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

https://doi.org/10.1016/S1386-1425(01)00460-7 Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 57, 13, pp. 2695-2702, 2001-11

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Spectrochimica Acta Part A 57 (2001) 2695-2702

SPECTROCHIMICA ACTA PART A

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# Step-scan Photoacoustic Fourier Transform and X-rays photoelectron spectroscopy of oil sands fine tailings: new structural insights

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Received 20 February 2001; accepted 17 March 2001

#### Abstract

The chemical and physical properties of clay suspensions from oil sands have profound effect not only on the bitumen extraction process but also on the tailing treatment and reclamation. Step-scan Photoacoustic Fourier Transform Infrared (S<sup>2</sup>PAS-FTIR) has been used to characterize the properties of clay suspensions. The photoacoustic spectral features of the fine solids (FS) fraction were found to vary drastically with the modulation frequency. This is attributed to the increase in the relative amount of bitumen-like matter in the bulk. A similar behavior was observed on the bi-wetted solid (BWS) fraction, in spite of the fact that the variation as a function of the modulation frequency is less significant. No such change is observed on hydrophobic solid (HPS) sample. These observations allow us to refine our pictorial image of the bitumen fraction materials structure. © 2001 Published by Elsevier Science B.V.

Keywords: Bitumen; Solids; PAS-FTIR; XPS; Depth profile

### 1. Introduction

Commercial oil sands mining plants in Northern Alberta currently use a modified Hot Water Extraction Process (HWEP) [1,2]. Oil sands are conditioned with hot water, steam and caustic to release the bitumen from the sand and other solids. This process produces tailings (presently exceeding one billion m<sup>3</sup>) with about 35% more volume than that occupied by the bituminous

sands before mining, prohibiting any economical reclamation scheme [3,4]. Furthermore, the bitumen fraction remaining with tailings (estimated to 2-6 wt.%) contributes to lower bitumen yield. Understanding the relationship between the structure and properties of oil sands components is essential in engineering a successful process. Presently there are no accurate models of these ill-defined materials embodying the spectroscopic data reported so far.

We have used oil-phase agglomeration techniques for the removal of residual organics and the fractionation of oil wettable solids from the

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aqueous tailing streams [3,4]. This treatment results in the sludge destabilization, which then differentiates into four distinct lavers - clear water, a colloidal suspension, a thin dark brown interface layer and a well compacted sediment. The colloidal fraction displays a propensity to form gels believed to be largely responsible for the water holding capacity of these sludges. The solids in the brown interface layer have a relatively high organic carbon content compared with the other solid fractions. The organic matter associated with the solids from the brown interface laver is insoluble in toluene and has been designated as strongly bound organic humic matter. These organic rich solids could also play a significant role in the formation of sludge structure because they are wettable by both oil phase and water, that is they have a bi-wetted surface, hence the designation bi-wetted solids (BWS). The BWS are capable of forming a strongly flocculated structure through interaction with free bitumen and naphta present in sludge [5,6].

In this article, we report Step-scan Photoacoustic Fourier Transform Infrared (S<sup>2</sup>PAS-FTIR) data of three organic coated mineral fractions of Syncrude fine tailings samples. PAS-FTIR spectroscopy can probe layers of several µm thick [7]. It is particularly suitable for the characterization of powder samples with strong IR absorption characteristics. As for other IR techniques. PAS-FTIR directly probes chemical bonds. Thus, information on composition, structure and even conformation can be obtained. The technique is especially appealing because it requires neither vacuum nor special sample preparation techniques [7]. Furthermore, S<sup>2</sup>PAS-FTIR could be used to probe selectively different layers, by simply changing the modulation frequency [8-11]. Depending on the sample, the probing depth could be varied from around  $1-100 \mu m$ .

# 2. Experimental

## 2.1. Fractionation scheme

A fractionation scheme has been developed to separate so-called bi-wetted solids (BWS) and hy-

drophobic solids (HPS) from both Syncrude and Suncor fine tailing samples [5,6].

## 2.1.1. Separation of hydrophobic solids (HPS)

A sample of fine tailings (500 g) was gently agitated with stainless steel balls in a rotating polyethylene bottle in order to collect residual bitumen and hydrophobic solids as a surface coating on the balls. The balls were washed with toluene on a 100-mesh screen in order to separate them from the associated organic matter. The toluene slurry was then centrifuged at  $500 \times g$  for 30 min to separate the hydrophobic solids, which were washed several times with more toluene to remove bitumen and then dried at  $110^{\circ}$ C.

## 2.1.2. Separation of bi-wetted solids (BWS)

The clean tailings after the removal of bitumen and associated hydrophobic solids were agitated in a Waring Blendor at 15 000 rpm for 30 min and allowed to settle for 30 min under gravity. During this time, the tailings separated into two distinct layers - BWS and coarse inert solids settled to the bottom as a black layer while most of the clay solids (fine solids) remained in suspension. The suspension fraction was decanted off and the sediment gently mixed with pond water by stirring with a spatula in order to separate occluded fine solids. The sediment was again allowed to gravity settle for another 30 min. at which time the suspension was once more decanted. This procedure was repeated several times until the amount of fine solids remaining in suspension was negligible. The sediment was then washed several times with pond water to remove coarse inert solids by differential settling. This time most of the BWS remained in suspension, while inert solids settled as a clean compact sediment. The BWS suspensions were centrifuged at  $500 \times g$  for 30 min and the wet cake was dried at 110°C.

# 2.1.3. Separation of fine solids (FS)

The suspension fraction obtained during the separation of BWS solids was centrifuged at  $500 \times g$  for 4 h to reduce the solids content from 6.4 to 2.8 w/w%. It was decanted from the wet cake and centrifuged again at  $500 \times g$  for 20 h. The wet cake was dried under vacuum at 110°C.

#### 2.2. Analytical techniques

PAS-FTIR spectra were recorded with a Bruker FTIR spectrometer, model IFS 66. Except for the modulation frequency value, spectra were recorded under the same conditions using a MTEC 300-photoacoustic cell (MTEC Photoacoustics Inc., Ames, IA). Since the PAS signal is inversely proportional to the modulation frequency, a lower amplifier gain is used at lower modulation frequency, to avoid signal saturation. Helium was used as the carrier for the photoacoustic cell signal. Step-scan measurements were recorded using phase modulation approach [7].

XPS data were obtained with a KRATOS AXIS HS X-ray photoelectron spectrometer (Kratos, UK). The size of the analyzed area was about 1 mm<sup>2</sup>. Monochromatized Al  $K_{\alpha}$  radiation was used for excitation and a 180° hemispherical analyzer with a three-channel detector was employed. The X-ray gun was operated at 15 kV and 20 mA. High-resolution XPS spectra were collected using 40 eV pass energy. An electron flood gun neutralized sample charging during the exper-

0.04

0.03

0.02

732

iment. The take off angle data on the flat FS platelet were obtained by changing sample orientation versus the normal from 0 to 70°. This corresponds approximately to a change in the probing depth of ~80 to 27 Å [12].

#### 3. Results and discussion

Fig. 1 shows S<sup>2</sup>-PAS-FTIR spectra of FS platelets at different modulation frequencies. Spectra were normalized to the CH stretching peak around 2900 cm<sup>-1</sup>, to allow meaningful comparison.

Two groups of vibrational peaks are readily distinguished. The first group consists of organic based modes, such as CH stretching ( $\sim 2930$ cm<sup>-1</sup>) and bending (  $\sim 1460$  cm<sup>-1</sup>). The second group consists of inorganic based modes such as SiO (~1100 cm<sup>-1</sup>) and free OH (3600 cm<sup>-1</sup>) stretching [13,14]. Furthermore, characteristic OH stretching peaks are observed around 3300 cm<sup>-1</sup> on nearly all samples. Based on the position of the band maximum and on the broadness of the peak,



Fig. 1. S<sup>2</sup>PAS-FTIR spectra of FS platelet at different modulation frequencies. The spectra were normalized to the CH stretching peak around 2900 cm<sup>-1</sup>.



Fig. 2. S<sup>2</sup>PAS-FTIR spectra of FS powder at two different modulation frequencies. The spectra were normalized to the CH stretching peak around 2900 cm<sup>-1</sup>.

it can be assigned to the hydrogen bonded OH stretching mode [13]. The three peaks assigned to free OH stretching are observed at 3622, 3650 and 3696 cm<sup>-1</sup>, respectively. Similar free OH stretching peaks were observed on Kaolinite and bitumen solids [14,15]. Thus, the inorganic groups are probably from the clay component.

When the modulation frequency is increased from 11 to 732 Hz, the relative peak intensity of the inorganic functional groups increases significantly compared with those originated from organic functional groups. This feature is probably due to the change in composition of the FS platelet as a function of depth. Furthermore, as expected, the signal-to-noise decreases, when the modulation frequency is increased. Indeed, theoretical calculation predicts that in the case of thermally thick sample, the PAS signal is inversely proportional to  $f_{,,}^{3/2}$  where f is the modulation frequency [11].

As shown in Fig. 1, the spectrum recorded at 732 MHz is quite noisy. Thus, we have chosen 585 Hz as representative of high modulation region. Below, the two extreme frequencies, 11 and

585 Hz, are used as basis for comparing the PAS spectra of the different samples in the low and high frequency regions.

The same FS platelets have been ground to make fine powder. S<sup>2</sup>FTIR-PAS spectra were recorded at two modulation frequencies (Fig. 2). The spectral features of platelet and powder FS seem to be quite similar. However, the effect of the modulation frequency on the relative intensity of the inorganic peaks is less significant in the case of the powder FS. The relative intensity of the 1134 cm<sup>-1</sup> peak of the FS platelet increased 8-fold, when the modulation frequency is increased from 11 to 585 Hz. In the case of powder FS, the increase is 2-fold.

We also characterized the FS samples with XPS. All the platelets present two different sides — one side is smooth, shiny and blackish. The other side is rough and grayish. A FS platelet with a nominal size of  $5 \times 5 \text{ mm}^2$  and about 1 mm thick was chosen. As shown in Table 1, the two sides give different results. The results for powder appear to be in the middle. The shiny and smooth side contains less carbon than the rough side.

Elements	Atomic percent							
	1st side: 80 Å	1st side: 51 Å	1st side: 27 Å	2nd side: 80 Å	Powder: 80 Å			
С	12.4	14.0	17.7	30.0	20.5			
0	59.3	58.6	54.9	50.6	53.8			
Si	15.0	14.6	14.8	11.4	13.8			
Al	13.2	12.8	12.7	8.1	11.9			

Table 1 Elemental atomic concentrations of FS obtained with  $\rm XPS^{a}$ 

<sup>a</sup> The platelet FS contains a smooth (1st) and a rough (2nd) side. The variable angle (corresponding to variable depth profile) XPS data are given only on the smooth side. No change is observed on the XPS peaks from the rough side as a function of take-off angle.

Furthermore, increasing the take-off angle away from the normal to the surface (thus, decreasing the number of probed layers) leads to an increase in the relative carbon concentration. At 0° takeoff angle (corresponding to a sampling depth of 80 Å), the carbon atomic concentration of the shiny side (1st side) is about 12.4%. The carbon concentration increases to 17.7% at a takeoff angle of 70° (corresponding to a sampling depth of 27 Å). At the same time, Si and Al atomic concentrations decreased.

The variable takeoff angle data seems to indicate that the very top layer contains larger amount of organic matter. This confirms the model viewing the clays as partially coated with strongly bond organic [14,16]. However, based on the XPS data, it is difficult to explain the presence of an intense XPS signal from inorganic (Si, Al) even at low take-off angle (sampling depth of about 27 Å).

We have suggested that organic rich solid from Athabasca oil sands are patchy conferring a biwettable property [14]. Indeed ToF-SIMS, which is sensitive to only the very top layer ( $\sim 1-10$  Å) gives rise to ion peaks of both organic and inorganic origin [14]. However, this does not explain why the present S<sup>2</sup>PAS-FTIR data is showing the dominance of organic within the bulk of the material.

The spectra of BWS sample at 11 and 585 Hz shows that the inorganic peaks (SiO and OH) are much weaker, consistent with XPS data (Table 2). In fact, the XPS data show that the top layer contains about three times more carbon than FS samples. However, the relative intensities of the organic and inorganic components (Fig. 3) are similar to what is observed on powder FS.

Fig. 4 shows the S<sup>2</sup>FTIR-PAS spectra of the HPS sample. As it is the case of the precedent samples, peaks assigned to organic and inorganic groups were detected. The inorganic peaks are relatively weaker compared with those observed on FS and BWS. The relative intensity of the organic and inorganic peaks does not seem to change significantly with the modulation frequency. XPS data of HPS show that carbon is the dominant element (Table 2). This explains probably the absence of variation of the PAS spectrum as a function of the probed depth.

A possible model explaining the S<sup>2</sup>PAS-FTIR data is depicted in Fig. 5. In this model, we propose that colloidal particles containing large quantity of bitumen be trapped between ultrafine solid particulate. The relative concentration of these bitumen colloids is suggested to increase in the bulk. This explains also the origin of differ-

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Elemental atomic concentrations of FS, BWS and HPS obtained with  $\ensuremath{XPS^a}$ 

Elements	Atomic percent		
	FS (powder)	BWS	HPS
С	20.5	60.8	85.5
0	53.8	25.9	10.3
Si	13.8	8.3	2.9
Al	11.9	5.0	1.3

<sup>a</sup> The platelet FS is comprised of a smooth (1st) and a rough (2nd) side.



Fig. 3. S<sup>2</sup>PAS-FTIR spectra of BWS (powder) at two different modulation frequencies. The spectra were normalized to the CH stretching peak around 2900 cm<sup>-1</sup>.



Fig. 4. S<sup>2</sup>PAS-FTIR spectra of HPS (powder) at two different modulation frequencies. The spectra were normalized to the CH stretching peak around 2900 cm<sup>-1</sup>.

ence in composition between the two platelets' sides. The side containing more carbon seems to reflect more the bulk composition of the platelet. The surface composition of the powder sample appears to be intermediary between the two sides' composition of the platelet.

#### 3.1. Model and process implications

Based on the approximate relation:  $L(\mu m) = 180 \times (f)^{-1/2}$ , where f is the modulation frequency, the depth profiled L at 11 and 585 Hz modulation frequencies are 54 and 7  $\mu m$ , respectively. This implies that the relative concentration of inorganic decreases, as we probe deeper within the material in the case of FS and BWS samples.

Based on TEM data [16], it has been shown that the ultrafine solids are thin particles (about 10 nm) with lateral expansion of about 100 nm or more. The top layer composition of these ultrafine solids probed by XPS shows the presence of both organic and inorganic functional groups [14]. In our model, we view these fine solids (FS) samples

Simplified conceptual diagram of



Fig. 5. Simplified conceptual diagram of a fine solid sample. The layered model contains ultrafine solids coated with thin organic layer 'sandwiching' colloidal bitumen particles.

as a stacking of ultrafine solids with bitumen-like colloidal particles trapped in between.

A consequence of this model is that in the case of FS significant amount of bitumen matter in the form of colloidal particle is trapped between the ultrafine solids. The trapped bitumen is a potential contributor to coke formation and is also a source of an inefficient bitumen recovery Fig. 5. Furthermore, it is detrimental for future reclamation process. Thus grounding of these bitumen solid ultrafines will allow exposition of more bitumen to the surface and facilitate a further separation between solid and bitumen.

### 4. Conclusions

Physico-chemically distinct samples of FS, HPS and BWS were separated from the fine tailings using a new flocculation/agglomeration method. The S<sup>2</sup>FTIR-PAS presented in this paper allowed us to refine our pictorial model of the ultrafine solids. The relative contribution of the organic versus inorganic components varies significantly in the case the FS platelet. However, this variation is reduced significantly in FS powder, HPS and BWS samples. The fine solids contain colloidal particles of bitumen trapped between ultrafine clays coated with humic matter.

#### Acknowledgements

This work was supported by the National Research Council of Canada.

#### References

- [1] M.B. Hocking, J. Chem. Educ. 54 (1977) 725-729.
- [2] N. Berkowitz, J.G. Speight, Fuel 54 (1975) 138-142.
- [3] A. Majid, J.A. Ripmeester, Fuel 65 (1986) 1714-1727.
- [4] A. Majid, B.D. Sparks, Proc. International Symposium on Waste Processing and Recycling in Mining and Metallurgical Industries, in: S.R. Rao, L.M. Amaratunga, D.A.D. Boate, M.E. Chalkley (Eds.), The Metallurgical Society of the Can. Institute of Mining, Metallurgy and Petroleum, Montreal 1992, pp. 125–134.
- [5] A. Majid, B.D. Sparks, Fuel 75 (1996) 879-884.
- [6] A. Majid, B.D. Sparks, Structure Formation in Oil Sands Fine Taillings Resulting from Floculation of coarse Bi

Wetted Solids by Bitumen Bridging, NRC report No. EC-1281-93S, August 1993.

- [7] J.F. McClelland, R.W. Jones, S. Luo, L.M. Seaverson, in: P.B. Coleman (Ed.), Practical Sampling Techniques for Infrared Analysis, CRC Press, Boca Raton: FL, 1993 Chapter 5.
- [8] R. Palmer, R. Dittmar, Thin Solid Films 223 (1993) 31-38.
- [9] D.L. Drapcho, R. Curbelo, E.y. Jiang, R. Crocombe, W.J. McCarthy, Appl. Spectr. 51 (1997) 453–460.
- [10] E.Y. Jiang, Appl. Spectr. 53 (1999) 583-587.
- [11] A. Rosencwaig, A. Gersho, J. Appl. Phys. 47 (1976) 64– 69.

- [12] B.D. Ratner, D.G. Castner, in: J.C. Vickerman (Ed.), Surface Analysis, Wiley, New York, 1997, p. 43.
- [13] F. Bensebaa, T.H. Ellis, Progr. Surf. Sci. 50 (1995) 173– 185.
- [14] F. Bensebaa, G. Pleizier, B.D. Sparks, Y. Deslandes, K. Chung, Surf. Interf. Anal. 30 (2000) 207–211.
- [15] H.W. Van der Marel, H. Beutelspacher, Atlas of Infrared spectroscopy of Clay Minerals and Their Admixtures, Elsevier, Amsterdam, 1976, p. 57.
- [16] L.S. Kotlyar, B.D. Sparks, J. Woods, S. Raymond, Y. Le Page, W. Shelfantook, Petroleum Sci. Technol. 16 (1998) 1–19.