



## NRC Publications Archive Archives des publications du CNRC

### **Organic coated solids in Athabasca bitumen : Characterization and process implications**

Bensebaa, Farid; Kotlyar, Luba S.; Sparks, Bryan D.; Chung, Keng H.

This publication could be one of several versions: author's original, accepted manuscript or the publisher's version. / La version de cette publication peut être l'une des suivantes : la version prépublication de l'auteur, la version acceptée du manuscrit ou la version de l'éditeur.

For the publisher's version, please access the DOI link below. / Pour consulter la version de l'éditeur, utilisez le lien DOI ci-dessous.

#### **Publisher's version / Version de l'éditeur:**

<https://doi.org/10.1002/cjce.5450780402>

*Canadian Journal of Chemical Engineering*, 78, 4, pp. 610-616, 2000-08

#### **NRC Publications Record / Notice d'Archives des publications de CNRC:**

<https://nrc-publications.canada.ca/eng/view/object/?id=f3d24143-1342-4954-bf80-d3f55d359a56>

<https://publications-cnrc.canada.ca/fra/voir/objet/?id=f3d24143-1342-4954-bf80-d3f55d359a56>

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at

<https://nrc-publications.canada.ca/eng/copyright>

READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L'accès à ce site Web et l'utilisation de son contenu sont assujettis aux conditions présentées dans le site

<https://publications-cnrc.canada.ca/fra/droits>

LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D'UTILISER CE SITE WEB.

#### **Questions?** Contact the NRC Publications Archive team at

PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the first page of the publication for their contact information.

**Vous avez des questions?** Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n'arrivez pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.



# Organic Coated Solids in Athabasca Bitumen: Characterization and Process Implications

Farid Bensebaa<sup>1</sup>, Luba S. Kotlyar<sup>1\*</sup>, Bryan D. Sparks<sup>1</sup> and Keng H. Chung<sup>2</sup>

<sup>1</sup>National Research Council of Canada, Institute for Chemical Process and Environmental Technology, Montreal Road Campus, Ottawa, ON K1A 0R6, Canada

<sup>2</sup>Synchrude Canada Ltd., Edmonton Research Centre, 9421-17th Avenue, Edmonton, AB T6N 1H4, Canada

Oil sands deposits in Northern Alberta contain about 1.3 trillion barrels of crude oil equivalent. Nearly three-quarters of these reserves are found in the Athabasca region. About one-tenth of the Athabasca formation lies within 50 m of the surface and is economically accessible by conventional surface mining techniques (Hocking, 1977; Berkowitz and Speight, 1975).

Commercial oil sands mining plants currently use a modified hot water extraction process (HWE) in which oil sands are conditioned with hot water, steam and caustic to release the bitumen. Gravity separation and air flotation of the ore slurry produce bitumen froths that still contain significant amounts of water and solids. The conventional froth-cleaning procedure includes dilution with partly aromatic naphtha, followed by centrifugation. At this stage some intractable solids and water still remain with the treated bitumen. The major constituent of these residual solids (BS) is ultra-fine, aluminosilicate clay crystallites with surfaces coated by toluene insoluble organic matter (TIOM). In the bitumen phase the ultra-fine solids associated with the water droplets. These droplets, or clusters, exist as a stable colloidal dispersion in the maltene component of bitumen (Kotlyar et al., 1998a).

Before bitumen upgrading, the naphtha diluent and other volatile components in the cleaned, diluted bitumen are removed by atmospheric topping at elevated temperature. The mineral solids and salt remain with the topped bitumen and during bitumen upgrading they may be entrained with volatile overheads and carry over to other process units. The high chloride content of the salt residue causes corrosion and fouling problems in downstream upgrading units. Because of the amount and type of organic matter associated with the BS component it is a potential contributor to coke formation, both in reactor vessels and on catalysts (Chung et al., 1997, 1998). Also, entrainment of BS particles is known to cause fouling in packed-bed hydrotreaters. This problem can lead to excessive pressure build-up and premature shutdown of the units (Chan et al., 1994).

In order to overcome such process-related problems, it is critical to develop a better understanding of the nature of these intractable solids. In particular, it is of interest to determine whether there is a difference between the bulk and surface properties of the BS associated with ores from diverse sources. For this work, two BS samples were separated from oil sands sampled from marine and estuarine ores known to behave differently during bitumen separation. These samples were subjected to characterization by several complementary bulk and surface analytical techniques.

Bitumen, separated from oil sands by the hot water extraction process, contains ultra-fine (< 200 nm), inorganic solids (BS). Surfaces of BS particles are coated with toluene insoluble organic matter (TIOM). This organic material is polar and aromatic with contributions from both humic and asphaltene-like components. Although the surfaces of BS particles are dominated by TIOM, the coverage is patchy rather than continuous. As a result, these solids are capable of stabilizing fine water emulsions in the bitumen phase. The nature of the organic matter on the surfaces of the particles is such that it has a high propensity to form coke. Therefore, these particles can also play a role in fouling on equipment and catalysts.

Le bitume séparé des sables pétroliers par le procédé d'extraction à air chaud, contient des solides inorganiques (BS) ultrafins (<200 nm). Les surfaces des particules BS sont recouvertes de matière organique insoluble au toluène (TIOM). Cette matière organique est polaire et aromatique avec des contributions provenant de composés humiques et proches de l'asphalte. Bien que les surfaces des particules BS soient dominées par le TIOM, le revêtement est irrégulier plutôt que continu. Par conséquent, ces solides sont capables de stabiliser des émulsions aqueuses fines dans la phase du bitume. La nature de la matière organique sur les surfaces des particules est telle qu'elle a une forte propension à former du coke. Ces particules peuvent donc jouer un rôle dans l'encrassement des équipements et des catalyseurs.

**Keywords:** oil sands, bitumen, organic coated solids, ultra-fines.

During their existence, sediments deposited in the oil sands basin have been exposed to both humic and hydrocarbon components. Therefore, humic acid (HA) and the pentane insoluble asphaltene fraction from bitumen (PIB) were also analyzed for comparison purposes.

## Materials and Methods

Synchrude Canada Ltd. Edmonton Research Centre supplied the oil sands and PIB sample. The PIB sample

\*Author to whom correspondence may be addressed. E-mail address: luba.kotlyar@nrc.ca

**Table 1.** Elemental analysis of ultra-fine solids (BS) associated with bitumen from various sources.

Solids	Source	Composition (w/w% of sample)			
		C	H	N	S
BS-1	Bitumen from marine ore	21.0	2.3	0.5	2.5
BS-2	Bitumen from estuarine ore	26.0	3.1	0.6	1.2
BS <sup>a</sup>	Bulk bitumen	18.3–30.8	2.2–3.3	0.1–0.8	1.2–3.3
Hydrophilic ultra-fines	Mature fine tailings	0.8	0.4	0.0	0.0

<sup>a</sup>Range of compositions for solids separated from coker feed bitumen, primary froth bitumen, rag layer and PIB (Kotlyar et al., 1999).

was the insoluble material remaining after supercritical fluid extraction of bitumen with pentane (Chung et al., 1998). Humic acid was a commercial sample from Aldrich Chemical.

### Separation Schemes

A batch extraction unit (BEU) was used to separate bitumen froth from oil sands (Syncrude Analytical Methods, 1979). One part by weight of froth was heated and mixed with 0.45 parts by weight of hot toluene on a high intensity Spex shaker for 5 min. Centrifugation of the bitumen solutions for 10 min at a relative centrifugal force (RCF) of 1500 gravities produced toluene solutions with water and solids levels similar to those found in diluted bitumen from the conventional HWEP. The bitumen solutions were concentrated using a RapidVap evaporation system. The BS were recovered by centrifuging 5 w/w% toluene solutions of each bitumen sample at an RCF of 366 000 gravities for one hour. Prior to characterization the BS were washed completely free of bitumen by repeated treatments with a mixture of toluene and water until the toluene phase was colourless. The solids from marine and estuarine oil sands were designated BS-1 and BS-2, respectively. As received, the PIB sample contained about 7 w/w% of associated inorganic components; these solids were removed by the same centrifugation technique.

### Analysis

Elemental analysis for carbon, hydrogen, nitrogen and sulfur was accomplished using a LECO CHNS-932 analyzer. Metals were determined by DC Arc Emission Spectroscopy (DCAES).

X-ray photoelectron spectroscopy (XPS) data were obtained with a KRATOS AXIS HS X-ray photoelectron spectrometer (Kratos, Manchester, UK). The size of the analyzed area was about 1 mm<sup>2</sup>. Monochromatized Al K<sub>α</sub> radiation was used for excitation and a 180° hemispherical analyzer with a three-channel detector was employed. The X-ray gun was operated at 15kV and 20mA. Throughout the study the spectrophotometer was run in fixed analyzer transmission (FAT) mode, with electrostatic magnification. The pressure in the analyzer chamber was always in the range 10<sup>-8</sup> to 10<sup>-9</sup> Torr. Survey and high resolution XPS spectra were collected using 160 and 40 eV pass energy, respectively. An electron flood gun neutralized sample charging during the experiments. Binding energy (BE) data were not referenced. Atomic composition was estimated using

standard software and tabulated sensitivity factors provided with the instrument.

Time-of-flight secondary ion mass spectroscopy (ToF-SIMS) measurements were made with a KRATOS PRISM instrument (Kratos, Manchester, UK). The sample was bombarded with 25 keV Ga<sup>+</sup> ions; the current was less than 10<sup>-9</sup> A. Data acquisition required between 60 and 200 s. The total primary ion dose was always less than 10<sup>12</sup> ions/cm<sup>2</sup>, which is within the static limit for SIMS experiments. Charge neutralization was accomplished by means of a beam of electrons synchronously pulsed on every primary gun cycle and in anti-phase with the ion extraction voltage. Survey and high-resolution ToF-SIMS spectra were obtained using a resolution time of 10 ns and 1.25 ns, respectively.

PAS-FTIR spectra were recorded with a Nicolet spectrometer, model IFS 66. All spectra were recorded under the same conditions using an MTEC 100 photo-acoustic cell.

The inorganic samples were also examined by transmission electron microscopy (TEM), using a Philips CM20 200 kV electron microscope equipped with an Oxford Instruments Energy Dispersive X-ray Diffraction (LINK EDX) detector and a charge-coupled device (CCD) camera. The CCD camera produces electronically enhanced image contrast, allowing extremely thin objects to be viewed at high resolution. The EDX detector allows detection and quantitation of elements heavier than nitrogen. Use of the TEM in the diffraction mode produces standard electron diffraction patterns that, in conjunction with EDX analysis, allow mineral identification.

## Results and Discussion

### Bulk Analysis

Table 1 summarizes results for elemental composition of the BS from various sources. Regardless of their origin, these BS particles have similar compositions; however, they are quite different to similar-sized solids found in HWEP mature fine tailings (MFT) streams, i.e., hydrophilic ultra-fines (Kotlyar et al., 1993, 1999). An important feature of the BS is that they are associated with an appreciable amount of TiOM with organic carbon representing more than 18 w/w% of the samples. By comparison, hydrophilic ultra-fines have a bulk carbon level of less than 1 w/w%. Alumino-silicate, ultra-fine clays, i.e., crystallites with a lateral extension of less than 200 nm and thickness of about

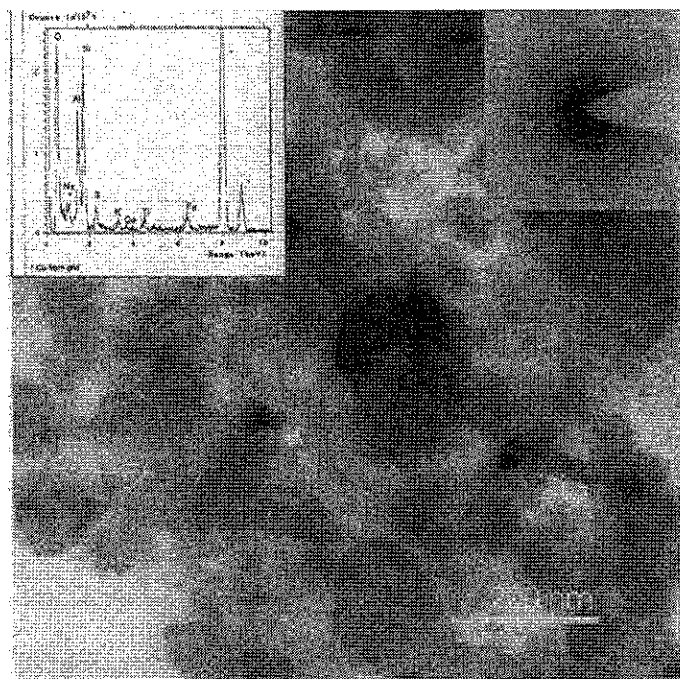


Figure 1. TEM, EDX and electron diffraction patterns for a typical sample of bitumen associated solids sample (BS).

10 nm, are the major contributors to the BS solids, see Figure 1. By comparison, the finest fraction of MFT comprises clay particles, possibly beidellite, with a major dimension of 50 nm and only one layer (10 Å) thick (Kotlyar et al., 1998b). Sulfur bearing particles occur as pyrite, whereas titanium is present as titanium oxide. Compared to hydrophilic ultra-fines, BS have a higher contribution from bulk S, Fe, Ti (see Tables 1 and 2). Relatively high Ni and V concentrations suggest the presence of tightly bound 'asphaltene-type' components. In asphaltenes these heavy metals occur as vanadium and nickel porphyrins, or chelated compounds (Jacobs and Filby, 1983). A comparison with the metal contents determined for hydrophilic ultra-fines is given in Table 2.

PAS-FTIR spectra for the BS-1, BS-2, PIB and HA, samples are shown in Figure 2. This technique directly probes chemical bonds and is particularly suitable for the characterization of powder samples with strong IR absorption characteristics, providing compositional and structural information. Because

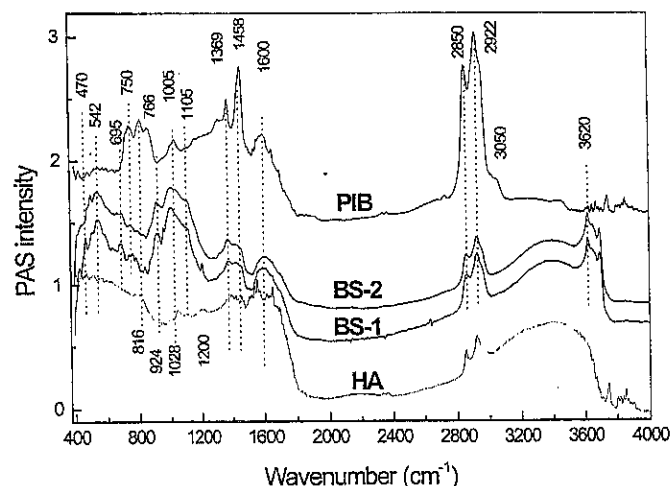


Figure 2. PAS-FTIR spectra for BS-1, BS-2, PIB and HA.

layers several  $\mu\text{m}$  thick are probed, the application of PAS-FTIR to ultra-fine BS particles is considered to be a bulk technique. All the peak assignments are based on previously published data (Lin-Vien et al., 1991, Van der Marel and Beutelspacher, 1976).

For both BS samples the presence of Al or Si is indicated by intense peaks positioned at about 466, 502 and 550  $\text{cm}^{-1}$ ; a medium peak at 913  $\text{cm}^{-1}$  corresponds to the OH bending mode from Al-OH and Si-OH groups while the peaks at 1005, 1028 and 1105  $\text{cm}^{-1}$  originate from Si-O stretching modes. However, a possible contribution from SO, -CH and -CO vibrational modes at 1005 and 1028  $\text{cm}^{-1}$  cannot be ruled out. Both BS samples also display peaks at 3622, 3650 and 3696  $\text{cm}^{-1}$  assigned to free OH stretching.

Aliphatic -CH<sub>3</sub> bending and -CH<sub>2</sub> scissoring bands at 1369 and 1458  $\text{cm}^{-1}$  and -CH<sub>2</sub> stretching bands at 2850  $\text{cm}^{-1}$  and 2922  $\text{cm}^{-1}$  detected for the BS samples may originate from either PIB or HA type components. A relatively intense peak (C=C stretching) at 1600  $\text{cm}^{-1}$  in the spectra for PIB and both BS samples suggests that the former may be the source of conjugated bonds in the TIOM. Peaks around 3300  $\text{cm}^{-1}$  (hydrogen bonded -OH stretching mode) are observed for HA and both BS samples. This indicates a similarity between TIOM and humic matter.

The PAS-FTIR results also demonstrate some differences in TIOM associated with the marine and estuarine samples. For

Table 2. Metal analysis of ultra-fine solids (BS) associated with bitumen from various sources.

Solids	Composition (w/w% of sample)							
	Fe	Mn	Ca	Ti	V	Ni	Mg	Al
BS-1	5.1	0.1	0.5	2.2	0.03	0.02	0.4	6.4
BS-2	3.9	0.2	0.5	1.3	0.03	0.01	0.5	7.2
BS <sup>a</sup>	3.8-6.0	0.08-0.2	0.5-0.9	1.3-3.0	0.03-0.04	0.01-0.03	0.4-0.6	6.2-9.6
Hydrophilic ultra-fines	1.3	0.1	0.5	0.2	0.005	0.004	0.3	n.a.

<sup>a</sup>Range of values for solids separated from coker feed bitumen, primary froth bitumen, rag layer and PIB (Kotlyar et al., 1999).  
n.a. Value not available.

**Table 3.** X-ray photoelectron spectroscopy (XPS) results for ultra-fine solids (BS) associated with bitumen from various sources.

Solids	Composition (Atomic Percent)							
	C	Si	Al	S	Fe	O	Ca	Mg
BS-1	47.1	8.0	4.6	1.4	0.6	37.0	0.7	0.2
BS-2	36.7	10.7	6.9	n.d.	0.6	44.7	n.d.	n.d.
BS <sup>a</sup>	37.7–57.0	4.7–10.6	3.4–7.6	0.8–1.6	0.2–1.1	29–42	n.d.	n.d.
PIB	92.0	n.d.	n.d.	2.5	n.d.	5.2	n.d.	n.d.
HA	78.7	n.d.	n.d.	1.0	n.d.	18.3	n.d.	n.d.
Hydrophilic ultra-fines	3.0	17.3	6.3	n.d.	n.d.	65.0	n.d.	n.d.

<sup>a</sup>Range of values for solids separated from coker feed bitumen, primary froth bitumen, rag layer and PIB (Kotlyar et al., 1999).  
n.d. Not detected.

**Table 4.** Binding energy (BE) and atomic concentration for carbon and sulfur components.

Species	Binding energy e(V)	Atomic Percent				
		BS <sup>a</sup>	BS-1	BS-2	HA	PIB
C-H & C-C	283.5–283.9	42.5–45.9	38.4	33.9	66.9	88.5
C-OH & C-O-C	285.2–286.4	5.8–7.5	5.3	1.4	6.3	2.4
C=O & C(OH)=O	287.1–288.7	2.4–3.4	2.4–3.4	1.4	5.5	1.2
Thiophene	162.6–163.0	n.a.	0.9	n.d.	0.6	2.5
SO <sub>x</sub>	167.2–167.8	n.a.	0.5	n.d.	0.4	n.d.

<sup>a</sup>Range of values for solids separated from coker feed bitumen, primary froth bitumen, rag layer and PIB (Kotlyar et al., 1999).  
n.d. Not detected.  
n.a. Not available.

example, peaks at 744, 812 and 870 cm<sup>-1</sup> (out-of-plane -CH aromatic bending mode) are characteristic of both the PIB and BS-1 samples. These peaks are practically non-existent in the HA and BS-2 samples. Also, the peak at about 1200 cm<sup>-1</sup> (-C-O stretching mode of the C-O-C group) is detected only on the HA and BS-1 samples.

### Surface Analysis

Characterization of the first 7 nm of sample surfaces was carried out by X-ray photoelectron spectroscopy. A summary of the major elements detected for the BS, PIB and HA samples is shown in Table 3; hydrophilic ultra-fines from MFT are included for comparison (Kotlyar et al., 1993). The important factor to be noted is that the organic carbon, associated with the BS samples, is strongly concentrated at the surface. Values of 40 to 60 atomic percent are detected. By comparison, hydrophilic ultra-fines has a surface carbon concentration of only 3 atomic percent. The carbon envelope in the XPS spectrum can be deconvoluted to provide information on carbon functionalities. The results of such de-convolution are presented in Table 4. The peaks at the lowest binding energy (283.5 to 283.9 eV) are assigned to carbon atoms linked only to other carbon (C-C) or hydrogen atoms (C-H). Another peak, shifted by approximately

1.5 eV, corresponds to carbon atoms linked to carbon or hydrogen atoms and one oxygen atom via a single bond (C-OH or C-O-C). Carbon peaks corresponding to carbonyl (C=O) and acid or ester (O-C=O) functions are shifted from the C-C peak by about 3 and 4 eV, respectively. From the point-of-view of oxygen functionality, BS-1 is closer to HA while BS-2 has similarities with PIB. A lower oxygen functionality for estuarine BS demonstrates a more paraffinic nature for its surface organic matter. These results indicate sufficient differences in both amount and type of surface organic matter associated with BS solids. This may be an important factor in determining the interaction between these solids and bitumen.

For the BS-2 sample no sulphur peak is detected with XPS. However, BS-1 gives rise to two very distinct S2p bands. These bands are separated by about 4 eV and are ascribed to two chemically different sulphur states. The first band, peaking at 167.4 eV, is attributed to sulphur in sulphoxide groups. The second band, peaking at 163.0 eV, corresponds to thiophenic sulfur (Jimenez Mateos and Fierro, 1996; Bensebaa et al., 1998). Table 4 shows that, while the PIB sample does not give rise to any oxidized sulphur peaks, both types of sulphur are detected in the HA sample. Thus, from the point of view of sulphur content, HA and BS-1 again present some similarities. Also, Ca and Mg, are present at the BS-1 but not BS-2 surfaces, see Table 3.

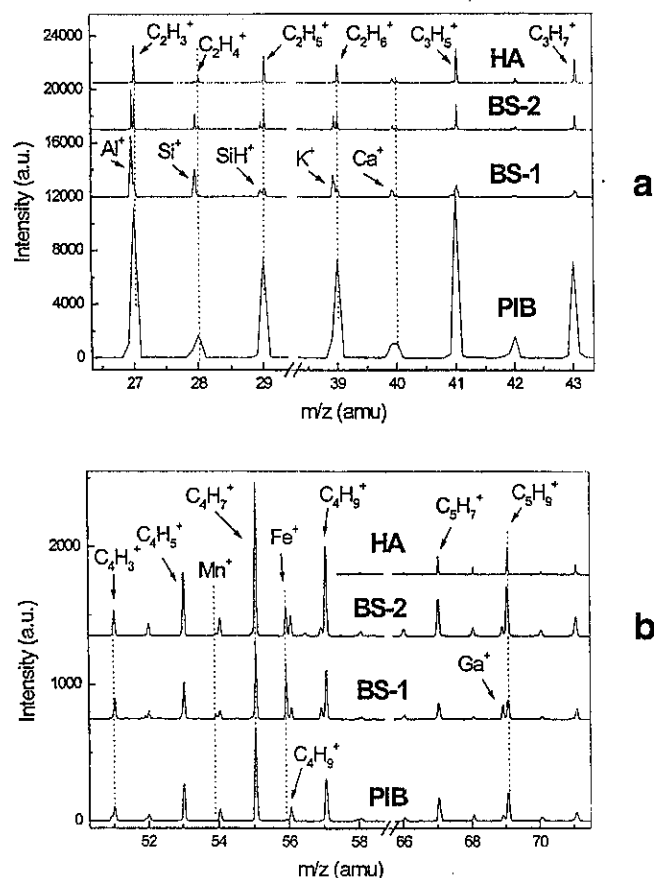


Figure 3. ToF-SIMS spectra for BS-1, BS-2, PIB and HA: (a) 26-43 amu; and (b) 50-72 amu mass range.

ToF-SIMS spectroscopy provides a tool for probing the first 1 nm of the surface layer. The ToF-SIMS spectra are shown on Figures 3 and 4. Except for the PIB sample all spectra were run under high-resolution conditions. The peak assignments are based on values published in reference handbooks (Briggs, 1986; Newman et al., 1991). Several physico-chemical and geometrical factors contribute to the intensity of each peak. Therefore, the peak intensity may not always correlate directly with component concentrations on the surface. However, it is possible to compare the relative concentrations of specific ion fragments observed.

The lower and higher mass peaks seen at 27 amu and 28 amu correspond to  $\text{Al}^+$  and  $\text{C}_2\text{H}_3^+$  and  $\text{Si}^+$  and  $\text{C}_2\text{H}_4^+$  while those around 29 amu are assigned to  $\text{SiH}^+$  and  $\text{C}_2\text{H}_5^+$ , see Figure 3a. The  $\text{Al}^+$ ,  $\text{Si}^+$  and  $\text{SiH}^+$  peaks dominate in both BS samples, whereas organic fragments are dominant in the HA and PIB spectra. By normalizing the amount of Al in each BS spectra and comparing the relative intensity of  $\text{Al}^+$  and  $\text{C}_2\text{H}_3^+$  peaks for each sample, we can estimate that there is about four times more hydrocarbon in the top surface layer of BS-1 than in the same region of BS-2. Both BS samples give rise to relatively strong peaks for  $\text{K}^+$ ,  $\text{Ca}^+$ ,  $\text{Mn}^+$  and  $\text{Fe}^+$  at the nominal peak masses of 39 and 40 amu (Figure 3a) and 54, 56 amu, see Figure 3b. The major peak at 41 amu is assigned to  $\text{C}_3\text{H}_5^+$ . The very weak  $\text{Si}^+$  peak observed for the HA spectrum is probably from trace contamination while the  $\text{Ga}^+$  peak at a nominal mass of 69 amu is attributed to primary ions from the Gallium source.

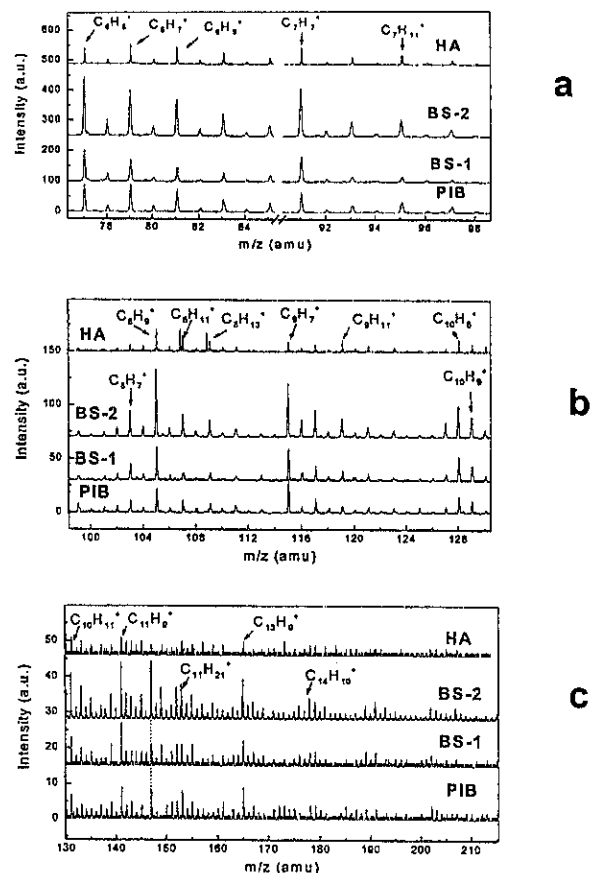


Figure 4. ToF-SIMS spectra for BS-1, BS-2, PIB and HA: (a) 76-98 amu; (b) 100-130 amu; and (c) 130-210 amu mass ranges.

The fact that ToF-SIMS is able to detect inorganic elements on the BS samples allows us to conclude that the surface layer of organic material is patchy, rather than continuous, in both cases. This determination provides molecular evidence for the observation that these solids show bi-wettable characteristics towards water and hydrocarbon liquids (Kotlyar et al., 1998a).

Peaks assigned to organic matter fragments dominate the spectra at higher ion masses. The major peaks in the mass range of 76 to 98 amu are attributed to:  $\text{C}_6\text{H}_5^+$ ,  $\text{C}_6\text{H}_7^+$ ,  $\text{C}_6\text{H}_9^+$ ,  $\text{C}_6\text{H}_{11}^+$ ,  $\text{C}_7\text{H}_7^+$ ,  $\text{C}_7\text{H}_9^+$  and  $\text{C}_7\text{H}_{11}^+$  ion fragments containing one benzene ring, see Figure 4a. Although these peaks are found in the spectra for all four samples they have different absolute intensities in each case. In the mass range 99 to 132 amu the dominant peaks are attributed to:  $\text{C}_8\text{H}_7^+$ ,  $\text{C}_8\text{H}_9^+$ ,  $\text{C}_8\text{H}_{11}^+$ ,  $\text{C}_8\text{H}_{13}^+$ ,  $\text{C}_9\text{H}_7^+$ ,  $\text{C}_9\text{H}_{11}^+$ ,  $\text{C}_{10}\text{H}_8^+$ ,  $\text{C}_{10}\text{H}_9^+$  ion fragments, see Figure 4b. The peaks at 106.9 and 108.9, on the spectrum for the HA sample, are attributed to silver contamination. The spectra on Figure 4c show the peaks for a mass range greater than 130 amu. These peaks are attributed to the ion fragments from multiple aromatic rings, namely:  $\text{C}_{10}\text{H}_{11}^+$ ,  $\text{C}_{11}\text{H}_9^+$ ,  $\text{C}_{11}\text{H}_{21}^+$ ,  $\text{C}_{13}\text{H}_9^+$  and  $\text{C}_{14}\text{H}_{10}^+$ . The first four of these fragments contain two aromatic rings while the last has three.

### Conceptual Description of Solids

Based on the detailed characterization of the solids associated with bitumen it is possible to develop a conceptual view of the

nature of the particle surfaces. A simplified diagram is shown on Figure 5. The most important observation is that particle surfaces are not completely covered by organic matter; in the diagram, the gray areas represent exposed clay mineral. The organic matter on the surface shows characteristics of both humic and asphaltic type materials. Because the solids were deposited in the sedimentation basin as a result of soil erosion by water and wind we may assume that they were associated with plant humic matter prior to contact with hydrocarbons. Humic matter will therefore constitute the bulk of the organic matter directly adsorbed to the clay surfaces; in the diagram this layer is represented by the diagonal shading. There is an indication that some of the organic matter may be chemically bound. It is well known (Senesi and Miano, 1995) that humic acids strongly interact with other polar molecules. In bitumen, multi-ring compounds fit this requirement. Significant amounts of one to three ring molecules are detected on the clay surfaces and are depicted by the gray molecules on the diagram. The components derived from bitumen can adsorb onto the existing humic-coated surfaces, exposed mineral or, overlapping these areas. While this description is undoubtedly simplistic it does provide a coherent explanation of the characterization data.

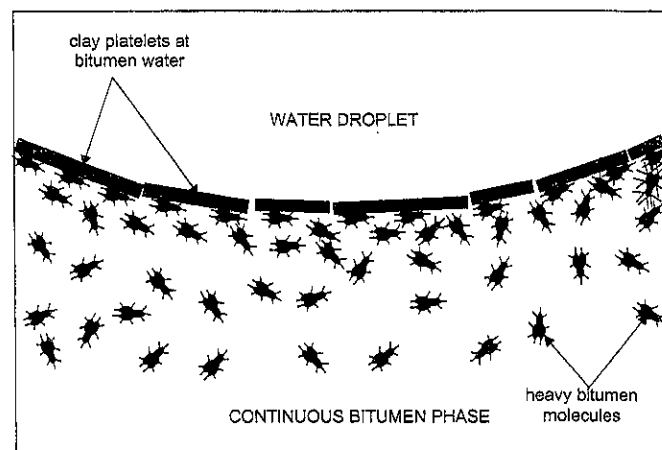


Figure 6. Emulsion stabilization by clay-asphaltenes film formation at a bitumen-water interface.

### Process Implications

The most significant conclusion from this work is that the surface characteristics will impart a bi-wettable nature to these solids. This means that the particles are able to interact with

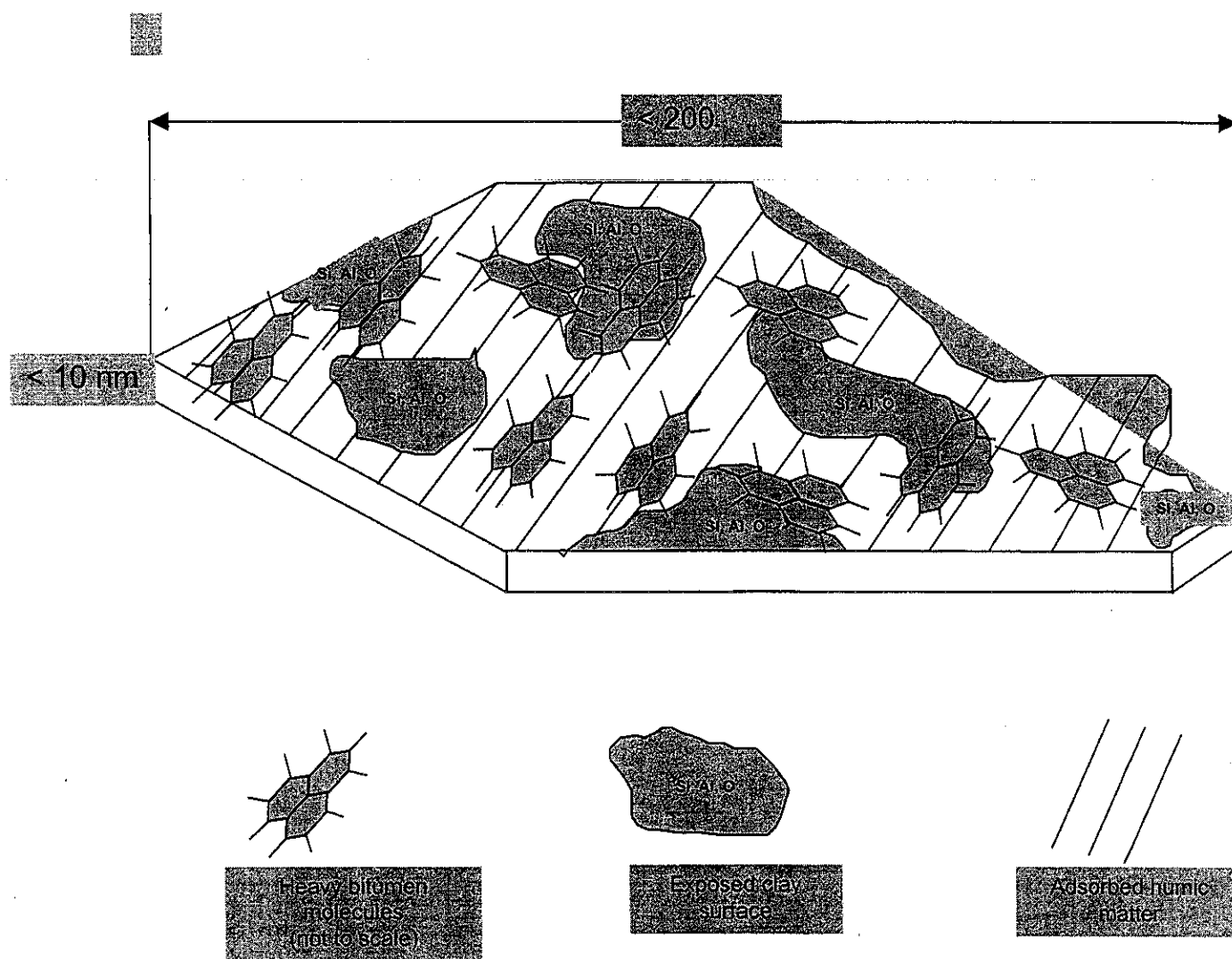


Figure 5. Simplified conceptual diagram of clay particles coated with organic matter.

both water and oil and consequently they will tend to collect preferentially at interfaces. This behaviour allows bi-wettable solids to stabilize emulsions; Figure 6 demonstrates how this occurs. Clay platelets are shown attached to the interface between a water droplet and a bulk bitumen phase. The particles may be orientated in a number of alternative ways, i.e., edgewise, as fans or, as some form of micelle-like structure. Because of the strong interaction between heavy components in bitumen and the surface organic matter associated with the particles, additional asphaltic material will be drawn towards the interface from the bulk bitumen phase. The end result is an armoring of the interface by a film comprising clay and asphaltic material. This film prevents coalescence of droplets and produces an extremely stable emulsion. The extremely small particle size allows the stabilization of very small emulsion droplets. Because of the intractable nature of these stable emulsions, mineral solids and soluble salts are retained in the bitumen after froth cleaning. These components are then introduced into the upgrading units where they cause fouling and corrosion.

## Conclusions

1. Solids retained by bitumen after separation from marine (BS-1) and estuarine (BS-2) oil sands are mainly aluminosilicate, ultra-fine clays.
2. Regardless of their source, these solids have a similar elemental composition that is quite different to that determined for the hydrophilic ultra-fines found in mature fine tailings produced by the HWEP.
3. The organic matter (TIOM) associated with different BS samples has a bulk composition with similarities to both humic matter and asphaltene.
4. The TIOM found on the surfaces of both BS-1 and BS-2 samples is characterized by multi-aromatic ring systems.
5. ToF-SIMS measurements show that there is significantly more organic matter in the top surface layers of BS-1 compared to BS-2. The polarity of TIOM on BS-1 is closer to that for humic acid (HA) while that on BS-2 is more similar to the pentane insoluble fraction of bitumen (PIB). The lower polarity of TIOM on estuarine BS demonstrates a more paraffinic nature for this material. This may be an important factor in determining the degree of interaction between these solids and bitumen.
6. Surface analysis by XPS shows that S, Ca and Mg are present at the surface of particles in BS-1 but not BS-2. The sulphur detected in BS-1 and HA is present as sulphoxide and thiophenic types.
7. ToF-SIMS shows that Al, Si, Fe and Ti are exposed in the very top surface layers, demonstrating that coverage by organic matter is patchy rather than continuous. This determination provides a molecular basis for the observed bi-wettable characteristics of BS.
8. Because of the intractable nature of the emulsions stabilised by ultra-fine clays, mineral solids and soluble salts are retained in the bitumen after froth cleaning. These components are then introduced into the upgrading units where they cause fouling and corrosion.

## Acknowledgements

The authors thank Anna Delgado (IRC/NRC) for making the PAS-FTIR measurements. Financial assistance from AOSTRA is gratefully acknowledged.

## Nomenclature

BE	binding energy
BS-1	bitumen associated solids from marine oil sands
BS-2	bitumen associated solids from estuarine oil sands
EDX	energy dispersive X-ray diffraction
HA	humic acid
HWEP	hot water extraction process
PAS-FTIR	photoacoustic Fourier transform infrared
PIB	pentane insoluble bitumen fraction (non-humic or asphaltic component)
ToF-SIMS	time-of-flight secondary ions mass spectroscopy
TEM	transmission electron microscopy
TIOM	toluene insoluble organic matter
XPS	X-ray photoelectron spectroscopy

## References

- Bensebaa, F., Y. Zhou, Y. Deslandes, E. Kruus and T.H. Ellis, "XPS Study of Metal-Sulfur Bonds in Metal-Alkanethiolate Materials", *Surface Science Letters* **405**, L472-L476 (1998).
- Berkowitz, N. and J.G. Speight, "The Oil Sands of Alberta", *Fuel* **54**, 138-149 (1975).
- Briggs, D., "SIMS for the Study of Polymer Surfaces: A Review", *Surf. Interface Anal.* **9**, 391-404 (1986).
- Chan, E.W., K.H. Chung, M. Veljkovic, and J.K. Liu, "Hydrodynamics and Fines Capture in Packed Bed Hydrotreaters", in "Proc. Int. Petroleum and Petrochem. Technol. Symposium", September, 1994, Beijing, China (1994).
- Chung, K., C. Xu, Y. Hu, R. Wang, "Supercritical Fluid Extraction Reveals Resid Properties", *Oil Gas J.* **60**, 66-70 (1997).
- Chung, K., C. Xu, M. Gray, Y. Zhao, L. Kotlyar, B. Sparks, "The Chemistry, Reactivity and Processability of Athabasca Bitumen Pitch", *Reviews in Process Chemistry and Engineering* **1**, 41-79 (1998).
- Hocking, M.B., "The Chemistry of Oil Recovery from Bituminous Sands", *J. Chem. Educ.* **54**, 725-729 (1977).
- Jacobs, F.S. and R.H. Filby, "Solvent Extraction of Oil Sands Components for Determination of Trace Elements by Neutron Activation Analysis", *Anal. Chem.* **55**, 74-77 (1983).
- Jimenez Mateos, J.M. and J.L.G. Fierro, "X-ray Photoelectron Study of Petroleum Fuel Cokes", *Surf. Interf. Anal.* **24**, 223-236 (1996).
- Kotlyar, L.S., Y. Deslandes, B.D. Sparks, H. Kodama, R. Schutte, "Characterization of Colloidal Solids from Athabasca Sludge", *Clays and Clay Minerals* **41**, 341-345 (1993).
- Kotlyar, L.S., B.D. Sparks, J. Woods, S. Raymond, Y. Le Page and W. Shelfantook, "Distribution and Types of Solids Associated with Bitumen", *Petr. Sci. Tech.* **16**, 1-5 (1998a).
- Kotlyar, L.S., B.D. Sparks, J. Woods, Y. Le Page, "Effect of Particle Size on the Flocculation Behaviour of Ultra-Fine Clays in Salt Solutions", *Clay Minerals* **33**, 103-107 (1998b).
- Kotlyar, L.S., B.D. Sparks, J. Woods, K.H. Chung, "Solids Associated with the Asphaltene Fraction of Oil Sands Bitumen", *Energy and Fuels* **13**, 346-350 (1999).
- Lin-Vien, D., N.B. Colthup, W.G. Fateley and J.G. Grasselli, "The Handbook of Infrared and Raman Characteristics Frequencies of Organic Molecules", Academic Press Publishers, Boston, MA (1991), pp. 485-490.
- Newman, J.C., B.A. Carlson, R.S. Michael and T.A.H. Hohlt, "Static SIMS Handbook of Polymer Analysis", Perkin Elmer Publishers, Eden Prairie, MN (1991), pp. I-LXXVI.
- Senesi, N. and T.M. Miano, "The Role of Abiotic Interactions with Humic Substances on the Environmental Impact of Organic Pollutants" in "Environmental Impact of Soil Component Interactions", Huang, P.M., J. Berthelin, J.M. Bollag, W.B. McGill, A.L. Page, Eds., Lewis Publishers, London, UK (1995), pp. 311-336.
- "Syncrude Analytical Methods of Oil Sand and Bitumen Processing", Syncrude Canada Ltd., Edmonton, AB (1979), p. 23.
- Van der Marel, H.W. and H. Beutelspacher, "Atlas of Infrared Spectroscopy of Clay Minerals and their Admixtures", Elsevier Publishers, Amsterdam, The Netherlands (1976), p. 57.

Manuscript received August 30, 1999; revised manuscript received March 8, 2000; accepted for publication March 13, 2000.