



Full Length Article

Spatially resolved organic coating on clay minerals in bitumen froth revealed by atomic force microscopy adhesion mapping



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HIGHLIGHTS

- PeakForce QNM-AFM was applied for the first time to study organic matter associated with oil sands fine solids.
- The patchy-distributed organic coating on clay particles was directly visualized.
- The surface coverage and average thickness of the organic coating on clay basal faces were quantitatively determined.
- The organic matter associated with the fine solids was found to be softer than asphaltene fraction of oil sands bitumen.

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ABSTRACT

Mineral solids in oil sands are often coated with organic matter. These organically-modified mineral solids hinder bitumen aeration and stabilize water-in-oil emulsions, leading to low bitumen recovery and poor bitumen product quality. The study of these organic coating on the fine solids has been elusive due to the nanometer length scale and the unsuitability of sampling in high vacuum sample chambers. In the present work, we report the first attempt of using PeakForce Quantitative Nanomechanical Mapping (QNM) Atomic Force Microscopy (AFM) to study the organic matter adsorption on fine mineral solids extracted from bitumen froth. Taking advantage of the simultaneous nano-scale resolution topographic imaging and adhesion force mapping enabled by PeakForce QNM-AFM, the mineral and organic components in the bitumen froth fine solids were clearly distinguished due to their variations in shapes and mechanical properties. The inhomogeneous spatial distribution of adhesion force on surfaces of platy particles indicated the existence of organic patches on clay minerals. The area percentage of surface organic matter coverage on the clay basal faces was calculated to be $17 \pm 6\%$, and the average thickness of the organic coating was estimated to be 1.4 nm based on the adhesion force maps. The organic matter associated with the mineral solids, which cannot be washed off by toluene, was different from asphaltenes in terms of mechanical properties. More specifically, the irreversibly-adsorbed organic matter on clay minerals was found to be softer than the asphaltene fraction of oil sands bitumen.

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1. Introduction

The adsorption of organic matter on mineral surfaces is a subject of interest in a variety of disciplines, such as petroleum geology, pharmacy, cosmetics, and ceramics [1,2]. In oil sands processing, the organic matter associated with the oil sands fine solids can significantly affect the behavior of the fine solids, significantly impacting the bitumen production process [3,4]. For example, the current warm-water oil sands extraction process in the

Fort McMurray region in northern Alberta, Canada, generates a bitumen froth as an intermediate product. The fine solids in the bitumen froth are believed to play a vital role in stabilizing water-in-oil emulsions and thus degrading bitumen quality as the emulsions are difficult to separate from the bitumen froth [4,5]. The emulsion stabilizing property of the fine solids is caused by their bi-wet characteristics, due to hydrocarbon coating [6]. Therefore, an understanding of the structures and properties of the organic matter associated with these fine solids is essential for oil sands processing.

Characterization studies reported in literature [4,6,7] indicated that the organic matter associated with the fine solids derived from oil sands was polar and aromatic, similar to asphaltene fraction of oil sands bitumen. However, no prior studies compared the

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mechanical properties of the adsorbed materials. Clay minerals are the main components of the mineral solids in Alberta oil sands [8,9]. The organic matter can modify the clay minerals either by adsorbing on the clay surfaces as an organic coating, or by cementing the mineral particles into organic-mineral aggregates as “glue” [8,10–13]. As the organic matter may appear as nano- or submicron domains on clay surfaces [3,14], ultra-high resolution techniques are needed to study the organic coating on the clay surfaces. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) have been used [4,15]. However, the thin film thickness of organic coating [3] and the poor conductivity of clay minerals (a carbon or metal coating is needed to avoid sample charging) make it challenging to visualize the organic coating on mineral solids by these imaging techniques. The surface analysis techniques such as X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectroscopy (ToF-SIMS) have also been applied, and the organic coverage on clay surfaces is proposed to be patchy and discontinuous based on the detectable signals of inorganic elements (such as Al and Si) in the topmost layer (2–5 nm) [4,8,16]. However, determination of the spatial distribution and thickness of the organic matter adsorbed on the clay minerals has not been possible.

Another challenge in imaging of organic-clay mixtures is their tendency to aggregate. Six et al. [17] and Sohi et al. [18] successfully disrupted the organic-mineral aggregates in soil by ultrasonic treatment and then separated the organic matter by centrifugation. Their approach suggested that ultrasonication followed by centrifugation was a practical way to separate the organic matter in the fine solids aggregates.

Atomic force microscopy (AFM), invented in the early 1980s, is a powerful tool for surface analysis with nano- or even atomic resolution [19,20], but measurement of the mechanical properties of materials is difficult using contact or tapping mode of AFM [21]. PeakForce Quantitative Nanomechanical Mapping (QNM) mode of AFM, recently developed by Pittenger et al. [22], can quantitatively and unambiguously measure the mechanical properties (e.g. adhesion and modulus) [23]. This method is particularly useful for analyzing samples with different material components showing variations in mechanical properties, such as shales [24], polymers [25], and biological materials [26].

In this study, we apply PeakForce QNM-AFM for the first time, to our knowledge, to study the organic matter associated with the fine solids extracted from bitumen froth. Different components (i.e. platy clays, organic coating, separated organics, and submicron particles) were identified by topographic imaging and adhesion force mapping. The spatial distribution of organic coating on clay minerals was directly visualized, and its surface coverage and adsorption layer thickness on the clay basal faces were quantitatively determined. This work shows that PeakForce QNM-AFM can be a useful technique in analyzing the organic contamination of a mineral surface. The results lead to a better understanding of the structures and properties of the organic matter associated with the fine solids derived from oil sands.

2. Materials and methods

2.1. Materials

Three samples were analyzed to enable quantitative comparisons: a model mineral (kaolinite), a model organic (C_7 asphaltenes), and the fine solids extracted from the bitumen froth. The high purity kaolinite powders were purchased from ACROS organics. The C_7 asphaltenes were precipitated from Athabasca bitumen using *n*-heptane and provided by Imperial Oil Limited. The bitumen froth sample was acquired from CanmetENERGY, Devon,

Alberta, courtesy of Imperial Oil Limited. The fine solids in the bitumen froth were extracted by filtration using 0.22 μm pore size GVWP Millipore filter membrane. The filtration was conducted at 55 kPa vacuum pressure under room temperature ($\sim 22^\circ\text{C}$). To obtain the fine solids, one gram of the bitumen froth was diluted by 100 mL toluene to form a suspension for filtration. When all the liquid passed through the filter, the filter cake was washed by toluene until the filtrate became colorless. The filter cake solids were dried at 65°C for 24 h and then collected for AFM measurements. The fine solids were mainly composed of organically-modified clay minerals with a total organic carbon content of 15 wt% [8]. Detailed information on the mineralogical and chemical compositions of these fine solids can be found in our previous work [8].

2.2. Sample preparation for AFM measurements

The kaolinite or bitumen froth fine solids suspension was prepared by mixing the solid particles with deionized water (Milli-Q, Millipore) at a concentration of 1 mg/mL, followed by 30 min ultrasonication (Model FB15064, Fisher Scientific). After 2 h of standing, a drop of the solution ($\sim 10\ \mu\text{L}$) was cast on a $1\ \text{cm}^2$ SiO_2 substrate (nanoFAB, University of Alberta) which had been prewashed successively in 10 mL methanol and 10 mL water and blown dry with N_2 gas to remove any contaminants and impurities from the surface. The drop was allowed to dry at ambient conditions for 2 h and kept inside a petri dish before AFM measurements to avoid contamination by ambient particles.

The asphaltene sample was dissolved in toluene by ultrasonication to make 0.005 wt% asphaltene solution. A drop of this solution was cast on the SiO_2 substrate. The drop was allowed to dry at ambient conditions for 2 h. After toluene evaporation, only the solid asphaltenes adhered to the substrate. The substrate with the asphaltenes was kept inside a petri dish before AFM measurements.

To separate the organic matter in the bitumen froth fine solids aggregates, the fine solids sample was mixed with toluene at a concentration of 1 mg/mL, followed by 30 min ultrasonication. The solution was centrifuged for 3 h at 2000g using a Model C1301 Spectrafuge Mini Centrifuge (Labnet international, Korea). After centrifugation, the organic matter was expected to concentrate in the supernatant due to its lower density than the minerals. A drop of the supernatant solution was cast on the SiO_2 substrate. The drop was allowed to dry at ambient conditions for 2 h and kept inside a petri dish before AFM measurements.

2.3. Adhesion characterization by PeakForce QNM mode of AFM

The AFM measurements were performed in PeakForce QNM mode using Bruker Icon AFM (Santa Barbara, CA) at ambient conditions (temperature $22 \pm 1^\circ\text{C}$, relative humidity $15 \pm 4\%$). A Pt-Ir coated silicon probe (SCM-PIT, Bruker) with tip radius of 20 nm and cantilever spring constant of 2.8 N/m was used to obtain the topography and adhesion images. Detailed description for the working principles of PeakForce QNM-AFM can be found elsewhere [22,27]. Briefly, the sample surface is measured by the deflection of the cantilever, and a force-distance curve is obtained for each image pixel. The *z*-piezo in PeakForce QNM mode is driven with a sinusoidal waveform (rather than a triangular waveform in conventional modes), which allows direct force control of damaging lateral forces. Fig. 1 shows the schematic force-distance curves of a typical PeakForce QNM-AFM measurement during approach and retraction of the tip. The peak force value of the force-distance curves is used as the imaging feedback parameter, and the maximum pull-off force during the retraction of the tip is designated as adhesion force. The topography and adhesion images

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