core samples (5 estuarine and 5 marine) from the Aurora and North mine operations of the company. Each core was carefully homogenized in a Comomil before subsampling; individual samples were kept frozen until required for testing. For the supercritical extraction tests, four oil sands were selected from this group of 10. These included two easily processable estuarine ores (E3 and E7) and two marine ores with either mediocre (M18) or very poor (M13) recovery. Figure 1,¹⁴ shows recoveries for these ores as a function of their clay and ultra-thin illite contents; these were the two clay

mineral properties correlating best with BEU bitumen recoveries. Accordingly, the four oil sands selected for the current study encompassed the whole range of bitumen recoveries, clay content, and ultra-thin illite concentration encountered in the recovery study.

2.2. Separations. Bitumen was extracted from each oil sands by the standard Soxhlet Dean and Stark method, with toluene as the solvent.¹⁸ Particle size distributions of the dried solids were determined using a laser diffraction technique,¹⁹ in which fines are defined as the size fraction comprising $< 44 \mu\text{m}$ solids and clay are defined as the size fraction comprising $< 2.8 \mu\text{m}$ solids.

Soxhlet extraction of oil sands with toluene yielded bitumen solutions in toluene and bitumen-free solids. The extracted solids and bitumen solutions were dried to constant weight at 80°C in a vacuum concentrator at a pressure of 76 cm of mercury. The solvent-free bitumen samples were then redissolved in toluene at a 1:1 volume ratio before treatment, with a large excess of *n*-pentane for quantitative separation of the asphaltene fractions.²⁰ Any solids present in the bitumen were reported entirely with the separated asphaltene and were removed quantitatively by an ultracentrifugation procedure.²¹ High-performance liquid chromatography (HPLC) SARA separation^{22,23} on the desolventized maltene fractions from the parent bitumens yielded saturates (sat), aromatics (ar), and resin (res) fractions. On the basis of increasing relative polarity, the resin components were further divided into three subfractions (R1, R2, and R3).²⁴

Bitumen-free solids, after toluene extraction, were subjected to SCFE with methanol using customized equipment. Supercritical methanol, preheated to 250°C , was delivered at a flow rate of 5 mL/min to a 50 mL extraction cell also set at 250°C and containing about 50 g of the dried, toluene-extracted oil sands solids. System pressure was controlled to about 140 atm by manually opening and closing a heated restrictor valve. Extract was collected for a total of 100 min into a 1 L conical flask set in an ice bath. The methanol solutions from supercritical extraction were dried to a constant weight, then redissolved in toluene, and ultracentrifuged to remove any associated solids. The amount of ME, which varied from ~ 0.03 to 0.1 wt % of the bitumen-free solids, was in line with values determined by others.² Because the amounts of solvent-free ME material were small, it was necessary to combine the production from several extractions to provide enough material for analyses. In one case, E7, the amount of ME was so low that even multiple extractions did not produce enough material for complete characterization.

Bitumen recovery tests were made in a standard BEU cell; the detailed procedure is described elsewhere.¹⁸ The same commercial process water and caustic addition (0.08 wt % of oil sands feed) was used in each test.

2.3. Analyses. Carbon, hydrogen, nitrogen, and sulfur contents were determined using a LECO CHNS-932 analyzer.

Table 1. Basic Characterization and BEU Bitumen Recovery Data for the Four Ores Selected for This Work

(a) Oil Sands Compositions and BEU Recoveries					
sample ID	bitumen ^a (wt % oil sands)	water (wt % oil sands)	solids (wt % oil sands)	bitumen recovery (%)	
				primary	total
E3	9.8	6.8	83.4	84.8	93.3
E7	14.7	1.3	84.0	5.5	92.4
M13	9.9	6.1	84.0	15.3	31.7
M18	7.9	8.6	83.5	34.5	57.5

(b) Weight of Subfractions in 50 g of Toluene-Extracted Oil Sands Solids						
sample ID	extract (g/50 g)	fines (g/50 g)	clay minerals (g/50 g)			
			illite	kaolinite	illite	kaolinite
E3	0.0521	15.0	2.8	1.6	1.1	0.1
E7	0.0169	2.5	0.4	0.4	0.1	0.1
M13	0.0580	12.9	3.9	1.7	1.8	0.1
M18	0.0640	20.9	3.1	1.8	1.6	0.1

^a By difference. ^b Mass fraction of illite and kaolinite crystallites with a thickness $q = 1-3$, where q is the number of composite layers per individual crystallite derived from XRD measurements.¹⁴

Molecular-weight determinations were carried out on sample solutions (0.5 w/w %) in tetrahydrofuran. Number average molecular weights (MW_n) were measured by gel permeation chromatography (GPC) calibrated with polystyrene reference standards.²⁴ A recent discussion on the validity of asphaltene molecular-weight determination by this technique and others has been published elsewhere.²⁵

X-ray photoelectron spectroscopy (XPS) characterization of the samples was provided by a Kratos Axis Ultra unit with a monochromated Al X-ray source. Three analyses were performed on each sample to ensure reproducibility. The same experimental conditions and data analysis procedures, as described elsewhere,²⁴ were used to analyze the measured XPS data. Quantification was performed using sensitivity factors from the Scofield element library included with the CasaXPS (version 2.2.107) data processing software; such measurements are reproducible to within 10% standard deviation as a percentage of the average value (RSD).

¹H NMR measurements were made with a Varian Unity Inova 400 MHz spectrometer, using a 5 mm, 4 nucleus probe. Measurements for ¹³C NMR were made with the same spectrometer and a 5 mm broadband probe.²⁴

3. Results and Discussion

3.1. Standard Oil Sands Characterization. The basic characterization and BEU bitumen recovery data for the four ores selected for this work are given in Table 1. On the basis of fines and bitumen contents (Table 1a), sample E7 was a high-grade low fines ore, E3 and M13 were typical average ores, while M18 was a lower grade sample with high fines content. Of particular interest are the high proportions of illite and ultra-thin illite in the clay fractions (Table 1b). M18 was unusual in that it was the only ore with significant amounts of dolomite and calcite detectable by XRD. Significant amounts of chlorite, as measured by XRD, were observed only in the marine oil sands.¹⁴

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Table 2. Elemental Analysis of ME Samples

sample ID	H/C	N (wt %)	S (wt %)	N/S
E3	1.42 ± 0.05	1.3 ± 0.07	5.3 ± 0.1	0.56 ± 0.01
E7	1.39	1.3	5.5	0.54
M13	1.50 ± 0.05	1.5 ± 0.1	5.4 ± 0.1	0.63 ± 0.02
M18	1.47 ± 0.05	1.4 ± 0.02	5.3 ± 0.1	0.60 ± 0.04

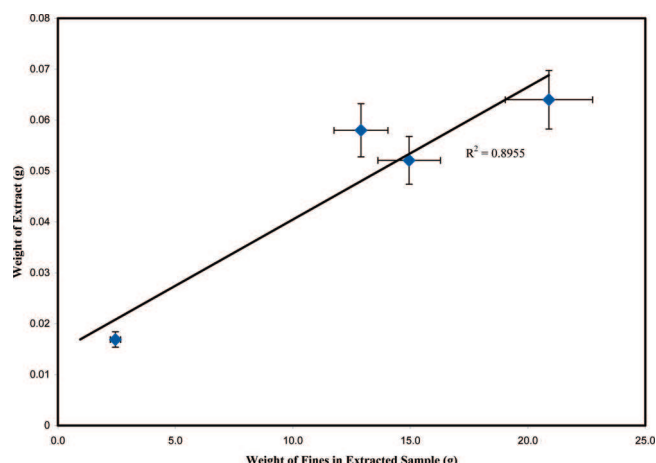
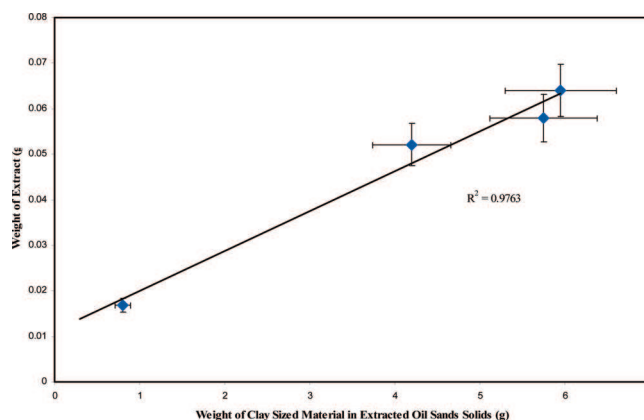
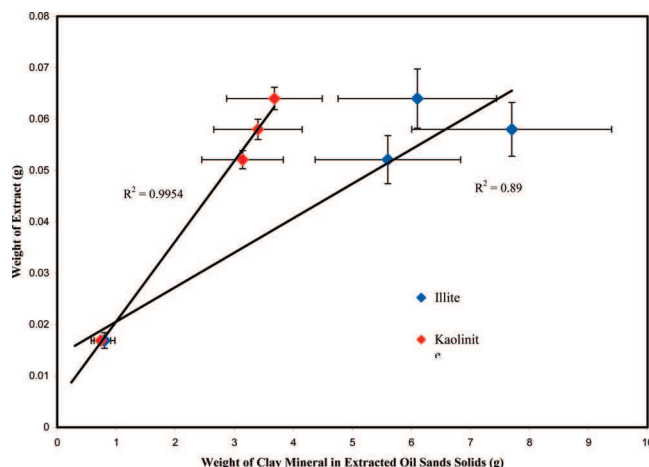
**Figure 2.** Correlation between normalized weights of ME and fine solids in bitumen-free oil sands solids samples.**3.2. Yields and Elemental Compositions of Extracts.**

Table 2 summarizes the elemental analysis (CHNS) for the extracts from the different oil sands samples; there was insufficient E7 sample for multiple analyses, and no standard deviations could be determined in this case. On the basis of the measurement precisions, we cannot differentiate between the extracts based on simple elemental analysis. It thus appears that the residual organic material extracted by SCFE is similar in each case; it is quite possible that the same bitumen components are being adsorbed to different extents based on the type, amount, and surface areas of the clay minerals present in the parent oil sands solids.

3.3. Correlation with Clay Mineral Properties. The weight of ME correlated quite well with the total weight of both fines- and clay-sized particles in the four samples of bitumen-free, oil sands solids tested (see Figures 2 and 3). The nonzero intercept of the trend line with the vertical axis indicates that the coarser solids contribute very little to organic retention compared to the clay fraction. This is not unexpected given that the clay-sized material comprises the largest source of surface area in these samples.¹⁴

The concentrations of individual major clay minerals, illite and kaolinite, also correlated quite well with the extract yield (see Figure 4). Previously, it was noted that, for these¹⁴ and other²⁶ oil sands, the illite/kaolinite mass ratio increased with decreasing particle size. Figure 5 shows that illite was essentially the only clay mineral present in the ultra-thin clay mineral fraction (i.e., the mass fraction of clay minerals comprising crystallites with thicknesses q of 1–3 composite layers). While the fit is not as good as for the individual bulk clay minerals, the results in Figure 5 show that the amount of residual organic matter extracted by SCFE also correlated quite well with the ultra-thin illite content of these oil sands samples.

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**Figure 3.** Correlation between normalized weights of ME and clay-sized solids in bitumen-free oil sands solids samples.**Figure 4.** Correlation between normalized weights of ME, illite, and kaolinite in bitumen-free oil sands solids samples.

In summary, the yield of MEs separated by SCFE correlated well with properties of the finer size fractions of the mineral solids. The close association with clay mineral properties suggests that the residual organic matter was primarily associated with these minerals. The toluene solubility of the SCFE extract separated from solids, previously exhaustively extracted by the same solvent, is an indication that it was strongly bound to the solids. Because clay minerals constitute the solids fraction with the largest surface area in these samples,¹⁴ it is then reasonable to infer that the residual organic matter was originally mostly adsorbed onto clay mineral size fractions prior to its supercritical extraction with methanol. This combination of fine particle size and organic coating provides the essential ingredient for an emulsion-forming entity that occurs naturally in oil sands.

3.4. Comparison of SCFE MEs with SARA Fractions from Bitumen. Following Mercier et al.,²⁷ we compare elemental ratios for the ME samples to those for the SARA fractions from the parent bitumens (see Table 3). Here, we note that H/C ratios for the ME fractions are closer to the SARA resin components than any other fraction. On the other hand, the N/C values for the extracts are as high as those for asphaltenes

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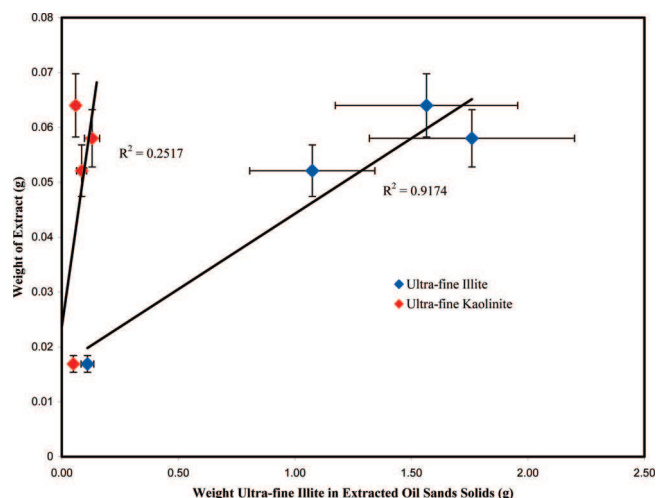


Figure 5. Correlation between normalized weights of ME, ultrafine illite, and kaolinite in bitumen-free oil sands solids samples.

Table 3. Comparison of Basic Properties for MEs and SARA Fractions from Bitumen

(a) Estuarine Oil Sands						
fraction	E3			E7		
	H/C	N/C	S/C	H/C	N/C	S/C
saturates	1.91	0.002	0.001	1.90	0.004	0.002
aromatics	1.55	0.002	0.017	1.49	0.002	0.019
resin 1	1.47	0.005	0.032	1.42	0.005	0.033
resin 2	1.34	0.010	0.029	1.30	0.011	0.029
resin 3	1.44	0.012	0.031	1.40	0.012	0.030
asphaltene	1.21	0.013	0.039	1.21	0.013	0.038
ME	1.42	0.015	0.027	1.39	0.016	0.029
standard deviation	±0.11	±0.0005	±0.0007	±0.10	±0.0005	±0.0003

(b) Marine Oil Sands						
fraction	M13			M18		
	H/C	N/C	S/C	H/C	N/C	S/C
saturates	1.82	0.002	0.001	1.93	0.003	0.001
aromatics	1.56	0.002	0.018	1.57	0.002	0.018
resin 1	1.37	0.005	0.031	1.50	0.005	0.030
resin 2	1.29	0.010	0.028	1.42	0.010	0.028
resin 3	1.32	0.011	0.031	1.43	0.012	0.031
asphaltene	1.22	0.013	0.039	1.20	0.014	0.039
ME	1.50	0.018	0.028	1.47	0.017	0.028
standard deviation	±0.05	±0.0006	±0.003	±0.008	±0.0003	±0.0003

and significantly higher than the values for the corresponding resin fractions. The selectivity for nitrogen compounds in their interaction with illite,^{27,28} zeolite,²⁹ and smectite^{30,31} materials is well-documented. While the S/C atomic ratio values for the ME samples are similar to those for the resin fractions, they

have a tendency to be marginally less than the asphaltene results. In this regard, Mercier et al.²⁸ also observed that illite preferentially adsorbs nitrogen compounds over those of sulfur. In contrast, other workers believe that the hydrophilic–hydrophobic character of clays is related to their relative wettability by asphaltenes and water, whereby asphaltenes are preferentially adsorbed onto kaolinite, while illite shows more affinity for water.^{32,33}

The bar chart in Figure 6a compares MW_n values for the ME fractions and SARA components from the parent bitumens. The much lower molecular weight of the ME samples compared to asphaltenes clearly eliminates this bitumen component as a *direct* source for the residual organic material separated by supercritical extraction. Molecular weights for the extracts were most closely aligned with those for the resins, making these bitumen fractions the most likely source for the ME material. If resins are the primary source for the strongly bound ME organic matter, the higher nitrogen contents (Figure 7) in the extracts are in accordance with previous studies,²⁸ while the similar sulfur (Figure 8) values are not.

3.5. Surface Analysis and Chemical Group Speciation. XPS provides a tool for probing the first 7 nm of a surface layer; the resulting spectra can be mathematically deconvoluted to allow for chemical group speciation. Table 4 compares the distributions of sulfur and nitrogen types for two bitumen subfractions (R3 and asphaltenes), with the ME fractions from the corresponding bitumen-free oil sands solids. The sulfur species from the bitumen fractions were predominantly thiophenic, with some contribution from sulphides and sulfoxides; the R3 subfractions from E3 and M13 were exceptional in this regard. Apart from sample M18, by far the highest concentrations of sulphone and sulfoxide species were found in the ME samples. It should also be mentioned that sulfoxides have also been detected in the TIOM separated from bitumen-free oil sands solids by extraction with mixed solvents.²

In accordance with other work on organo-clay model systems,²⁸ our results support the observation that pyrrole nitrogen species play an important role in the retention of organic matter by illite; on the basis of the precision of the results ($RSD = \pm 10\%$), the proportion of pyrroles in R3, asphaltene, and ME samples is not significantly different. However, the contribution of pyridines to the extracts is significantly higher than values determined for the corresponding R3 and asphaltene fractions. The reason for this is unclear, but it may be related to the fact that some particle surfaces in oil sands solids were in contact with humic matter^{2,34} before ingress of the hydrocarbon phase. Thus, the amount of clay exposed to adsorption of hydrocarbon will be governed by the *in situ* microenvironment, and this may have changed surface selectivity^{29,30} compared to the clean surfaces used in model studies.²⁸ Specific adsorption of pyridine is of particular interest because it is often used to alter the wettability of surfaces.³¹ Although there is no overall difference in the amount of sulfur compound

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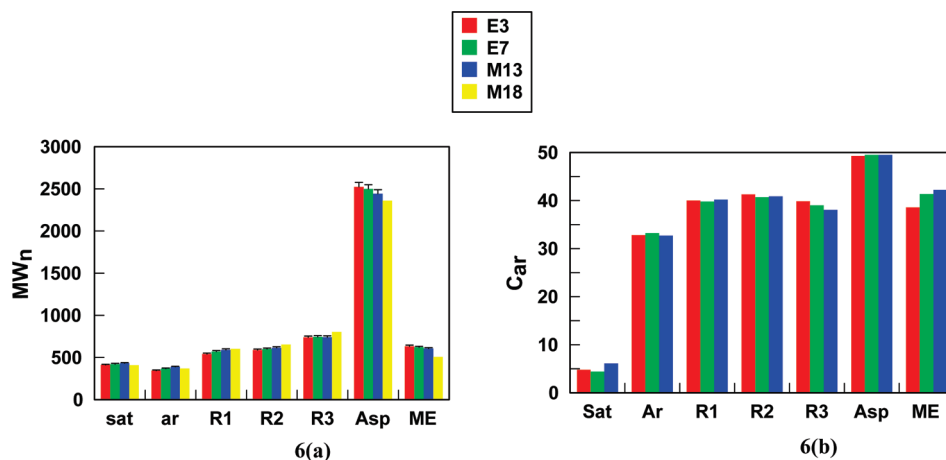


Figure 6. GPC number average molecular weights and ¹³C NMR aromaticities (C_{ar}) for bitumen fractions and ME from oil sands solids.

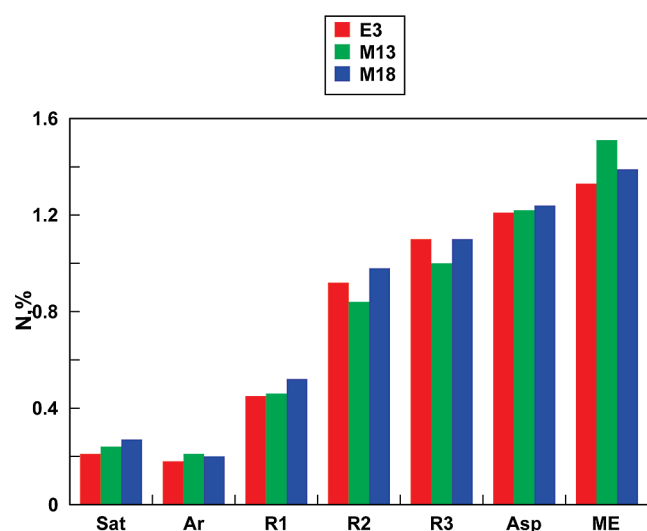


Figure 7. Nitrogen contents for MEs and SARA subfraction from bitumen.

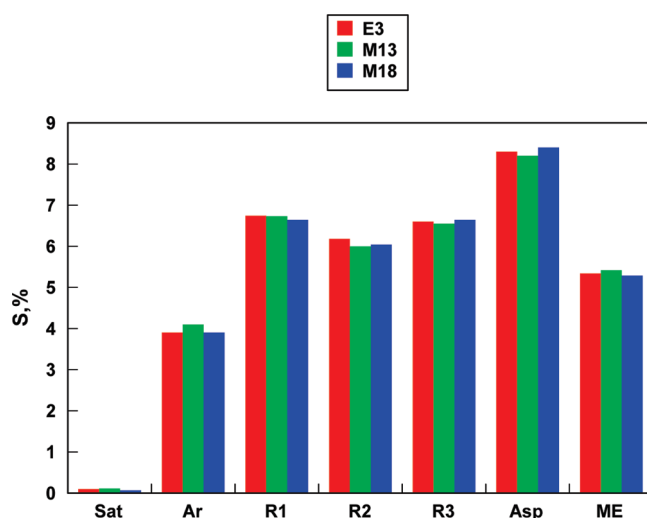


Figure 8. Sulfur contents for MEs and SARA subfraction from bitumen.

detected by XPS, there is a notable tendency for sulfoxides and, particularly, sulfones to be concentrated in the MEs

Table 4. Nitrogen and Sulfur Types in Bitumen Fractions and MEs^a

species	species distribution in sample (% of total)							
	E3		M13		M18			
	R3	asphal- tene	ME	R3	asphal- tene	ME	R3	asphal- tene
sulfur								
thiophenic	74.0	74.8	49.8	65.9	68.5	55.6	68.0	68.9
sulphide	26.0	17.6	8.9	34.1	15.4	10.6	13.3	14.2
sulphoxide	bdl ^b	7.7	28.0	bdl	13.6	21.8	18.8	14.2
sulphone	bdl	bdl	13.6	bdl	2.5	12.0	bdl	2.8
nitrogen								
pyrrole	81.0	74.0	66.7	69.2	78.1	59.7	80.7	78.5
pyridine	19.0	26.0	33.3	30.8	21.9	40.3	19.3	21.5

^a The RSD value for these measurements is $\pm 10\%$. ^b bdl = below detection limit.

obtained in this work. This selectivity suggests that the sulfur species in the ME samples are more polar than the thiophenes and sulfides that predominate in the resin source materials.

3.6. Structural Analysis of Organic Fractions. Well-established ¹H and ¹³C NMR spectroscopic techniques measure the proportion of protons and carbons in specific molecular environments.^{35,36} The proportion of protons or carbons in each environment is determined as a fraction of the total number of protons or carbons by comparing the integrated areas for each environment to the total peak areas on the ¹H and ¹³C spectra; dependent upon signal-to-noise ratios, the measurement of peak areas is typically better than $\pm 1\%$ RSD. The bar graph in Figure 6b compares aromaticities, from ¹³C NMR, for each of the ME samples and the bitumen SARA fractions. Again, we see that the greatest similarity is between the ME and resin fractions.

Average structural parameters, expressed as numbers of protons and carbon atoms in an average single molecule, were calculated from measurements of NMR assignments

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Table 5. Calculation of Average Structural Parameters Derived from ^1H and ^{13}C NMR^a

symbol	average parameter	equation
C_{ar}^n	number of aromatic carbon atoms in an average single molecule	$C_{ar}^n = C^n C_{ar}/100$
H_{ar}^n	number of aromatic hydrogen atoms in an average single molecule	$H_{ar}^n = H^n H_{ar}/100$
C_{al}^n	number of aliphatic carbon atoms in an average single molecule	$C_{al}^n = C^n - C_{ar}^n$
H_{al}^n	number of aliphatic hydrogen atoms in an average single molecule	$H_{al}^n = H^n - H_{ar}^n$
C_c^n	number of carbon atoms at condensed points in an aromatic ring system in an average single molecule	$C_c^n = C_{ar}^n - H_{ar}^n - C_{\alpha}^n - O^n$
C_{α}^n	number of alkyl substituents on an aromatic ring system in an average single molecule	$C_{\alpha}^n = H_{al}^n H_{\alpha}/r_{al} \times 100$
r_{al}	ratio of aliphatic hydrogen to carbon	H_{al}^n/C_{al}^n
K	degree of condensation of aromatic ring system	C_c^n/C_{ar}^n
$C_{29.7}^n$	number of carbon atoms contained at 29.7 ppm in an average single molecule	$C_{29.7}^n = C^n C_{29.7}/100$
$C_{14.2}^n$	number of carbon atoms contained at 14.2 ppm in an average single molecule	$C_{14.2}^n = C^n C_{14.2}/100$

^a C^n , H^n and O^n are the number of carbon, hydrogen, oxygen atoms in an average single molecule.

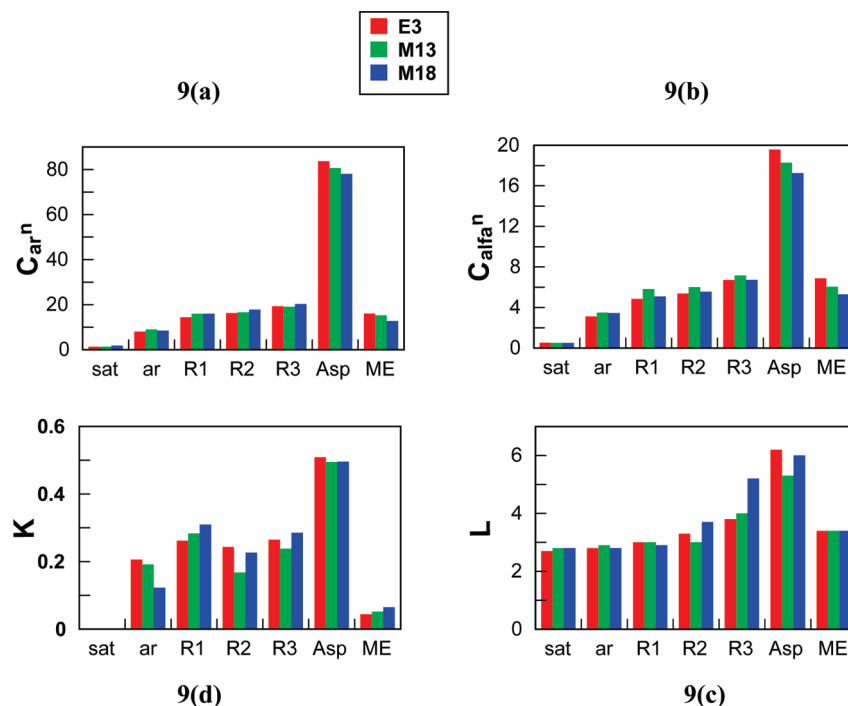


Figure 9. Calculated structural parameters for bitumen fractions for all bitumen fractions and ME samples: (a) number of aromatic carbons (C_{ar}^n), (b) number of alkyl substituents on aromatic ring systems (C_{α}^n), (c) lengths of paraffinic straight chains substituents on aromatic ring systems (L), and (d) degree of condensation of aromatic ring systems (K).

and molecular-weight data by procedures described previously;³⁷ combined RSD values for these calculations are about $\pm 10\%$. Parameter notations and the equations used in the calculations are listed in Table 5. The trend in average chain length was estimated from results for $C_{29.7}^n/C_{14.2}^n$ ratios. Results for several important features are summarized in Figure 9. The number of aromatic carbons (C_{ar}^n) (Figure 9a) and alkyl substituents on aromatic ring systems (C_{α}^n) (Figure 9b) as well as the lengths of paraffinic straight chains (L) (Figure 9c) for the resin subfractions were all quite similar, within experimental error, to those for the ME sample. However, the degree of aromatic ring condensation (K) (Figure 9d) for the ME samples is much lower than that for every other parent fraction, except saturates. The reason for this is unclear, but each SARA fraction is a complex mixture of compounds with a range of molecular weights that are separated primarily on the basis of differences in polarity. The more actively adsorbed polar nitrogen compounds could be part of the resin fraction, despite a discrepancy in the number of condensed rings. An alternative explanation is that some molecular cracking has occurred at

the relatively high temperature (250 °C) maintained during supercritical extraction. In that case, the ME fractions could also originate from asphaltenes. However, while mild cracking of asphaltene molecules causes a reduction in the molecular weight, the overall structure, including a high degree of ring condensation, is maintained.³⁸

3.7. Connection with Poor Bitumen Recovery. Several researchers have postulated a connection between poor bitumen recoveries and wettability of oil sands solids clay fractions.^{39,40} In results published in a recent paper, we particularly associated the decreased recovery of bitumen with a critical amount of ultra-thin illite.¹⁴ Colloidal clays, particularly those $< 0.3 \mu\text{m}$ in diameter, can detrimentally

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affect bitumen recovery by forming thixotropic structures in the middlings phase that inhibit separation of released bitumen.^{17,41} Another mechanism for bitumen losses, more relevant to the work described here, involves stabilization of bitumen-in-water emulsion droplets by biwetttable particles with a contact angle of 60–90°. Such solids preferentially collect at oil–water interfaces;^{8,9} related sliming effects also prevent the particle–air interaction in flotation.⁴² Previous work has indicated that adsorption of organic material on ORS particles from oil sands solids is patchy,⁴³ and this has also been indicated in model studies with asphaltene.²⁸ Such a pattern of adsorption will produce biwetted solids capable of forming bitumen-in-water emulsions. The final droplet size is a function of the particle diameter; i.e., finer particles are capable of producing smaller droplets that are less floatable.^{8,11} Not all of the oil sands clay fraction will have been exposed to organic matter to the same extent either during deposition or while *in situ*. Uncontaminated, hydrophilic clay will remain easily dispersible in the aqueous phase.⁴¹ Dependent upon the amount of biwetted ultrafines present, more or less of the oil phase can be stabilized as small droplets. The proportion of finer droplets will then govern overall bitumen recovery.¹¹

4. Conclusions

SCFE with methanol was used to separate a toluene-insoluble residual organic matter from each of four bitumen-free oil sands with very different bitumen recovery profiles. The composition and structural parameters of the MEs were compared to corresponding parent bitumen fractions from a modified HPLC SARA separation technique. Except for the much lower degree of aromatic ring condensation, the molecular parameters of the extract fractions were most aligned with the parent bitumen resins than any other fraction. In each case, the predominant sulfur species were

thiophenic, but in most cases, sulphones and sulfoxides were more prevalent in the MEs than in any possible bitumen source component. The ratio of nitrogen/sulfur was about the same for each of the four MEs, indicating a similar chemical group composition. In comparison to the source hydrocarbons, there was a concentration of pyridines compared to pyrroles.

The amount of residual organic material extracted by methanol under supercritical conditions correlated well with the total clay and reasonably well with the ultra-thin illite contents for the four samples tested. The close association with high surface area clay minerals suggests that the residual organic matter was originally adsorbed onto clay minerals *in situ*. Adsorbed pyridine and pyrrole compounds measured as a surface layer are capable of changing the wettability of clay substrates. The natural occurrence of biwetted clay particles in oil sands is a prerequisite for the formation of bitumen-in-water emulsion droplets that are too small to be successfully recovered by flotation. Such a mechanism could explain differences in bitumen separation efficiencies between oil sands, where all other characteristics are quite similar. However, because of the limited data set used here, more work will be necessary to fully evaluate this effect.

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Nomenclature

BEU = batch-extraction unit
 GPC = gel permeation chromatography
 HPLC = high-performance liquid chromatography
 ME = methanol extract
 MW_n = number average molecular weight
 NMR = nuclear magnetic resonance
 ORS = organic-rich solids
 R1, R2, and R3 = resin subfractions from enhanced HPLC SARA separation
 RSD = standard deviation as a percentage of the average value
 SARA = saturates, aromatics, resins, and asphaltenes
 SCFE = supercritical fluid extraction
 TIOM = toluene-insoluble organic matter
 XPS = X-ray photoelectron spectroscopy

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