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Role of Caustic Addition in Bitumen-Clay Interactions

Marjan Tamiz Bakhtiari[†], David Harbottle[†], Meghan Curran[†], Samson Ng[‡], Jonathan Spence[‡], Robert Siy[‡], Qingxia Liu[†], Jacob Masliyah[†] and Zhenghe Xu^{†}*

[†] Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta, T6G 2G6, Canada

[‡] Syncrude Canada Ltd., Edmonton, Alberta, T6N 1H4, Canada

Abstract

Coating of bitumen by clays, known as slime coating is detrimental to bitumen recovery from oil sands using the warm slurry extraction process. Sodium hydroxide (caustic) is added to the extraction process to balance many competing processing challenges which include undesirable slime coating. The current research aims at understanding the role of caustic addition in controlling interactions of bitumen with various types of model clays. The interaction potential was studied by quartz crystal microbalance with dissipation monitoring (QCM-D). After confirming the slime coating potential of montmorillonite clays on bitumen in the presence of calcium ions, interaction of kaolinite and illite with bitumen was studied. To make our study more closely related to industrial applications, tailings water from bitumen extraction tests using Denver flotation cell at different caustic additions was used. At caustic dosage up to 0.5 wt.% of oil sands ore, a negligible coating of kaolinite on the bitumen was determined. However, at lower level of caustic addition illite was shown to attach to the bitumen, with the interaction potential decreasing with increasing caustic dosage. Increasing concentration of humic acids as a result of increasing caustic dosage was identified to limit the interaction potential of illite with bitumen.

This fundamental study clearly shows that the critical role of caustics in modulating interactions of clays with bitumen depends on the type of clays, guiding the multi-billion dollar oil sands industry to identify clay type as a key operational variable.

Keywords: slime coating, clays, bitumen, caustic and humic acids

* Author to whom correspondence should be addressed. Email address: zhenghe.xu@ualberta.ca

1 INTRODUCTION

In 2013 Alberta, Canada produced an average 331.4 thousands (10^3) m³/d of crude bitumen, of which around 47% was extracted by surface mining¹ and warm slurry extraction process. The water-based extraction process relies on the efficient detachment of bitumen from solids, namely liberation,²⁻⁴ and the subsequent attachment of bitumen to air bubbles, namely aeration.⁵⁻¹¹ Collectively the two elemental steps lead to flotation of bitumen to form a froth that is further processed to remove unwanted solids and water prior to upgrading. The quantity of solids recovered in the froth is controlled by carryover (entrainment) and the extent to which bitumen droplets are contaminated by fine particles, commonly referred to as slime coating. Slime coating phenomenon has long been proposed to account for poor bitumen recovery and is often prevalent mechanism for low bitumen recovery and poor froth quality when processing poor oil sands ores.¹² In this case, the clays attach to the surface of the bitumen droplet, forming a layer of clays that impede the attachment of a flotation air bubble to a liberated bitumen droplet, which is considered as one of the major reasons for poor processability of high fines oil sands ores.¹³ The attached clays to the bitumen surface can also cause problems in bitumen froth treatment by forming a rag layer.¹⁴⁻¹⁶

The mechanism for bitumen slime coating has recently been studied in detail by Masliyah et al. using atomic force microscopy (AFM) and zeta potential distribution measurement.^{12, 17- 23} While oil sands ores are a complex mixture of clays including kaolinite, illite, chlorite, montmorillonite, not all the clays cause slime coating. By systematically studying model clays, researchers have shown the detrimental impact of montmorillonite and illite, although to a less extent, on bitumen recovery by slime coating.^{18, 21} While the electrical double layer force between the two interacting species (bitumen and clay particles) is important, it is often the case that both surfaces are negatively charged, leading to a repulsive electrostatic interaction. However, with the addition of divalent cations such as calcium, montmorillonite slime coats strongly on bitumen under the oil sands processing conditions while kaolinite does not. The contrasting behavior for clays of equivalent zeta potentials (kaolinite and montmorillonite at pH's > 8) showed that the clay type and its interaction with calcium play an important role in the slime coating.¹⁸ As proposed by Masliyah et al.,^{18, 21} calcium ions can act to bridge bitumen and clays, with the level of slime coating being related to the calcium ion – clay binding strength. The cationic exchange capacity of different clays has been highlighted to account for these differences, with montmorillonite being of a high adsorption density (high charge to surface area) achieved by ion exchange.^{18, 24} Using AFM to study the interaction potential between bitumen and clays (montmorillonite and kaolinite) in the presence of calcium, Liu et al.¹² measured a stronger adhesion force (four times greater) between bitumen and montmorillonite than between bitumen and kaolinite. The same technique was applied to study the interactions between bitumen and real mineral fines recovered from good and poor processing ores. Strong attraction and adhesion forces were measured in the case of fines recovered from the poor processing ore, with the strength of interaction being related to the increased hydrophobicity of

the fines from the poor processing ore, leading to a greater additional attractive force due to hydrophobic effect.²⁰

While extensive research has been conducted on kaolinite and montmorillonite, little is known about the slime coating potential of illite, another abundant clay mineral in oil sands ores. Ding et al.²³ considered the effect of increased illite concentration in the slurry on bitumen extraction performance. By varying the illite concentration up to 5 wt.% (based on mass of oil sands) the authors measured a gradual reduction in bitumen recovery from ~96 % to ~80 % at 35°C and pH 4.9 (naturally buffered condition). At an equivalent pH, slime coating of bitumen by illite was confirmed by zeta potential distribution measurement. In an early study, Masliyah et al. also observed slime coating of clay as a reason to hinder bitumen-bubble attachment when they studied bitumen-air bubble interaction in the presence of illite particles.²⁵

From a processing perspective it is highly desirable to minimize slime coating so that the bitumen recovery and bitumen froth quality can be improved. For this purpose industry typically adds process aids to the extraction process to keep the operating temperature low while increasing the bitumen recovery.^{26, 27} One of the common process aids is NaOH. Addition of caustic (NaOH) to the process water increases the water pH. In doing so, an optimum in bitumen recovery is often achieved by balancing the contributions from bitumen liberation, coalescence, aeration and slime coating.^{3, 28-30}

The objective of the current study is to advance understanding of bitumen slime coating by studying the particle-bitumen interactions using quartz crystal microbalance with dissipation monitoring (QCM-D). Research to date has highlighted the detrimental impact of montmorillonite on bitumen slime coating in the presence of divalent cations. However, slime

coating is often encountered when processing oil sands ores that contain very little montmorillonite. Therefore, a systematic study using laboratory extracted tailings water at different caustic loadings is conducted to identify the slime coating potential of more prevalent clays such as kaolinite and illite. The critical role of water chemistry, in particular the Ca^{2+} ion concentration, carboxylic surfactant and humic acids concentrations in slime coating will be considered.

2 MATERIALS AND EXPERIMENTAL METHODS

2.1 Minerals

Kaolinite, illite and montmorillonite were obtained from Ward's Natural Science (Rochester, NY). The clay particle sizes were reduced to sub-micron by wet-grinding for 60 hr, with the continual addition of water to compensate its evaporation. The particle sizes of the three minerals after grinding were measured using a Mastersizer 3000 (Malvern Instruments, UK) with the average particle size (d_{50}) measured to be 0.25, 0.14 and 0.29 μm for kaolinite, illite and montmorillonite, respectively. Clay suspensions were prepared to 0.1 wt.% in either Milli-Q[®] water or tailings water with the pH adjusted to 8.5 (see discussion below on the preparation of tailings water). All particle suspensions were mildly sonicated to disperse particles prior to the QCM-D measurement.

2.2 QCM-D measurement principle

Quartz Crystal Microbalance with Dissipation (QCM-D) is a research tool that has been widely used to study solid-solid and solid-liquid interactions.³¹⁻³⁸ The basic principle of the technique relies on monitoring the resonance frequency and dissipation of a piezoelectric quartz crystal

sensor. The application of QCM-D as an ultrasensitive mass balance originates from the work of Sauerbrey,³⁹ who established an empirical relationship between the added (deposited) mass to the sensor and the resonance frequency shift of the sensor given by Eq. 1.

$$-\Delta f = \frac{nf_0 \Delta m}{\rho_q t_q} = \frac{n\Delta m}{c} \quad (1)$$

where, n is the overtone number, f_0 is the fundamental resonance frequency, ρ_q (2648 kg/m³) is the density of quartz, t_q (3.3×10⁻⁴ m) is the thickness of the quartz crystal and c (0.177 mg/m²·Hz for a 5 MHz sensor) is the sensitivity constant.

The Sauerbrey relationship is often used only to approximate the deposited mass, since most systems studied do not satisfy the model criteria of rigid deposits. Frequently, the deposited film may exhibit viscoelastic properties where the frequency is influenced by the mechanical properties of the film, including the shear modulus and viscosity.⁴⁰ For such systems the deposited mass is not 100% coupled with the oscillatory motion of the crystal. In this case, the apparent mass is better described using both frequency and dissipation responses of the sensor,⁴¹ with dissipation defined as the loss of energy per oscillation period divided by the total energy stored in the system and is given by Eq. 2.

$$D = \frac{E_{\text{Dissipated}}}{2\pi E_{\text{Stored}}} \quad (2)$$

With a substantial change in the sensor dissipation, usually considered to be > 5% of the frequency shift, the apparent mass of the deposited viscoelastic film can be modeled using the Voigt-Voinova equation (Eqs. 3, 4 and 5),^{40, 42} by considering the shift in both the sensor

frequency and dissipation. In the following equations subscripts 0, 1 and 2 represent the quartz sensor, the adsorbed viscoelastic layer, and the Newtonian fluid, respectively.

$$\Delta f \approx -\frac{1}{2\pi\rho_0 h_0} \left\{ \frac{\eta_2}{\delta_2} + \left[h_1 \rho_1 \omega - 2h_1 \left(\frac{\eta_2}{\delta_2} \right)^2 \frac{\eta_1 \omega^2}{\mu_1^2 + \omega^2 \eta_1^2} \right] \right\} \quad (3)$$

$$\Delta D \approx \frac{1}{2\pi f \rho_0 h_0} \left\{ \frac{\eta_2}{\delta_2} + \left[2h_1 \left(\frac{\eta_2}{\delta_2} \right)^2 \frac{\eta_1 \omega^2}{\mu_1^2 + \omega^2 \eta_1^2} \right] \right\} \quad (4)$$

$$\delta = \sqrt{\frac{2\eta_2}{\rho_2 \omega}} \quad (5)$$

where h is the thickness, ρ is the density, η is the viscosity, μ is the shear modulus and ω is the angular frequency.

Compared with zeta potential distribution measurement, a unique advantage of using QCM-D to study slime coating or particle interactions of non-ideal systems is that it does not have the limitation that the interacting species have to have a significant difference in zeta potential of the interacting species.

2.3 Preparation of QCM-D sensor surface

The piezoelectric quartz sensor was first pretreated to prepare a thin bitumen layer on the sensor surface. A 5 MHz AT-cut piezoelectric silica sensor was first cleaned by Ultraviolet (UV)/ozone for 10 min followed by washing in a 2 wt.% sodium dodecyl sulfate (SDS) (99% Sigma Aldrich) solution for 30 min. The sensor was then rinsed with excess Milli-Q[®] water and dried with pure nitrogen. Finally, the sensor was once again treated with UV/ozone, then exposed to dichloro-dimethylsilane (DDMS) (Fisher Scientific) vapors for 2 min and cured in an oven at 80 °C for 24 hr to transform the surface from hydrophilic to hydrophobic. The contact angle of the

hydrophilic (untreated) and hydrophobic (treated) surfaces were determined to be 18° and 104° respectively. Hydrophobization of the silica surface ensured that the thin layer of bitumen remained stable when submerged in tailings water.

Vacuum Distillation Unit (VDU) feed bitumen, supplied by Syncrude Canada Ltd., was used throughout the study. To prepare the bitumen layer on the hydrophobically modified QCM-D sensor surface, 5 wt.% bitumen in toluene solution (HPLC grade, Fisher Scientific) was prepared and centrifuged at 20,000 g for 15 min with the centrifugation step repeated 5 times to remove almost all the fines in the bitumen. A spin coater (Laurell WS-400A-6NPP/Lite) was used to prepare a smooth bitumen film on the hydrophobized silica sensor. Rotating at 2000 rpm for 50 s, 4 drops of the diluted bitumen solution were added drop wise to the spinning sensor, ensuring complete wetting of the surface prior to further drop addition. To form a uniform surface and remove any excess solvent, the sensor was rotated at 4500 rpm for an additional 40 s. Before and after coating, the resonance frequency of the sensor was measured using the E4 QCM-D (Q-Sense AB, Sweden). Combining the two data sets using the “stitch” command in the Q-Tools software (Q-Sense, Sweden), the approximate layer thickness (DDMS + bitumen) was determined to be ~200 nm.

2.4 Preparation of tailings water

Tailings water was generated from oil sands extraction studies using Denver cell flotation at 45°C . 500 g of oil sands ore (composition shown in Table 1) was slurried for 5 min at 1500 rpm in 900 g of process water (chemical composition shown in Table 2). Caustic (reagent grade NaOH from Fisher Scientific) was added to the process water at concentrations between 0 wt.% and 0.5 wt.% based on the mass of oil sands. After slurrying, 150 mL/min air was introduced

into the flotation cell with bitumen froth being continually removed over 10 min. A more detailed description of the flotation procedure is provided by Zhou et al.⁴³ To remove fine and ultra-fine solids from the tailings water (the water left in the cell after flotation test), the tailings water was centrifuged at 20,000 g for 30 min. The centrifuged samples then underwent vacuum filtration (0.1 μm filter) to remove nearly all the solids.

Table 1. Composition of oil sands ore (wt.%)

Water	Solids	Bitumen	Fines*
			(wt.% of solids)
8.3	83.5	8.2	15.4

* Fines are defined as solid particles less than 44 μm .

Table 2. Chemistry of process water

pH	Concentration of ions (ppm)			
	K ⁺	Na ⁺	Ca ²⁺	Mg ²⁺
8.5	23	660	40	17

2.5 QCM-D measurement procedure

The frequency and dissipation of the piezoelectric sensor were monitored using a Q-Sense E4 unit. Prior to each measurement, flow modules and tubing were sonicated in 1 wt.% Hellmanex II (Hellma, Germany) solution and subsequently rinsed with excess Milli-Q[®] water and dried with nitrogen. To eliminate concern of deposition due to gravity, the E4 unit was inverted such that any deposition is a direct consequence of bitumen slime coating. At high pH it was difficult

to maintain a stable bitumen layer, possibly due to the low interfacial tension between bitumen and water, which may cause emulsification of bitumen into the aqueous phase and lead to potentially uneven bitumen-water interface. Therefore, all tailings water was adjusted to pH 8.5. The pH adjustment was not expected to influence the concentration of soluble carboxylic surfactants of pKa value \sim pH 4.5. For all the experiments the fluid temperature was maintained at 22 ± 0.02 °C and the flow rate at 0.15 mL/min. At the start of each measurement a stable baseline was established in pH 8.5 Milli-Q[®] water and maintained for a further 4 – 5 min. To minimize sensor disturbance during fluid exchange, the peristaltic pump was temporarily adjusted to no flow during fluid exchange. Tailings water was then introduced into the flow cell without fines to establish a second baseline. A second exchange of the fluids introduced tailings water containing 0.1 wt.% clay particles. The suspension was continually pumped through the flow module until a stable baseline had been reached. Finally, the suspension was switched to tailings water. It should be noted that all QCM-D experiments were repeated at least once. The experimental variability was measured to be less than 10%.

2.6 Analysis of carboxylic surfactant concentration in tailings water

For determination of carboxylic surfactant concentration in tailings water, 50 g of tailings water was acidified to pH 2.3 using reagent grade hydrochloric acid (Fischer Scientific) diluted to different molarities (0.5, 5 and 10 N). The acidified carboxylic surfactants in the neutral form were extracted into Optima grade dichloromethane (DCM) (Fisher Scientific) from acidified tailings water using 2:1 tailings water to DCM volume ratio by liquid-liquid extraction. The extraction was repeated three times to recover nearly all of the carboxylic surfactants, as shown

in Figure 1, with a weak broad band around 1743 cm^{-1} of the Fourier transform infrared (FTIR) absorbance spectrum of the 3rd extraction.

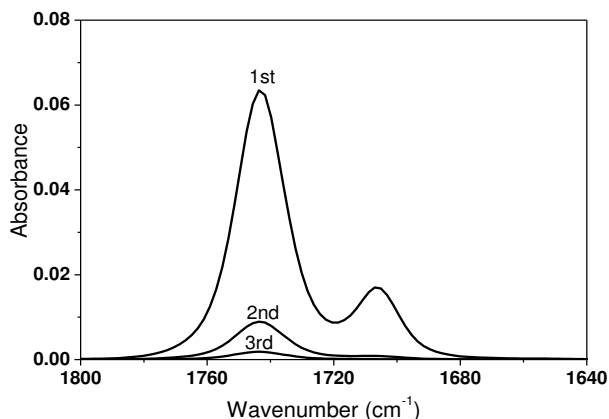


Figure 1. FTIR spectra of extracted carboxylic surfactants from tailings water in dichloromethane. Extraction was performed in three steps.

The three DCM extraction samples were combined and then placed in a vented fume hood to evaporate the solvent under filtered air ($45\text{ }\mu\text{m}$ filter). The remaining residue was re-dissolved in 20 g of fresh DCM and the solubilized sample was analyzed by FTIR (Bio-Rad FTS 6000, Cambridge, USA).^{44, 45} A KBr super-sealed liquid transmission cell (International Crystal Laboratories) with 3 mm path length was used as the sample holder and the measurement chamber was continuously purged with dry air. The instrument resolution was set at 4 cm^{-1} and the spectra were collected in the mid-IR range between $4000\text{-}400\text{ cm}^{-1}$ using a deuterated triglycine sulfate (DTGS) detector. The background (DCM) and sample spectra were obtained after 128 co-added scans. To determine the concentration of carboxylic surfactants, the sum of measured absorbance intensity of the carboxyl functional groups at ~ 1743 (monomer) and $\sim 1706\text{ cm}^{-1}$ (dimers) was equated to a mol/L standard calibration curve. The calibration curve was

prepared using four standard model compounds: dodecanoic acid (98%, Sigma Aldrich), dicyclohexyl acetic acid (99%, Sigma Aldrich), 1-methyl-cyclohexane carboxylic acid (99%, Sigma Aldrich) and *trans*-4-pentylcyclohexane carboxylic acid (99%, Sigma Aldrich).

3 RESULTS AND DISCUSSION

3.1 QCM-D method evaluation

Frequently, slime coating phenomena have been investigated by zeta potential distribution analysis.^{12, 18-23} The technique has identified specific conditions which promote slime coating of montmorillonite on bitumen and coal in the presence of divalent cations.^{18, 46} Therefore, the interaction between montmorillonite, with bitumen in the absence and presence of calcium was chosen to validate the QCM-D technique. Figures 2a and b show the raw QCM-D data of the sensors' third overtone for montmorillonite and bitumen surface. In the absence of Ca^{2+} (Figure 2a) a baseline was first established using 1mM KCl in Milli-Q[®] water. After ~300 s the 0.1 wt.% montmorillonite in 1mM KCl aqueous suspension of pH 8.5, was continuously pumped through the flow cell for almost 20 min. Both the frequency and dissipation response of the sensor remained unchanged, indicating no interaction (deposition) of montmorillonite with (on) bitumen. Repeating the flow experiment in the presence of 40 ppm Ca^{2+} , the results in Figure 2b clearly show a significant negative frequency shift ($\Delta f/n \sim -70 \text{ Hz}$) and positive dissipation shift ($\Delta D \sim +35 \times 10^{-6}$) with the flowing of the montmorillonite suspension after a stable baseline. It should be noted that flowing through 40 ppm Ca^{2+} solution in Milli-Q[®] water without any clay particles addition did not show any noticeable change in both frequency and dissipation of the sensor, indicating the change was caused by the presence of both Ca^{2+} ions and montmorillonite clays. Based on the Sauerbrey equation, a negative frequency shift would

indicate an apparent mass increase of the sensor and hence suggest the deposition of montmorillonite particles on the bitumen coated sensor.

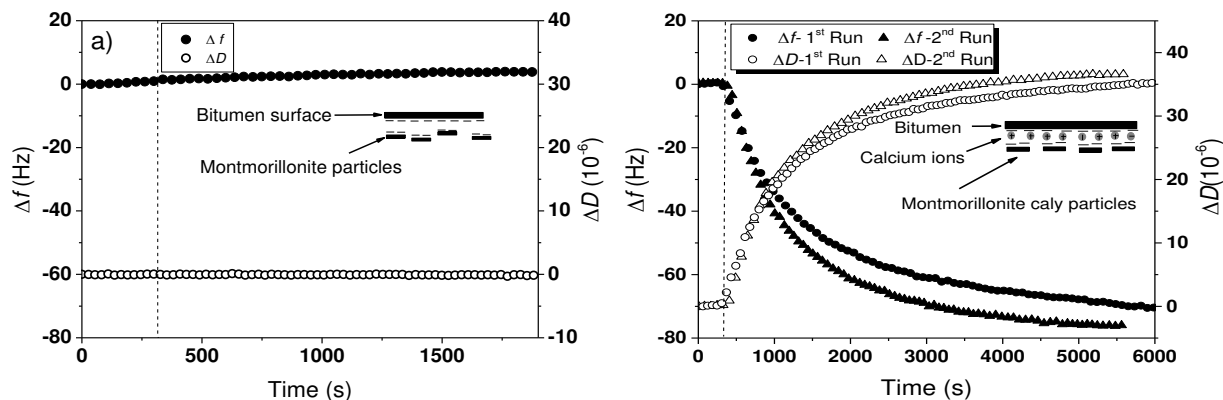


Figure 2. Interaction between montmorillonite clay particles and bitumen surface in 1 mM KCl solution at pH 8.5, a) without Ca^{2+} and b) with addition of 40 ppm Ca^{2+} (1 mM CaCl_2). Dashed line indicates fluid switching from background (Milli-Q[®] water at pH 8.5) to montmorillonite suspension.

Optical microscope and SEM images of the sensor surface were analyzed after completion of the QCM-D experiments to confirm slime coating of montmorillonite clay particles on bitumen immobilized on silica sensor. As shown in Figure 3a, a heterogeneous layer of particles was observed to be deposited on and engulfed within the bitumen layer. At lower resolution (Figure 3b) the surface coverage of montmorillonite on bitumen is clearly visible. The particle surface coverage was determined by grayscale image analysis using ImageJ software to be 16% of the total sensor area. Assuming the density of montmorillonite particle as $\sim 2.7 \text{ g/cm}^3$,⁴⁷ and with a sensor area of 1.21 cm^2 , the mass of particles deposited per unit area based on 16% surface coverage is calculated to be $6.67 \text{ }\mu\text{g/cm}^2$.

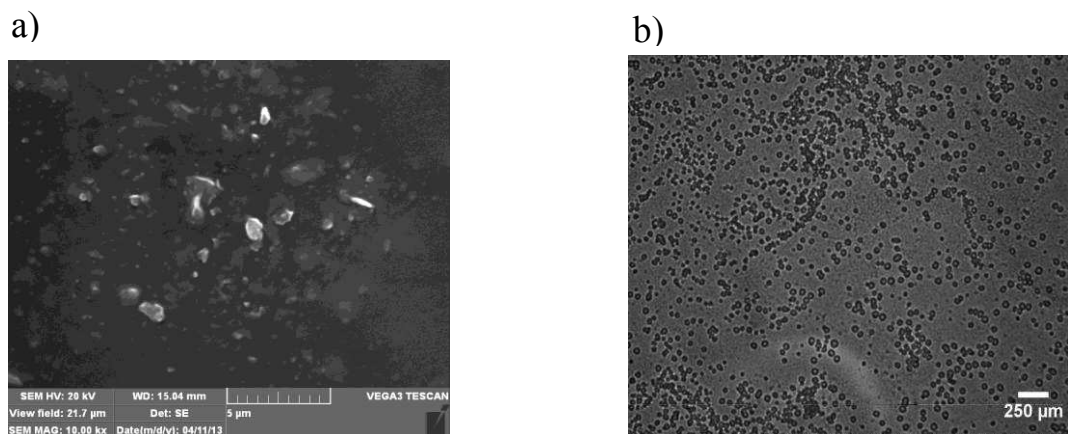


Figure 3. (a) SEM and (b) optical microscope images of deposited montmorillonite particles on the surface of bitumen coated sensor. Fluid conditions: 0.1 wt.% montmorillonite suspension in 1mM KCl solution with 40 ppm Ca^{2+} (1mM CaCl_2) at pH 8.5.

The apparent mass deposited (Figure 4) is calculated using the Voigt model (using Q-Tools software) from the frequency and dissipation responses of the third and fifth sensor overtones to be $8.80 \mu\text{g}/\text{cm}^2$. Close agreement between the two approaches confirms that QCM-D is a suitable technique to assess slime coating potential.

3.2 Slime coating potential of kaolinite and illite particles in tailings water

Kaolinite: Figure 5 shows the QCM-D response for the interaction between bitumen and kaolinite clay particles in tailings water prepared at different caustic levels (a → d: 0, 0.05, 0.1 and 0.5 wt.% NaOH). The addition of caustics increases pH of tailings water, which causes continuous drift of baselines due to undesired emulsification of coated thin bitumen layer, making the interpretation of the QCM-D experimental results difficult if not impossible. For the purpose of studying the effect of surfactant and humic acids in the tailings water by isolating the variation of pH due to NaOH addition, the pH of the tailings water was first adjusted to pH 8.5 in this set of measurements. Decreasing pH over the current range retained all the surfactant and

humic acid in tailings water that their effect can be effectively studied. In all the cases a stable baseline was first established with pH 8.5 Milli-Q[®] water. Then the desired tailings water (with no fines) was pumped through the flow module resulting in a negative frequency shift, with the magnitude of the shift increasing in the order of 0 wt.% NaOH (-3.5 Hz), 0.05 wt.% NaOH (-8.3 Hz), 0.1 wt.% NaOH (-32.8 Hz) and 0.5 wt.% NaOH (-49.3 Hz). The decrease in the resonance frequency during this step results from the adsorption of natural surface active species released from bitumen during extraction, which will be discussed later in the paper. Once the resonance frequency and dissipation reached a steady state condition, tailings water containing 0.1 wt.% kaolinite clay particles was allowed to flow through the cell. Independent of the caustic dosage, the addition of kaolinite clay did not change the steady-state resonance (both frequency and dissipation) of the sensor, suggesting that none of the experimental conditions promoted slime coating of bitumen by kaolinite particles.

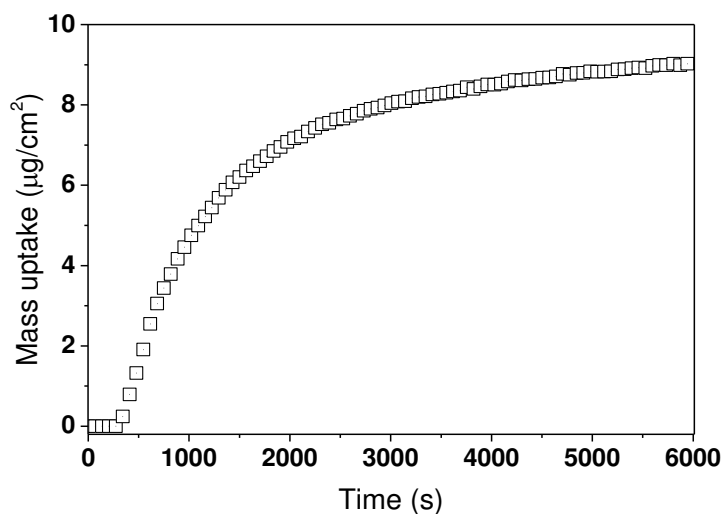


Figure 4. Apparent mass of montmorillonite particles deposited on bitumen coated sensor surface as determined by Voigt model (using Q-Tools software). Fluid conditions: 0.1 wt.% montmorillonite suspension in 1mM KCl solution with 40 ppm Ca²⁺ (1mM CaCl₂) at pH 8.5.

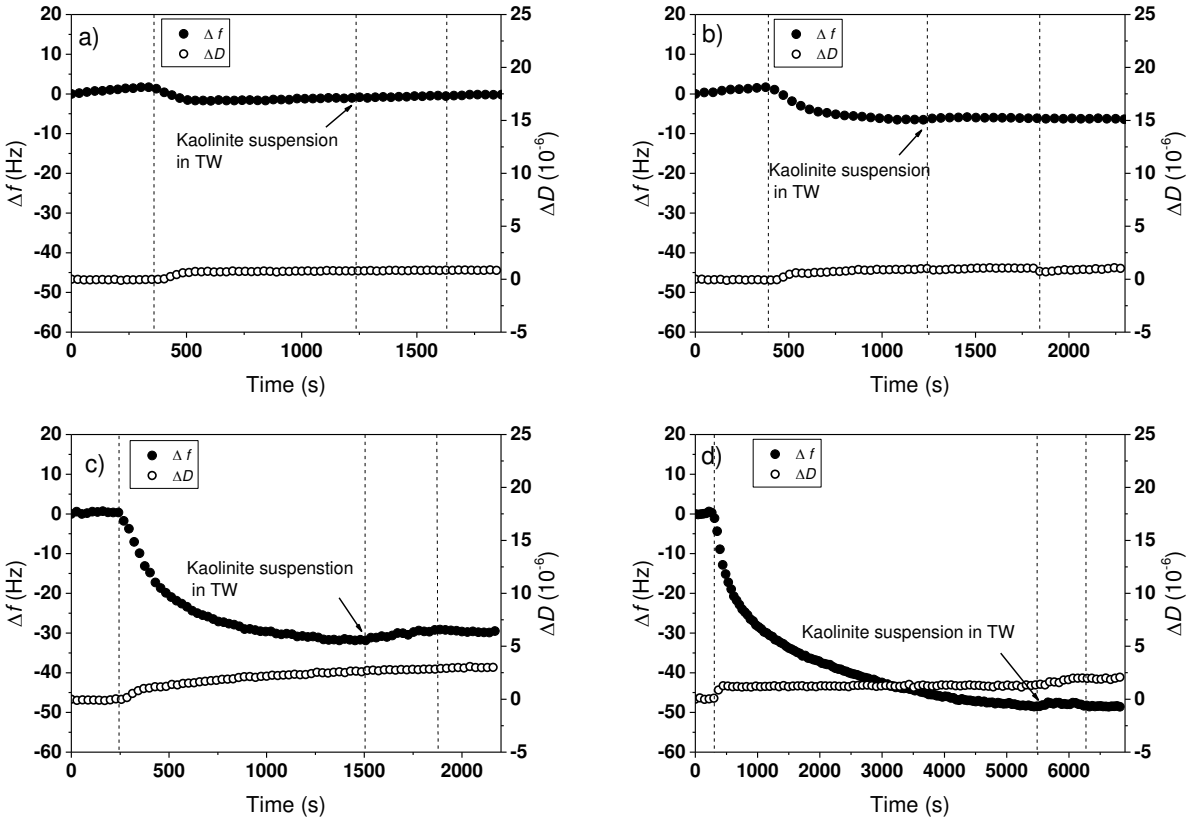


Figure 5. Interactions between kaolinite particles and bitumen surface in tailings water prepared with different levels of caustic additions during bitumen extraction: a) 0 wt.% NaOH, b) 0.05 wt.% NaOH, c) 0.1 wt.% NaOH and d) 0.5 wt.% NaOH with initial suspension particle concentration of 0.1 wt.%. Dashed lines indicate fluid switching (from left to right: background to tailings water; tailings water to kaolinite suspension in tailings water; tailings water rinse).

TW: tailings water

The results presented in Figure 5 suggest that uncontaminated (hydrophilic) kaolinite, albeit abundant in oil sands ores, does not cause slime coating of bitumen under bitumen extraction conditions at pH 8.5. These observations are in complete agreement with results from earlier studies using model clay particles.^{17, 18}

Illite: Figure 6 shows the QCM-D response for bitumen – illite interaction under the same experimental conditions as for kaolinite. With Milli-Q[®] water and tailings water baselines established, tailings water containing 0.1 wt.% illite clay particles was allowed to flow through the cell. At low caustic dosage (0 wt.% and 0.05 wt.%), the presence of illite clay particles in tailings water was shown to decrease the resonance frequency beyond the tailings water baseline, by an additional -15.2 Hz and -6.1 Hz for 0 wt.% and 0.05 wt.% caustic dosage, respectively. Based on our QCM-D validation experiments, a decrease in the resonance frequency with the presence of particles would indicate particle deposition on bitumen and hence, bitumen slime coating. The positive dissipation shift is a further validation of particle deposition on the bitumen coated sensor. At higher caustic dosages (0.1 wt.% and 0.5 wt.%), introducing the illite particles did not cause a noticeable change in the resonance frequency and dissipation of the sensor. Such response is similar to the response presented in Figures 2a and 5a-d where slime coating was not measured. It can be concluded that illite slime coating on bitumen occurred without or at low caustic addition, with the slime coating diminishing at higher levels of caustic addition. This trend is in agreement with the common observation of improved froth quality at higher level of caustic addition.⁴⁸ To the author's knowledge this is the first study that identifies illite as a problematic oil sands clay component that causes slime coating under common processing conditions. The presence of ultra-thin illite (<0.3 μm) particles in oil sands ores was shown to decrease the bitumen recovery.^{49, 50}

Calculating the deposited particle mass by the Voigt model, the deposited mass was determined to be in the range of 0.5 – 0.6 $\mu\text{g}/\text{cm}^2$ for both the 0 and 0.05 wt.% caustic samples, see Figure 7. At high caustic concentrations the degree of slime coating decreased with minimal or no interaction between bitumen and illite particles. It is worth noting that at low caustic

concentrations, the deposited mass is an order of magnitude smaller than montmorillonite in the presence of Ca^{2+} .

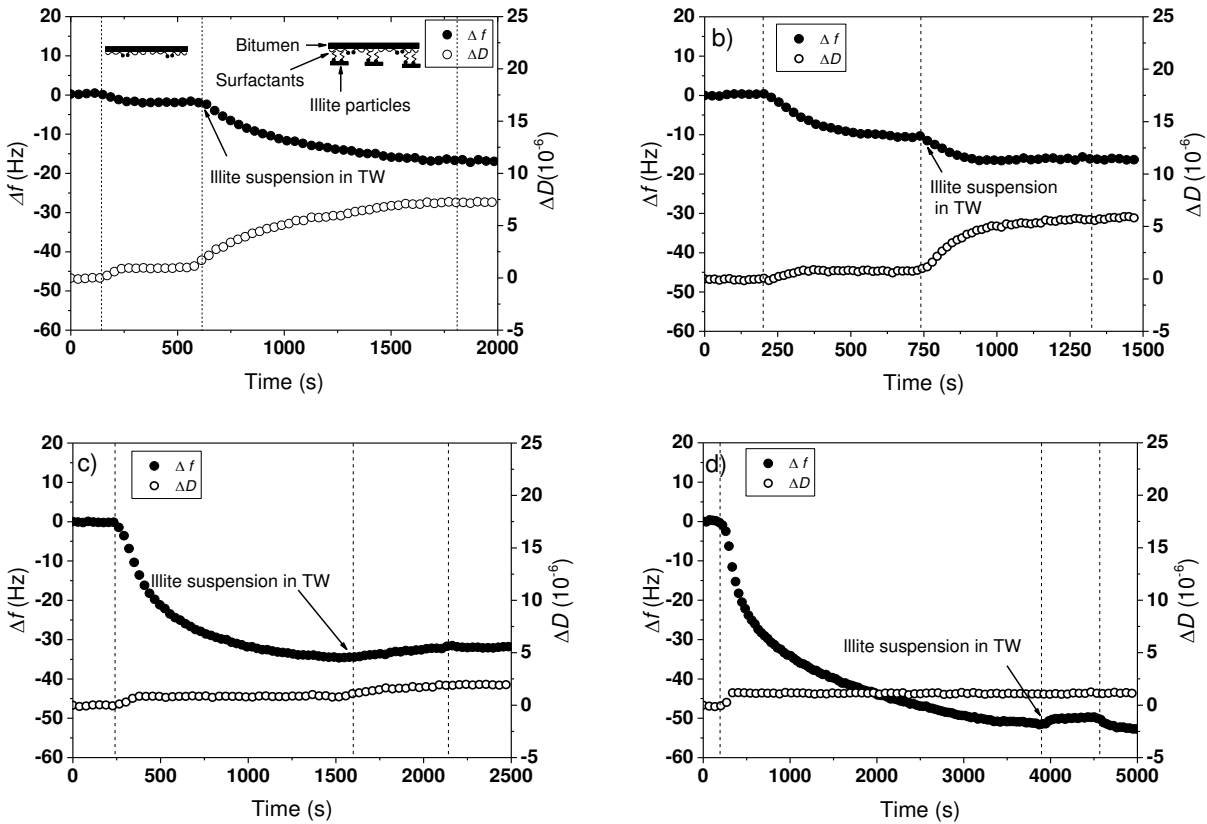


Figure 6. Interactions between illite particles and bitumen surface in tailings water prepared with different levels of caustic addition during bitumen extraction: a) 0 wt.% NaOH, b) 0.05 wt.% NaOH, c) 0.1 wt.% NaOH and d) 0.5 wt.% NaOH with initial illite clay particle concentration of 0.1 wt.%. Dashed lines indicate fluid switching (from left to right: background to tailings water; tailings water to illite suspension in tailings water; tailings water rinse).

To further understand the critical conditions which promote and hinder illite-bitumen interaction, not only is it important to characterize the water chemistry, but one should also consider the effect of water chemistry on the bitumen prior to illite clay particle addition. Laboratory

extracted tailings water was analyzed to determine the carboxylic surfactants and the divalent cations (Ca^{2+} and Mg^{2+}) concentrations at different levels of caustic addition. As shown in Table 3, an increase in the caustic addition (\uparrow pH) results in an increase in the soluble carboxylic surfactants concentration and a decrease in both the Ca^{2+} and Mg^{2+} ion concentrations, both trends in agreement with previously published data.^{29, 51}

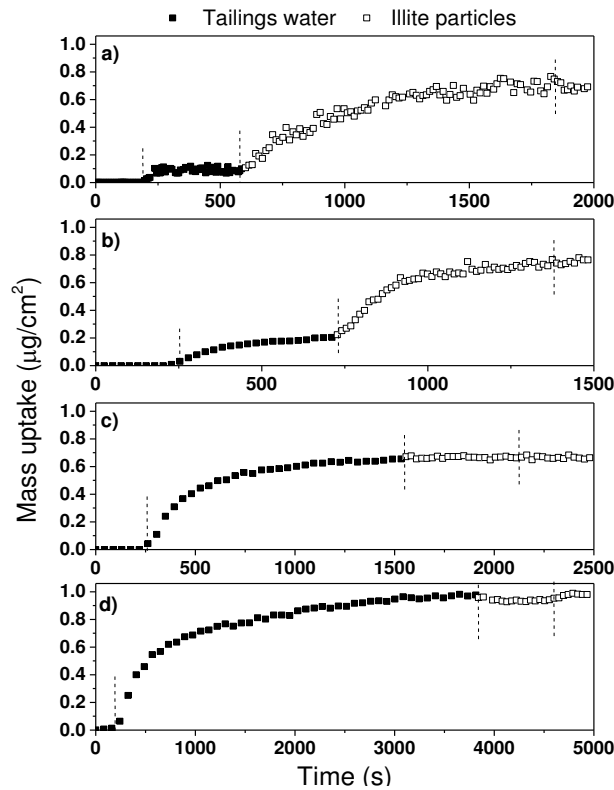


Figure 7. Apparent deposited mass caused by tailings water and illite clay particles on bitumen surface determined by Voigt two layers model (using Q-Tools software) at increasing caustic concentrations: a) 0 wt.% NaOH, b) 0.05 wt.% NaOH, c) 0.1 wt.% NaOH, d) 0.5 wt.% NaOH. Dashed lines indicate fluid switching (from left to right: background to tailings water; tailings water to illite suspension in tailings water; tailings water rinse)

Table 3. Characterization of tailings water prepared with different levels of caustic addition during bitumen extraction.

NaOH (wt.% of oil sands)	pH*	Carboxylic surfactant (10^{-5} mol/L)	Ion content (ppm)	
			Ca ²⁺	Mg ²⁺
0	8.5	29.2	25.6	13.7
0.05	9.3	36.9	10.1	6.3
0.1	10.2	41.4	4.7	0.7
0.5	12.6	48.8	2.1	0.1

* The pH in the table is the original pH of the tailings waters. For the QCM-D tests the pH of the tailings waters were adjusted to 8.5.

As previously shown in Figures 5 and 6, switching the fluid from Milli-Q[®] water to tailings water in the absence of clay particles results in a frequency shift that is dependent on caustic addition (pH). However, this dependency does not always scale linearly with solution pH as shown in Figure 8. By increasing the pH of tailings water, the $-\Delta f$ response of the bitumen coated sensor is shown to increase significantly between 0.05 wt.% NaOH (pH 9.3) and 0.1 wt.% NaOH (pH 10.2), which is not in accordance with an incremental increase in both the pH and carboxylic surfactant concentration. With the sensor frequency response being influenced by adsorbed mass, the non-linear response to caustic addition may indicate the adsorption (inclusion) of an additional soluble species at higher pH (pH >9.3).

On visual inspection of the tailings waters, a noticeable discoloration (browning) was observed with increasing caustic addition as shown in Figure 9. Analysis of the soluble species by FTIR

identified the additional species to be humic acids. The observed extraction/leaching of humic acids into the aqueous phase at high pH is in agreement with previous studies.⁵²⁻⁵⁵ The release of humic acids in more alkali conditions could account for the observed ‘jump’ in resonance frequency shift between pH 9.3 and pH 10.2, as a result of humic acids adsorption on bitumen-coated silica sensors. It is also interesting to note that the adsorption of humic acids by illite clay was observed by discoloration of the tailings water prepared with 0.5 wt. % NaOH to a less brownish color when illite clay particles were added to the tailings water sample.

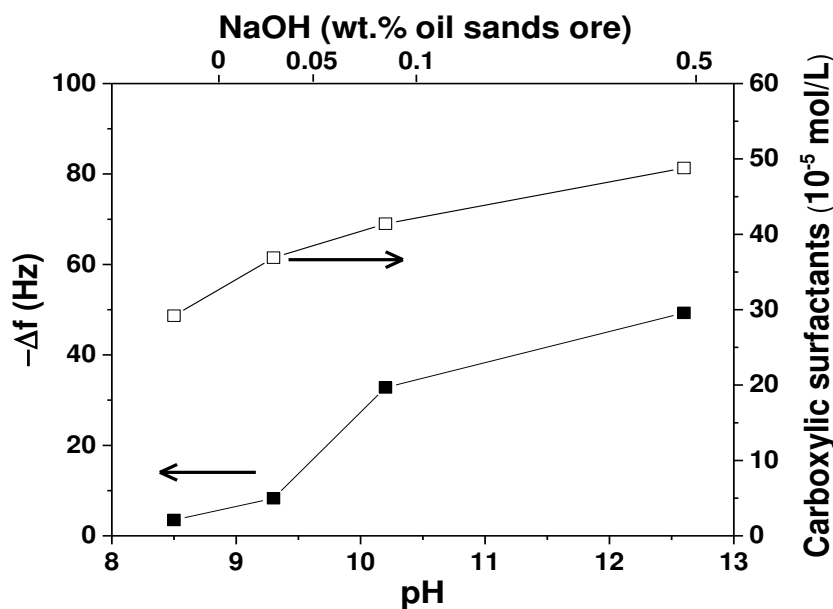


Figure 8. Variation in the resonance frequency of bitumen coated sensors upon switching of fluid from Milli-Q[®] water to tailings water without clay particles (left axis), and the corresponding tailings water carboxylic surfactants concentration (right axis) as a function of pH/caustic level.

The similar darkness of the tailings water prepared by bitumen extraction with 0.5 wt.% NaOH addition to that of solutions prepared in Milli-Q water of 50 ppm humic acids confirmed qualitatively that the tailings water contains 50 ppm humic acids. To determine the contribution

of humic acids adsorption to the overall mass gain, two simple QCM-D tests were conducted. For the first test, 50 ppm humic acids (MP Biomedicals, Canada) were dissolved in 1 mM KCl solution at pH 8.5. After establishing a sensor baseline (1 mM KCl at pH 8.5) the humic acids solution was introduced with no measurable shift in the frequency and dissipation of the bitumen coated sensor (data not shown). Therefore, humic acids alone (dissolved in simple electrolyte solution) do not interact to any measurable extent with bitumen. For the second test, humic acids were dissolved in tailings water (0 wt.% NaOH) to determine whether the presence of co-surfactants (carboxylic acids) and/or multivalent cations would trigger the adsorption of humic acids. With a baseline established (0 wt.% NaOH tailings water at pH 8.5), the switching to the tailings water containing 50 ppm humic acids led to a decrease in the resonance frequency and a small increase in the dissipation of the bitumen-coated sensor. A new baseline in the presence of 50 ppm humic acids was established indicating their added contribution in the presence of other soluble species such as surfactants and/or multivalent cations. However the exact mechanism for interaction is not known.

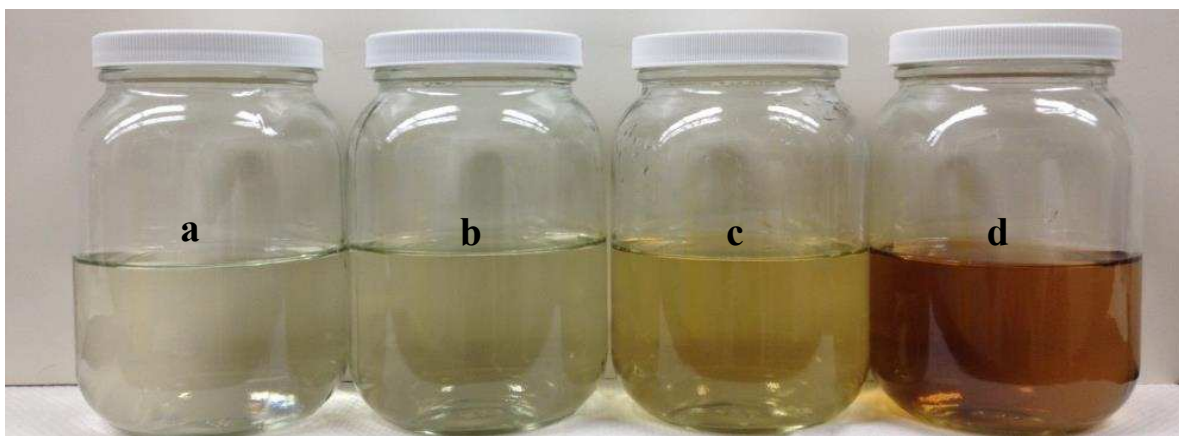


Figure 9. Changes in the color of laboratory extracted tailings water with increasing caustic addition during bitumen extraction :a) 0 wt.% NaOH (pH 8.5), b) 0.05 wt.% NaOH (pH 9.3), c) 0.1 wt.% NaOH (pH 10.2) and d) 0.5 wt.% NaOH (pH 12.6).

These simple experiments have confirmed that the role of humic acids in tailings water should not be disregarded and could potentially influence the particle-bitumen interaction. The results presented in Figures 9 and 10 suggest that the ‘sharp decrease’ in resonance frequency between pH 9.3 and pH 10.2 (shown in Figure 8) results from the added contribution of humic acids.

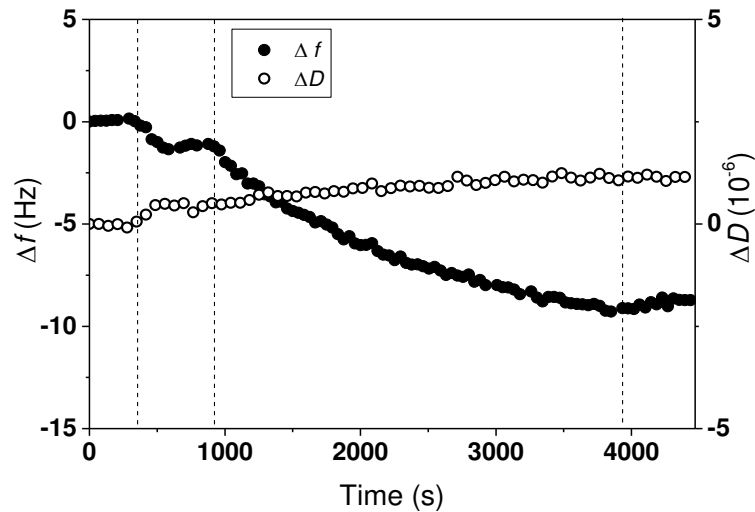


Figure 10. Frequency and dissipation shifts of bitumen-coated QCM-D sensor during the introduction of tailings water (0 wt. % NaOH) followed by introduction of tailings water containing humic acids of the same pH. Dashed lines indicate the switching of the fluid (from left to right: background to tailings water; tailings water to tailings water containing 50 ppm humic acids; and tailings water rinse).

3.3 Effect of water chemistry on illite – bitumen slime coating

3.3.1 Calcium effect

An increase in tailings water pH led to a decrease in the soluble divalent cation concentration as shown in Table 3. This decrease is mostly due to the precipitation of calcium ions with carbonate

ions to form calcium carbonate, or with carboxylate ions to form calcium carboxylate.⁵⁶⁻⁵⁸ Previous research has demonstrated the pivotal role of Ca^{2+} on slime coating of bitumen by montmorillonite model particles.¹⁸ To determine whether the decrease in Ca^{2+} accounts for the observed reduction in illite-bitumen slime coating potential at higher level of caustic addition, 40 ppm calcium was added to 0.1 wt.% NaOH tailings water (critical condition where slime coating of illite diminished). However, the added calcium was also consumed (measured concentration = 3.8 ppm) and the concentration did not increase. The consumption of calcium cations is due to the precipitation of calcium in forms of carbonate, carboxylate or humate.^{56, 58, 59} Therefore QCM-D experiments in tailings water were not considered. The role of calcium on illite-bitumen slime coating was studied in 1mM KCl solution at pH 8.5.

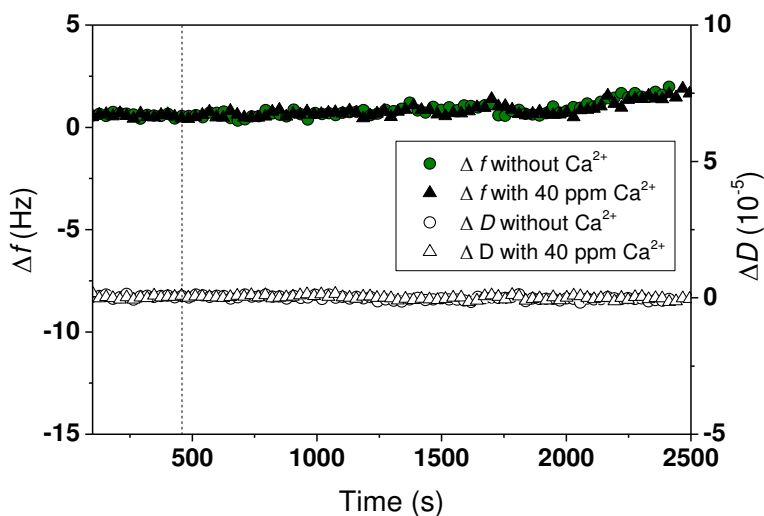


Figure 11. Interaction between illite particles and bitumen surface in 1 mM KCl solution at pH 8.5, with and without the addition of 40 ppm Ca^{2+} (1 mM CaCl_2). Dashed line indicates fluid switching from background (Milli-Q[®] water at pH 8.5) to illite suspension.

Figure 11 shows the QCM-D response of a bitumen-coated sensor in the presence of an illite suspension dispersed in 1mM KCl solution with and without the addition of 40 ppm Ca^{2+} . Both

experiments are comparable and show no response to the introduction of the illite clay particle suspension. Hence, under the current experimental conditions, calcium concentration does not appear to impact the slime coating potential of illite clay particles.

3.3.2 *Surfactants and humic acids effect*

The effect of surfactants and humic acids on illite-bitumen slime coating was assessed by considering three separate experiments: i) 0 wt.% NaOH tailings water, ii) 0.5 wt.% NaOH tailings water and iii) 0.5 wt.% NaOH tailings water with humic acids extracted. To extract the humic acids a similar procedure was followed to that previously described in Section 2.6. Briefly, the tailings water was acidified to $\text{pH} < 2$ to precipitate the humic acids. Before removing humic acids, in order to avoid loss of carboxylic surfactants the acidified tailings water sample was extracted by DCM. The DCM was then evaporated and carboxylic surfactants remained in the container. The carboxylic surfactant-free tailing water was then centrifuged to remove precipitated humic acid. The supernatant was collected and the recovered carboxylic surfactants were re-dispersed in it. Surfactant concentration was measured 49.5×10^{-5} mol/L using DCM extraction and FTIR analysis.

Firstly, the dependence on surfactant concentration can be considered by comparing experiment i) (tailings water obtained with 0 wt.% NaOH) with experiment iii) (tailings water obtained with 0.5 wt.% NaOH addition and humic acids being extracted). As shown in Figure 12 for the low surfactant concentration solution (0 wt.% NaOH tailings water), switching of fluids from background to tailings water results in a small change in both the frequency and dissipation of the sensor, indicative of the low surfactant concentration. With the introduction of illite clay particles the frequency ($\Delta f \sim -14\text{Hz}$) and dissipation responded rapidly to reach a new steady state condition. In the absence of illite particles, the frequency shift in the tailings water of high

surfactant concentrations (obtained with 0.5 wt.% NaOH and humic acids being extracted) is greater than that in the tailings water obtained using 0 wt.% NaOH, with the dissipation shift being almost the same. With the addition of illite particles both the frequency ($\Delta f \sim -11\text{Hz}$) and dissipation responses of the sensor support the interaction of illite and bitumen, although the rate of interaction appears slower in the case of higher surfactant concentrations. The change in deposition rate may be influenced by the charge density which is dependent on the surface surfactant concentration.²⁰ The interaction strength between the clay particles and bitumen is lower as shown by the increase in frequency during tailings water wash.

The role of humic acids was illustrated by comparing the results of the experiments conducted using tailings water with 0.5 wt.% NaOH addition with and without the humic acids being extracted. While the QCM-D test performed using this tailings water without humic acids showed slime coating of bitumen by illite particles, the contrasting results were obtained when conducting the test using the same tailings water without removing the humic acids. Firstly, with the addition of tailings water (no illite particles) the solution containing humic acids results in a greater frequency shift, which is comparable with the earlier observations presented in Figure 10. Secondly, the addition of illite particles is shown to have minimal effect on the resonant frequency and dissipation of the sensor. This behaviour is in contrast to the particle deposition obtained in the same tailings water with humic acids being removed.

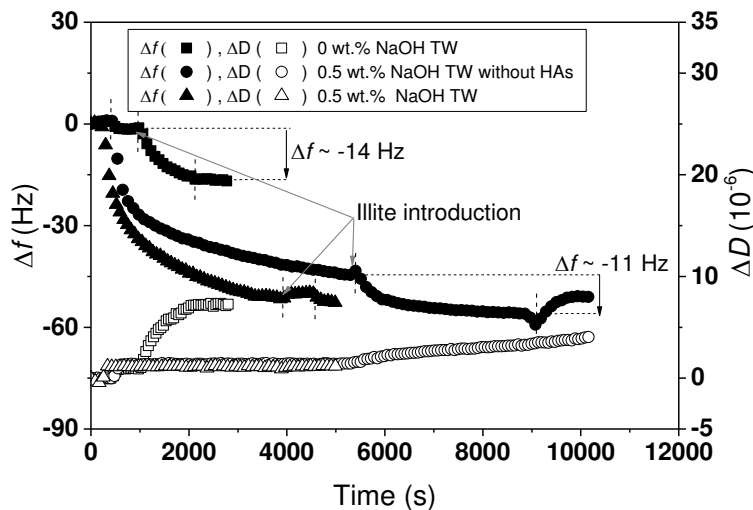


Figure 12. Effect of surfactant concentration (■ and ●) and humic acids concentration (▲ and ●) on the slime coating potential of illite on bitumen. Dashed lines indicate switching of the fluid (from left to right: background to tailings water; tailings water to illite suspension in tailings water (0.1 wt.%); and tailings water rinsing). HAs: humic acids.

To further assess the critical role of humic acids in determining the interaction between illite particles and bitumen, humic acids extracted from 0.5 wt.% NaOH tailings water were added to 0 wt.% NaOH tailings water. Without humic acids addition an attractive interaction (deposition) between bitumen and illite particles was observed, see Figure 13. In the presence of humic acids, the switching from background to tailings water once again resulted in a greater frequency shift of the bitumen-coated sensor. Again the frequency and dissipation responses remain insensitive to the addition of illite particles in the tailings water containing humic acid. While both humic acids extraction (Figure 12) and addition (Figure 13) have been considered, the conclusion remains the same where slime coating potential between illite particles and bitumen is diminished in the presence of humic acids.

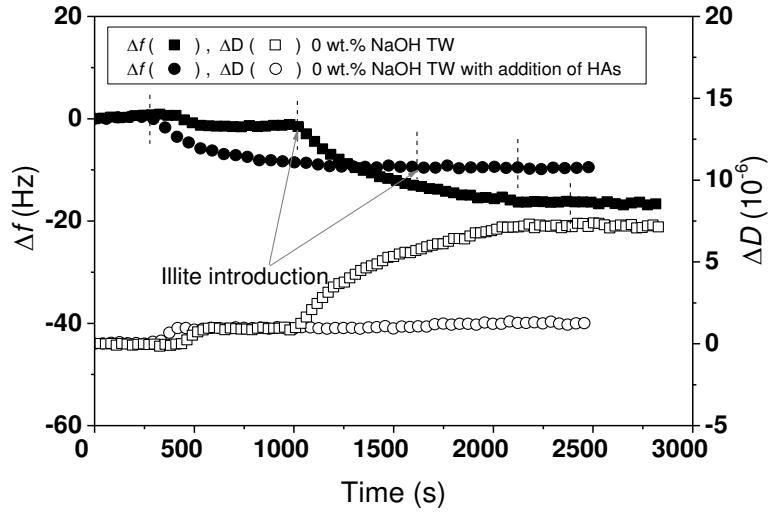


Figure 13. Effect of humic acids (addition) on the interaction of illite clay particles with bitumen. Dashed lines indicate fluid transitions (from left to right: background to tailings water; tailings water to illite suspension in tailings water (0.1 wt.%); tailings water rinse). HAs: humic acids.

Table 4 summarizes the bitumen-illite interaction (slime coating) at different conditions studied in this work. The reduction in illite-bitumen slime coating with increased humic acids concentration is evident, yet the mechanism for the diminishing effect is non-trivial. With negligible gravity contribution (upturned experimental setup and colloidal particles), the colloidal interaction may be suitably described by the DLVO theory, which considers an attractive van der Waals force and a repulsive electrical double layer force.^{60, 61} A general rule of thumb for colloidal stability/instability transition is a surface/Stern potential around ± 30 mV.

Table 4. Summary of the bitumen-illite interaction (slime coating) at different conditions

Water sample	Bitumen-illite interaction at original condition				Bitumen-illite interaction at new condition		
	CS* (10 ⁻⁵ mol/L)	Ca ²⁺ (ppm)	Release of HA**	SC***	Ca ²⁺ added (ppm)	HA**	SC***
Milli-Q® water	0	0	n/a	No	40	-	No
0 wt.% NaOH TW	29.2	25.6	Very low	Yes (strong)	-	added	No
0.05 wt.% NaOH TW	36.9	10.1	Very low	Yes (strong)	-	-	-
0.1 wt.% NaOH TW	41.4	4.7	Low	No	40	-	No
0.5 wt.% NaOH TW	48.8	2.1	High	No	-	removed	Yes (weak)

* CS: Carboxylic surfactants; ** HA: Humic acids; *** SC: Slime coating; n/a: not available.

For illite clay particles dispersed in 0 wt.% NaOH tailings water without and with humic acids (addition), the particle zeta potentials remained almost unchanged at – 35mV, similar to the zeta potential of bitumen that was measured to be – 55 mV using a ZETAPALS (Brookhaven Instruments, NY, USA). With negligible dependence on the presence of humic acids and high surface potentials, it appears that classical DLVO theory alone cannot describe the illite-bitumen slime coating behavior. The lack of agreement with DLVO is not unexpected as many other forces (steric and hydrophobic) often influence the interaction potential.^{62, 63} To assess the hydrophobic interaction, the wettability of both bitumen and illite clay particles was studied. Quantitative measurement of the contact angle of fine particles is extremely challenging and often qualitative approaches are considered. In the current study the Water Droplet Penetration

Time (WDPT) method was chosen to compare the wettability of illite particles prepared in Milli-Q[®] water containing 40 ppm Ca²⁺ and 0 wt.% NaOH tailings water without and with 50 ppm humic acids addition. Further details on the WDPT method can be found elsewhere.⁶⁴ In the current study, illite clay particles were agitated in each solution for 2 hrs, filtered and dried at 50°C, and compressed into a 1 inch pellet. One drop of water (~ 12.5 mm³) was then placed on the pellet surface and the drop penetration time was measured using the DSA 10 tensiometer (Kruss, Germany) imaging software. Taking an average of 6 measurements, the WDPT for illite particles treated in Milli-Q[®] water with 40 ppm Ca²⁺ as the base line was measured to be 26±4.8 s, which increased to 45.2±2.4 s and 45.83± 6.6 s when the illite particles were agitated in 0 wt.% NaOH tailings water without and with 50 ppm humic acids, respectively, prior to making the pellets. The results suggest that the wettability of illite particles decreased (became less hydrophilic) in the presence of surfactants, accounting for the observed deposition of illite on bitumen in 0 wt.% NaOH tailings water. To assess the wettability of bitumen after addition of humic acids, a bitumen-coated sensor was submerged in 0 wt.% NaOH tailings water (without and with 50 ppm humic acids) for 1 hr, and then gently blow-dried with nitrogen. One droplet of water was placed on the surface and the three phase contact angle was measured using the DSA 10 tensiometer (Kruss, Germany) imaging software. The contact angle of water droplet on bitumen after being submerged in tailings water of 0 wt% caustic addition as baseline was determined to be ~ 86° and it decreased to ~ 44° after it was submerged in tailings water of 0 wt.% caustic addition but containing 50 ppm humic acids. The significant reduction in the bitumen contact angle (42°) corresponds for the decreased hydrophobicity of bitumen in the presence of 50 ppm humic acids. With decreased hydrophobicity of the bitumen surface due to the adsorption of humic acids containing water-loving carboxyl and hydroxyl functional groups,

⁵⁴ the attractive hydrophobic interaction between the bitumen and illite particles weakens, potentially lowering the interaction potential between illite and bitumen. Figure 14 schematically describes the interaction between bitumen and illite in tailings water with and without humic acids. While the illite clay particles are naturally hydrophilic, adsorption of natural surfactant in the tailings water makes them slightly hydrophobic as shown by an increase in WDPT, which induces illite coating on bitumen. Although the strong adsorption of humic acids on illite in 0 wt.% NaOH tailings water containing 50 ppm humic acids does not greatly modify either the wettability or the surface charge of the particles, it does induce steric repulsion between humic acids adsorbed on both bitumen and illite⁶⁵⁻⁶⁷, reducing the deposition activity of illite clay particles which is highly desirable. Further work in this area is needed to further explore the nature of interaction.

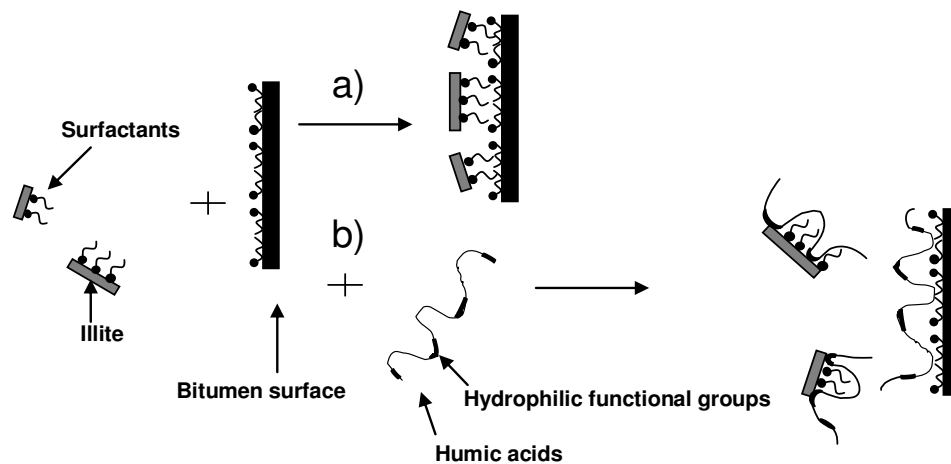


Figure 14. Model of interaction between illite and bitumen in tailings water, a) without and b) with humic acids.

4 CONCLUSIONS

In the current study QCM-D has been used to measure particle-bitumen slime coating at a fundamental level. By measuring the deposition of montmorillonite clay particles on bitumen in presence of 40 ppm Ca^{2+} cations (at pH 8.5), it was found that QCM-D can be used as a suitable technique for monitoring bitumen-clay interactions at different conditions. The research considered the role of water chemistry (divalent ion concentration, carboxylic surfactant concentration and humic acids concentration), that was controlled by caustic addition to flotation tests, on the deposition potential of the two most abundant clays typically found in the oil sands ore; kaolinite and illite. While kaolinite model clay particles used in this work were not observed to deposit on the bitumen coated sensor, illite model clay particles were observed to slime coat when dispersed in 0 wt.% and 0.05 wt.% NaOH tailings water, with the effect diminishing at higher caustic concentrations. With the surfactant being shown to provide favorable conditions for slime coating, the diminishing effect at higher caustic concentrations has been associated with the release of humic acids. Two experiments with humic acids extracted or added to the system provided compelling evidence for the critical role of humic acids in reducing illite-bitumen slime coating. The reduction in slime coating was attributed to the wettability change of the bitumen layer and steric hindrance caused by adsorbed humic acids.

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REFERENCE

- (1) Teare, M.; Cruickshank, R.; Miller, S.; Overland, S.; Marsh, R. AER ST98-2014: Alberta's Energy Reserves 2013 and Supply/Demand Outlook 2014-2023. **2014**.
- (2) Basu, S.; Nandakumar, K.; Masliyah, J. A study of oil displacement on model surfaces. *J. Colloid Interface Sci.* **1996**, *182*, 82-94.
- (3) Masliyah, J.; Zhou, Z.; Xu, Z.; Czarnecki, J.; Hamza, H. Understanding water-based bitumen extraction from Athabasca oil sands. *Can. J. Chem. Eng.* **2004**, *82*, 628-654.
- (4) Srinivasa, S.; Flury, C.; Afacan, A.; Masliyah, J.; Xu, Z. Study of bitumen liberation from oil sands ores by online visualization. *Energy Fuels* **2012**, *26*, 2883-2890.
- (5) Clark, K. A. The separation of the bitumen from Alberta bituminous sands. *Bull. Can. Inst. Min. Metall.* **1929**, *22*, 1385-1395.
- (6) Clark, K. A. Hot-water separation of Alberta bituminous sand. *Trans. Can. Inst. Min. Metall.* **1944**, *47*, 257-274.
- (7) Sanford, E., Processibility of Athabasca oil sand: Interrelationship between oil sand fine solids, process aids, mechanical energy and oil sand age after mining. *Can. J. Chem. Eng.* **1983**, *61*, 554-567.
- (8) Flynn, M.; Bara, B.; Czarnecki, J.; Masliyah, J. An investigation of the effect of air addition during oil sand conditioning. *Can. J. Chem. Eng.* **2001**, *79*, 468-470.
- (9) Gu, G.; Sanders, R.; Nandakumar, K.; Xu, Z.; Masliyah, J. A novel experimental technique to study single bubble-bitumen attachment in flotation. *Int. J. Miner. Process.* **2004**, *74*, 15-29.

- (10) Su, L.; Xu, Z.; Masliyah, J. Role of oily bubbles in enhancing bitumen flotation. *Miner. Eng.* **2006**, *19*, 641-650.
- (11) Wang, L.; Dang-Vu, T.; Xu, Z.; Masliyah, J. H. Use of short-chain amine in processing of weathered/oxidized oil sands ores. *Energy Fuels* **2010**, *24*, 3581-3588.
- (12) Liu, J.; Xu, Z.; Masliyah, J. Interaction forces in bitumen extraction from oil sands. *J. Colloid Interface Sci.* **2005**, *287*, 507-520.
- (13) Gu, G.; Xu, Z.; Nandakumar, K.; Masliyah, J. Effects of physical environment on induction time of air-bitumen attachment. *Int. J. Miner. Process.* **2003**, *69*, 235-250.
- (14) Jiang, T. M.; Hirasaki, G. J.; Miller, C. A.; Ng, S. Effects of Clay Wettability and Process Variables on Separation of Diluted Bitumen Emulsion. *Energy Fuels* **2011**, *25*, 545-554.
- (15) Jiang, T.; Hirasaki, G. J.; Miller, C. A.; Ng, S. Wettability alteration of clay in solid-stabilized emulsions. *Energy Fuels* **2011**, *25*, 2551-2558.
- (16) Kiran, S. K.; Acosta, E. J.; Moran, K. Study of Solvent-Bitumen-Water Rag Layers. *Energy Fuels* **2009**, *23*, 3139-3149.
- (17) Kasongo, T.; Zhou, Z.; Xu, Z.; Masliyah, J. Effect of clays and calcium ions on bitumen extraction from Athabasca oil sands using flotation. *Can. J. Chem. Eng.* **2000**, *78*, 674-681.
- (18) Liu, J.; Zhou, Z.; Xu, Z.; Masliyah, J. Bitumen-clay interactions in aqueous media studied by zeta potential distribution measurement. *J. Colloid Interface Sci.* **2002**, *252*, 409-418.
- (19) Liu, J.; Xu, Z.; Masliyah, J. Studies on bitumen-silica interaction in aqueous solutions by atomic force microscopy. *Langmuir* **2003**, *19*, 3911-3920.

- (20) Liu, J.; Xu, Z.; Masliyah, J. Interaction between bitumen and fines in oil sands extraction system: Implication to bitumen recovery. *Can. J. Chem. Eng.* **2004**, *82*, 655-666.
- (21) Liu, J.; Xu, Z.; Masliyah, J. Role of fine clays in bitumen extraction from oil sands. *AICHE J.* **2004**, *50*, 1917-1927.
- (22) Zhao, H.; Long, J.; Masliyah, J. H.; Xu, Z. Effect of divalent cations and surfactants on silica-bitumen interactions. *Ind. Eng. Chem. Res.* **2006**, *45*, 7482-7490.
- (23) Ding, X.; Repka, C.; Xu, Z.; Masliyah, J. Effect of illite clay and divalent cations on bitumen recovery. *Can. J. Chem. Eng.* **2006**, *84*, 643-650.
- (24) Wallace, D.; Tipman, R.; Komishke, B.; Wallwork, V.; Perkins, E. Fines/water interactions and consequences of the presence of degraded illite on oil sands extractability. *Can. J. Chem. Eng.* **2004**, *82*, 667-677.
- (25) Moran, K.; Yeung, A.; Masliyah, J. Factors affecting the aeration of small bitumen droplets. *Can. J. Chem. Eng.*, **2000**, *78*, 625-634.
- (26) Long, J.; Drelich, J.; Xu, Z.; Masliyah, J. H. Effect of operating temperature on water-based oil sands processing. *Can. J. Chem. Eng.* **2007**, *85*, 726-738.
- (27) Harjai, S. K.; Flury, C.; Masliyah, J.; Drelich, J.; Xu, Z. Robust Aqueous-Nonaqueous Hybrid Process for Bitumen Extraction from Mineable Athabasca Oil Sands. *Energy Fuels* **2012**, *26*, 2920.
- (28) Schramm, L. L.; Stasiuk, E. N.; Turner, D. The influence of interfacial tension in the recovery of bitumen by water-based conditioning and flotation of Athabasca oil sands. *Fuel Process Technol.* **2003**, *80*, 101-118.

- (29) Schramm, L. L.; Smith, R. G. Two classes of anionic surfactants and their significance in hot water processing of oil sands . *Can. J. Chem. Eng.* **1987a**, *65*, 799-811.
- (30) Flury, C.; Afacan, A.; Tamiz Bakhtiari, M.; Sjoblom, J.; Xu, Z. Effect of caustic tpe on bitumen extraction from Canadian oil sands. *Energy Fuels* **2014**, *28*, 431-438.
- (31) Ivanchenco, M.; Kobayashi, H.; Eduard, A.; Dobrova, N. Studies on polymer-solutions, gels and grafted layers using the quartz-crystal microbalance technique. *Anal. Chim. Acta* **1995**, *314*, 23-31.
- (32) Rodahl, M.; Kasemo, B. Frequency and dissipation-factor responses to localized liquid deposits on a QCM electrode. *Sens. Actuators B: Chem.* **1996**, *37*, 111-116.
- (33) Notley, S.; Eriksson, M.; Wagberg, L. Visco-elastic and adhesive properties of adsorbed polyelectrolyte multilayers determined in situ with QCM-D and AFM measurements. *J. Colloid Interface Sci.* **2005**, *292*, 29-37.
- (34) Fatisson, J.; Domingos, R. F.; Wilkinson, K. J.; Tufenkji, N. Deposition of TiO₂ nanoparticles onto silica measured using a quartz crystal microbalance with dissipation monitoring. *Langmuir* **2009**, *25*, 6062-6069.
- (35) Alagha, L.; Wang, S.; Xu, Z.; Masliyah, J. Adsorption kinetics of a novel organic-inorganic hybrid polymer on silica and alumina studied by quartz crystal microbalance. *J. Phys. Chem. C* **2011**, *115*, 15390-15402.
- (36) Wang, S.; Segin, N.; Wang, K.; Masliyah, J. H.; Xu, Z. Wettability control mechanism of highly contaminated hydrophilic silica/alumina surfaces by ethyl cellulose. *J. Phys. Chem. C* **2011**, *115*, 10576-10587.

- (37) Alagha, L.; Wang, S.; Yan, L.; Xu, Z.; Masliyah, J. Probing adsorption of polyacrylamide-based polymers on anisotropic basal planes of kaolinite using quartz crystal microbalance. *Langmuir* **2013**, *29*, 3989-3998.
- (38) Gotoh, K.; Nakata, Y.; Tagawa, M. Evaluation of particle deposition in aqueous solutions by the quartz crystal microbalance method. *Colloids Surf. Physicochem. Eng. Aspects* **2006**, *272*, 117-123.
- (39) Sauerbrey, G. Z. Verwendung von schwingquarzen zur wägung dünner schichten und microwägung. *Phys.* **1959**, *155*, 206-222.
- (40) Cho, N.; Kanazawa, K. K.; Glenn, J. S.; Frank, C. W. Employing two different quartz crystal microbalance models to study changes in viscoelastic behavior upon transformation of lipid vesicles to a bilayer on a gold surface. *Anal. Chem.* **2007**, *79*, 7027-7035.
- (41) Rodahl, M.; Hook, F.; Krozer, A.; Brzezinski, P.; Kasemo, B. Quartz crystal microbalance setup for frequency and Q-factor measurements in gaseous and liquid environments. *Rev. Sci. Instrum.* **1995**, *66*, 3924-3930.
- (42) Voinova, M. V.; Rodahl, M.; Jonson, M.; Kasemo, B. Viscoelastic acoustic response of layered polymer films at fluid-solid interfaces: Continuum mechanics approach. *Phy. Scr.* **1999**, *59*, 391-369.
- (43) Zhou, Z.; Kasongo, T.; Xu, Z.; Masliyah, J. Assessment of bitumen recovery from the Athabasca oil sands using a laboratory Denver flotation cell. *Can. J. Chem. Eng.* **2004**, *82*, 696-703.

- (44) Clemente, J.; Fedorak, P. A review of the occurrence, analyses, toxicity, and biodegradation of naphthenic acids. *Chemosphere* **2005**, *60*, 585-600.
- (45) Scott, A. C.; Young, R. F.; Fedorak, P. M. Comparison of GC–MS and FTIR methods for quantifying naphthenic acids in water samples. *Chemosphere* **2008**, *73*, 1258-1264.
- (46) Xu, Z.; Liu, J.; Choung, J. W.; Zhou, Z. Electrokinetic study of clay interactions with coal in flotation. *Int. J. Miner. Process.* **2003**, *68*, 183-196.
- (47) Mitchell, J. K. *Fundamentals of soil behaviour*; John Wiley & Sons, Inc.: New York, 1976; , pp 44-45.
- (48) Romanova, U. G.; Valinasab, M.; Stasiuk, E. N.; Yarranton, H. W.; Schramm, L. L.; Shelfantook, W. E. The effect of oil sands bitumen extraction conditions on froth treatment performance. *J. Can. Pet. Technol.* **2006**, *45*, 36-45.
- (49) Mercier, P. H. J.; Patarachao, B.; Kung, J.; Kingston, D. M.; Woods, J. R.; Sparks, B. D.; Kotlyar, L. S.; Ng, S.; Moran, K.; McCracken, T. X-ray diffraction (XRD)-derived processability markers for oil sands based on clay mineralogy and crystallite thickness distributions. *Energy Fuels* **2008**, *22*, 3174-3193.
- (50) Fu, D. B.; Woods, J. R.; Kung, J.; Kingston, D. M.; Kotlyar, L. S.; Sparks, B. D.; Mercier, P.; McCracken, T.; Ng, S. Residual organic Matter associated with toluene-extracted oil sands solids and its potential role in bitumen recovery via adsorption onto clay minerals. *Energy Fuels* **2010**, *24*, 2249-2256.

- (51) Wik, S.; Sparks, B. D.; Ng, S.; Tu, Y.; Li, Z.; Chung, K. H.; Kotlyar, L. S. Effect of process water chemistry and particulate mineralogy on model oilsands separation using a warm slurry extraction process simulation. *Fuel* **2008**, *87*, 1394-1412.
- (52) Majid, A.; Ripmeester, J. A. Isolation and characterization of humic acids from Alberta oil sands and related materials. *Fuel* **1990**, *69*, 1527-1536.
- (53) Majid, A.; Sparks, B. D.; Ripmeester, J. A. Isolation and characterization of humic matter from Syncrude sludge pond tailings. *Fuel* **1992**, *71*, 165-168.
- (54) Gutierrez, L.; Pawlik, M. Influence of humic acids on oil sand processing. Part I: Detection and quantification of humic acids in oil sand ores and their effect on bitumen wettability. *Int. J. Miner. Process.* **2014**, *126*, 117-125.
- (55) Gutierrez, L.; Pawlik, M. Influence of humic acids on oil sand processing. Part II: Relationship between bitumen extraction, humic acids concentration and power draw measurements on oil sand slurries. *Int. J. Miner. Process.* **2014b**, *126*, 126-135.
- (56) Dai, Q.; Chung, K. H.; Czarnecki, J. Formation of calcium carbonate in the bitumen/aqueous sodium hydroxide system. *AOSTRA J. Res.* **1992**, *8*, 95-101.
- (57) Zhao, H.; Dang-Vu, T.; Long, J.; Xu, Z.; Masliyah, J. H. Role of bicarbonate ions in oil sands extraction systems with a poor processing ore. *J. Dispersion Sci. Technol.* **2009**, *30*, 809-822.
- (58) Masliyah, J.; Czarnecki, J.; Xu, Z. *Handbook of theory and practice of bitumen recovery from Athabasca oil sands, Vol. 1: Theoretical Basis.*; Kingsly Knowledge Publishing: Canada and United States, 2011.

- (50) Wik, S.; Sparks, B. D.; Ng, S.; Tu, Y.; Li, Z.; Chung, K. H.; Kotlyar, L. S. Effect of bitumen composition and process water chemistry on model oilsands separation using a warm slurry extraction process simulation. *Fuel* **2008**, *87*, 1413-1421.
- (60) Derjaguin, B.; Landau, L. Theory of the stability of strongly charged lyophobic sols and of the adhesion of strongly charged-particles in solutions of electrolytes. *Acta Physicochim URSS* **1941**, *14*, 633-662.
- (61) Verwey, E. J. W.; Overbeek, J. T. G. *Theory of the stability of lyophobic colloids*; Elsevier publishing Co., Inc.,: Amsterdam, 1948.
- (62) Churaev, N. V.; Derjaguin, B. V. Inclusion of structural forces in the theory of stability of colloids and films. *J. Colloid Interface Sci.* **1985**, *103*, 542-553.
- (63) Yoon, R. -.; Yordan, J. L. Critical rupture thickness of thin water films on hydrophobic surfaces. *J. Colloid Interface Sci.* **1991**, *146*, 565-572.
- (64) Dang-Vu, T.; Jha, R.; Wu, S.; Tannant, D. D.; Masliyah, J.; Xu, Z. Wettability determination of solids isolated from oil sands. *Colloids Surf. A-Physicochemical Eng. Aspects* **2009**, *337*, 80-90.
- (65) Ksiezopolska, A.; Pazur, M. Surface properties of bentonite and illite complexes with humus acids. *Clay Miner.* **2011**, *46*, 149-156.
- (66) Kretzschmar, R.; Hesterberg, D.; Sticher, H. Effects of adsorbed humic acid on surface charge and flocculation of kaolinite. *Soil Sci. Soc. Am. J.* **1997**, *61*, 101-108.
- (67) Goodwin, J. W. *Colloids and Interfaces with Surfactants and Polymers : An Introduction*; John Wiley: Chichester, England, 2004.