Characterization of Clays from Poorly Processing Oil Sands using Synchrotron Techniques

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ABSTRACT

Conventional laboratory x-ray diffraction techniques are generally used to characterize minerals in oil sand ores and other extraction process streams and can usually provide mineralogical insight into reasons for poor processability. Often, however, a greater level of detail is required to quantify low levels of mixed layering in clay minerals and the multitude of non-clay minerals in the ores. The more intense x-ray sources available at synchrotrons with their inherent high resolution and tunable wavelength can often help in providing this level of detail. In addition, x-ray microscopy can help to characterize the organic contaminants that commonly affect clay behaviour in industrial processes. In this study, low levels of mixed layering of smectite were observed in the kaolinite and illite phases using synchrotron x-ray diffraction, in addition to heavy minerals undetectable using a laboratory rotating anode x-ray source. Using scanning transmission x-ray microscopy, the speciation of carbon components adsorbed on clay minerals after bitumen extraction suggests a preferential affinity of the clay minerals for high-molecular-weight aromatics in bitumen.

Key words: STXM, SXRD, Emulsions, Bitumen, Oil sand clays

INTRODUCTION

The oil sand deposits in northern Alberta currently account for over 50% of Canada's crude oil production. Surface-mined oil sands operations are currently restricted to the McMurray Formation in the Athabasca oil sands deposit of northern Alberta, Canada. The Athabasca deposit is usually described as fluvial in the lower McMurray Formation, estuarine in the middle McMurray Formation and marine in the upper McMurray Formation. Bitumen content is quite variable across the formation, with a mineable range between 6 and 18 wt%.

The clay mineralogy, though variable across the formation, is primarily kaolinite and illite with high concentrations of illite-smectite and kaolinite-smectite mixed layers and minor quantities of chlorite and chloritic intergrades. Discrete smectite is sometimes found in small concentrations in the marine deposits.

In addition to clay minerals, the clay-sized fraction (minus 2-μm) contains significant amounts of iron oxides, iron carbonate, and titanium oxides.

The bitumen resource is conventionally extracted by a water-based flotation technique that involves high mechanical energy input at 45 to 55°C and a pH between 7 and 8.5. Clay minerals in oil sands are known to exhibit biwettable behaviour with the result that, during bitumen extraction, the bulk of the clay minerals report to the water-saturated tailings stream, while a significant portion of the clay minerals and the naturally oleophilic minerals (compounds of iron, titanium, and zirconium) float with the bitumen phase.

The extractability of bitumen from oil sands depends to a great extent on properties affecting bitumen liberation from sand grains on one hand, and those affecting flotation of bitumen through a water column on the other. Water chemistry that favours a dispersed clay slurry allows better bitumen separation from sand grains and better bitumen flotation whereas a coagulating chemistry (with high concentrations of divalent or trivalent ions) tends to inhibit bitumen flotation, but enhances the tailings properties. Ore desiccation, weathering, and oxidation change the bitumen surface structure and chemistry with an attendant greater affinity for mineral surfaces.

Such interactions inhibit bitumen liberation from the minerals and impede the air bubble–bitumen attachment required for flotation. The hydrophobic sites created on clay mineral surfaces result in their biwettable behaviour, which provides a bridge for
bitumen carryover with the tailings and mineral carryover with the froth product, along with a propensity for forming stable emulsions during froth treatment \cite{6,8,9}. Hindrances to both bitumen liberation from mineral surfaces and flotation are typically ameliorated with caustic additions and higher extraction temperatures \cite{10}. The elevated pH releases natural carboxylate surfactants, which lower the oil/water interfacial tension with an attendant reduction in the hydrophobicity of mineral surfaces \cite{11-13}. The resulting dispersed clay slurry creates a slow-settling tailings stream that requires extensive containment facilities and limits the release of water for recirculation to extraction. The processability problems associated with variations in bitumen chemistry and oil sands mineralogy have provided the impetus for a great deal of study into clay-bitumen interactions. While clay-bitumen interactions have been extensively investigated using a wide range of surface-sensitive techniques \cite{6,9,14,20}, it has been difficult to examine samples as-is in the wet, undisturbed state. Consequently, most of the speciation studies have focused on dried mineral and organic solids. The present study is part of an ongoing investigation to evaluate the selectivity of the different organic components in bitumen for specific sites on different clay minerals in oil sands using synchrotron-based scanning transmission x-ray microscopy (STXM) and x-ray powder diffraction (SXRD) techniques. The study could provide a basis for identifying a mineral or organic marker that could potentially be used to predict processability and tailings management issues. STXM is uniquely suited to investigating froth and tailings streams by combining chemical speciation of organics and minerals with high-resolution microscopy in the undisturbed wet state. For SXRD, the improved resolution and wavelength tunability offered by synchrotron sources allow the use of powder diffraction to quantify low levels of interstratification in oil sand clay minerals \cite{22} and differentiation of the myriad of oleophilic heavy minerals in oil sands.

Using a variety of surface-sensitive techniques such as x-ray photoelectron spectroscopy (XPS) and time-of-flight ion mass spectroscopy (ToF-SIMS), several studies have shown that minerals are often coated with toluene-insoluble aromatic polar organic matter derived from humic and asphaltene-like substances \cite{3,18}. The polar compounds were identified as a complex mixture of carboxylic acids, sulfoxides, and alcohols. Some of the observed toluene-insoluble organics are water-soluble surfactants based on sulphanic and naphthenic acids \cite{6,11,13}. These water-soluble surfactants are capable of stabilizing multiple emulsions. At the pH of the extraction process, these organic substances cannot compete with water on the hydrophilic sites on clay surfaces but preferentially adsorb on hydrophobic sites, the neutral siloxane surface of kaolinite, or via an exchangeable cation on clay mineral surfaces \cite{25}. The specificity of adsorption sites on clay mineral surfaces is dependent on the charge distribution and hence on the mineralogy. Understanding these interactions in terms of bitumen chemistry and clay mineralogy can be important in optimizing the extraction and tailings operations in commercial oil sands plants. The unique characterization opportunities offered by synchrotron sources are ideally suited to the characterization of these clay-organic interactions.

**MATERIALS AND METHODS**

**Materials**

To estimate the range of mineral composition in oil sands, several samples from three different leases with varying degrees of processability were analyzed over a period of five years. The samples cut across fluvial, estuarine, and marine streams generated from a low-grade ore with low bitumen recovery. The ore is characterized by high iron and humic acid concentrations in the connate water.

The second sample is a low-solids naphtha-diluted bitumen with highly stable multiple emulsions typically observed during froth treatment from a poorly processing ore. This is a commercial plant sample that was collected during a process upset condition. The aim was to investigate the water/organic interface for potential emulsion stabilizing functional groups.

The third sample is a pentane-insoluble bitumen asphaltene. The bitumen was recovered during froth treatment of a regular ore.

**X-Ray Diffraction**

SXRD experiments were conducted on the middlings and diluted bitumen minerals to determine the composition. Bitumen was removed from the minerals by refluxing the middlings and diluted bitumen samples in hot toluene (Dean-Stark extraction). The SXRD experiments were conducted on the middlings and diluted bitumen samples in hot toluene (Dean-Stark extraction). The SXRD experiments were conducted at the NSLS high-resolution powder diffraction SUNY X3B1 bending magnet beamline. All diffraction data reported here were collected at \( \lambda = 0.70011\text{Å} \) in a capillary between 6 and 30° 2θ at 0.005° per step. The wavelength was selected using a silicon double crystal monochromator. A corundum NIST standard was used to calibrate the wavelength. In a typical diffraction experiment, the intensity of the incoming beam is monitored by an ion chamber and normalized to account for beam decay in the primary beam. A post-sample diffracted beam Ge(111) crystal analyzer is used to ensure very high resolution. A commercial Rietveld refinement program, TOPAS™, was used for mineral quantification. In general, only microstructural parameters were refined. Phases in high concentrations sometimes lend themselves to occupancy and atomic position refinements with large constraints.

Laboratory x-ray diffraction experiments were conducted with a Rigaku cobalt rotating anode RU200B diffractometer. A Bruker D8 Advance diffractometer equipped with parabolic Co monochromating mirrors on the incident and
diffracted beam sides was used for some of the experiments. Mineral quantification was also conducted with TOPAST™. Analysis of the laboratory x-ray diffraction patterns was based on minerals identified using synchrotron x-rays, which have better detection limits for minor to trace minerals.

**Scanning Transmission X-Ray Microscopy**

Scanning transmission x-ray microscopy (STXM) experiments were performed using a SUNY-SB microscope (Fig.1) on beamline X1A at the National Synchrotron Light Source (NSLS)²⁴.

![Fig.1. Schematic of the STXM setup on beamline X1A at the NSLS](image)

STXM is based on a Fresnel zone plate optic that focuses soft x-rays on a small spot ~35 nm in diameter. A thin sample transparent to x-rays is raster-scanned through the focus and the detected x-ray transmission is used to form a transmission image on a pixel-by-pixel basis. The selection of an imaging x-ray wavelength that correspond to a specific electronic transition, such as the C 1s→π*transition of an aromatic group, imparts chemical contrast to these STXM images. Similarly, one can also perform x-ray absorption near-edge spectroscopy (XANES) on specific sub-micron domains, permitting chemical speciation at this scale. The sensitivity of XANES is particularly useful for the chemical characterization of complex organic materials²⁵,²⁶, "Spectromicroscopy" is the combination of these types of microscopy and spectroscopy, and spectroscopic series of images can contain a wealth of spatially resolved chemical information²¹.

In order to avoid artifacts from the sample drying, the middlings sample was examined as liquid slurry using a wet STXM cell²⁷. An aliquot of the minus 2-μm middlings slurry was placed between two Si₃N₄ membranes and sealed. This sample dried out during the data collection, but this is not thought to have affected the interpretation of the results. Other samples were examined as dried films cast onto a Si₃N₄ membrane; the sample of asphaltene from a toluene solution and the sample of diluted bitumen from a sonicated water solution. The mineral fraction of naphtha-diluted bitumen was first isolated by Dean-Stark extraction, leaving minerals with strongly adsorbed toluene-insoluble organics. This fraction was cast onto a Si₃N₄ membrane from a water suspension.

The microscope was used to record a series of images across the carbon K-edge to identify the carbon-rich areas. XANES spectra were collected from several regions within an image frame to provide chemical information.

**RESULTS AND DISCUSSION**

**Mineral Composition of Athabasca Oil Sands and some Process Streams**

The concentrations of bitumen and minerals in oil sand ores vary significantly but the bitumen chemistry and mineralogy are less varied. While the mineralogy of the clay fraction (minus 2-μm) is actually the most important determinant of interaction with the organic phase, the interaction is based on size for convenience given the variation in the active sorption sites and concentrations of minerals in the clay fraction. Table 1 gives a range of mineral compositions in the minus 2-μm fraction observed in samples from different areas of three oil sands leases. Conventional x-ray diffraction data were collected using Rigaku RU200B and Bruker D8 diffractometers. The mixed-layered clay minerals were quantified using NEWMOD™, based on the extent of mixed layering established from synchrotron x-ray data²². The discrete minerals were quantified using TOPAST™. The minus 0.3-μm fraction, which has been observed by several authors to interact the most with organics, comprises primarily kaolinite and illite with minor degrees of smectite interstratification (an average of 10 and 25%, respectively, in the minus 0.2-μm fraction) and minor concentrations of discrete kaolinite, illite, and lepidocrocite (FeO(OH)). Trace amounts of discrete smectite are sometimes observed in marine oil sands²².

<table>
<thead>
<tr>
<th>No. of samples</th>
<th>Ore</th>
<th>Froth</th>
<th>Tailings</th>
</tr>
</thead>
<tbody>
<tr>
<td>61</td>
<td>22</td>
<td>54</td>
<td></td>
</tr>
<tr>
<td>K(90)-Smectite</td>
<td>0.23</td>
<td>0.22</td>
<td>0.16</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>5.67</td>
<td>31.58</td>
<td>14.79</td>
</tr>
<tr>
<td>I(85)-Smectite</td>
<td>0.70</td>
<td>0.38</td>
<td>0.58</td>
</tr>
<tr>
<td>Illite</td>
<td>3.23</td>
<td>6.21</td>
<td>2.24</td>
</tr>
<tr>
<td>Chlorite</td>
<td>0.9</td>
<td>0.1</td>
<td>0.8</td>
</tr>
<tr>
<td>Quartz</td>
<td>3.13</td>
<td>6.10</td>
<td>5.57</td>
</tr>
<tr>
<td>Rutile + Anatase</td>
<td>0.2</td>
<td>1.10</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Siderite</td>
<td>0.1</td>
<td>1.11</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Pyrite+Marcasite</td>
<td>0.2</td>
<td>1.2</td>
<td>&lt;0.1</td>
</tr>
</tbody>
</table>

In addition to clay minerals, naturally oleophilic heavy minerals concentrate in the bitumen phase at the pH of extraction. The sheer number of mineral types in the froth stream necessitates the use of a high-resolution synchrotron x-ray source to identify and quantify the mineral phases by powder diffraction. This is illustrated in Fig.2 for one of the froth solids in Table 1. The laboratory x-ray data (B) were
collected with a Rigaku cobalt rotating anode operating at 40 kV and 180 mA. Diffraction data were collected between 6 and 60° 2θ at 0.02° per step for 5 s using a 0.3-mm receiving slit. The splits observed in the peaks of the synchrotron data are due to other minerals in the sample. In this particular sample, at least 14 minerals were identifiable in the synchrotron data, out of which the strongest peaks for ilmenite, marcasite, and a sodium borate mineral were not present in the laboratory data.

Mineral Composition of Middling Solids

The bulk properties of the middlings are given in Table 2. The sample was generated from a noncaustic batch extraction of a poorly processing low-grade ore. The ore is characterized by an unusually high concentration of soluble Fe in the connate water, and by 35% bitumen oxidation. The mineral composition was obtained from laboratory x-ray diffraction data. The concentrations of the mixed-layered clay minerals were obtained by NEWMOD™ modeling, and the other minerals were quantified using TOPAS™. The mineral composition of the middlings is not unusual for fine tailings suggesting that the reason for poor processability may not be mineral-based.

Table 2. Middlings properties of a poorly processing low-grade ore

<table>
<thead>
<tr>
<th>Middlings</th>
<th>Bitumen (wt%)</th>
<th>Minerals (wt%)</th>
<th>Water (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.3</td>
<td>6.5</td>
<td>93.2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>wt% on mineral basis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolinite + K-S</td>
</tr>
<tr>
<td>Illite + I-S</td>
</tr>
<tr>
<td>Chlorite</td>
</tr>
<tr>
<td>Quartz</td>
</tr>
<tr>
<td>Rutile+Anatase</td>
</tr>
</tbody>
</table>

*S-K: kaolinite (90)-smectite, I-S: illite (85)-smectite

Spectroscopy of Diluted Bitumen and Asphaltenes.

Figure 4 shows the carbon XANES spectrum of a diluted bitumen sample and an asphaltene model. The XANES spectrum of the diluted bitumen sample was collected on an oil drop obtained in a water-continuous area of emulsion from a plant upset condition. These spectra show a distinct transition at 285 eV characteristic of C=C double bonds (C \( \rightarrow \pi^*_{C=C} \)) and a band at 287.5 eV characteristic of saturated carbon chains (C \( \rightarrow \sigma^*_{C-H} \)). In the diluted bitumen sample, the aromatic feature arises from the naphtha diluent, increased relative to the spectrum of bitumen in Fig.6.

The composition was determined by Rietveld analysis implemented in TOPAS™. Both illite-smectite (85:10) and kaolinite-smectite (90:10) were detected in significant concentrations but they were modeled as anisotropic strain–broadened forms of discrete illite and kaolinite, respectively. The mineralogy is dominated by clay and oleophilic minerals. The uncertainty in the quantification is given in brackets in Fig.3.

Once the minerals have been identified using SXRD, it becomes fairly straightforward to use the phases as starting structures for data collected with conventional laboratory XRD, which are more easily accessible.
Fig. 4. XANES spectra of a diluted bitumen and an asphaltene model.

**X-Ray Microscopy of Middlings Slurry**

Figure 5 shows two images from the middlings minus 2-μm fraction.

The left image, taken below the carbon K-edge highlights a densely packed clay region. The right image, taken at the energy of the C 1s → π* transition (285 eV), highlights unsaturated carbon. A continuous oil area is seen at the bottom left of the 285 eV image, and several clay areas (circled) can be correlated with a carbon phase. XANES spectra collected from the oil-continuous phase and the two clay particles in the frame are shown in Fig. 6.

The XANES spectrum of the oil-continuous phase is primarily saturated alkane, from the intense C 1s → σ* band at 288 eV, with some unsaturation (285 eV) and a small carbonyl content (289 eV), likely a COOH group. The XANES spectrum extracted from the clay particles shows a stronger 285 eV peak than the oil-continuous phase, indicating that the "carbon on clay" contains more C=C bonds than the bulk oil. The sharp peak at 297 eV is the K 2p edge from an illite particle.

**X-Ray Microscopy of Diluted Bitumen Minerals**

Figure 7 shows a series of STXM images around the carbon K-edge of the toluene-insoluble organics bound to the diluted bitumen minerals. Some of the clay mineral particles in the images contain carbon-rich regions (top left of the 285 eV image).

The carbon absorption spectra shown in Fig. 8 indicate that the bound organics are primarily aromatic, similar to the organics-on-clay in Fig. 5. Also shown in Fig. 8 is the absorption spectrum of a carbonate at 290.2 eV. The illite K 2p edge observed in the spectra confirms that clay-rich regions were being evaluated. Further attempts are being made to differentiate between the illitic and kaolinitic clays.

Fig. 7. STXM images across the carbon K-edge of toluene-extracted diluted bitumen minerals. The circled particle in the 290.2 eV image is a carbonate.

The carbon absorption spectra shown in Fig. 8 indicate that the bound organics are primarily aromatic, similar to the organics-on-clay in Fig. 5. Also shown in Fig. 8 is the absorption spectrum of a carbonate at 290.2 eV. The illite K 2p edge observed in the spectra confirms that clay-rich regions were being evaluated. Further attempts are being made to differentiate between the illitic and kaolinitic clays.
Fig. 8. Carbon absorption spectra of diluted bitumen minerals with toluene-insoluble organic coating. The spectra correspond to the image frames in Fig. 7.

CONCLUSIONS

This study demonstrates that synchrotron-based scanning transmission x-ray spectromicroscopy and x-ray powder diffraction are useful tools for probing mineral-organic interactions in oil sands processes. As the resolution achievable at STXM beamlines continues to improve, new information on the chemistry and morphology of adsorbed organics on clays will expand the fundamental understanding of the sorption sites on clay surfaces and preferentially adsorbed functional groups.

The partitioning of polar aromatic compounds on the clay surfaces confirms earlier studies using NMR, FT-IR, XPS, and ToF-SIMS. Further work is being conducted on a wide range of oil sands process streams to enable more precise speciation of both mineral and associated organics by STXM, and to further improve the technique for these types of complex samples.

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