Role of Sodium Hydroxide in Bitumen Extraction: Production of Natural Surfactants and Slime Coating

by

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ABSTRACT

Alkaline environment by addition of NaOH in bitumen extraction process often shows a positive effect on bitumen recovery from Athabasca oil sands by mining-extraction method. NaOH ionizes organic acids in the bitumen to produce surfactants. These species are essential for bitumen liberation. Understanding the role of NaOH in the processing of different types of oil sands ores is important in designing the processes to enhance bitumen recovery from variable oil sands ores and minimizing bitumen loss in the tailings.

This study focuses on responses of 15 different ores to the addition of variable amount of NaOH in generation/release of natural surfactants from the ores. An existing FTIR technique was modified to quantify the concentration of carboxylic surfactants in tailings water. The results showed that the concentration of carboxylic type of surfactants in tailings water depends not only on the amount of NaOH addition, but also on bitumen content and composition, concentration of divalent cations and concentration of carbonate/ bicarbonate ions in the ores. The content of pyrite in the fines fraction of the solids was found also to affect the release of carboxylic type of natural surfactants in tailings water.

The critical role of NaOH addition in levitating bitumen slime coating (bitumen-clay interaction) on a single ore using QCM-D method was also studied. The QCM-D measurements showed that illite clay particles formed layers of slime on bitumen in tailings water prepared at weak alkaline conditions while kaolinite did not.

A key contribution of this work was to identify the positive effect of humic acids released from ores processed at high pH (pH > 10) on avoiding the slime coating of bitumen by clays. After determining a strong adsorption of humic acids by illite clays, the results of QCM-D measurements showed that the presence of humic acid released in tailings water at high pH reduced slime coating of bitumen by illite clay particles, which was initiated by the presence of surfactants in tailings water. The results revealed that the reduction in the slime coating was attributed to the increased hydrophilicity of the bitumen layer and steric hindrance caused by adsorbed humic acids on both bitumen and illite surfaces.

PREFACE

The design of the experiments, data analysis and the preparation of the manuscript of this dissertation were carried out by the author under supervision of the research supervisors: Dr. Xu and Dr. Masliyah. Excluding the below mentioned experiments and analysis, all the experimental work in this work was conducted by the author.

- Preparation of the tailings water (by Denver flotation cell) for the purpose of quantification of surfactants was performed by Ms. Meghan Curran, MSc. student and Ms. Qian Zhu, graduated MSc. student at University of Alberta, Department of Chemical and Materials Engineering.

- AAS analysis was performed by Mr. Shiraz Merali in University of Alberta, Department of Chemical and Materials Engineering.

- Quantification of bicarbonate ions in tailings water were performed by Mr. Allan Harms, University of Alberta, Erath Sciences Building.

- XRF and XRD samples preparation and analysis were performed by Dr. Xiaowen Liu, visiting professor from Central South University of China and Mr. Shiraz Merali in University of Alberta, Department of Chemical and Materials Engineering.

- Bitumen liberation tests from ores were performed by Mr. Tong Chen, MSc. student at University of Alberta, Department of Chemical and Materials Engineering.

- Bitumen liberation tests using micropipette method were performed with the help of Mr. Bauyrzhan Primkulov, MSc student at University of Alberta, Department of Chemical and Materials Engineering.

Dedicated to my parents

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NOMENCLATURE

- Symbols

pKa: Acid dissociation constant
K_{sp}: Solubility product constant
Q_{sp}: Ion product quotient
A : Hamaker constant
ϕ : Zeta potential

- Abbreviations

NAs: Naphthenic acids
HAs: Humic acids
TW: Tailings water
PW: Process water
OSPW: Oil sands process water
FTIR: Fourier transform infrared
DCM: Dichloromethane
DDMS: dichlorodimethylsilane
ppm: Part per million
EDX: Energy-dispersive X-ray
MS: Mass spectrometry
AAS: Atomic absorption spectroscopy
DCMER: Dichloromethane extracted residue
CSFTW: Carboxylic surfactants-free tailings water
QCM-D: Quartz crystal microbalance with dissipation
XRD: X-ray diffraction
XRF: X-ray fluorescence
μm: micrometer
BEU: Batch extraction unit
DOC: Dissolved organic carbon
DBL: Degree of bitumen liberated
DLVO: Derjaguin-Landau-Verwey-Overbeek

CHAPTER 1

1 Introduction and Objectives

1.1 Introduction

Currently, ~47% of the total bitumen recovered in Alberta, Canada is by surface mining (Teare et al., 2014) and warm water extraction process. The warm water extraction process involves two elemental steps: liberation and aeration. In liberation process bitumen is detached from sand grain (Basu et al., 1996; Masliyah et al., 2004; Srinivasa et al., 2012) while in aeration, the detached bitumen attaches to air bubbles and moves to the surface of the pulp to form froth, leading to separation of bitumen from remaining water and solids (Clark, 1929; Clark, 1944; Sanford, 1983; Flynn et al., 2001; Gu et al., 2004; Su et al., 2006; Wang et al., 2010). The efficiency of these two steps is critical for good bitumen recovery and the subsequent upgrading process. In oil sands industry, chemical additives, such as caustic (sodium hydroxide, NaOH), are usually added into the extraction water to optimize the interactions between bitumen, solids and air in order to improve bitumen recovery. It is believed that NaOH can react with organic acids in the bitumen phase, which releases natural surfactants to water phase (Schramm and Smith, 1987). These charged surfactants, mainly carboxylates and sulfonates, adsorb on the surface of bitumen, and air bubbles, resulting in the increase in the surface hydrophilicity and surface electric charges (Bowman, 1967; Mistra et al., 1981; Schramm and Smith, 1987). By addition of caustic, in the liberation step the charged surfaces of bitumen and sands cause a large repulsive force that increases the initial 10 nm thickness of the water film between bitumen and sands (Takamura, 1982), hence improves the detachment efficiency of bitumen from solids. However, the fine solids would effectively disperse in the aqueous phase due to the increased surface charge of solids. The high repulsive force between bitumen and air bubbles on the other hand, hinders the bitumen-air attachment and lowers the bitumen recovery. Schraam et al. (1987a) suggested critical surfactant concentrations of $(1.2\times10^{-4}\pm15\%N)$ and $(1.5\times10^{-4}\pm15\%N)$ for carboxylate and sulfate/sulfonate surfactants respectively in order to reach optimum bitumen recovery. These concentrations can be obtained by controlling the amount of NaOH added to the extraction process.

Slime coating is also an important issue in oil sand extraction process. In the slime coating, fine solids or clays attach to bitumen droplets when the surface characteristics of fines are altered either by adsorption of ions or organic materials. Slime coating is one of the factors that can diminish bitumen recovery and froth quality (Masliyah et al., 2004). Kasongo et al. (2000) showed that co-addition of montmorillonite with calcium ions to extraction test can reduce bitumen recovery. Also, it was found that slime coating is often encountered in poor processing ores, which have a relatively large amount of fine solids (Liu et al., 2005). When slime coating occurs, if the attached fine solids or clays are hydrophilic the formed layer of slime impedes the attachment of bitumen droplets to air bubbles, leading to a reduction in bitumen recovery (Gu et al., 2003; Masliyah et al., 2004). In the case where the attached particles are hydrophobic, the slime coated bitumen is able to attach to air bubbles, reducing froth quality without depressing bitumen recovery (Masliyah et al., 2011).

1.2 Research objectives

Enhancing bitumen recovery and froth quality are the main reasons for addition of NaOH to oil sands extraction process. It has been reported that the impact of NaOH on bitumen recovery arises mainly due to the increase in the generation of natural surfactants. It was found that the amount of surfactants produced depends on ore types. However, few studies have been conducted on the relationship between the concentration of surfactants released and ore characteristics. Also, the changes in the water chemistry caused by NaOH and its role in the interactions between different species in oil sands ores have not been investigated systematically. Study of these interactions is important since they are known to affect the extraction efficiency. The goal of this research is to better understand the impact of NaOH addition to oil sands extraction processes on bitumen recovery performance. The investigations in this research study are focused on achieving the following objectives:

- Analyze natural surfactants and other co-extracted organic materials in tailings waters prepared by performing flotation tests over the range of caustic levels.

- Study the role of caustic (NaOH) and characteristics of oil sands in production of natural surfactants from different ores.

- Understand the effect of water chemistry caused by NaOH addition on bitumen-clays interactions (slime coating).

1.3 Thesis organization

Chapter 1

- Provides an introduction to the subject matter of the thesis and describes objectives of this study.

Chapter 2

- Provides a review on previous studies on addition of NaOH as process aid to oil sands extraction and its role in production of natural surfactants and humic substances followed by general overviews on the role of pH and natural surfactants in determining oil sands processability, bitumen liberation and aeration and slime coating. Quantification methods for natural surfactants and the effect of surfactants on wettability and electric surface potentials of particles and bitumen are discussed as well.

Chapter 3

- Presents the modified FTIR method for quantification of carboxylic surfactants in standard solutions and tailings water.

- Shows the results of the effect of other extractable organic materials (such as humic acids) on quantification of carboxylic surfactants in the tailings water.

- Study the application of surface tension measurement for qualitative analysis of the presence of sulfonic surfactants in tailings water.

Chapter 4

- Compares the effect of caustic (NaOH) addition at different dosages on production of natural surfactants from different ores.
- Studies the possible correlations between the concentration of released carboxylic surfactant measured in tailings water and ore composition (bitumen, fine, solid and water content), connate water and tailings water chemistry and mineral composition of ores.
- Investigates the effect of divalent cation addition and weathering (oxidizing) of ores on processability of the ores and production of carboxylic surfactants.

Chapter 5

- Evaluates application of QCM-D technique to study slime coating of clays on bitumen.
- Investigates the effect of clay type (montmorillonite, illite and kaolinite) and water chemistry (surfactants, calcium ions and humic acids concentrations) on bitumen-clay interactions.

Chapter 6

- Summarizes conclusions from this work and presents the possible extension of current studies.

Appendices

- Present the additional results to each chapter of this thesis.

CHAPTER 2

2 Literature Review

2.1 Alberta oil sands

Alberta, Canada, has the third largest oil reserves in the world after Saudi Arabia and Venezuela with 1.8 trillion barrels of oil sands in place. These resources are mainly located in Athabasca, Cold Lake, and Peace River in the province of Alberta. Total proven oil reserves in Alberta are approximately 170 billion barrels, of which 168 billion barrels are economically recoverable from bitumen with current technology (Alberta Government, Spring 2014). The bitumen from these reserves is recovered either by surface mining method, which is applicable where the overburden is less than 75 meters, or in-situ method for deeper deposits. It was reported that in 2013, ~ 47% of the total bitumen recovered in Alberta was extracted by surface mining method and processed using the warm slurry extraction process (Teare et al., 2014).

2.2 Oil sands compositions

Alberta's oil sands consist of 4-14% of bitumen (oil), 2-15% water, and 80-85% sands (including clays and minerals) by mass. Oil sands are commonly categorized as good (high grade), average and poor (low grade) processing ores depending on the bitumen and fines content of the oil sands ores. Fines are defined as solids smaller than 44 μm. In general, good ores contain in excess of 11 wt.% bitumen and poor ores contain less than 8 wt.%. Ores with 8-11 wt.% bitumen are considered average ore (Masliyah et al., 2011). It has been shown that there is a trend between bitumen content and fines percentage in oil sands ores. In general, high grade ores contain less fines and low grade ores are associated with more fine solids (Cameron Engineers. 1978). Such distinct differences have a marked effect on bitumen recovery performance.

In addition to bitumen, water and sands, oil sands also contain a lot of clay minerals (< 2 μm), which are part of the solids fraction. These clay minerals are mostly kaolinite (~69%), illite (~28%), chlorite (~1%) and montmorillonite (~0.3 %) (Mitchell, 1976). The clay minerals play an important role in ores' processability and tailings management due to their cation exchange capacity (CEC) and swelling characteristics. Mixed layer minerals such as kaolinite-smectite and illite-smectite have been reported too. Table 2.1 summarizes the clay minerals in the Athabasca oil sands according to different references. The information in Table 2.1 has been collected by Kaminsky, (2008).

There are also various inorganic cations and anions in oil sands ores. Shown in Table 2.2 is a list of main ions present in process water and connate water of good and poor processing ores. The chemistry of connate water (formation water) is analyzed by mixing equal mass of de-ionized water with oil sands ore. After mixing, the oil phase was removed and the aqueous phase was centrifuged at 20,000 g for 30 minutes. The supernatant was then analyzed to obtain the concentration of different ions (Zhao et al., 2009). Compared with poor ores, good ores generally contain smaller amounts of potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}) and sulfate (SO_4^{2-}) ions but contain more sodium and chloride (Cl^-) ions. Calcium, magnesium and bicarbonate ions have been shown to play a significant role in determining oil sands processability. Fong et al. (2004) investigated model oil sands and showed that the addition of 35-50 ppm of Ca^{2+} or 9-40 ppm of Mg^{2+} has a detrimental effect on bitumen recovery. In another study, Zhao et al. (2009) found that by precipitating calcium cations with bicarbonate ions solid-bitumen interactions could be reduced, resulting in an improved bitumen recovery.

The successful application of hot/warm water extraction technology for recovering bitumen from oil sands is based on the water-wet or hydrophilic characteristics of the sand grains in Athabasca's oil sands. Shown in Figure 2.1 is a suggested model structure for Athabasca oil sands, in which the bitumen is separated from sands by a thin layer of water (Cottrell, 1963; Mossop, 1980; Takamura, 1982). The oil sands from other regions such as Utah, USA, where sands are hydrophobic, are not processed by the same extraction method. For those types of ores, solvent extraction method is used (Hupka and Miller, 1993).

The first method used to extract bitumen from oil sands ores was the Clark hot water extraction process (HWEP) with operating temperature of ~70 to 80 °C (Clark, 1929; Clark and Pasternack, 1932; Clark, 1944). Because of high operating costs and greenhouse gas emissions, the process was changed to cold water process (Sury, 1990) or low energy extraction (LEE) in which the temperature was set to 25 °C. Currently the warm water extraction process (40-55° C) is widely used for bitumen extraction (Long et al., 2007). The schematic of water-based extraction process is shown in Figure 2.2.

Table 2.1. Summary of literature on the clay mineralogy of Athabasca oil sands (Kaminsky, 2008).

Authors	Reported mineralogy of clay (<2 µm) fraction	
Bayliss & Levinson (1976)	kaolinite, illite, up to 10% mixed layers, up to 6% chlorite and up to 1% montmorillonite	247 core ore samples
Camp (1976 a, b)	kaolinite, illite, mixed-layer clays, chlorite & smectite	ore and fine tailings
Yong & Sethi (1978)	kaolinite, illite, mixed-layer clays, chlorite & smectite, up to 4% amorphous Fe_2O_3	Suncor pond fine tailings
Kessick (1979)	kaolinite, illite	extraction tailings
Dusseault & Scafe (1979)	illite, kaolinite, vermiculite, illite-vermiculite, kaolinite-vermicuilite	outcrop and borehole ore samples in McMurray formation
Roberts et al. (1980)	kaolinite, illite, 0.9–3% smectite, 1–6% chlorite, 0.1–6% mixed-layer clays	Suncor pond fine tailings
Ignasiak et al. (1983)	kaolinite, illite/smectite (<10% smectite interlayers)	froth solids
Kotlyar et al. (1984)	kaolinite, illite	ore & froth solids
Kotlyar et al. (1985)	kaolinite, illite	froth solids
Ignasiak et al. (1985)	kaolinite, illite, trace amounts of chlorite and smectite in some samples	ore
Scott et al. (1985)	kaolinite and illite, trace quantities of smectite, vermiculite, chlorite and mixed-layer clays	ore & fine tailings
Kotlyar et al. (1987)	kaolinite, illite, up to 90% amorphous minerals	ore
Dusseault et al. (1989)	kaolinite, illite, smectites, vermiculites, mixed-layer clays	ore samples from various formations
Kotlyar et al. (1990)	kaolin, illite, up to 92% poorly crystalline minerals (allophane?)	Syncrude estuarine and marine ore
Ripmeester et al. (1993)	kaolinite, illite, trace amounts of smectites	fine tailings
Kotlyar et al. (1993)	kaolinite, illite, trace amounts of smectite and vermiculite	Suncor fine tailings
Cloutis et al. (1995)	kaolinite, illite	oil sand samples from Syncrude and Suncor leases
Kotlyar et al. (1995)	kaolinite, illite	Suncor fine tailings
Dudas, M.J (1998)	kaolinite, hydrous mica	5 fine tailings samples from Suncor, Syncrude and Oslo
Omotoso et al. (2002)	kaolinite, illite, mixed layer clays (kaolinite-smecite/illite- smectite)	mature fine tailings from Syncrude and Suncor ponds
Omotoso et al. (2004)	kaolinite, illite, mixed layer clays (kaolinite-smectite/illite smectite) and chlorite (in some samples)	mature fine tailings from Syncrude pond, thickener overflow and froth tailings
Wallace et al. (2004)	kaolinite, "degraded illite	ore samples
Omotoso et al. (2006)	kaolinite, illite, mixed layer clays (kaolinite-smecite/illite- smectite), trace amounts of discrete smectite in marineores	61 ore samples, 22 froth samples, 54 tailings samples from 3 different leases
Mercier et al. (2008)	kaolinite, illite	Syncrude fine tailings

Table 2.2. Ions in connate water of good and poor ores and process water (Zhao et al., 2009).

Water sample	Concentration of ions (ppm*)								
	K^+	Na^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_3^-	SO_4^{2-}	HCO_3^-	pH
Connate water (good ore)	5.2	62.4	0.1	0.3	308.3	-	13.5	22.9	7
Connate water (poor ore)	19.8	18.1	18.4	32.0	1.1	-	118.4	37.8	7.4
Process water	14-20	494-617	15-22	27-48	368-513	0-4	63-115	597-649	8

*ppm or mg/L is milligram (mg) of ion per kilogram (kg) of oil sands for connate water samples and milligram (mg) of ion per liter (L) of process water for process water sample. Water-based bitumen extraction process

In this process, oil sands ores are first crushed and slurried with water either in mixing boxes, stirred tanks, cyclo-feeders (Syncrude), or rotary breakers (Suncor and Shell Albian). The slurry is then mixed with warm process water, process aids (e.g. NaOH) and air, and transferred to a large primary separation vessels/cells (PSV/PSC) via tumblers or hydrotransport pipelines. During transportation, bitumen is liberated from the sand grains and attached to the air bubbles, lowering the apparent density of bitumen, thereby enabling successful separation through flotation. In PSV/PSC, where flotation takes place, the liberated bitumen from sand grains floats to the top (froth), while solids settle to the bottom of PSV as a result of gravity separation. A typical composition of the collected froth at the top is around 60 % bitumen, 30 % solid and 10 % water. The froth is then de-aerated and sent to froth treatment units for upgrading. Tailings slurry at the bottom of PSV is transferred to thickeners and then to tailings ponds to separate the solids and recycle the water.

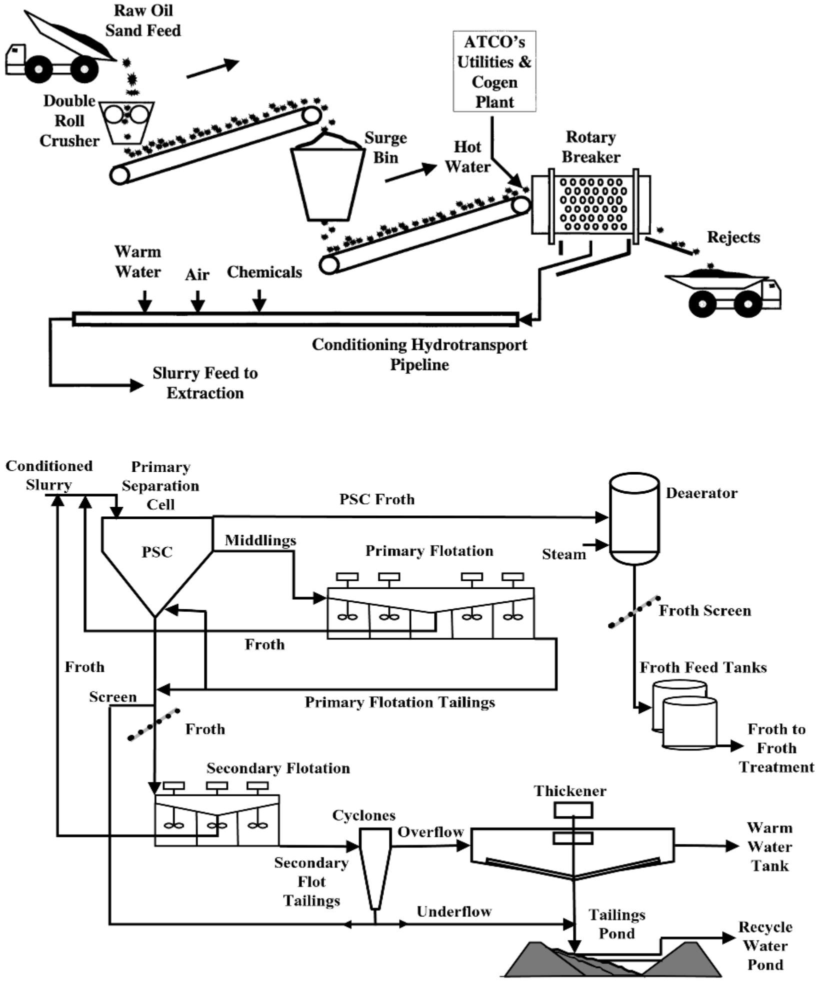


Figure 2.1. Schematic of water-based extraction process (Masliyah et al., 2004)

2.2.1 *Laboratory extraction units*

The first batch pilot plant was used by Clark to simulate the bitumen recovery from oil sands ore (Clark, 1929). Laboratory extraction unit was built for simulation of bitumen recovery or investigation of the impact of different parameters on bitumen recovery. Batch extraction units (BEU) by Syncrude Canada Ltd. (Sanford and Seyer, 1979; Mikula et al., 2007; Romanova et al., 2006; Mikula, 2007) and Denver flotation cells

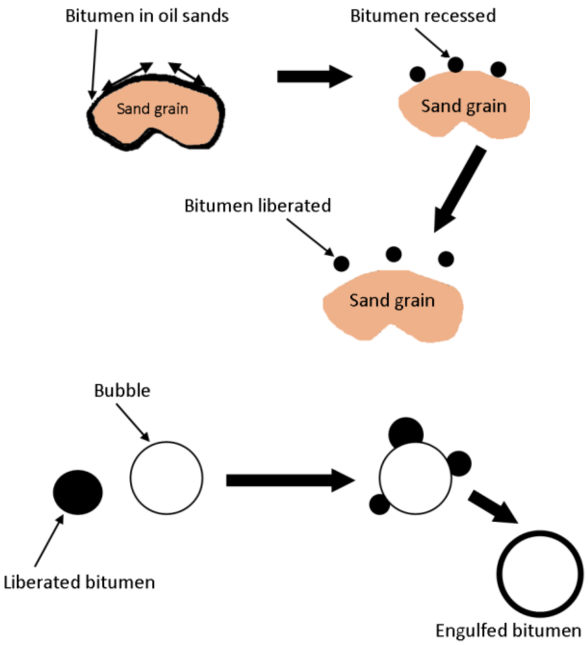
(Zhou et al., 2004; Kasongo et al., 2000) were the laboratory scale units used to study the processability of oil sands ores. In both methods, 500 g of oil sands ore and 900~1000 mL of process water were used. However, BEU provides lower shear rate to the process than Denver cell. Also, the airflow rate was different in each method. The froth from BEU is similar to the traditional commercial process (tumblers) while Denver flotation cell is closer to process with hydrotransport conditioning (Romanova et al., 2006). Also, in BEU froth was produced in two stages: primary froth and secondary froth. From primary froth primary bitumen recovery is calculated, which is typically used to scale up to plant operation. The total bitumen recovery is obtained from both the primary and secondary froth. With Denver Cell only total bitumen recovery value is reported. Another difference is the temperature sensitivity: It was reported that Denver cell is more sensitive to temperatures below 50 °C (Romanova et al., 2006).

Laboratory scale pipeline loop, or Laboratory hydrotransport extraction system (LHES), was first designed and constructed with 4 L capacity. The LHES uses visualization techniques to capture images from the slurry, which provides more information from a single test (Wallwork et al., 2003; Wallwork et al., 2004).

2.2.2 Extraction elements

Generally, an extraction process, which occurs in hydrotransport pipelines and PSVs has two elementary steps: liberation and aeration. In the liberation step the bitumen is recessed and detached from sand grains (Figure 2.3 a) (Basu et al., 1996; Srinivasa et al., 2012). The detached bitumen droplets then partially coalesce and at the same time attach to air bubbles, known as aeration step (Figure 2.3 b) (Flynn et al., 2001; Gu et al.

2004; Su et al., 2006). Due to the density difference, bitumen-air bubble aggregates float to the surface of the PSVs. At temperatures above 45 °C or in hot water extraction processes bitumen droplets engulf air bubbles, while at lower temperatures bitumen droplets only attach to the air bubbles. Temperature can also alter the slurry viscosity, which can affect the rising velocity of the air bubble-bitumen aggregates (Seyer and Gyte, 1989; Long et al., 2007). In the extraction process, factors such as ore grade, pH, surfactants concentration and the presence of different ions especially divalent cations can significantly affect the efficiency of the extraction elements and consequently the bitumen recovery.



a) b)

Figure 2.2. a) Bitumen liberation, and b) bitumen aeration (Zhao et al., 2009)

2.2.2.1 Bitumen liberation

In bitumen liberation from sands, the bitumen-sand interface is replaced by bitumen-water and sand-water interfaces. The interfacial energy associated with bitumen-sand separation is given by Eq. 1, where *ΔG* is Gibbs free energy, *ΔA* is the surface area and *γ* is interfacial tension. Subscripts *B*, *S* and *W* represent bitumen, sand and water, respectively. The corresponding forces are shown in Figure 2.4.

$$\frac{\Delta G}{\Delta A} = \gamma_{SW+}\gamma_{BW} - \gamma_{BS} \qquad (1)$$

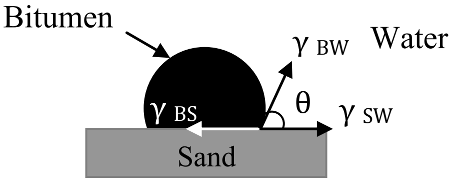


Figure 2.3. Interfacial energies involved in bitumen liberation

From Eq. 1, it is clear that a reduction in bitumen-water and sand-water interfacial tensions and an increase in bitumen-sand interfacial tension favor bitumen liberation. Increase in pH can increase hydrolysis of sands (wettability), which can consequently reduce sand-water interfacial tension. Additionally, by increasing pH, bitumen-water interfacial tension can be reduced due to the release of natural surfactants and changes in the surface charges. By inserting Young's equation (Eq. 2) in Eq. 1, the total interfacial energy for bitumen liberation can be calculated using Eq. 3:

$$\gamma_{BS} - \gamma_{SW} = \gamma_{BW} \cos\theta \qquad \text{Young's equation} \qquad (2)$$

$$\frac{\Delta G}{\Delta A} = \gamma_{BW}(1 - \cos\theta) \geq 0 \qquad (3)$$

Before separation of bitumen from sand, the recessed bitumen droplet on sand has a contact angle less that 90° ($\cos\theta > 0$). Also, bitumen-water interfacial tension has a positive value. Therefore, the term $\frac{\Delta G}{\Delta A}$ is positive and liberation of bitumen from sand (complete detachment) is thermodynamically unfavorable unless the sands are completely hydrophilic ($\theta = 0$). Therefore, for the complete detachment of bitumen from sands, additional forces (hydrodynamic or mechanical energy) are required (Masliyah et al., 2011).

2.2.2.2 Bitumen aeration

For bitumen aeration, a bitumen-air attachment should occur. Eq. 4 shows the interfacial energy associated for the bitumen-air attachment. The involved interfacial forces are shown in Figure 2.5.

$$\frac{\Delta G}{\Delta A} = \gamma_{BA} - (\gamma_{BW} + \gamma_{AW}) \qquad (4)$$

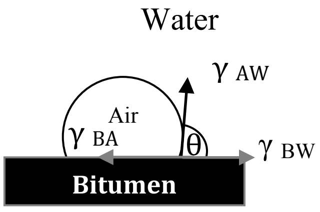


Figure 2.4. Interfacial energies involved in bitumen aeration

By introducing Young's equation (Eq. 5), Eq. 4 can be represented as Eq. 6:

$$\gamma_{BA} - \gamma_{BW} = \gamma_{AW} \cos\theta \qquad \text{Young's equation} \qquad (5)$$

$$\frac{\Delta G}{\Delta A} = \gamma_{AW} (\cos\theta - 1) \qquad (6)$$

The above equation shows that at contact angles greater than zero the term $\frac{\Delta G}{\Delta A}$ is negative, which makes the attachment of bitumen-air bubble thermodynamically favorable. The larger contact angle makes the term $\frac{\Delta G}{\Delta A}$ more negative, which is beneficial for attachment. However, increasing pH decreases the interfacial tension of water-air bubbles, which is not favorable for bitumen-air bubble attachment since $\frac{\Delta G}{\Delta A}$ will have a smaller negative value (Masliyah et al., 2011).

From comparison of the favorable interfacial energy conditions for bitumen liberation and aeration, one can conclude that increasing pH helps bitumen liberation while it is detrimental for bitumen aeration. Therefore, it is important to control the pH of the flotation in a range in which optimum recovery is achieved.

2.3 Role of NaOH in extraction process

In industry, process aids are usually introduced for enhancing bitumen recovery. The commonly used process aids are alkaline chemicals, polymers, surfactants or diluents (Schramm, 2000; Flury et al., Christopher 2014; Long et al., 2011; Li, 2008; Hupka et al., 1983). Although other sources of process aids have shown better performance than NaOH, NaOH is still the most widely used process aid due to its lower cost. The optimum concentration of NaOH as a process aid depends on the ores' composition and characteristics. It has been shown that ores with higher fines content need more NaOH to reach optimum bitumen recovery (Figure 2.6) (Sanford, 1983). Schramm and Smith (1987) investigated the role of caustic (NaOH) on the processing performance of oil sands ores of different grades. Using a laboratory scale batch-extraction unit (BEU), they reported that average ores responded well to caustic addition, showing a clear optimum in bitumen recovery, whilst caustic addition was shown to hinder bitumen recovery in good ores and provide only a slight improvement for poor ores.

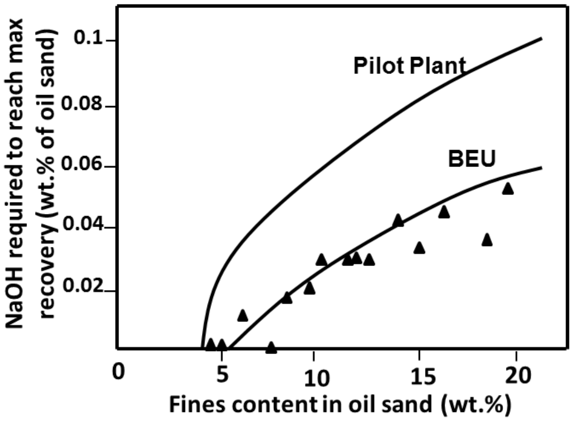


Figure 2.5. Effect of fines content on NaOH required for achieving the maximum recovery (Sanford, 1983)

2.3.1 Release of surfactants

NaOH is considered to be an activating agent that promotes the release of surfactants from organic acids existing naturally in bitumen. Using foam fractionation and spectroscopic characterization, it was shown that the surfactants produced in the process water are mainly carboxylic ($RCOO^-$) with the possible presence of the sulfonic salts (RSO^{3-}). The following reactions illustrate how base reacts with organic acids in the bitumen to produce the ionized form of surfactants (Bowman, 1967; Baptisa and Bowman, 1969; Sanford and Seyer, 1979; Sanford, 1983).

$$RSO_3H + OH^- \leftrightarrow RSO_3^- + H_2O$$

$$RCOOH + OH^- \rightarrow RCOO^- + H_2O$$

Mistra et al. (1981) reported that paraffinic carboxylate surfactants were the principal surfactant released in the processing of Utah tar sands. During 1980s, Schramm et al. have done several studies on isolation and quantification of natural surfactants in hot water extraction process and their relationship with bitumen recovery (Schramm et al., 1984; Schramm et al., 1984; Schramm and Smith, 1985; Schramm and Smith, 1987). In their studies, natural surfactants were isolated from a large sample of tumbler slurry from Syncrude's continuous pilot plant using centrifugation and ultra-filtration followed by six-stage foam fractionation. By characterizing the isolated surfactants using proton and carbon-13 NMR, they found that the fractionates predominantly consist of aliphatic carboxylates with hydrocarbon chains of at least five carbons (typically C15-C17) and aliphatic sulfonates having hydrocarbon chains of at least five carbons. Methoxyl, aromatic and humic materials were also found. In addition, they introduced critical surfactant concentrations of $(1.2\times10^{-4} \pm 15\% N)$ and $(1.5\times10^{-4} \pm 15\% N)$ for carboxylate and sulfate/sulfonate surfactants, respectively, which are required in order to achieve maximum bitumen recovery (Schramm and Smith, 1987).

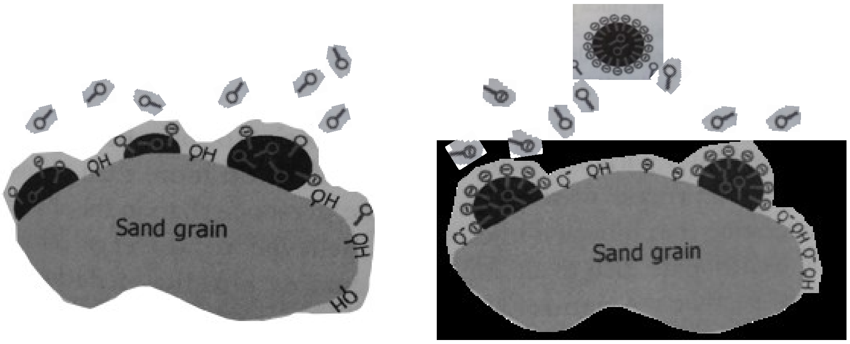
2.3.2 Changing surface properties

The increase in the slurry pH and the release of natural surfactants, which adsorb on surfaces and interfaces, alter the surfaces properties; thereby affect the efficiency of the extraction elements. During liberation, upon water-bitumen contact, these charged surfactants adsorb at the bitumen-water interface, with the hydrophilic head and hydrophobic tail positioned towards their favorable phases. The charged surface increases the repulsive interactions between bitumen and sands, leading to improved bitumen liberation. It was shown that bitumen and sands became more negatively charged with increasing pH (Schramm and Smith, 1985; Liu et al., 2002; Liu et al., 2003; Liu et al., 2004b). An online visualization technique was used to show that liberation of bitumen from sands was enhanced at higher pH (Srinivasa et al., 2012; Flury et al., 2014). Contact angle measurements also showed that bitumen wettability increased when pH was raised. Contact angles decreased from 58° to 38° when pH was increased from 8.5 to 11.3 (Flury et al., 2014).

NaOH also increases deprotonation of hydrolyzed sands. At high pH the hydrolized surface deprotonates and therefore becomes negatively charged according to the following equations. This phenomenon can help bitumen liberation by increasing the electrostatic repulsive forces between bitumen and sands (Figure 2.7).

$$SiOSi + H_2O \rightarrow 2SiOH$$

$$SiOH + OH^- \rightarrow SiO^- + H_2O$$



a) b)

Figure 2.6. Effect of NaOH on release of surfactants and hydrolysis of sands. a) Low pH, b) High pH (formation of micelles, deprotonation of sands) (Masliyah, 2011).

In the presence of calcium ions the deprotonated sites on sands adsorb calcium ions, making them more positively charged and suitable for attracting anionic surfactants (reactions are mentioned below). Surfactant adsorption on sands' surfaces renders sands more hydrophobic. In the case of fine solids and clays, the hydrophobized particles can float by attaching to air bubbles, which consequently can reduce the froth quality.

$$SiO^- + Ca^{2+} \rightarrow SiO^-Ca^{2+}$$

$$SiOH + CaOH^+ \rightarrow SiO\ Ca^+$$

$$SiOCa^+ + RCOO^- \rightarrow SiOCaOOCR$$

Liu et al. (2003) used zetaphormetry to measure the zeta potential of silica particles at different pH values. It was shown that silica particles became more negatively charged in 1 mM KCl solution when pH was increased. An increase in repulsive forces between silica and bitumen with increasing pH was measured. In another study, it was shown that the zeta potential of kaolinite and illite clays became more negative at higher pH values but remained almost unchanged for montmorillonite (Liu et al., 2002).

Although the liberation step benefits from the addition of NaOH, this is not the case for the aeration step. Due to the surfactants adsorption, the bitumen surface becomes more negatively charged and less hydrophobic. Hence, the attachment of a rising air-bubble onto a bitumen droplet becomes less efficient. Using induction time measurement (following the method provided by Gu et al., (2003)), it was found that addition of NaOH or NH_4OH to oil sands ore increases the attachment time of bitumen droplet to the air bubble. In the case of NaOH more surfactant was released, the bitumen surface was more negatively charged, and induction time had a greater value (Flury et al., 2014).

2.3.3 Consumption of divalent cations

Addition of NaOH to the flotation tests also consumes divalent cations in the slurry. The presence of divalent cations such as calcium and magnesium has been reported always problematic. Kasongo et al. (2000) reported that the addition of montmorillonite clays alone to flotation tests do not change the bitumen recovery, but it reduced the recovery by ~30% when it was co-added with 40 ppm calcium cations. Basu et al. (2004) found that montmorillonite in the presence of calcium ions can reduce the rate of bitumen displacement on a glass slide. The role of divalent cations at pH< 9 is more significant in controlling oil sands processability. At sufficiently high pH, divalent cations precipitate in the form of carbonates or hydroxide, hence they are less likely to affect bitumen recovery or froth quality (Dai et al., 1992; Fong et al., 2004). Fong et al. (2004) used model oil sands and showed that by increasing the alkalinity of the process water in the extraction test the concentration of the remaining magnesium ions in the solution decreased from 40 ppm at pH 6 to almost zero at pH 10.7. This is due to the very low solubility product of magnesium hydroxide (1.5×10^{-11}). Half of the initial concentration of calcium ions (50 ppm at pH 6) was also consumed when pH was increased to 12.

2.3.4 Release of toluene insoluble organic materials (humic substances)

2.3.4.1 Origin of humic substances

Humic substances are natural organic matters (NOM), which can be found in soil, water, lake sediments, peats, brown coals, and shales. They are formed by biochemical and chemical reactions of plants and microbial remains during decays. In general, humic substances are categorized into three groups: i) fulvic acids, soluble in water at all pH values, ii) humic acids, soluble at pH above 2 and iii) the water-insoluble humin (Stevenson, 1982). Humic substances can change the color of their solution. Humic substances with higher molecular weight and carbon content change their solutions color to dark brown or grey (Figure 2.8).

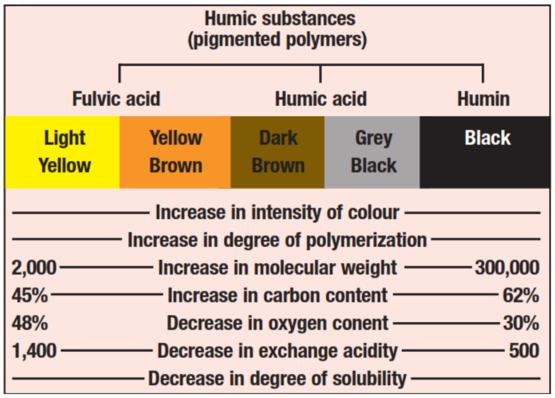


Figure 2.7. Classification and chemical properties of humic substances (Stevenson, 1994)

Among the above-mentioned humic substances, humic acids are the one that has been mostly reported in oil sands ores. Majid et al. extracted and characterized humic acids isolated from Alberta oil sands and Syncrude sludge tailings pond. He used NaOH or a mixture of NaOH and $Na_4P_2O_7$ to extract humic acids (Majid at al., 1991; Majid et al., 1992; Majid and Ripmeester, 1990). These materials (humic acids) are mixtures of aromatic and aliphatic macromolecules, which contain phenolic OH groups, nitrogen and oxygen as bridge units, and COOH groups. The hypothetical structure of humic acid is shown in Figure 2.9. Using alkaline solution to extract humic acids, it was revealed that poor ores or oxidized (weathered) ores released more humic acids than good ores (Ignasiak et al., 1985; Gutierrez and Pawlik, 2014b). Also, using 13C NMR analysis, it was shown that humic acids from Utah oil sands were more aliphatic while humic acids from Athabasca oil sands were more aromatic (Kotlyar et al., 1989; Kotlyar et al., 1988).

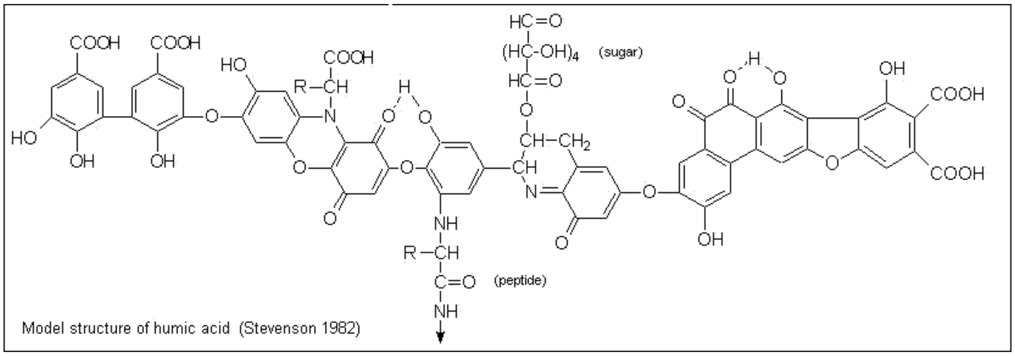


Figure 2.8. Model structure of humic acids (Stevenson, 1982)

2.3.4.2 Effect of humic acids on surface properties

In the studies on wettability and characterization of organic coated solids in Athabasca oil sands, it was reported that these solids were coated with toluene insoluble organic materials (TIOM) which were mostly humic matters (Kotlyar et al., 1988; Kotlyar et al., 1988; Kotlyar et al., 1989; Darcovich et al., 1989; Bensebaa et al., 2000; Sparks et al., 2003). Darcovich demonstrated that the solids, which were associated with humic matters, had moderately more hydrophobic characteristics. He also showed that the degree of hydrophobicity depended on the insoluble organic carbon content (IOCC) (Darcovich et al., 1989). Gutierrez and Pawlik (2014a) showed that bitumen became more hydrophilic in the presence of humic acids, with the effect of humic acids on bitumen wettability diminishing with pH increasing from 3 to 10. They proposed that humic acids make bitumen hydrophilic if they are part of the internal/surface bitumen structure, which happens when ores are oxidized.

The adsorption of humic acids on minerals had been investigated in several studies. It was found that the adsorption of humic acids on bohemite and goethite minerals was enhanced at low pH and reduced at intermediate and high pH (Fairhurst and Warwick 1998). In the same study it was shown that the zeta potential of minerals had more negative values in the presence of humic acids. The changes in the zeta potential were more significant at low pH. The adsorption of peat humic acids (PHA) on kaolinite and illite clays was confirmed by zeta potential measurements and FTIR analysis. The negative zeta potential values of kaolinite suspension in the presence of humic acids and 0.01 M $CaCl_2$ decreased by 30 mV in the pH range of 4-7 and 10 mV for pH values greater than 7. For illite suspensions, the addition of humic acids decreased the zeta potential values by 10 to 15 mV for pH values bellow 9. This value decreased to 2-5 mV at pH values greater than 9 (Martinez et al., 2010). In the study of the effect of humic acids on the floatability of graphite in aqueous solutions humic acids were found to adsorb on the surface of graphite over the pH range of 3 to 11, and made graphite more negatively charged and more hydrophilic, which depressed floatability of graphite particles (Wong and Laskowski, 1984).

2.4 Quantification methods of natural surfactants

The following methods have been used for the quantification of natural surfactants (carboxylate and sulphate/sufonate) and naphthenic acids (the major compounds of carboxylic surfactants) in oil sands process water (OSPW).

2.4.1 Acid titration

This method was used by Schramm et al. (1984) and was the first surfactant assay reported for oil sands process samples. In this method the water sample was centrifuged and titrated by HCl up to pH 4.5 to determine the total carboxylic surfactant concentration. Because surfactants have the tendency to concentrate at the interfaces, another sub-sample was then foam-fractionated until the residue was completely stripped off the surfactants (verified by surface tension measurements) (Bowman, 1967). The residue and foam fractionate samples were then titrated with HCl to determine the surface-active and non-active fractions of carboxylic surfactants. This method was restricted to the analysis of carboxylic surfactants only and it was very time consuming due to the foam fractionation stage and the incomplete separation of surface active species by foam fractionation. An approximate error of 10% was reported. Additionally, the presence of bicarbonates caused an interference to the acid titration endpoint.

2.4.2 Cationic surfactants titration

2.4.2.1 Two phase titration method using cationic surfactants

The widely used two-phase titration method was first introduced by Epton (1948). In this titration method, chloroform was used as the organic phase and methylene blue as indicator. Methylene blue is cationic and highly soluble in chloroform in salt form. Hyamine or cetyltrimethylammoniumbromide (CTAB) is used as the cationic surfactant (titrant). When a cationic surfactant is added, the dye in the indicator reacts with cationic surfactants. At 3:1 volume ratio of aqueous to chloroform phase, equal colour intensity in the two phases shows the end point and equivalence between anionic and cationic surfactants in the system. This method can measure both carboxylic and sulfonic surfactant concentration. The major challenge with this method is that it is hard to find the endpoint, which is operator-dependent. Chloroform is also hazardous. There have been alternatives to Epton's two-phase titration method with different indicators, cationic surfactants or pH condition for titration (Cullum, 1994).

2.4.2.2 One phase titration method using cationic surfactants

This method is based on the formation of complexes of anionic surfactants and a cationic surfactant (CTAB) as titrant. To determine the endpoint, the surface tension of the solution was monitored by using the maximum bubble pressure technique or by automated Wilhelmy plate method. Endpoint is where the surface tension is equal to surface tension of de-ionized water. This method also measures both carboxylic and sulfonic surfactants. For measuring each of the surfactants, a sample of solution was titrated with HCl to pH 3 to convert all the carboxylic surfactants to acid form and the solution was then titrated with cationic surfactants. Therefore, with this titration, only the concentration of sulphate/sulfonate surfactants can be measured. Concentration of carboxylic surfactant can be calculated by deduction of sulphate/sulfonate surfactants concentration from the total concentration of surfactant. Total concentration of anionic surfactant can be determined by titrating a sample of solution at its original pH (Schramm et al., 1984; Schramm, 2000).

2.4.2.3 Surfactant sensitive electrode

This method is based on the potentiometric titration with surfactants of opposite charges. In this method anionic surfactants are titrated by cationic surfactants. The titration is monitored by a surfactant-sensitive electrode and the endpoint is observed as the inflection point of the potential jump. The advantage of this method is that it is reproducible and there is no organic waste remaining after the titration (Cullum, 1994).

2.4.3 Methods for quantification of naphthenic acids

Naphthenic acids, which are the main components of carboxylic acids, are released in to the oil sands process water during bitumen extraction process. According to environmental regulations, it is important to control the amount of the naphthenic acids released to surface water and ground water due to their toxicity and environmental issues. There are several methods developed for quantification of these compounds. Each technique has its own limitations and requires special sample preparation. Differences between the measured concentrations of naphthenic acids using different techniques have been reported. Different analytical methods can be used for quantifying naphthenic acids. High Performance Liquid Chromatography (HPLC) and Gas chromatography (GC), which are mostly coupled with mass spectrometer as detector; spectroscopy methods such as Fourier Transform Infrared (FTIR) and fluorescence spectroscopy; or mass spectrometry alone are also among the common analytical methods.

2.4.3.1 High Performance Liquid Chromatography (HPLC)

High Performance Liquid Chromatography (HPLC) was used by Miwa (2000) for measuring carboxylic acids in foods and beverages. Different carboxylic acids were separated at different retention times in HPLC column and were detected by UV-visible detector. In this method, the carboxylic acids were derivatized to their hydrazine form so that they can be detected by UV-visible detector. The concentration of carboxylic acids was quantified according to calibration curves made with a standard sample. HPLC method with different derivatization methods was used by other researchers to quantify naphthenic acids in aerobic laboratory cultures (Clemente et al., 2003) and oil sands water samples (Yen et al., 2004). Wang and Kasperski (2010) used HPLC-MS/MS to detect naphthenic acids in standard solutions.

2.4.3.2 Gas chromatography (GC)

Naphthenic acids can be derivatized and analyzed by Gas chromatography (GC). Different derivatization techniques and detectors can be used for GC analysis. They can be derivatized and vaporized to their methyl esters forms and analyzed by Gas chromatography (GC) with a flame ionization detector. GC analysis yields an unresolved hump that was integrated and its area was constructed to the calibration curve for quantification of naphthenic acids (Herman et al., 1994; Jones et al., 2001). Mass spectrometry (MS) is common detector, which can be coupled with GC for characterization of naphthenic acids (Scott et al., 2008).

2.4.3.3 Fluorescence spectrometry

Recently a fluorescence technique has been proposed as a quick technique, which can detect naphthenic acids, and other dissolved organic materials (DOM) in OSPW without any pre-treatment for the samples. In fluorescence techniques, a loosely held electron in an atom or a molecule is first excited to a higher energy level by the absorption of energy, for example, by absorbing a photon. Then the electron returns to its original energy level by emission of light, where fluorescence can be observed. In the study of fluorescent organic matter, compounds that absorb light are called chromophores whereas compounds that absorb and re-emit light are called fluorophores (Hudson et al., 2007).

Fluorescence spectroscopy techniques are used to detect compounds with aromatic rings such as proteins, surfactants, humic and fulvic acids, phenols, polyaromatic hydrocarbons, and oils, which have fluorophoric characteristics. Although classical naphthenic acids do not have aromatic rings, this method has been used for monitoring and quantifying (semi-quantitative method) naphthenic acids in OSPW (Mohamed et al., 2008; Kavanagh et al., 2009; Rowland et al., 2011). The quantified materials are thought to be potentially naphthenoaromatic compounds formed by aromatic compounds and naphthenic acids co-existing in the OSPW (Kavanagh et al., 2009).

Comparing fluorescence spectrometry technique for quantification of naphthenic acids with other different methods such as Fourier transform infrared (FTIR) and ultra performance liquid chromatography-time of flight mass spectrometry (UPLC-TOF/MS), fluorescence technique was shown to overestimate the concentration of naphthenic acids (Lu et al., 2013).

2.4.3.4 FTIR method

This is the standard method for quantification of total naphthenic acids in process water or waste water in the oil sands industry. The method was initially developed by Syncrude Canada Ltd. (Jivraj et al., 1995). In this method, the water sample is acidified and naphthenic acids are extracted into dichloromethane (DCM) by liquid-liquid extraction. FTIR instrument was then used to quantify the naphthenic acids concentration in the samples. The absorbance peaks at ~1743 cm^{-1} and ~1706 cm^{-1} correspond to the monomer and dimer forms of carboxylic (-COOH) functional groups, respectively. Concentrations of naphthenic surfactants were then determined according to calibration curve constructed with solutions of commercial naphthenic acids in dichloromethane with known concentrations (Clemente and Fedorak, 2005). In a comparison of FTIR method with gas chromatography-mass spectrometry (GC-MS), the detection limits were reported to be 0.01 mg/L and 1 mg/L for GC-MS and FTIR, respectively. It was found that the GC–MS method was more selective in quantification of naphthenic acids while FTIR method overestimated the concentration of naphthenic acids (Scott et al., 2008). That is because FTIR quantifies all the DCM extractable carboxylic compounds and it cannot identify the difference between the classical and non- classical naphthenic acids.

2.4.3.5 Other methods

Headley et al. (2002) used solid phase extraction with a divinyl benzene support sorbent to extract and concentrate naphthenic acids from aqueous samples. A solvent was used to elute the naphthenic acids from the sorbent. The naphthenic acids concentration in the concentrated sample was then measured by negative-ion Electrospray Ionization Mass Spectrometry (ESI/MS). Similar methods with different solvent or extraction method were used in other studies (Headley et al., 2007; Rogers et al., 2002; Martin et al. 2008). More detailed studies and quantification methods of naphthenic acids can be found in the review studies carried out by Clemente and Fedorak (2005) and Zhao et al. (2012). Mass spectrometry (MS) alone can be also used for analysis of naphthenic acids. In MS methods, the chemical compounds should be first ionized to generate charged molecules. Then it uses the mass to charge ratios (m/z) to characterize the elemental compositions and the chemical structures of molecules. Different techniques for ionization of chemical compounds can be used.

2.5 Bitumen slime coating

Slime coating occurs when clay particles attach to the surface of a bitumen droplet and form a layer of slime (clays). This layer of slime hinders the effective attachment of air bubbles to liberated bitumen droplets and has a negative impact on froth quality and overall bitumen recovery. Slime coating is one of the reasons proposed for low bitumen recovery of poor processing ores (Liu et al., 2005). Atomic force microscopy (AFM) and zeta potential distribution measurement have been used to study the mechanism of slime coating (Kasongo et al., 2000; Liu et al., 2002; Liu et al., 2003; Liu et al., 2004a; Liu et al., 2004b; Liu et al., 2005; Zhao et al., 2006; Ding et al., 2006). Figure 2.10 shows the schematic of slime coating measured by zeta potential distribution for a system that contains bitumen and clays, proposed by Liu et al., (2002).

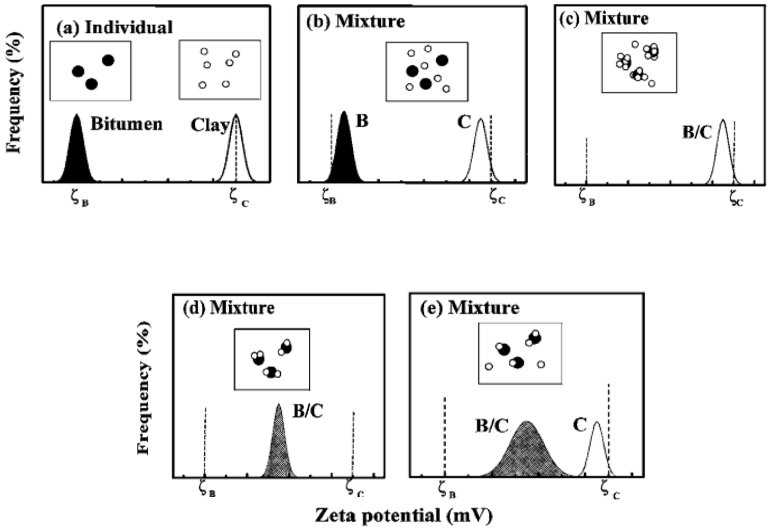


Figure 2.9. Schematic of zeta potential distribution for clay-bitumen system. a) zeta potential distribution of two components measured individually, b) binary mixture when slime coating does not occur, c) binary mixture when complete slime coating occurs, d) partial slime coating due to insufficient clays (strong attraction) and e) partial slime coating due to weak attraction (Liu et al., 2002).

In studying the slime coating, if both bitumen and clay particles carry relatively high like charges, slime coating will not occur. The electric charge on bitumen and clay particle generates a repulsive force barrier, which prevents the attachment of clay particles on bitumen droplet. However, presence of ions with opposite charge can diminish the repulsive interaction and induce attractive forces. By studying model clay particles, it was found that montmorillonite has detrimental impact on bitumen slime coating in the presence of calcium ions. Under the same condition it was found that kaolinite did not attach to bitumen droplet (Liu et al., 2002; Liu et al., 2004b). This observation was very important since it revealed that other than the charges of particles charges, clay type also plays an important role in slime coating. The cationic exchange capacity (CEC) of these clays has been highlighted to account for such differences (Liu et al., 2002; Wallace et al., 2004). It was shown that in the presence of calcium ions adhesion forces between bitumen and montmorillonite were stronger than bitumen and kaolinite (Liu et al. 2005). In another study, slime coating of bitumen by illite clays was studied by zeta potential distribution measurement in de-ionized water. Slime coating of bitumen by illite particles in presence of magnesium ions was measured at pH 4.9. By increasing pH to 8.5, slime coating was not observed Ding et al. (2006).

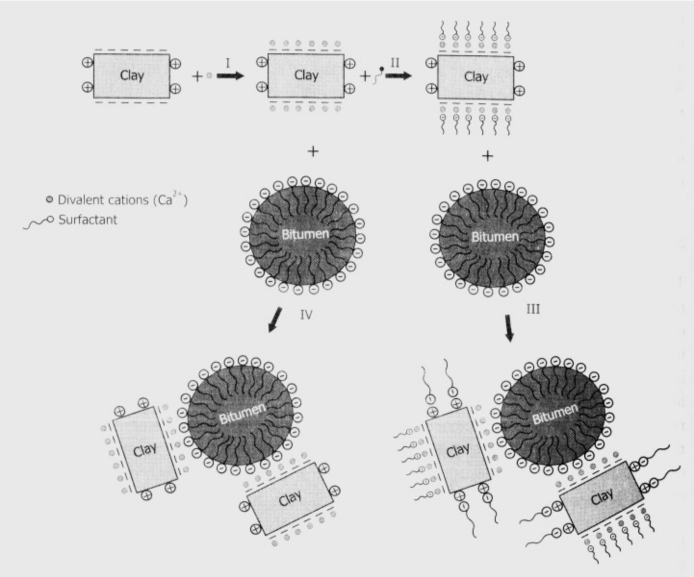


Figure 2.10. Schematic illustration of slime coating of clays on bitumen surface in the presence of calcium ions acting as a bridge (Masliyah et al., 2011).

Shown in Figure 2-11, Masliyah et al., (2011) proposed slime coating mechanism in the presence of calcium ions and surfactants. As illustrated calcium ions are bridging the negatively charged surfaces of bitumen and clays. Addition of caustic (NaOH) to oil sands flotation process was shown to decrease the concentration of calcium ions (Fong et al., 2004) and increase the negative surface charges on both bitumen and fine solids (Schramm et al., 1984), leading to a lower degree of slime coating.

Using AFM to study the interactions between bitumen and real mineral clays present in different grade processing ores, strong attraction and adhesion forces were measured for fines from the poor processing ores (Figure 2.12). The observed nature of the interaction was related to the increased hydrophobicity of fines from poor processing ores (Liu et al., 2004a).

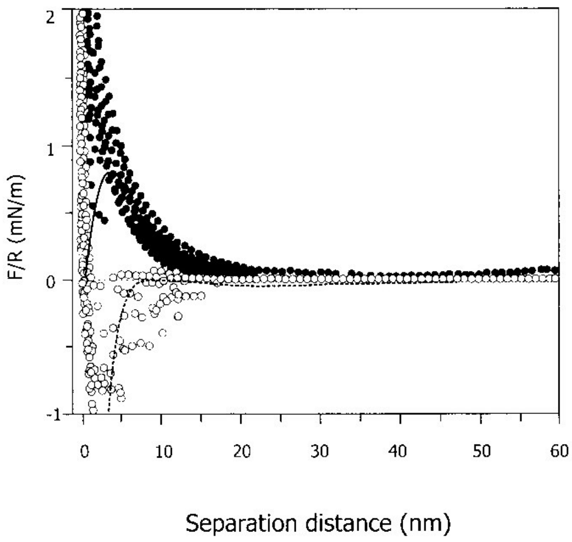


Figure 2.11. Interaction force in tailings water of pH 8.5 between bitumen and fines isolated from tailings of good (solid symbol) and poor (open symbol) processing ores (Liu et al., 2004a).

2.6 Ore oxidation

Ore oxidation, also known as ore aging, weathering or degradation has always been one of the challenges facing the oil sands industry due to its effect on reducing bitumen recovery. There have been several reasons reported for the observed decrease in the bitumen recovery of oxidized or degraded ores. Schramm et al. have done several studies on the processability of oxidized ores. They claimed that pyrite oxidation in oil sands ores can increase the acidity and dissolve calcium and magnesium carbonates. Released calcium ions consume carboxylic type of surfactants to form calcium carboxylate precipitates. The decrease in the concentration of carboxylic surfactant hinders the bitumen liberation, leading to a reduced bitumen recovery (Schramm and Smith, 1987a; Schramm and Smith, 1987b). Mikula et al. (2003) reported that no significant changes in iron or calcium concentration of oxidized ores were observed. However, changes in the bitumen chemistry were claimed to be the main reason for the decrease in bitumen recovery. By using Near Infrared Spectroscopy (NIR) with microscopic method, they found that there is a loss of aliphatic carbons in favour of hydroxyl groups in oxidized ores. They showed that for oxidized ores, the addition of process aids can increase bitumen recovery. Ren et al. (2009a) measured contact angles and revealed that mild bitumen oxidations during the weathering had a negligible effect on bitumen surface wettability. However, loss of formation water during weathering caused the intimate contact of bitumen with solids and resulted in adsorption of toluene insoluble organic materials (TIOM) onto sands surfaces, which made them more hydrophobic and hindered bitumen recovery. Using in-situ bitumen liberation visualization technique, Srinivasa et al. (2012) showed that ore weathering led to a severe degradation in bitumen liberation. It was also revealed that low bitumen recovery of oxidized ores is attributed to the deteriorated bitumen-air bubble attachment (Wallwork et al., 2003). Using oily bubbles (by the addition of kerosene) instead of air bubbles decreased the bitumen-air induction time (Su et al., 2006). The addition of 0.15 mL/min kerosene into air streams (feeding at 200 mL/min) introduced into the oil sands slurry in a laboratory pipeline increased the recovery of oxidized ores from ~10% to ~98 % (Wallwork et al., 2003).

Because of the significant role of surfactants in the oil sands extraction process, it is important to find the variables that can affect the concentration of surfactants released from ores in extraction process. This thesis is firstly focused on establishing a method for quantification of carboxylic surfactants produced from oil sands ores. Secondly, it is aiming to understand the role of NaOH, which is the main process aid used for enhancing the bitumen recovery, in changing the concentration of carboxylic surfactant generated from ore. Also the thesis is aiming to find the correlations between the ores' characteristics with produced carboxylic surfactant concentrations in tailings water. Thirdly, the role of water chemistry caused by addition of different dosages of NaOH to oil sands extraction process in bitumen-clay interactions will be investigated. These interactions are important and need to be controlled since they can decrease bitumen recovery and hinder froth quality.

CHAPTER 3

3 Analysis of Natural Surfactants in Tailings Water

3.1 Introduction

Role of NaOH in the oil sands extraction process is not only adjusting the pH of the slurry but also producing natural surfactants from bitumen. Natural surfactants, which are mainly carboxylic and sulfuric/sulfonic type (Schramm and Smith 1987a; Schramm et al., 1984) can change the electrical potential and hydrophobicity of surfaces and interfaces (Schramm and Smith, 1985; Schramm, 2000; Flury et al., 2014). It has been revealed that release of natural surfactants has a significant effect on bitumen recovery from oil sands ores (Schramm, et al., 1984; Schramm and Smith, 1985; Sanford and Seyer 1979). Schramm and Smith (1987a) showed that the optimum primary bitumen recovery was not correlated with the pH of the extraction, but it was obtained when surfactants concentrations were at certain levels.

Controlling the release of natural surfactants by the amount of NaOH added to the extraction test is important to manage the interactions between bitumen-sand, bitumen-bubble and sand-bubble in order to optimize the bitumen recovery. Different techniques have been used to measure surfactant concentrations in tailings water, such as foam fractionation followed by acid/base titration (Bowman, 1967; Schramm et al., 1984) or one phase or two phase titration by cationic surfactants (Cullum, 1994; Schramm et al., 1984; Schramm, 2000). In environmental researches, FTIR was a common method for quantifying the total concentration of naphthenic acids (NAs), which are the major compounds of carboxylic acids in the oil sands process water (OSPW) or tailings water (Holowenko et al., 2002; Scott et al., 2008).

While NaOH is added as process aid to flotation test to produce natural surfactants, other organic materials are also co-extracted from oil sands ores at high NaOH dosage (pH>10). These materials are mostly humic acids (Majid and Ripmeeter, 1990; Gutierrez and Pawlik 2014a). Humic acids are mixtures of aromatic and aliphatic macromolecules with hydroxyl and carboxyl functional groups (Stevenson, 1982). Release of these materials can influence the surface characteristics of fine solids and bitumen droplets, which consequently can affect the efficiency of bitumen recovery (Gutierrez and Pawlik 2014a; Gutierrez and Pawlik 2014b; Sparks et al., 2003; Darcovich et al., 1989).

The main objective of this chapter is to establish a method suitable for analyzing the concentration of free natural carboxylic surfactants in tailings water produced by performing flotation test (using Denver cell). To this end, FTIR method was used.[*] The effect of humic acids (which are co-extracted from oil sands ore at pH>10) on quantification of carboxylic surfactants in tailings water was studied. At the end, the presence of sulfonic acids (second type of surfactants) in tailings was investigated semi quantitatively using surface tension measurement technique.

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[*] Application of other methods such as fluorescence spectrometer for quantification of carboxylic surfactants was also examined. The results are shown in Appendix A.1.

3.2 Materials and Methods

3.2.1 Materials

Commercial mixture of naphthenic acids (NAs) from Sigma Aldrich was used as model compounds of carboxylic acids. Four different standard model compounds (Figure 3.1): 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) were used as the model compounds of carboxylic acids for preparing calibration curve. Reagent grade NaOH, HCl and H_2SO_4 were used to adjust pH. Humic acids (HAs) purchased from MP Biomedicals were used as received as the source of HAs. Sodium salt dodecylbenzene sulfonic acid and 1-dodecanesulfonic acid were used as model compounds of sulfonic acids.

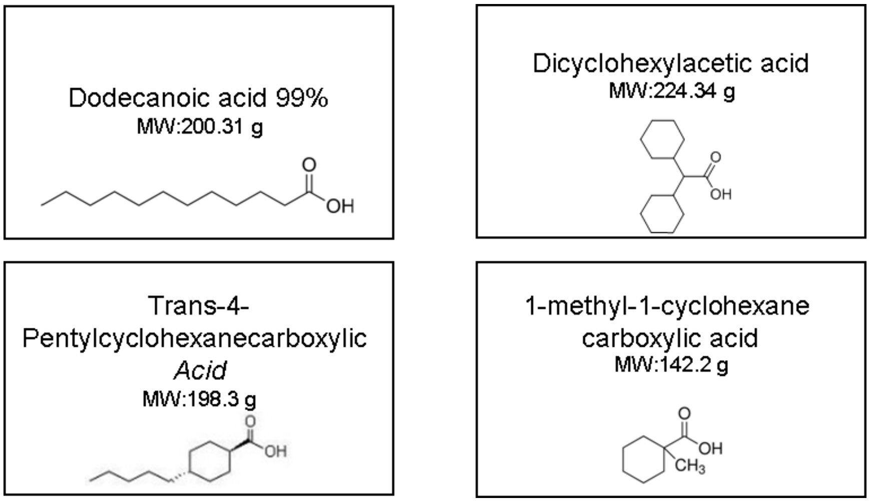

Figure 3.1. Four model compounds of naphthenic acids used to make calibration curve

Composition of the ore (MA) and chemistry of the process water used for flotation test and preparation of tailings water is shown in Table 3.1 and Table 3.2. Oil sands ore and process water were supplied by Syncrude Canada Ltd.

Table 3.1. Ore composition used for flotation test and preparation of tailings water

Ore composition (wt.%)			
Bitumen	Water	Solid	Fine (wt.% of solids)
8.2	8.3	83.5	15.4

Table 3.2. Chemistry of process water used for flotation test

Concentration of ions (ppm*)						pH
Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	HCO_3^{-}	CO_3^{2-}	
40	17	570	19	580	BDL	8.2

* milligram (mg) of ion per liter (L) of process water.
BDL: Bellow detection limit

3.2.2 Flotation test

A 1 liter Denver cell was used to perform the bitumen flotation test. The temperature was kept constant at 45°C by a water jacket connected to a thermal bath, while the concentration of sodium hydroxide (NaOH) added to oil sand ores was varied from 0 to 0.5 wt.% (weight of oil sands). For each test, 500 g of oil sands were dispersed in 900 g of process water (at 45 °C) with the required sodium hydroxide addition. NaOH was dissolved in process water prior to each flotation test. This slurry was mechanically agitated at 1500 rpm for five minutes (conditioning stage) and the froth was collected. Air was then introduced at 150 mL/min and froth was collected for additional ten minutes (Zhou et al., 2004).

3.2.3 Preparation of tailings water

The tailings water, which remained after each flotation test was centrifuged at 20,000 g for 30 minutes. The supernatant was then filtered three times using a 0.1 μm vacuum filter to remove all solids. The tailings water was then used for surfactant analysis and atomic absorption spectroscopy (AAS) analysis.

3.2.4 Atomic absorption spectroscopy (AAS)

Atomic adsorption spectroscopy (AAS) is an analytical technique that is used for quantitative analysis of chemical elements in a sample by measuring the absorbance of radiation by the chemical element of interest. Every atom has its own distinct absorbance wavelengths. Absorbance is directly proportional to the concentration of the analyte, which enables the qualitative analysis of a sample. The concentration is usually determined from a calibration curve obtained using standards of known concentration. In this study, AAS technique was used for determining concentrations of Na^+, K^+, Ca^{2+}, Mg^{2+} ions in tailings water samples.

3.2.5 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR measures adsorption of IR radiation by functional groups at specific wavelengths. This technique shines a beam containing many frequencies of light at once and measures the absorbance of the beam by the sample. The functional groups and molecular bonds in the sample are inferred from the spectra. The working principles of FTIR are shown in Figure 3.2. The instrument consists of a light source, a beam splitter, a fixed and a moving mirror and a detector. The beam splitter divides the beam from the source into two optical beams. A half goes to fixed mirror and the other half goes to moving mirror. Both beams recombined at the beam splitter and they transmit to the sample. Because the beam, which is reflecting off from the moving mirror is travelling different distances as the mirror is moving, the recombined beam includes different frequencies. The combination of beam splitter, fixed and moving mirror is called interferometer. The beam produced by interferometer is then reflected to the sample. The resulting signal from the detector, which is called interferogram (raw data) is processed and converted to a spectrum (light absorption at each wavenumber) by Fourier Transform algorithm.

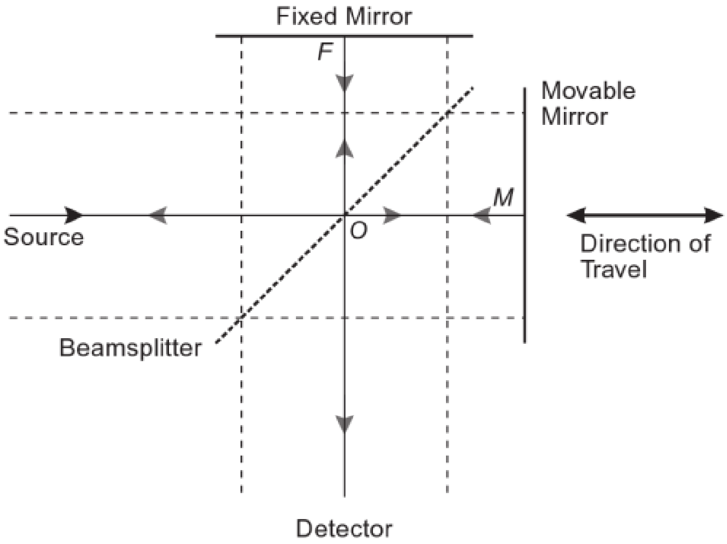

Figure 3.2. FTIR diagram (Griffiths et al., 2007)

3.2.5.1 Using FTIR to characterize solid samples

In this work, the spectra of solid samples were collected using a BioRad, FTS 6000. For the characterization of solid samples, the FTIR spectra of the samples were collected using the Diffuse Reflectance Infrared Fourier Transform technique (DRIFT), Figure 3.3. In this technique the sample should be used in powder form and diluted by well-mixing matrix such as KBr (1 - 5 % of sample in KBr on weight basis). KBr is used because it transmits most of IR radiation. This technique is conducted by focusing mid-infrared (4000-400 cm^{-1}) light onto the powder. The reflected light is then collected and sent to the IR detector. A Mercury Cadmium Telluride (MCT) detector was used. The detector was cooled down using liquid nitrogen at least 20 minutes before performing any measurements and the measurement cell was continuously purged by dry air. The background (KBr) and sample spectra were obtained following 128 co-added scans between the wavenumber ranges of 4000-400 cm^{-1}. The instrument resolution was set at 4 cm^{-1}.The reflectance is correlated with the concentration of the sample by the Kubelka-Munk function (Griffiths et al., 2007).

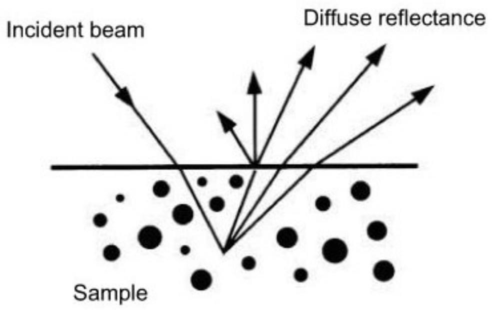

Figure 3.3. Schematic of reflected light from a powder sample in DRIFT analysis (Smith et al., 2009).

3.2.5.2 Using FTIR to analyze carboxylic surfactant in tailings water

In FTIR method, intensity of IR bands corresponding to carboxyl group (COOH) was used to quantify the concentration of carboxylic acids. FTIR method was used for quantification of naphthenic acids in oil sand process water (OSPW) or tailings water (Jivraj et al., 1995; Scott et al., 2008; Clemente and Fedorak, 2005). Naphthenic acids are categorized as a complex mixture of alkyl-substituted cyclic and acyclic aliphatic carboxylic acids (RCOOH). However, other types of carboxylic acid in the sample, e.g.

carboxylic acid with aromatic rings, can also contribute to the FTIR signals. Therefore, intensity of FTIR signals represents to the total concentration of all COOH groups in the sample.

For the extraction of carboxylic acids in tailings water samples, 50 g of tailings water were acidified to pH 2.3 using reagent grade hydrochloric acid (Fischer Scientific) of different molarities (10, 5 and 0.5 M). The carboxylic surfactants were removed from acidified tailings water by liquid-liquid extraction, using 2:1 volume ratio of tailings water to Optima grade dichloromethane (DCM) (Fisher Scientific). The extraction step was repeated three times to recover nearly all of the carboxylic surfactants. The DCM extracts were combined and then placed in a vented fume hood to evaporate the solvent under the filtered air (45 μm filter). The remaining residue was re-dissolved in 20 g of fresh DCM and the sample was analyzed by FTIR (Bio-Rad FTS 6000, Cambridge, USA) using KBr super sealed liquid cell. DCM was used as background.

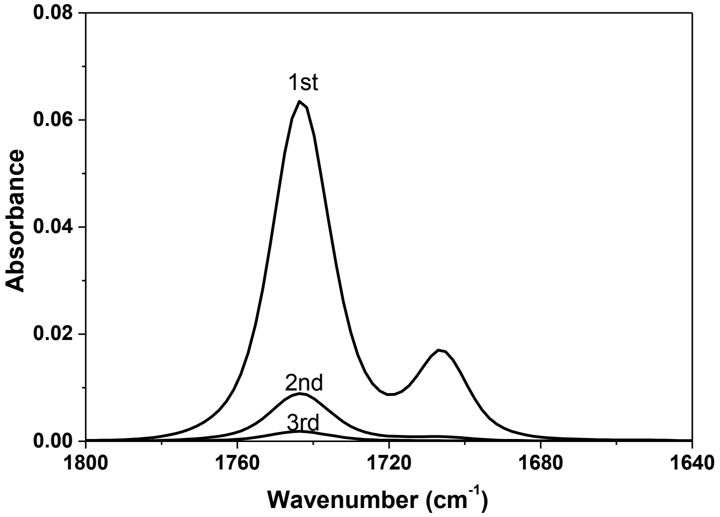

Figure 3.4. FTIR absorbance spectra of extracted carboxylic surfactants from tailings water in three steps.

Figure 3.4 shows FTIR spectrum after each extraction step. It is clear that after three extraction steps the amount of carboxylic compounds left in the sample may be considered negligible. To determine the concentration of carboxylic surfactant, the measured area under the peaks or absorbance intensity of the carboxyl functional groups at ~1743 (monomer) and ~1706 cm^{-1} (dimmers), which are the frequencies of carbonyl stretching vibration (shown in Figure 3.5), were equated to calibration curve value of known dilution that was made using standard solutions.

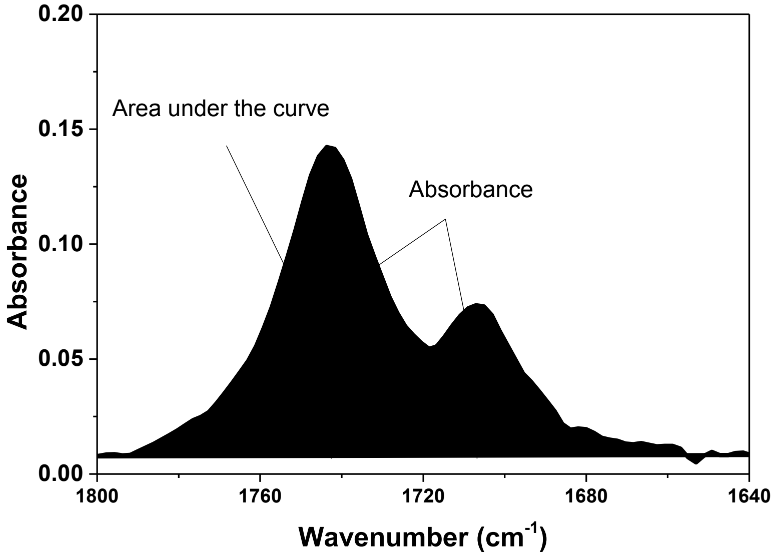

Figure 3.5. FTIR Absorbance spectrum of the carboxylic acids extracted from tailings water sample. DCM was used to extract carboxylic surfactants.

The following standards were used to make calibration curves:

- Sigma commercial mixtures of naphthenic acids
- Carboxylic acids extracted from tailings water (section 3.2.6)
- Four different standard model compounds (Figure 3.1)

In order to make the calibration curve, the stock solution of each standard with known concentration was first prepared in DCM. Diluted solutions of different concentrations were then made using the stock solution. The combined absorbance intensity or area under the peaks for each standard solution at ~1743 and ~1706 cm^{-1} were then plotted as a function of concentration of the standard sample. Based on the slope and the intercept of linear calibration curve and the measured IR absorbance of extracted sample, the concentration of extracted carboxylic surfactants can be determined. The calibration curve was updated every 3-4 months depending on the frequency of using the KBr super sealed liquid cell.

3.2.6 Extracting carboxylic acids from tailings water to prepare calibration curve

For comparison purpose, a calibration curve was prepared using real carboxylic acids (the ones which exist in tailings water) and was compared with the calibration curve prepared with Sigma NAs. In order to prepare calibration curve with the real carboxylic acids, 500 g of filtered tailings water (prepared with 0.5 wt. % NaOH addition to flotation test) was acidified (pH 2.3). The acidified tailings water was then extracted for carboxylic acids using liquid-liquid extraction method with DCM (Rogers et al., 2002). The DCM extracts, which contained the neutralized carboxylic acids, was then dried under the fume hood. The residue after the DCM was evaporated is called dichloromethane extracted residue (DCMER) in this work and was used to make calibration curve.

3.2.7 Extraction of humic acids from tailings water

Humic acids were released in tailings water when high dosage of NaOH (0.5 wt.% NaOH) was used to perform the flotation test. For characterization purposes, humic acids were extracted from tailings water. For this end, tailings water (0.5 wt.% NaOH) was first acidified to pH 2.3. However, acidification of tailings water precipitated both carboxylic surfactants and humic acids. In order to obtain humic acids only, the sample of the acidified tailings water was first extracted with DCM for extraction of carboxylic acids. In the extraction step as shown in Figure 3.6, the precipitated humic acids were placed between the DCM and acidified tailings water. DCM phase was then decanted from the separation funnel and the extraction step was repeated two more times. The residue (tailings water and humic acids) was transferred to centrifuge tube (30 ml) and centrifuged (at 12000 g) for 20 min. The supernatant was discarded and precipitates of humic acids were collected and dried under the fume hood.

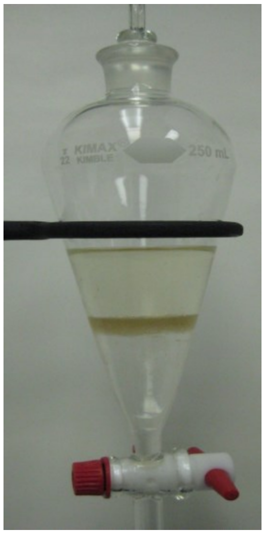

Figure 3.6. Extraction of acidified tailings water (0.5 wt.% NaOH) with DCM

3.2.8 Preparation of carboxylic surfactants - free tailings water (CSFTW)

Tailings water was stripped off carboxylic surfactants by extraction of acidified (pH 2.3) tailings water using DCM. The extraction step was repeated three times, and each time the DCM phase was separated. The resulted aqueous phase was then collected in a bottle and used for other experiments.

3.2.9 Surface tension measurement

Surface active materials lower the surface tension of solutions; hence surface tension measurement[*] is a suitable method to illustrate the presence of surfactants in tailings water. Surface tensions of tailings water were measured at room temperature using Processor Tensiometer K12 (Krüss, Hamburg, Germany). Flat Wilhelmy plate method was used for surface tension measurement. Accuracy of the instrument before each series of measurements was validated using Milli-Q® water (72.8 mN/m at room temperature). Any contaminant on the platinum plate was burnt with butane burner before each run. For each test, tailings water was placed in the a glass container and it was let to settle for 5 minutes. The measurements were then carried out three times for each sample. The plate was cleaned by rinsing with Milli-Q® water and burned by butane burner between the measurements.

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[*] The equations used for measuring surface tension of a liquid using flat Wilhelmy plate are shown in Appendix A.2.

3.3 Results and discussion

3.3.1 Quantitative analysis of carboxylic surfactant using DCM extraction method and FTIR analysis

For quantification of carboxylic surfactants using FTIR method, a calibration curve must be established as described in the materials and methods section. In order to find which calibration curve suits best for quantification of carboxylic surfactants in tailings water, both mg/L (ppm) and mol/L basis calibration curves were made and compared. Sigma commercial mixture of naphthenic acids, DCMER and individual compounds of naphthenic acids were used to prepare calibration curves.

3.3.1.1 Calibration curve in mg/L (ppm) prepared with Sigma NAs*

The commercial mixture of NAs is the most common standard NAs used for constructing calibration curve. Calibration curve was made by preparing a stock solution of ~1000 ppm Sigma NAs in DCM. Stock solution was then diluted to make NAs solutions at different concentrations. Shown in Figure 3.7 are the FTIR spectra for NAs solutions at various concentrations. As shown the absorbance at 1737 and 1699 cm^{-1} wave numbers, which correspond to COOH group (monomer and dimer), increases with the concentration of NAs in the samples.

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* In this chapter mg/L (or ppm) is milligram (mg) of naphthenic acids or carboxylic acids sample per liter (L) of water sample (Milli-Q water or process water).

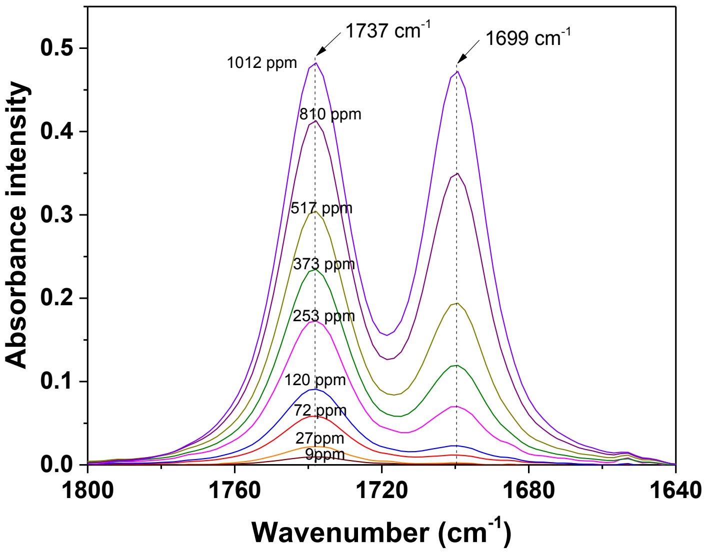

Figure 3.7. FTIR spectra of Sigma NAs in DCM at different concentrations

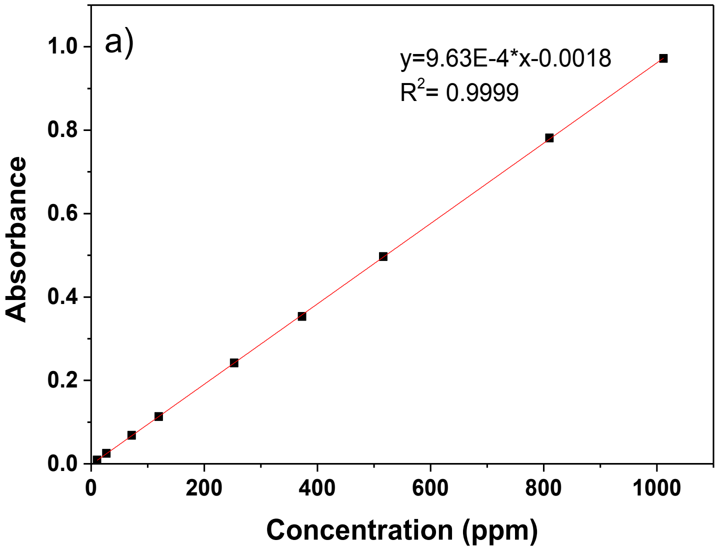

Figure 3.8. Calibration curves prepared with Sigma NAs

The corresponding total absorbance at 1737 and 1699 cm^{-1} versus concentration of NAs was plotted in Figure 3.8. The calibration curve exhibits good linearity.

3.3.1.1.1 Validation of DCM extraction method and FTIR analysis for quantification of COOH groups using calibration curve in mg/L (ppm) prepared with Sigma NAs

Solutions of known concentrations of commercial mixture of Sigma NAs were prepared in strongly basic (pH~12.2) solutions in Milli-Q® water. The solutions were extracted for naphthenic acids using DCM. The concentrations of extracted NAs were then calculated based on the measured IR absorbance values, using the standard calibration curve. Table 3.3 compares the actual concentrations of Sigma NAs solutions in Milli-Q® water with the measured concentrations using FTIR method. The maximum error in measurement was 4.8 %.

Table 3.3. Validation of DCM extraction method and FTIR analysis using calibration curve in mg/L (ppm) made with Sigma NAs

Sample	Actual concentration (ppm)	Measured concentration by FTIR (ppm)	Error (%)
1	20.8	21.8	4.8
2	50.4	52.6	4.3
3	103.8	99.3	4.3
4	200.9	192.3	4.2
5	316.0	306.6	2.9
6	496.3	486.3	2.0

3.3.1.2 Calibration curve in mg/L (ppm) prepared with DCMER

In this section before making calibration curve made with DCMER, mass spectrometry analysis of DCMER and Sigma NAs was performed to understand the difference between the carboxylic compounds exist in DCMER and Sigma NAs.[*] Shown in Figure 3.9 is the comparison between the results for Sigma NAs and DCMER obtained at negative charge mode analyzed by Electrospray Ionization Fourier Transform Ion Cyclotron Resonance (ESI-FT-ICR) Mass Spectrometry. The mass spectra in Figure 3.9 indicate that the relative distribution of carboxylic acids in DCMER is different from Sigma NAs. Also, the total number of peaks is higher in DCMER than in Sigma NAs. Naphthenic acids are identified with the general formula of $C_nH_{2n+z}O_{2,}$ where n is the carbon number and z refers to the hydrogen deficiency due to a ring formation (z = 0, -2, -4, -6,…). According to the mentioned formula of NAs, the major type of NAs found in Sigma NAs, have z = 0 or -2 while the NAs from DCMER predominantly have z = -4 or -6 showing that the DCMER sample has more cyclic or aromatic NAs. In the comprehensive study carried out by Grewer et al. (2010) on characterization of naphthenic acids from various sources, the same types of NAs (z = -4 or -6) were reported as the primary NAs in the OSPW.

In Figure 3.10, mass spectra of both samples between the m/z range of 236.9-239.9 are shown. As shown in the same (m/z) region, the number of peaks is higher for DCMER sample. The peaks marked as "?" shows the materials that do not match the classical formula of naphthenic acids. These materials could either be an oxy acids ($C_nH_{2n+z}O_x$, x=3, 4,..) or other DCM extractable materials (Grewer et al., 2010). The presence of DCM extractable materials can certainly affect the accuracy of the calibration curve.

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[*] Mass spectrometry of two other commercial mixtures of NAs for comparison purpose is shown in Appendix A.3.

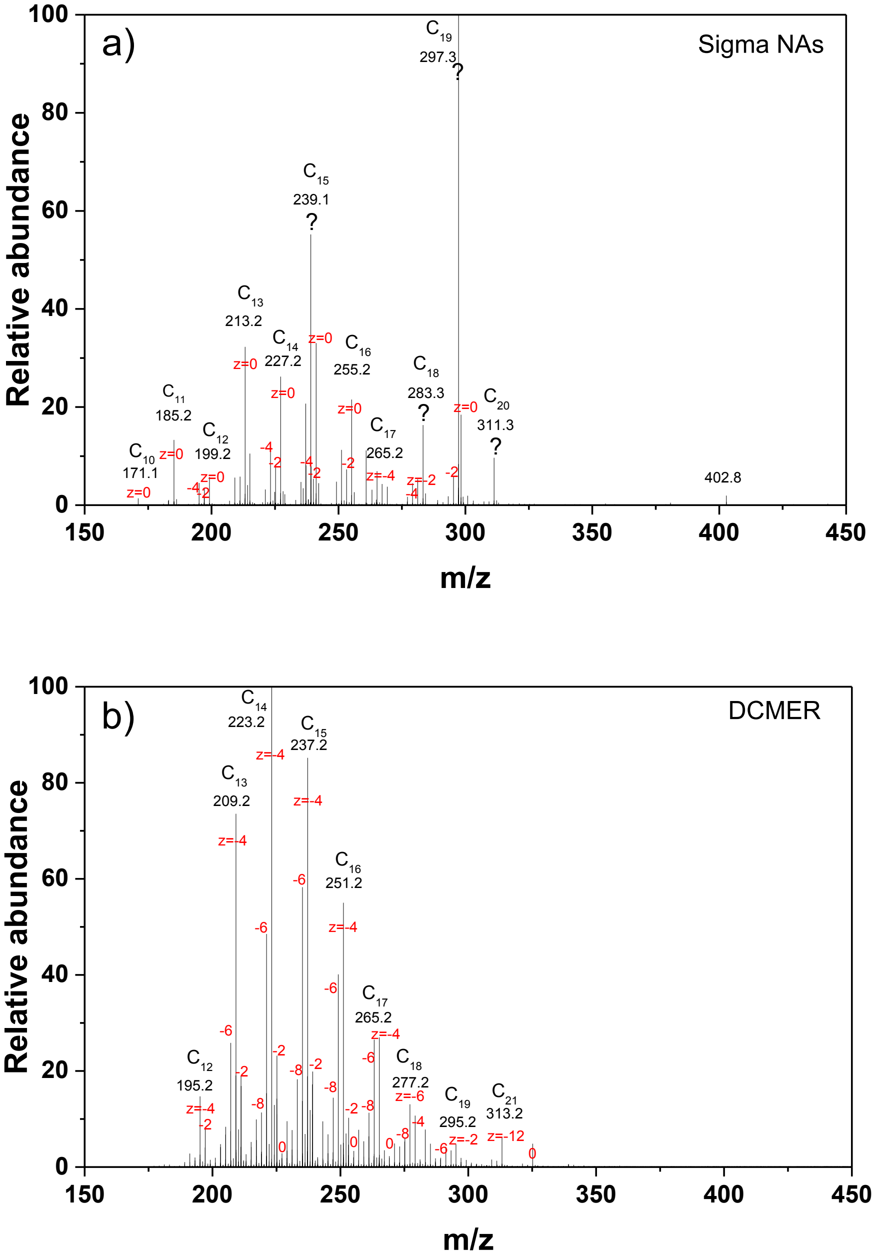

Figure 3.9. ESI-FT-ICR mass spectrometry of a) Sigma NAs and b) DCMER

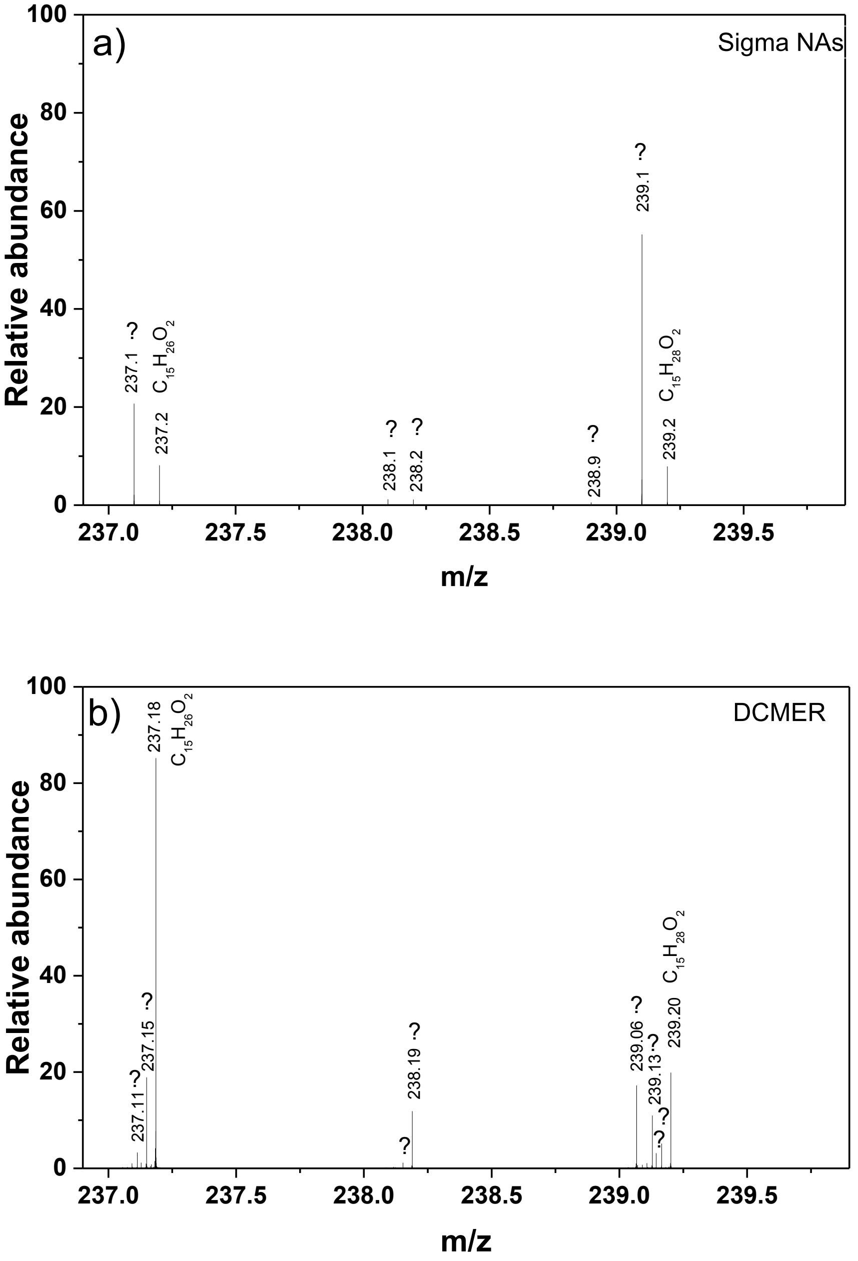

Figure 3.10. Mass scale expanded mass spectra of: a) Sigma commercial mixture of NAs and b) DCMER

The calibration curve made with DCMER was compared with the one made with Sigma NAs in Figure 3.11. As shown, at the same mass concentration in mg/L (ppm), the

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Sigma NAs sample exhibits higher IR absorbance, indicating the presence of more carboxyl group than DCMER. One possible explanation could be the compositional difference between the two samples. If the Sigma NAs contains more NAs with smaller molecular weight (MW), the molar concentration of carboxyl group will be higher in the sample. However, this is not the case here. Based on the ESI mass spectra (Figure 3.9), the DCMER actually contains more carboxylic acids distributed at lower m/z, with average MW of 244 g/mol comparing to Sigma NA, 254 g/mol. Another possible explanation could be the interference of other organic materials co-extracted from tailings water.

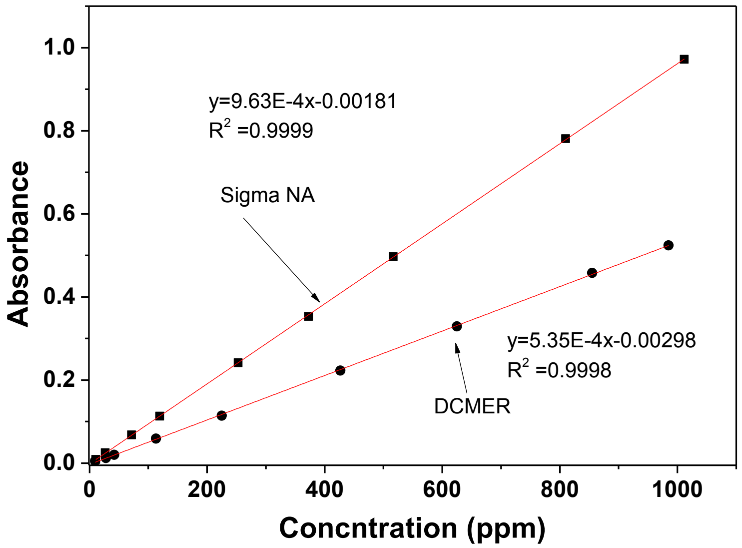

Figure 3.11. Comparison of mg/L (ppm) calibration curves prepared with Sigma NAs and DCMER.

In the research study conducted by Martin et al. (2008) using High Performance Liquid Chromatography/ Electrospray Ionization High Resolution Mass Spectrometry (HPLC/ESI HRMS), it was also shown that the response of the extracted NAs from oil sands process water diverges significantly from the commercial mixture of NAs. It was reported that this difference is due to the impurities co-extracted with naphthenic acids.

3.3.1.2.1 Validation of DCM extraction method and FTIR analysis for quantification of COOH groups using calibration curve in mg/L (ppm) prepared with DCMER

Solutions of DCMER in Milli-Q® water at pH 12.2 were prepared and solutions were extracted with DCM for carboxylic acids. FTIR was then used to measure the concentration of COOH group using calibration curve in mg/L prepared with DCMER. As shown in Table 3.4, the error in the measurements was less than 5% indicating that calibration curve made with DCMER works well for quantification of COOH groups in the solutions made with DCMER.

Table 3.4. Validation of DCM extraction method and FTIR analysis using calibration curve in mg/L (ppm) made with DCMER

Sample	Actual concentration (ppm)	Measured concentration by FTIR (ppm)	Error (%)
1	123	117.5	4.4
2	24.6	23.6	4.0

3.3.1.3 Calibration curves in mol/L using Sigma NAs and DCMER

Since the IR absorbance is proportional to molar concentration of carboxyl group, the calibration curves using molar concentrations (mol/L) were also created and compared. Using average molecular weight of Sigma NAs and DCMER obtained from ESI-FT-

ICR MS analysis, calibration curves in mol/L for both Sigma NAs and DCMER were plotted in Figure 3.12. As shown in Figure 3.12, the calibration curves in mol/L basis were also not converging and resulted in different concentrations of COOH group for the same IR absorbance intensity. The reason for this observation as discussed earlier is most probably due to the presence of other DCM extractable materials which are non-carboxylic compounds that contribute to the weight of the sample used for making calibration curve and calculation of average molecular weight.

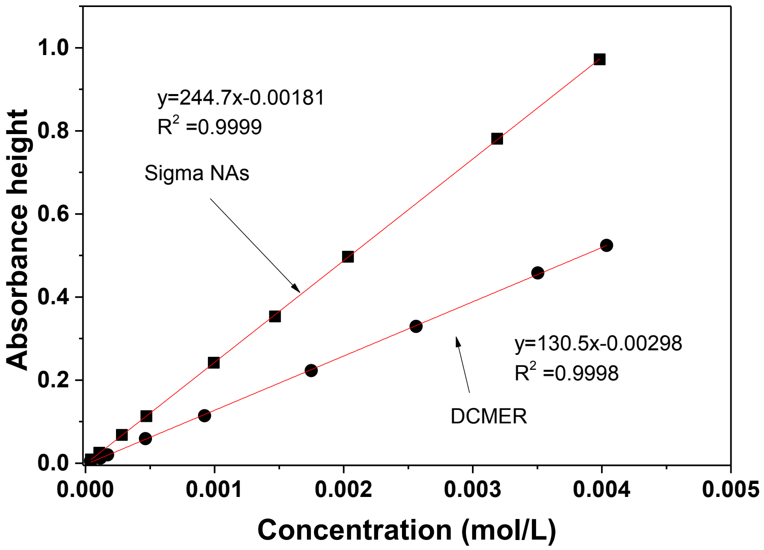

Figure 3.12. Comparison of mol/L calibration curves prepared with Sigma NAs and DCMER

The results of FTIR analysis for quantification of COOH group in solutions made with Sigma NAs and DCMER in Milli-Q® water suggest that each calibration curve can accurately predict the concentration of COOH groups when it is used to measure the concentration of the same sample in its solution. However, in case of quantification of carboxylic acids in the tailings water, for the same IR intensity each of these calibration curves will measure completely different concentrations. To find the best option for choosing calibration curve, which can predict concentration of carboxylic acids in different samples; calibration curves of known model compounds of naphthenic acids with known molecular weight on different basis (mg/L and mol/L) were prepared and compared. The results are shown in the next section.

3.3.1.4 Calibration curves prepared with four standard model compounds of naphthenic acids

Four different model compounds of NAs: 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) were used to make calibration curves. Figures 3.13a and b show the FTIR spectra of the four individual standards in solid phase (mixed with KBr) and liquid phase (dissolved in DCM). As shown in solid phase there is only one peak representing carbonyl functional group. The band is shown at 1700 cm^{-1} while in liquid phase two absorbance peaks correspond for carboxyl functional group (monomers and dimmers), which are slightly different for each compound and vary around ~1740 and ~1705 cm^{-1} wave numbers.

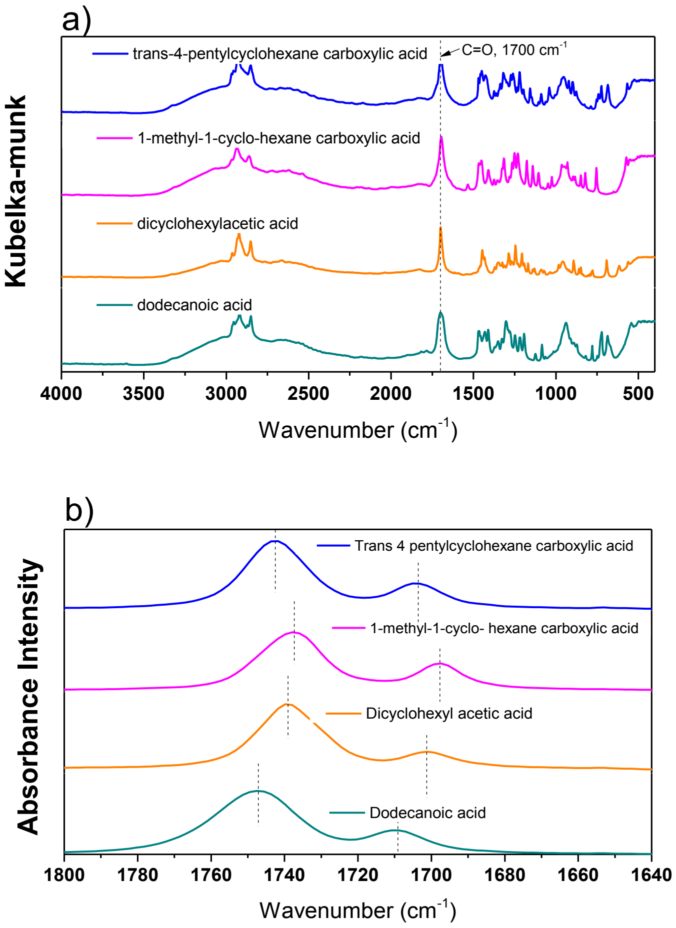

Figure 3.13. FTIR spectra of four standard model compounds of carboxylic acids, a) in powder form, mixed with KBr b) in liquid form, dissolved in DCM

Calibration curves based on mg/L (ppm) or mol/L versus absorbance or area under the peaks have been plotted in Figure 3.14. In general, mol/L calibration curves were converging (Figure 3.14 c and d) while mg/L (ppm) calibration curves didn't (Figure 3.14 a and b). These results show that the calibration curve in mg/L (ppm) unit can only be used to quantify the exactly same sample. In fact, the theory of IR to quantify NAs is based on the molar concentration of COOH group in the sample. Here, molar concentration of COOH is equal to molar concentration of model compound and that's why in Figures 3.14 c and d, all the curves almost collapsed and became independent of type of the model compound.

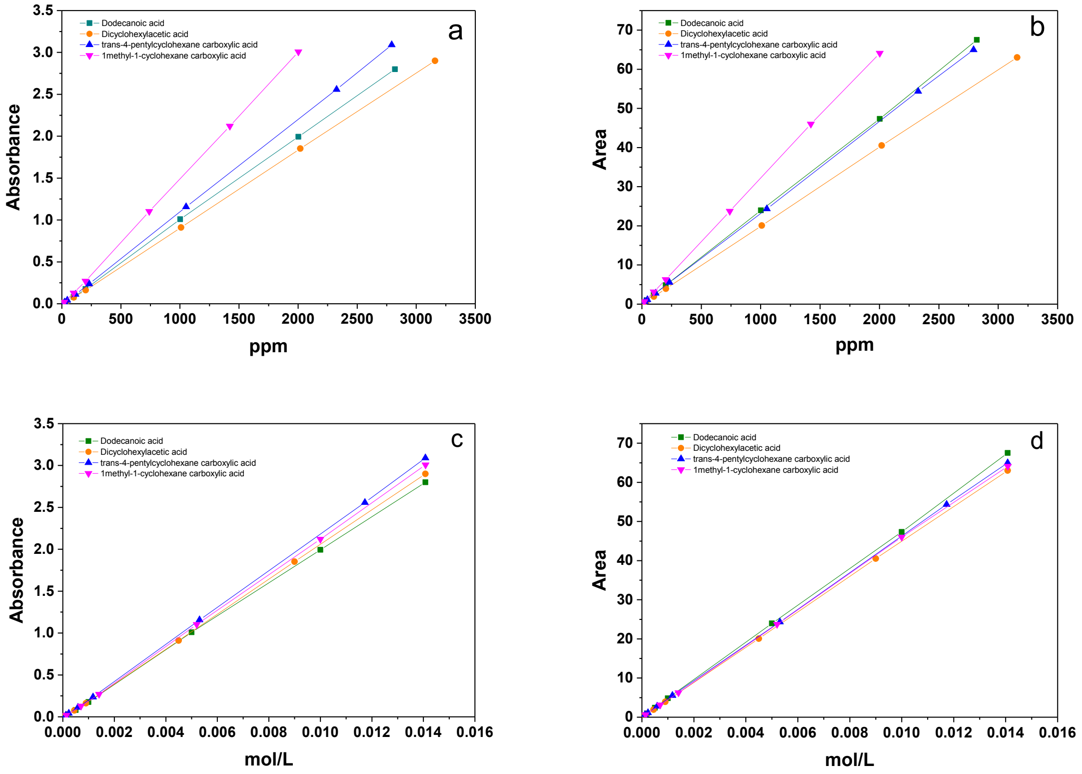

Figure 3.14. Calibration curves for individual model compounds: a) ppm as a function of absorbance, b) ppm as a function of area under the peaks, c) mol/L as a function of absorbance height d) mol/L as a function of area under the peaks

In Figure 4.13, calibration plots of area vs. concentration (mol/L) better collapsed; however DCM extracts of tailings water may contain impurities that can contribute to the peak area of the COOH groups. Hence, absorbance vs. concentration (mol/L) data points was used to make a unique calibration curve as shown in Figure 3.15.

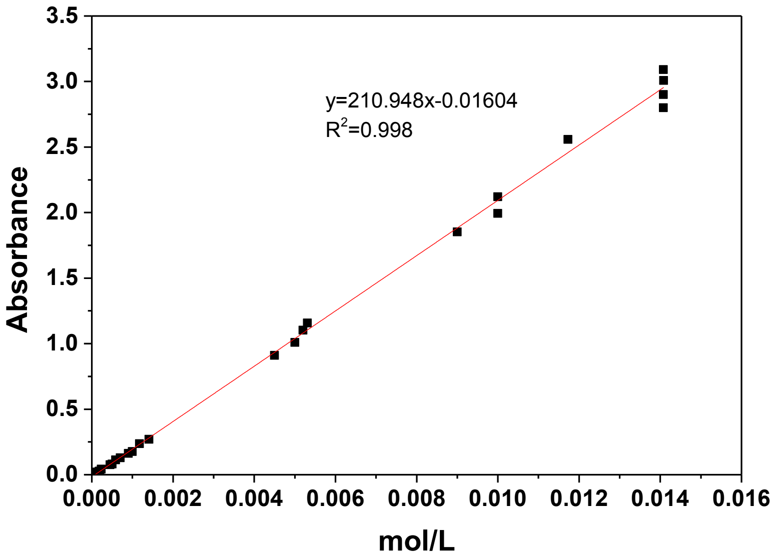

Figure 3.15. Calibration curves made with four model compounds, a) absorbance vs. mol/L, b) area vs. mol/L

3.3.1.4.1 Validation of DCM extraction method and FTIR analysis for quantification of COOH groups using calibration curve in mol/L prepared with model compounds

Solutions of mixtures of model compounds in Milli-Q® water (pH 12.2) were prepared at known concentrations. DCM extraction was used to extract COOH functional groups from the solutions. FTIR method was then used to quantify the COOH group using the mol/L calibration curve prepared with model compounds of naphthenic acids. Table 3.5 compares the concentration of COOH group in standard solutions measured by DCM extraction method followed by FTIR analysis using calibration curve in Figure 3.15a with the actual concentration of COOH group in the solutions. The accuracy of the measurements was validated according to the results shown in Table 3.5.

Table 3.5. Validation of DCM extraction method and FTIR analysis using calibration curve prepared with model compounds

Solution	Dicyclohexyl acetic acid (10^{-4} mol/L)	Dodecanoic acid (10^{-4} mol/L)	Trans -4- pentylcyclohexyl carboxylic acid (10^{-4} mol/L)	1 methyl-1- cyclohexane carboxylic acid (10^{-4} mol/L)	Total actual conc. (10^{-4} mol/L)	Measured conc. with FTIR (10^{-4} mol/L)	Error %
1	5.40	3.09	-	-	8.49	8.14	4.16
2	1.08	0.62	-	-	1.70	1.64	3.24
3	-	-	4.52	5.15	9.67	10.20	5.21
4	-	-	0.90	1.03	1.93	2.00	3.29

3.3.2 Release of humic acids from oil sands ore in flotation tests performed at high dosage of NaOH

In DCM extraction of tailings waters, which were prepared by addition of 0.5 wt. % NaOH to the flotation test, a precipitate layer was formed between the aqueous and DCM phase (Figure 3.16). This precipitate layer was formed neither in the tailings water prepared with low dosage of NaOH nor in the standard solutions of NAs prepared in Milli-Q water at high pH. The observed precipitate layer as it is discussed later in this chapter is mostly consisting of humic acids (HAs). The release of humic acids from oil sands ore by addition of sodium hydroxide has been reported also by other researchers (Majid et al., 1992; Gutierrez and Pawlik 2014a).

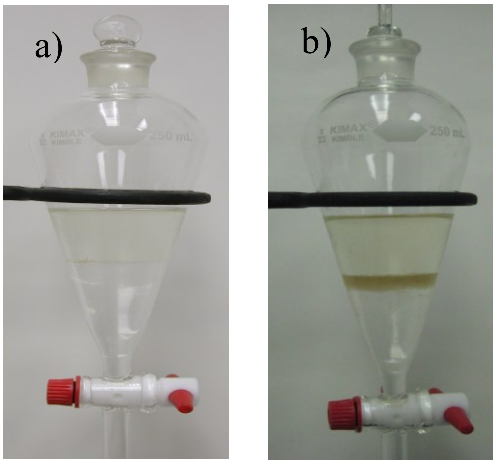

Figure 3.16. Formation of precipitate of humic acids after acidification and DCM extraction of tailings water, a) 0 wt.% NaOH TW , b) 0.5 wt.% NaOH TW

3.3.2.1 Characterization of precipitates

3.3.2.1.1 Colour comparison

Figure 3.17a shows solutions of commercial humic acids (MP Biomedical) in Milli-Q water at different concentrations. As shown, humic acids at very high concentration change the color of water to dark brown.

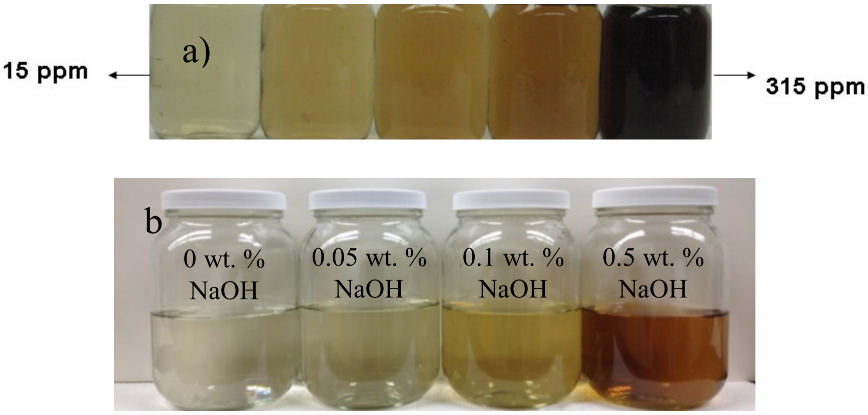

Figure 3.17. Color comparison of a) solutions of commercial humic acids at different concentrations in Milli-Q water with b) tailings water prepared with the addition of different concentrations of NaOH to Denver flotation cell.

Shown in Figure 3.17b are the tailings water samples prepared with MA ore at different NaOH levels. With increasing the amount of NaOH, the color of the tailings water becomes more brownish, indicating the release of more humic acids.

3.3.2.1.2 FTIR, EDX analysis of precipitates

FTIR analysis was performed to further characterize the precipitates. Shown in Figure 3.18 a is the FTIR spectrum of the extracted humic acids from tailings water prepared with the addition of 0.5 wt.% NaOH to flotation test. In order to recognize the main peaks, the spectrum was first compared with FTIR spectrum of commercial humic acids (MP Biomedical) in Figure 3.18 b. Except for the two bands at 640 and 1150 cm^{-1}, which are attributed to the formation of sodium sulphate (shown in Figure 3.19), the wave numbers of the other peaks are very similar to that of humic acids'. The broad absorption band in 2500-3500 cm^{-1} region mainly corresponds to the hydroxyl (O-H) group (in phenol or carboxyl) or N-H bond. It could be also due to the trapped water in the sample. The bands at 2860, 2930 and 2960 cm^{-1} indicate the symmetric and asymmetric stretching vibration of aliphatic C-H groups in the sample. The band at 1720 cm^{-1} is attributed to C=O stretching vibration of COOH and 1608 cm^{-1} is attributed to aromatic C=C or COO^- asymmetric stretching bonds. The band at 1460 cm^{-1} corresponds to C-O stretching of phenolic or C-H stretching of aliphatic group. And the band at 1380 cm^{-1} mostly corresponds to COO^- symmetric stretching bonds (Stuart, 2004; Tatzber et al., 2007).

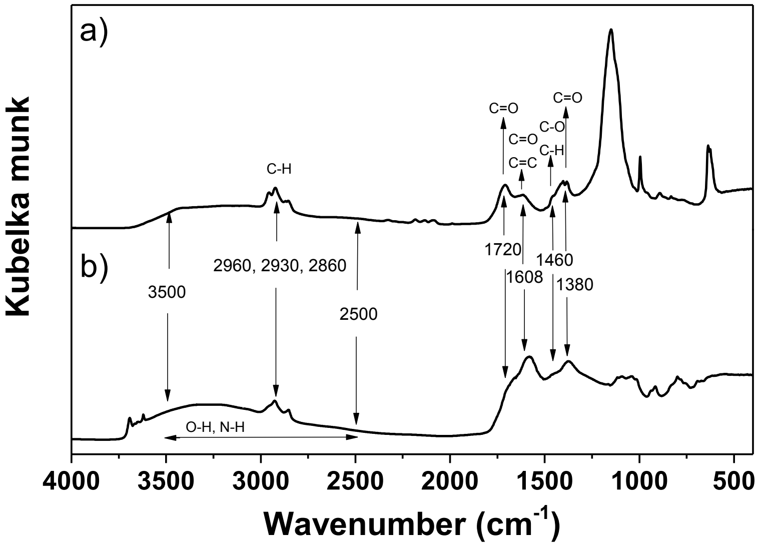

Figure 3.18. FTIR spectra of a) dried precipitate and b) commercial humic acids (MP Biomedical)

In the next step the FTIR spectra of the precipitates were compared with FTIR of Na_2SO_4 shown in Figure 3.19. Na_2SO_4 is formed because of the presence of NaOH (added to the flotation test) and H_2SO_4 (added for acidification).

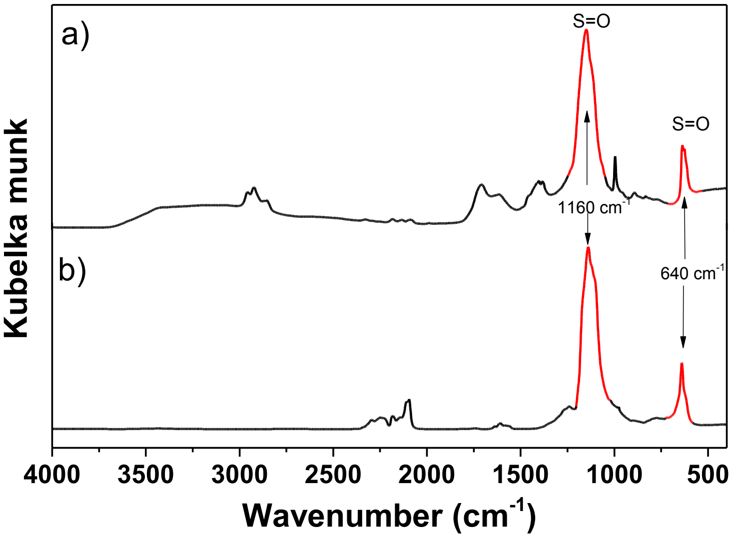

Figure 3.19. FTIR spectrum of: a) dried precipitate and b) Na_2SO_4

The bands at 1150 and 640 cm^{-1} in both spectra in Figure 3.19 are attributed to SO_4^- ions (Foil and Charles, 1952). The presence of sodium sulphate in the precipitate was shown by Energy Dispersive X-ray Spectroscopy (EDX) analysis given in Figure 3.20. The EDX was performed on the white particles found in the dried precipitates.

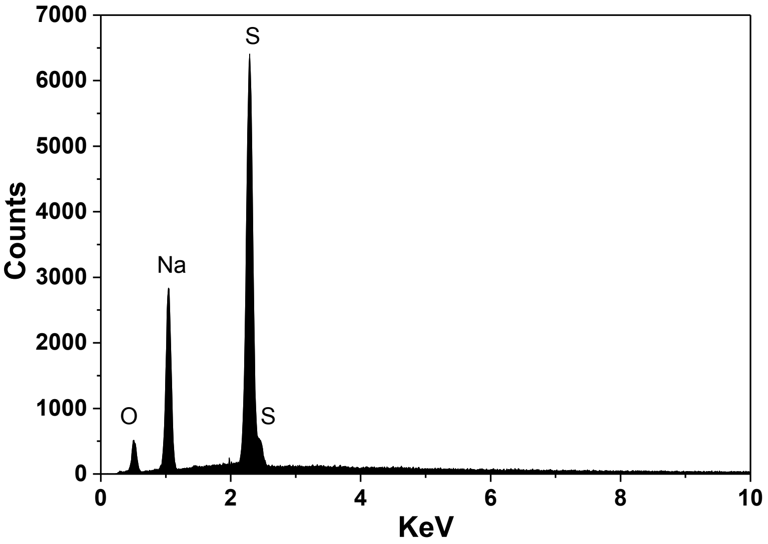

Figure 3.20. EDX analysis of white precipitate

3.3.2.2 Impact of humic acids on quantification of carboxylic surfactant

3.3.2.2.1 Addition of HAs to solutions of Sigma NAs

Humic acids have high content of carboxyl functional groups[*]. In order to understand whether they are co-extracted with carboxylic acids in DCM and affect quantification of carboxylic acids in tailings water the following tests were performed.[*]

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[*] The effect of humic acids on surface tension of Milli-Q water was studied in Appendix A.4.

Solutions of known concentration of HAs and Sigma NAs in Milli-Q at pH 12.2 were prepared. Sigma NAs were used since they contain a wide range of NAs compounds. FTIR analysis was used for quantification of COOH groups in the DCM solutions of extraction. As shown in Table 3.6, the addition of humic acids to NAs solution did not affect the measured concentration of NAs extracted into DCM. The difference in the actual concentration of NAs in the solutions and measured concentrations of NAs is within the error range. Humic acids are not soluble in dichloromethane; hence they are not co-extracted to the DCM phase.

Table 3.6. Addition of HAs to standard solution of Sigma NAs

Solution	NAs (ppm)	HAs (ppm)	NAs concentration measured by FTIR (ppm)	Error (%)
1	102	0	99.8	2.1
2	102	100	99.3	2.6
3	316	0	306.6	2.9
5	316	100	302.1	4.3

3.3.2.2.2 *Addition of Sigma NAs and extracted HAs to carboxylic surfactant-free tailings water (CSFTW)*

This section is to examine if other species in the tailings water such as different inorganic anions and cations or other organic matters can bind or trap carboxylic acids

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[*] Dilution of tailings water was performed to avoid the precipitation of humic acids in the acidification step of FTIR method. The effect of dilution on surfactants quantification is shown in Appendix A.5

and hinder the complete extraction of carboxylic acids in DCM. For this purpose, NAs solutions were prepared in CSFTW. Tailings water prepared with 0 wt.% NaOH (no NaOH was added to flotation test) was used to prepare CSFTW. Solutions of known concentration of NAs in CSFTW were prepared. After performing DCM extraction step, the concentration of NAs was measured by FTIR method. As shown in Table 3.7, the same amount of NAs added to the CSFTW was measured with FTIR, indicating that other species in tailings water did not affect the accuracy of DCM extraction and FTIR method. In a similar test NAs and extracted HAs (obtained from tailings water prepared with 0.5 wt.% NaOH) were co-added to CSFTW and the concentration of NAs was measured. Extracted HAs were used because the structure and properties of HAs from different sources can be different. Addition of extracted HAs also did not impact analysis of NAs in tailings water (Table 3.7) by DCM extraction and FTIR method. The error of the measurement was less than 1%.

Table 3.7. Addition of NAs and extracted HAs to carboxylic surfactants free - tailings water (CSFTW)

Solution	Description	Concentration of NAs added (ppm)	Concentration of NAs measured (ppm)	Error (%)
1	CSFTW + NAs	185.9	187.2	0.69
2	CSFTW + NAs+ Extracted HAs	185.9	184.6	0.96

3.3.2.2.3 Addition of HAs and Sigma NAs to tailings water

In this section, the impact of standard HAs (MP Biomedical) on measurement of COOH group in tailings water with DCM extraction and FTIR method was determined. In addition, co-addition of Sigma NAs with HAs to tailings water was examined. For this purpose solutions of known concentrations of Sigma NAs and commercial HAs in Milli-Q® water at pH 12.2 were prepared. These solutions were added to tailings water (0 wt.% NaOH) as shown in Table 3.8. The total concentration of COOH group in the solutions was measured and compared with actual concentration of COOH group. As shown in Table 3.8, FTIR method led to good results in measurement of COOH functional groups in the sample and the results were not influenced by HAs addition.

Table 3.8. Addition of HAs and NAs to 0 wt. % NaOH tailings water

Sample	**TW (g)**	**NAs Solution* (g)**	**HAs Solution** (g)**	**Carboxylic acids (ppm)**		**Error (%)**
				Actual	**Measured**	
Tailings water	50.0	-	-	-	85.4	-
Tailings water + NAs solution	44.0	6.0	-	95.7	92.3	3.6
Tailings water + HAs solution	44.0	-	6.0	75.1	75.7	0.7
Tailings water + NAs+HAs solutions	40.0	5.0	5.0	85.5	83.0	2.9

* Concentration of Sigma NAs solution: 172 ppm
** Concentration of HAs solution: 194 ppm

3.3.3 Qualitative analysis of sulfonic surfactants in tailings water

In order to qualitatively analyze the presence of other types of surfactants such as sulfonic acids in tailings water, surface tension measurement was performed. Experiments are based on the fact that the presence of surface active materials can reduce the surface tension of solutions (Rosen and Kunjappu, 2012). Using surface tension method to analyze the presence of surfactants in tailings water was also reported by Schramm et al. (1984).

3.3.3.1 Study the presence of surface active materials in CSFTW

Surface tension measurement of tailings water was performed before and after extraction of carboxylic surfactants and the result are illustrated in Figure 3.21. Increase of surface tension of tailings water after extraction of carboxylic surfactants to ~71 mN/m (very close to surface tension of de-ionized water (72.8 mN/m)) indicates that the amount of surfactants left in the tailings water should be very small or negligible. This test was conducted for tailings water obtained from four different ores prepared with different NaOH dosage. Same conclusion was drawn for all of them. AB and CNRL were high fines ores (20% <fines content < 40%) and MA and AZ were average fines ores (fines content < 20%).

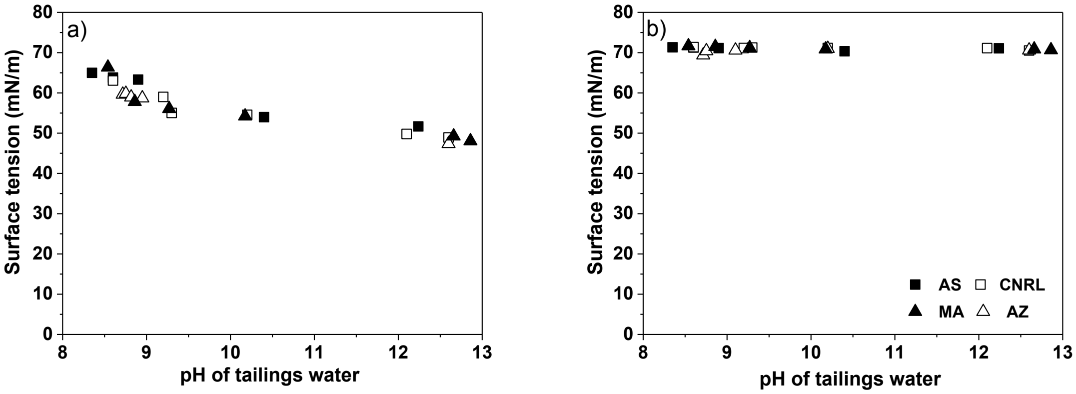

Figure 3.21. a) Surface tension of tailings water, b) surface tension of tailings water after extraction of carboxylic surfactants. Tailings water samples were prepared with the addition of variable NaOH dosage to flotation test (reflected in pH of tailings water).

3.3.3.2 Study the presence of surface active materials in precipitated humic acids

Extraction of carboxylic surfactants in DCM extraction method was performed at pH=2.3. At this pH humic acids were precipitated in the tailings waters prepared with the addition of 0.5 wt. % NaOH. In order to examine whether any surface active materials have been trapped in the precipitated layer while performing DCM extraction step, the following test was carried out. Precipitated HAs from 50 g of tailings water after extraction of carboxylic surfactants was dissolved in 50 g of Milli-Q® water and the surface tension of the solution was measured. Figure 3.22 compares the surface tension of tailings water of three ores (prepared with 0.5 wt.% NaOH) and extracted HAs solutions in Milli-Q® water at pH 12.2. As shown, surface tensions of HAs solution in Milli-Q® water is very close to 72.8 mN/m, indicating that the precipitated HAs did not carry or trap any surface active materials.

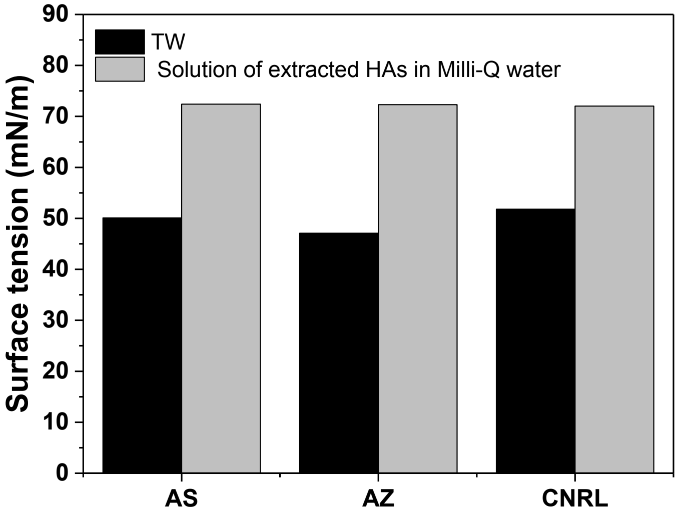

Figure 3.22. Comparison of the surface tension of tailings water samples prepared with the addition of 0.5 wt.% NaOH to flotation test with solutions of extracted HAs in Milli-Q® water.

3.3.3.3 Study the extractability of sulfonic acids in DCM at pH 2.3

Average pKa value of carboxylic acids is ~4.5 and extraction of carboxylic surfactants from tailings water was carried out at pH 2.3. Although the average pKa value of sulfonic acids is ~1 or even lower, in order to understand if any sulfonic surfactants have been extracted to DCM phase in the extraction process, the following test was performed. Solutions of standard sulfonic acids in tailings water (0 wt. % NaOH) were prepared at different concentrations: 0, 25 and 50 ppm. Carboxylic surfactants were then extracted. Surface tension of the tailings waters was measured before and after extraction of carboxylic surfactants. For both sulfonic acids model compounds, surface tension of the tailings water dropped after addition of sulfonic acids to the tailings water (Figure 3.23), with dodecylbenzene sulfonic acid showing more surface activity.

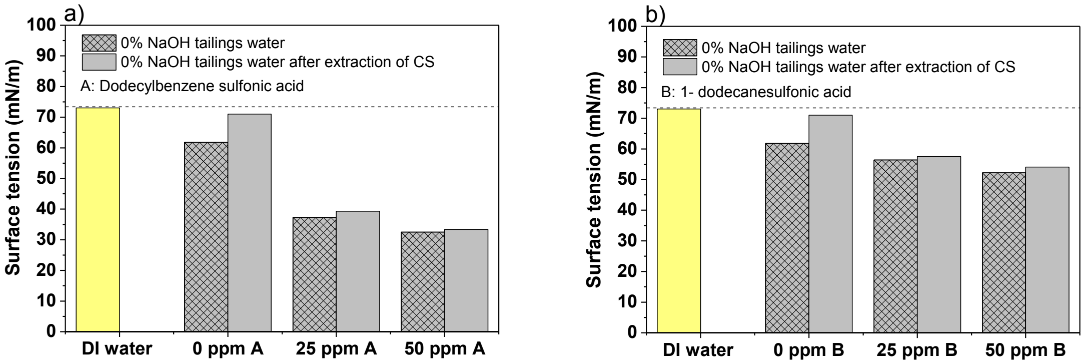

Figure 3.23. Effect of addition of sulfonic acids model compounds on surface tension of tailings water, a) dodecylbenzene sulfonic acid, b) dodecanesulfonic acid

Extraction of carboxylic surfactants at pH 2.3 increased only slightly the surface tension of tailings water, which shows that sulfonic acids in the tailings water were not co-extracted with carboxylic acids to DCM phase. Therefore, it can be concluded that carboxylic surfactants are the major surfactants in the tailings water and the amount of sulfonic surfactants (the other type of anionic surfactant) in tailings water is very small or insignificant.

3.4 Conclusions

In this chapter DCM extraction with FTIR method was validated for measuring the concentration of free carboxylic surfactants in tailings water. It was found that the concentration of the measured carboxylic surfactants is very much dependent on the choice of calibration curve used for FTIR analysis. The results showed that the mg/L (ppm) calibration curve can accurately predict the concentration of carboxylic or naphthenic acids in the solution when it is used for quantification of exactly the same sample. However, for the samples with unknown carboxylic acids compounds it is better to use the mol/L calibration curve, which is made with standard model compounds. The results indicated that despite the type and molecular weight of the model compounds, each mol of the studied compounds resulted in the same IR absorbance, which makes them an appropriate option for preparation of calibration curve.

It was also shown that humic acids were released from oil sands ore when high dosage of NaOH was added to flotation tests. Role of humic acids on quantification of carboxylic acids were studied in both standard solutions and tailings water samples. According to the results humic acids did not affect quantification of carboxylic surfactants using DCM extraction with FTIR method.

Increase in the surface tension of tailings water after extraction of carboxylic surfactants to the surface tension of de-ionized water (72.8 mN/m) confirmed that the amount of other surface active materials (sulphuric/sulphonate type of surfactants) in the tailings water was negligible. Using standard model compounds, it was shown that sulfonic surfactants with pKa values of ~1 were not co-extracted with carboxylic surfactants in DCM phase at pH of extraction (2.3).

CHAPTER 4

4 Effect of Ores' Characteristics on Production of Natural Surfactant from Oil Sands Ores by NaOH Addition

4.1 Introduction

Variability in ore composition and process chemistry makes ores to respond differently to NaOH addition in production of natural surfactants. It has been shown that at a given NaOH dosage different grades of ores produced different amount of surfactants (Schramm et al., 1984; Schramm and Smith, 1987a). The NaOH added can react with other compounds which consume NaOH and affect the production rate of surfactants. Examples of these compounds are divalent cations, polyvalent metal carbonates and sulfates (Smith and Schramm, 1992). In addition, adsorption of surfactants on the surface of mineral clays can also reduce the concentration of free surfactants in oil sands process water (Smith and Schramm, 1992; Amirianshoja et al., 2013). Weathering/oxidizing of ores also has been reported to reduce the rate of surfactant production. Schramm and Smith (1987a) showed that the reduction in the bitumen recovery of weathered ores was due to the low concentration of surfactants released from these ores. It was revealed that the addition of NaOH to weathered/oxidized ores can increase the production of surfactants and enhance bitumen recovery (Schramm and Smith, 1987a; Mikula et al., 2003).

The main objective of this chapter is to investigate the possible relationship between the production of natural surfactants from oil sands ores at different caustic levels with the composition of ores (bitumen, solid and water), mineral composition, connate water chemistry and ore weathering. Effect of divalent cation addition (calcium/magnesium) and weathering of ores on surfactant production and bitumen recovery were studied using Denver floatation cell and Dean Stark.

4.2 Materials and methods

4.2.1 Materials

The oil sands ores used in this study were supplied by Syncrude Canada Ltd. with the exception of CN912, which was supplied by Canadian Natural Resource Ltd. They are classified as: average, high and ultra-high fines ores. The Dean Stark analysis and wet solid sieving were employed to determine the mass content of water, solids, bitumen, and fines (fraction of solids less than 45 μm) in the ores. Certified ACS reagent grade toluene was used for bitumen/ solid/ water analysis using Dean Stark apparatus. The measured composition of ores used in this study is tabulated in increasing order with respect to fines content. Table 4.1. Process water used for flotation tests was supplied by Syncrude Canada Ltd. The chemistry of the process water used is shown in Table 4.2.

Reagent grade sodium hydroxide (Fisher Scientific) was used for increasing pH of the slurry during the flotation test. Calcium chloride and magnesium chloride (from Fisher scientific) were used to study the effect of divalent cation addition on bitumen recovery and carboxylic surfactant production. Kaolinite and illite from Ward's Natural Science were used as standard clays to study the role of clay type in changing the pH of the process water.

4.2.2 *Flotation test and Dean Stark apparatus*

A 1 L Denver cell was used to perform bitumen flotation test. The temperature was kept constant at 45°C by a water jacket connected to a thermal bath. Flotation tests were performed at six different sodium hydroxide dosages: 0, 0.01, 0.03, 0.05, 0.1, and 0.5 wt.% (based on weight of oil sands). For each flotation test, 500 g of oil sands ore with 900 g of process water were used at a desired NaOH dosage. NaOH was dissolved in process water prior to each flotation test. The slurry was mechanically agitated at 1500 rpm for five minutes (conditioning stage) and the bitumen froth formed was collected as primary froth. Air was then introduced at 150 mL/min and froth was collected for additional ten minutes (after 2, 5 and 10 min) (Zhou et al., 2004). Dean Stark apparatus was used to determine the composition of the collected froth (Starr & Bulmer, 1979), and bitumen recovery was determined as bellow. Figure 4.1 shows the Denver flotation cell and Dean Stark apparatus used in this work.

$$R(\%) = \frac{Bitumen\ in\ froth\,(g)}{Bitumen\ in\ feed\,(g)} \times 100$$

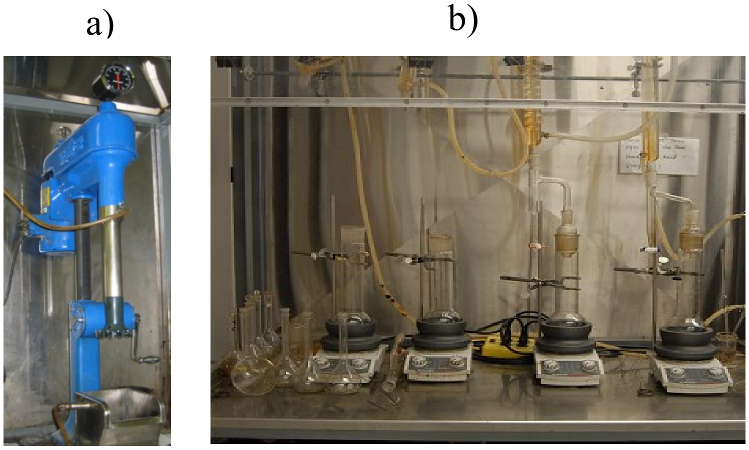

Figure 4.1. a) Denver Cell and b) Dean Stark

Table 4.1. Composition of oil sands ores used in this study

Ores				**Composition of ores (wt. %)**				**Concentration of ions in connate* water (mg/kg of oil sands)**						
#	Class	Name	pH of connate water	Water	Solid	Bitumen	Fines (wt. % of solids)	Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	HCO_3^-	$SO4^{2-}$
1	Average fines	MA	7.6	8.3	83.5	8.2	15.4	6.1	5.5	386.6	13.2	251.4	86	81.5
2		AO	7.2	3.5	85.6	10.7	19	35.3	12.4	5.7	10.9	1.2	33.4	38.0
3		AZ	7.0	3.7	84.7	11.6	20	14.7	6.6	42.7	15.13	1.9	32.8	34.6
4	High fines	AJ	7.0	3	87.4	9.2	25	54.8	17.9	28.1	19	5.7	3.7	60.1
5		AS08	7.2	7.1	83.9	9.4	25	8.3	5.1	84.1	16.1	11.7	43.7	57.1
6		AE	7.4	9.1	84.1	6.4	25.3	33.0	13.3	38.6	11.1	10.6	72.4	46.5
7		AA	7.4	6.3	84	9.9	30	5.2	-	46.6	23.9	2.5	64	31.8
8		AR	7.3	5.2	85.7	8.7	30.9	112.6	31.7	12.9	13.6	2.2	96.3	89.8
9		AB	7.7	6.7	83.7	10.2	35	0.72	3.5	81.1	16.8	16.3	84.9	36.9
10		AE13	7.8	4.9	86.8	8.3	35	1.3	1.2	56.9	18.6	30.35	54.7	31.45
11		CN912	8.5	7.4	84.3	8.3	37.5	2.3	2.2	650.9	16.1	360.9	307.2	81.9
12		AN	7.6	2.2	87.3	10.4	38	2.6	6.2	72.4	23.3	5.4	51.3	42.4
13		AS	7.3	3.8	86.4	9.8	39	93.2	63.0	89.6	22.1	1.1	54.5	145.2
14	Ultra high fines	AL	7.1	3.9	87	9.3	46	27.8	26.9	163.7	23.1	1.6	39.1	118.5
15		AB08	7.4	5.6	85.3	8.8	47	115.2	66.9	4.8	17.4	3.2	51.9	107.9

* The chemistry of connate water (formation water) was analyzed by mixing equal mass of de-ionized water with oil sands ore. After mixing, the oil phase was removed and the remaining aqueous phase was centrifuged at 20,000 g for 30 minutes. The supernatant was then analyzed to obtain the concentration of different ions (Zhao et al., 2009).

Table 4.2. Chemistry of process water

Concentration of ions (ppm*) in process water						pH
Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	HCO_3^{-}	CO_3^{2-}	
40	17	570	19	580	BDL	8.2

*milligram (mg) of ions per liter (L) of process water.
BDL: Bellow detection limit

4.2.3 Quantifying selected inorganic cations and anions in connate water of ores

The procedure, described by Zhao et al. (2009), was used to determine the concentrations of selected inorganic cations and anions in the connate water of ores. Slurry water was prepared by the addition of 1:1 mass ratio of boiling water to an oil sands ore. The mixture was first shaken for 2 minutes, followed by removing the oil phase formed at the top. The mixture was then centrifuged at 20,000 g for 30 minutes. The supernatant was then filtered (0.1 μm) and the concentration of selected ions was determined by atomic absorption spectroscopy (AAS). The results are shown in Table 4.1.

4.2.4 Ore weathering procedure

In order to study the effect of ore weathering (also known as aging or oxidation) on ore processability and production of natural surfactants (carboxylic surfactant), one centimeter thick layers of oil sands ores were placed in pans. The pans were then put in a vacuum oven for 2 days at 60 °C (Ren et al., 2009a). AE13 and AR ores were used for this part of the experiments.

4.2.5 Mineral composition of ores

Mineral composition of solids at different size fractions (>45 mμ, <45 mμ and <2mμ) of eight oil sands ores were determined by X-ray diffraction (XRD) and X-ray fluorescence (XRF) spectroscopy analysis. These measurements and analysis were performed by Dr. Xiaowen Liu and the results were used for parts of analysis in this study.

4.2.6 Extracting bitumen from ores by centrifugation

Three oil sands ores were centrifuged to extract their bitumen. The extracted bitumen was then used for measuring the concentration of carboxylic surfactant that initially exists in bitumen. Centrifugation method was used in order to keep light end compounds of bitumen with it. Centrifugation was performed using a Rotana 460R centrifuge (Hettich Centrifuges, UK) at 50 °C and 18000 g. Ores were first thaw out of the freezer for a couple of hours. The 120-mL stainless steel centrifuge tubes (Beckman Coulter Inc., Canada) were then filled up with ores to 2/3 of the volume of the tubes. They were then centrifuged for 2 hrs at 50 °C and 18000 g. Solids were then scooped out from the top of the tubes and more ores were added. This step was repeated until bitumen was floated on top of the solids. The bitumen was scooped out carefully and quickly before it soaked back into the solids. The procedure was repeated until enough amount of bitumen was extracted (Zhang, 2012; Wallace et al., 1984).

4.2.7 Quantifying surfactant in bitumen fraction of ores

0.5 g of bitumen extracted from ores by centrifugation was added to 60 g of Milli-Q water at pH 12.2. The mixture was shaken for 24 hours. The emulsified solution was then centrifuged and filtered (0.1 μm vacuum filter). The concentration of carboxylic surfactants was determined by FTIR method, described in Chapter 3.

4.3 Results and discussion

4.3.1 Concentration of carboxylic surfactant in tailings water prepared with different ores at different caustic levels

NaOH reacts with carboxylic acids in bitumen (reaction 1) and converts them from acid (neutral) form to salt (ionized) form, which has higher solubility in water.

$$RCOOH + OH^- \rightarrow RCOO^- + H_2O \qquad (1)$$

Concentrations of free carboxylic surfactant in tailings water of different ores prepared at different NaOH dosage were measured using DCM extraction and FTIR method described in Chapter 3. Figure 4.2[*] compares the concentration of free carboxylic surfactant in tailings water produced from different ores as a function of NaOH dosage (Figure 4.2a) and pH of tailings water (Figure 4.2b)[†].

As shown in Figure 4.2a, the addition of higher dosage of NaOH caused release of more carboxylic surfactants from all ores. However, at the same NaOH level, each ore produced tailings water of different pH values and different amount of carboxylic surfactant.

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[*] The raw data are shown in Appendix B.1 and B.2.

[†] In this work, Denver flotation cell was used to perform flotation tests. The effect of extraction methods (BEU vs. Denver cell) on production of natural surfactant was studied for AE13 ore. The results are shown in Appendix B.3.

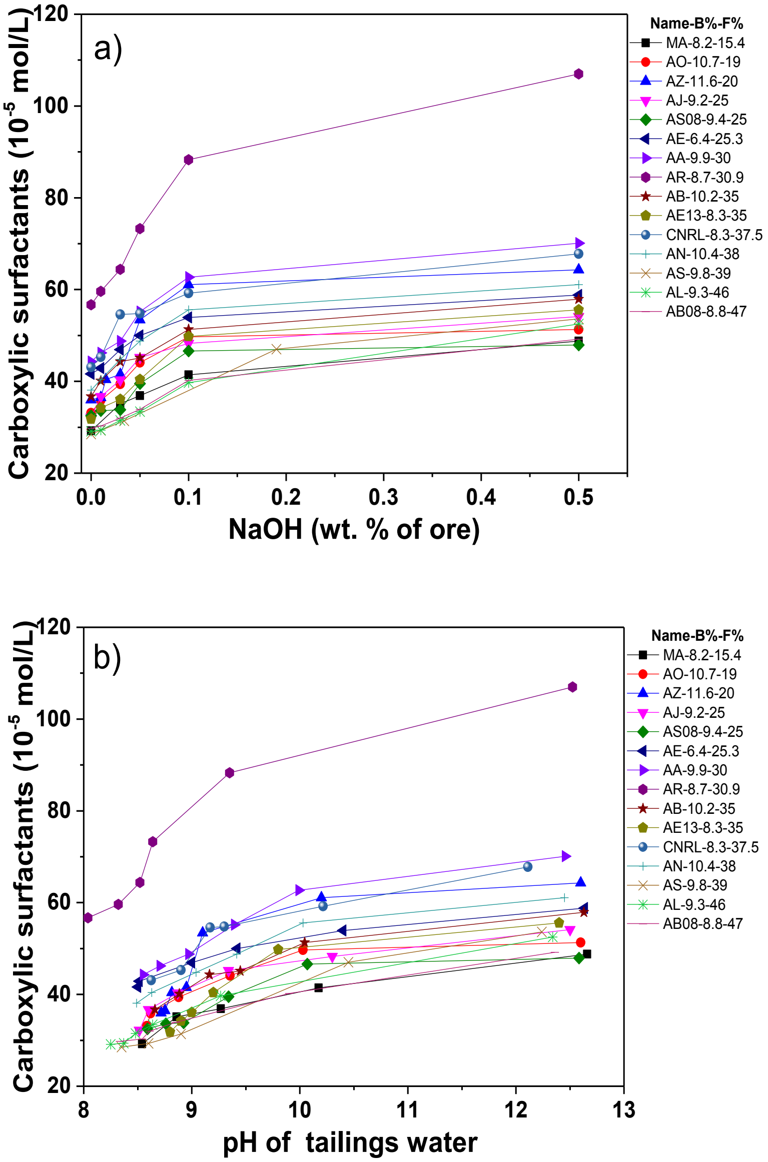

Figure 4.2. Concentration of free carboxylic surfactant in tailings water of different ores prepared at different NaOH dosage. a) as a function of NaOH (wt.% of ore) added to flotation test and b) as a function of pH of the tailings water. (In legends, B= Bitumen, F= Fine).

4.3.2 Variables affecting pH of tailings water

There are many variables in oil sands ores that can affect the pH of the produced tailings water. Added NaOH dosage, fines content, clay type, concentrations of divalent cations and bicarbonate ions, pH of connate water or combination of these variables are among the factors that can influence the pH of tailings water.

4.3.2.1 Role of fines content and clay type

Figure 4.3.a shows the pH of tailings water for different ores vs. NaOH dosage added to the test.* Although average fines ores have relatively high pH values comparing to other ores, no clear trend, such as $\text{pH}_{\text{average}} > \text{pH}_{\text{high}} > \text{pH}_{\text{ultra-high}}$ between the pH of tailings water and fines content of ores is observed. Especially for high fines ores, pH of tailings water varies in a wide range, showing that other parameters may also play a role. However, Figure 4.3.b shows that the pH of tailings water for average fines ores are consistently higher than that for ultra-high fines ores at the same NaOH dosage.

To clarify the role of fines content and fines type in changing the pH of tailings water, kaolinite and illite were added to process water at different concentrations and the pH of the suspension was measured afterwards.

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* The pH of tailings water for different ores vs. NaOH dosage added to the test based on fines content of ore is shown in Appendix B.4.

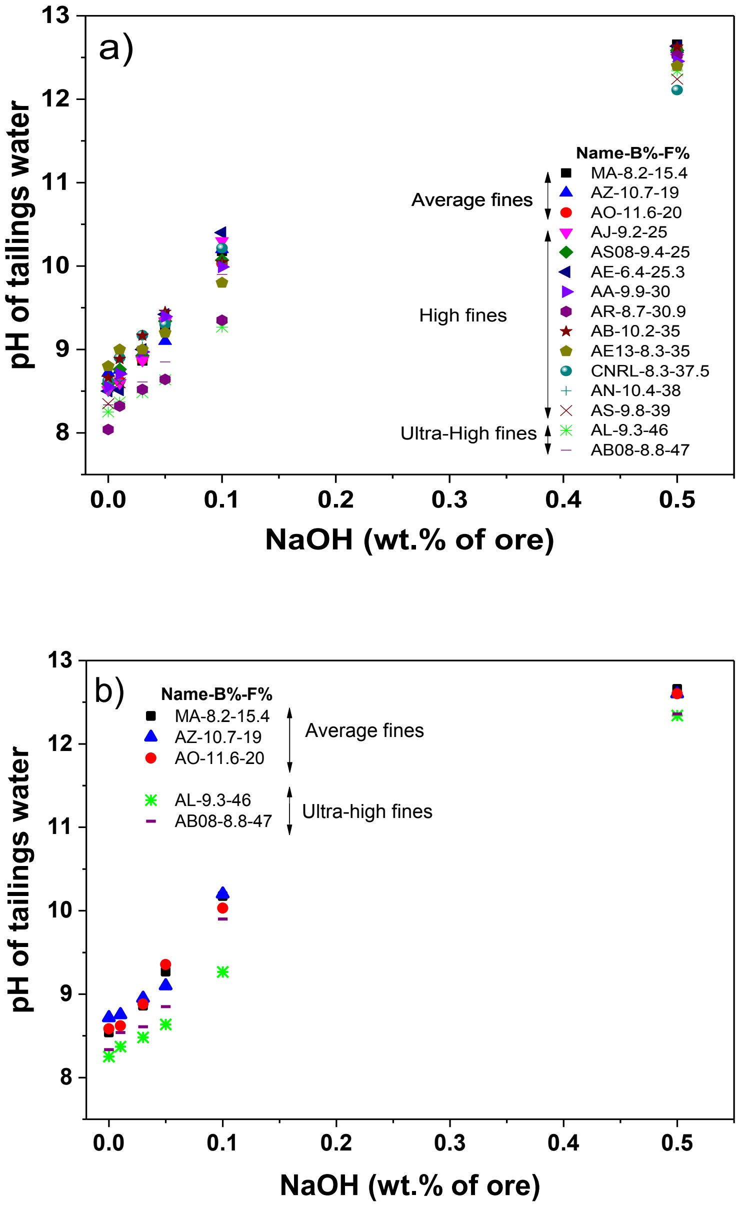

Figure 4.3. pH values of tailings water as a function of NaOH dosage, a) all ores, b) average and ultra-high fines ores.

The experiments for understanding the role of fines in changing the pH of tailings water were conducted separately for kaolinite and illite. The pH of the process water was also measured separately as control test at the same time intervals. For each test, the pH of the process water was measured before adding any clay. Then clay was added to the process water starting with 0.05 wt.% (mass ratio of clay in suspension), and the pH was measured shortly afterwards. The experiment was continued until the total cumulative concentration of clay in the suspension reached to 5 wt.%.

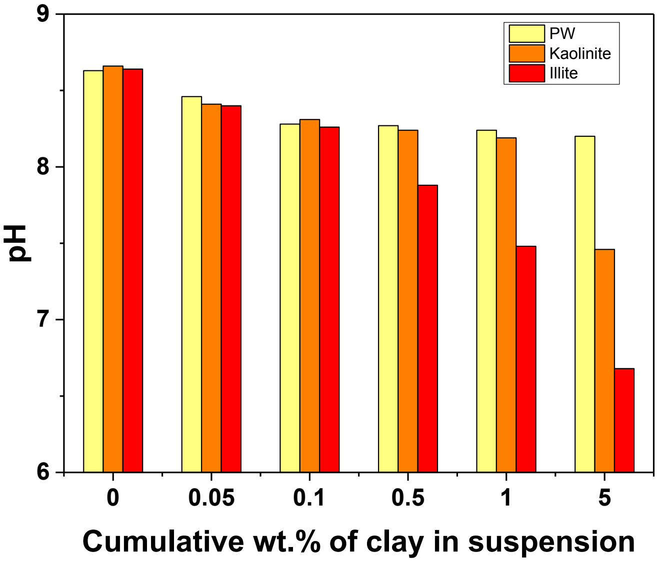

Figure 4.4. Effect of kaolinite and illite addition on pH of process water.

As shown in Figure 4.4, there is a slight reduction in pH with aging time of process water as anticipated. However, the effect of illite on reducing the pH is stronger than kaolinite. For example, the addition of kaolinite to process water started to reduce the pH when the total concentration of kaolinite in the suspension reached 5 wt.%, while illite reduced the pH after the addition of only 0.5 wt.%. This behavior of illite is attributed to the acidity of illite clays (Du et al., 1997). Ding et al. (2006) also observed a reduction in pH of tailings water by the addition of illite clays to floatation tests.

4.3.2.2 Role of divalent cations

Another important factor in changing the pH of tailings water is the concentration of divalent cations such as calcium and magnesium in the oil sands ores. Figure 4.5 shows the pH of the tailings water samples prepared with 0 wt.% NaOH for different ores as a function of calcium and magnesium concentration in their connate water. The general trend shows that tailings water of ores with higher concentrations of calcium and magnesium has lower pH values.

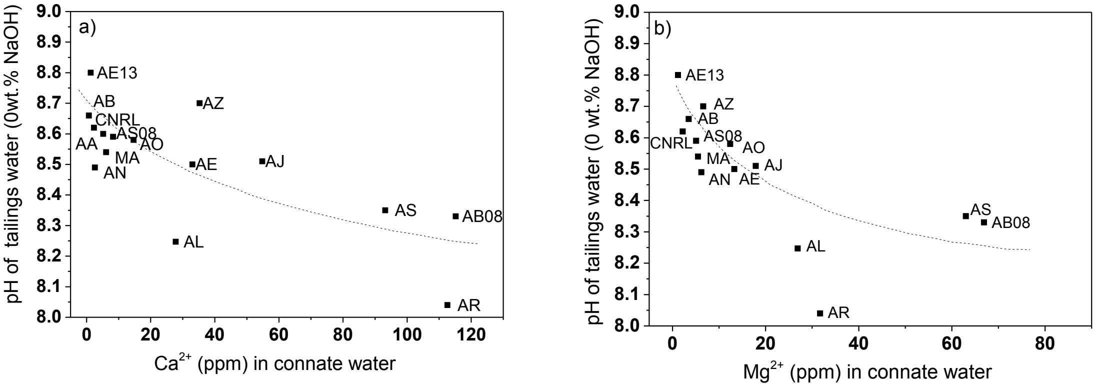

Figure 4.5. pH of tailings water (0 wt. % NaOH) of all ores versus concentration of a) Ca^{2+} and b) Mg^{2+} ions in connate water.

This finding suggests that calcium and magnesium ions consume hydroxyl ions; either directly in the forms of calcium or magnesium hydroxides (Wik, 2008) (reactions 2 and 3, respectively) or indirectly by precipitating carboxylate ions (reactions 4 and 5, respectively). By precipitating carboxylate ions, reaction (1) shifts to the right direction; therefore concentration of OH^- ions in the slurry drops.

$$Ca^{2+} + OH^- \leftrightarrow Ca(OH)_2 \downarrow \qquad K_{sp} : 5.02\times10^{-6}\, at\, 25^\circ C \qquad (2)$$

$$Mg^{2+} + OH^- \leftrightarrow Mg(OH)_2 \downarrow \qquad K_{sp} : 5.61\times10^{-12} at\ 25^\circ C \tag{3}$$

$$Ca^{2+} + RCOO^- \leftrightarrow Ca(RCOO)_2 \downarrow \tag{4}$$

$$Mg^{2+} + RCOO^- \leftrightarrow Mg(RCOO)_2 \downarrow \tag{5}$$

Below are other proposed reactions in which NaOH can be consumed in the slurry (Smith and Schraam, 1992). In these reactions, M represents polyvalent metal ions.

$$MCO_3 + NaOH + H_2O \leftrightarrow M(OH)_2 \downarrow + NaHCO_3$$

$$M(clays)_2 + 2NaOH \leftrightarrow M(OH)_2 \downarrow + 2Na(clay)$$

$$MSO_4 + 2NaOH \leftrightarrow M(OH)_2 \downarrow + Na_2SO_4$$

The role of calcium and magnesium ions in changing the pH of tailings water, concentration of produced carboxylic surfactant and bitumen recovery is discussed in detail in section 5.2.4.3, where calcium and magnesium ions were added to the flotation tests.

4.3.3 Role of ore composition in production of carboxylic surfactant from oil sands ores

4.3.3.1 Bitumen content of ores

Carboxylic surfactants are released from bitumen during the hot water extraction process. Therefore, the concentration of produced surfactants from each ore should be proportional to its bitumen content. To understand the relationship between the released carboxylic surfactant concentration and bitumen content in the ores, the concentrations of carboxylic surfactant for each ore prepared at different NaOH dosage were divided (normalized) by the bitumen content of the same ore and the results are compared.

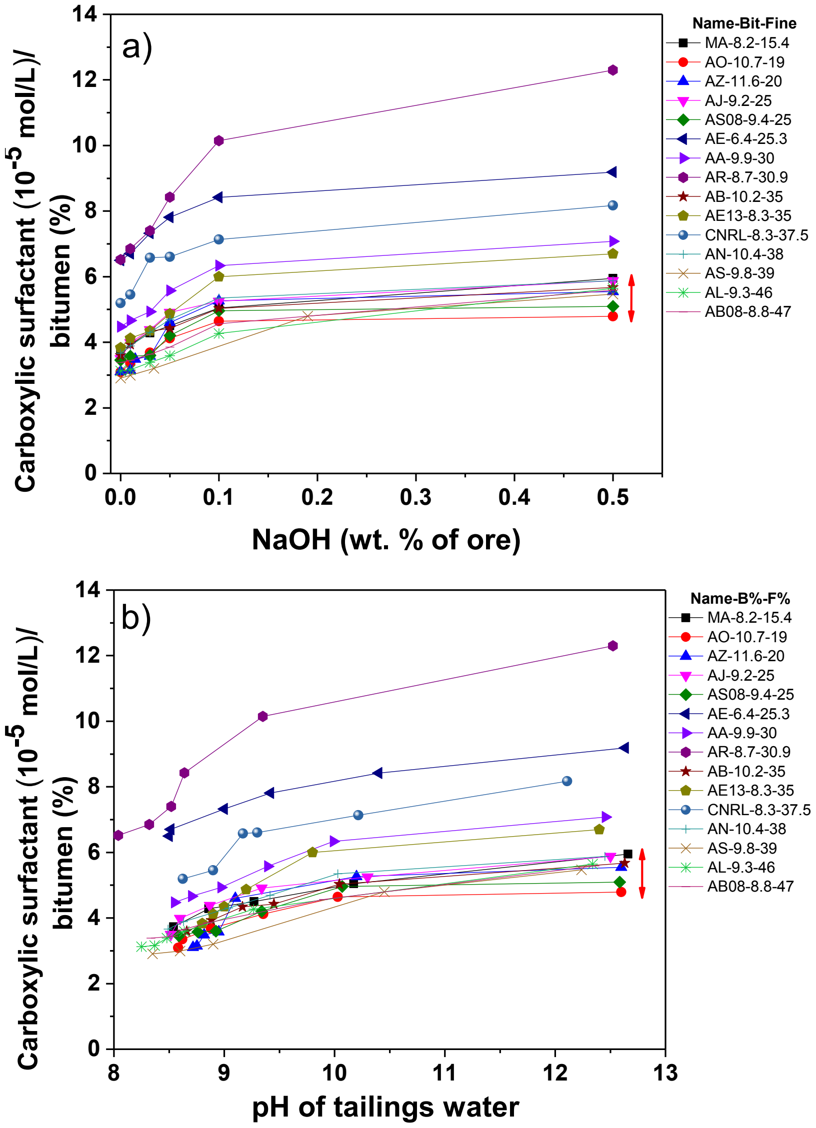

Figure 4.6. Concentration of free carboxylic surfactant in tailings water of different ores prepared at different NaOH levels divided by bitumen (%) in ores. a) as a function of NaOH (wt.% of ore), b) as a function of pH of tailings water (In legend, B: Bitumen, F: Fines).

As shown in Figure 4.6, the normalized plots of carboxylic surfactant concentration for 10 ores have almost collapsed in the same region, while for other ores (AR, AE, CNRL, and AA), it did not. This observation shows that the concentration of the released surfactants in the tailings water is not only determined by bitumen content of the ores and NaOH dosage added to the flotation test. For instance, Smith and Schramm (1992) showed that the addition of Ca-illite or Ca-kaolinite clays to batch extraction test reduced the amount of free carboxylic surfactant measured in the tailings water. Also the addition of multivalent metal carbonates and sulfates to batch extraction process of oil sands ores was found to have a detrimental effect on production of carboxylic surfactant.

4.3.3.2 Fine content of ores

Natural surfactants after getting released from bitumen during the hot water extraction process can attach to the surface of fine particles and clays either by bridging via divalent cations or by adsorption on the edges of clays (electrostatic attraction forces) (Masliyah, 2011). Therefore, the increase in the amount of fine solids in the oil sands ores can have an opposite impact in carboxylic surfactant concentration released in tailings water. Figure 4.8 indicates the concentration of free carboxylic surfactant in the tailings water multiplied by fine content of each ore as a function of pH of the tailings water.

As shown in Figure 4.7, no trend was observed. However, the graphs were divided into three regions for average fines (AV), high fines (HF) and ultra-high fines (UHF) ores with partial overlap. AR and CNRL were considered as outliers since they did not fit in the three regions.[*]

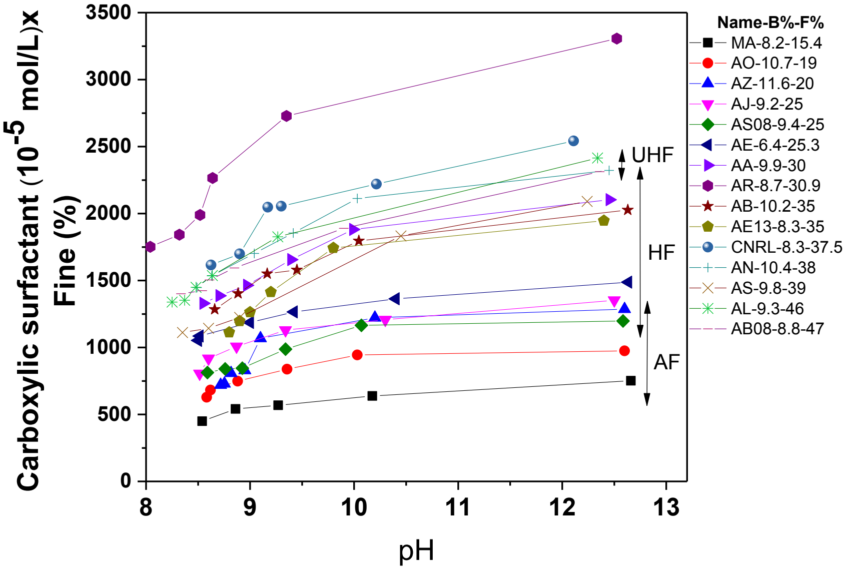

Figure 4.7. Concentration of free carboxylic surfactant in tailings water of different ores prepared at different NaOH levels multiplied by fine content (In legend, B: Bitumen, F: Fines).

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[*] No correlation or classification was observed between the produced free carboxylic surfactants concentration and solid content and water content of ores.

4.3.3.3 Bitumen and fine content of ores

In the next trial both bitumen and fine content were used to establish a trend for the produced surfactant concentration in tailings water. For this purpose concentrations of free carboxylic surfactants were multiplied by fine content (indirectly related) and divided by bitumen content (directly related) of each ore. Again the graphs were divided in three regions (Figure 4.8), obviously with less overlaps comparing to Figure 4.7. AR and CNRL remained as outliers.

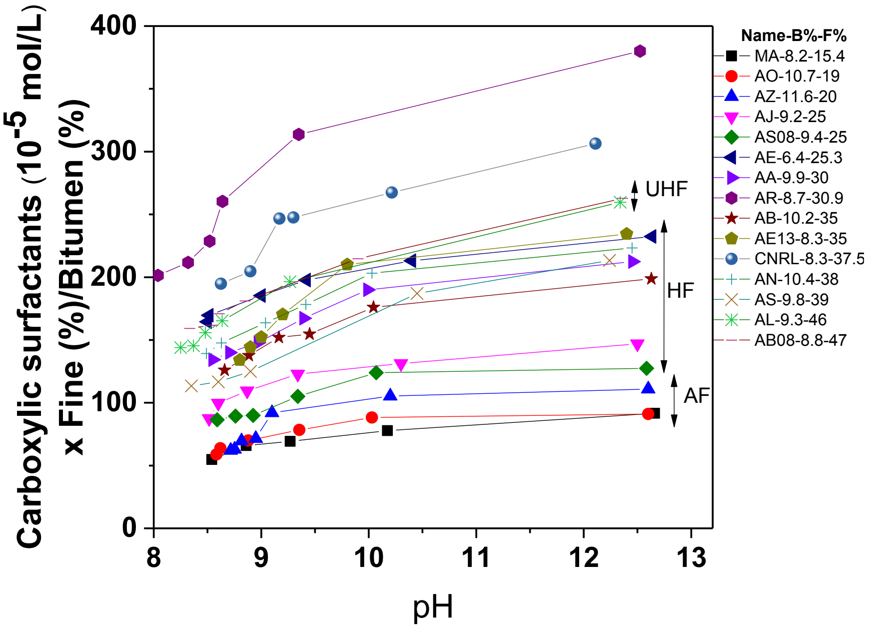

Figure 4.8. Concentration of free carboxylic surfactant in tailings water of different ores prepared at different NaOH levels multiplied by fine content, divided by bitumen content (In legend, B: Bitumen, F: Fines).

4.3.4 Role of bitumen chemistry in production of carboxylic surfactant from oil sands ores

In addition to bitumen content of ores, bitumen chemistry and the initial carboxylic surfactant concentration in bitumen fraction of ores is also an important factor in determining the final concentration of free carboxylic surfactant in tailings water. Physical and chemical properties of bitumen such as viscosity and SARA fractions (saturates, aromatics, resins and asphaltene) for different ores have been measured and compared in several studies (Woods et al., 2012). However, the quantity of the surfactant in bitumen fraction of oil sands ores has not been reported elsewhere yet. For this purpose, three different ores (AR, MA and AZ) were centrifuged to obtain bitumen. Carboxylic surfactants were then measured in the extracted bitumen[*]. Table 4.3 summarizes the measured carboxylic surfactants extracted from bitumen of each ore (column A). As shown, the same amount of surfactant was measured in 0.5 g bitumen of MA and AZ ores. However, AR produced the double amount of carboxylic surfactant compared with the other two ores. This difference clarifies why higher concentrations of free carboxylic surfactant were measured for AR and made it an outlier (Figure 4.2).

Table 4.3. Concentration of carboxylic surfactants (CSs) extracted from bitumen fraction of oil sands ores.

	A	B	C	D
Ore	CS (10^{-5} mol/L) in 0.5 (g) of bitumen	Bitumen (%) in ore	Bitumen (g) in 500 (g) of ore Bx500	Total CS (10^{-5} mol/L) in 500 g of ore CxA/0.5
AR	29.2	8.7	43.5	2540.4
MA	12.6	8.2	41	1033.2
AZ	12.6	11.6	58	1461.6

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[*] Bitumen viscosity for the extracted bitumen was also measured. The results are shown in Appendix B.5.

Total amount of carboxylic surfactant in the bitumen fraction of 500 g of studied ores was calculated and shown in column D of Table 4.3. These values were then used to normalize the concentration of free carboxylic surfactant in tailings water of AR, MA and AZ ores. Figure 4.9 compares the concentrations of free carboxylic surfactant measured in the tailings water of the studied ores before and after normalization as a function of pH of tailings water. As shown, the graphs for MA, AZ and AR ores are collapsed in Figure 4.9.b. This result indicates the importance of bitumen chemistry in addition to bitumen content and other parameters in determining the final concentration of carboxylic surfactant in tailings water.

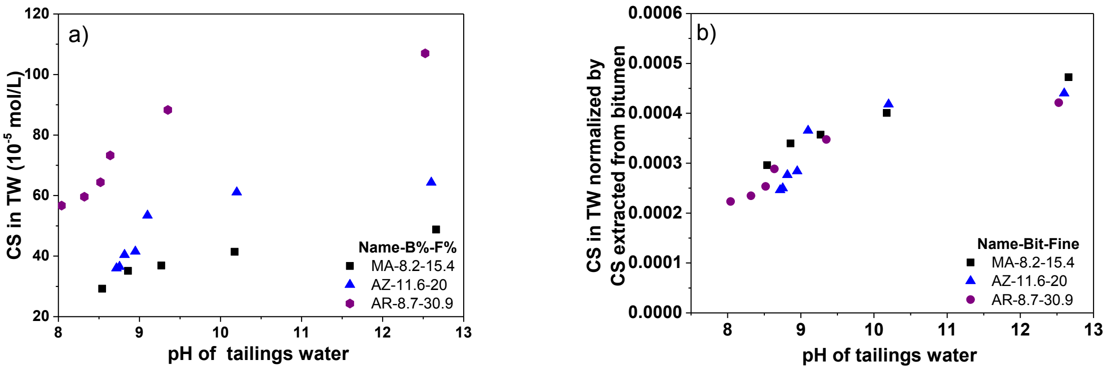

Figure 4.9. Concentration of free carboxylic surfactant (CS) in tailings water a) without normalization, b) with normalization. (Normalized by total carboxylic surfactant content in bitumen obtained from ores; In legends, B=Bitumen, F=Fines).

4.3.5 Role of divalent cations in production of carboxylic surfactant from oil sands ore

Presence of calcium and magnesium ions in the formation water of ores affect the concentration of free carboxylic surfactants released in tailings water. According to reactions (4) and (5), calcium and magnesium ions can precipitate carboxylate ions in the form of calcium or magnesium carboxylates and reduce the total concentration of free carboxylic surfactant in tailings water. On the other hand, carbonate ions or hydroxyl ions in the solution can affect the concentration of divalent cations by precipitating them in the form of calcium/magnesium carbonates (reaction 6 and 7) or calcium/magnesium hydroxides (reactions 2 and 3).

$$Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_3 \downarrow \qquad K_{sp} : 3.36\times10^{-9}\, at\, 25^\circ C \qquad (6)$$

$$Mg^{2+} + CO_3^{2-} \leftrightarrow MgCO_3 \downarrow \qquad K_{sp} : 6.82\times10^{-6}\, at\, 25^\circ C \qquad (7)$$

According to reactions 8, 9 and 10, concentration of carbonate ions in the solution depends on the concentration of bicarbonate ions and pH of the solution. The distribution of carbonate species as a fraction of total dissolved carbonate versus pH is shown in Figure 4.10 (Huang et al., 2011).

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \qquad (8)$$

$$H_2CO_3 + H_2O \leftrightarrow HCO_3^{-} + H_3O^{+} \qquad (9)$$

$$HCO_3^{-} + H_2O \leftrightarrow CO_3^{2-} + H_3O^{+} \qquad (10)$$

According to Figure 4.10, the maximum concentration of bicarbonate is found at pH 8.5. Among the studied ores (Table 5.1) CNRL had the highest pH of connate water (8.4), which accordingly had the maximum bicarbonate concentration in its connate water (307.1 ppm).

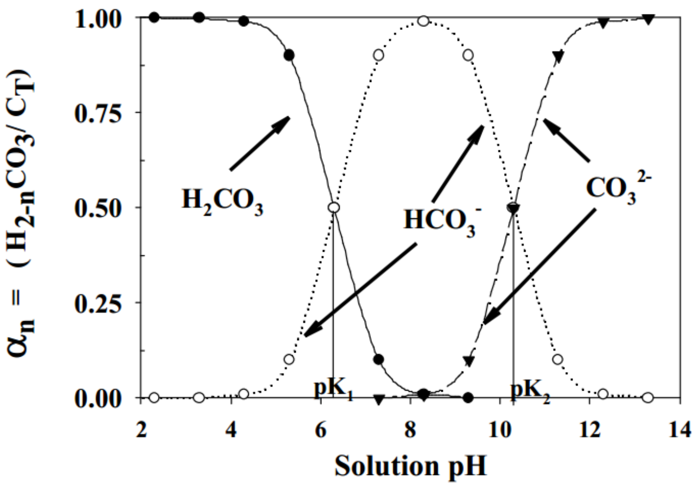

Figure 4.10. Distribution of carbonate species as a fraction of total dissolved carbonate in relation with solution pH (Huang et al., 2011).

The relationship between the concentration of divalent cations in connate water and tailings water with concentration of released carboxylic surfactant in tailings water is studied in sections 4.3.5.1 and 4.3.5.2. Also, in order to better understand the role of divalent cations in determining the processability of ores, calcium and magnesium were added to Denver flotation test and the results of bitumen recovery, pH of tailings water and concentrations of free carboxylic surfactant in tailings water at different caustic dosages were compared in section 4.3.5.3.

4.3.5.1 Relationship between the concentration of divalent cations in connate water and concentration of free carboxylic surfactant in tailings water

In Figure 4.11, the concentrations of free carboxylic surfactants in tailings water prepared with (0 wt.% NaOH) were plotted as a function of concentration of calcium and magnesium ions in connate water. Among all the ores studied, the ones with higher concentration of Ca^{2+} and Mg^{2+} produced less amount of carboxylic surfactant in tailings water. This can be explained by the fact that the high amounts of Ca^{2+} and Mg^{2+} ions precipitate more carboxylic surfactant. The only outlier is AR ore, which as shown previously had exceptionally higher concentration of carboxylic surfactant in its bitumen fraction.

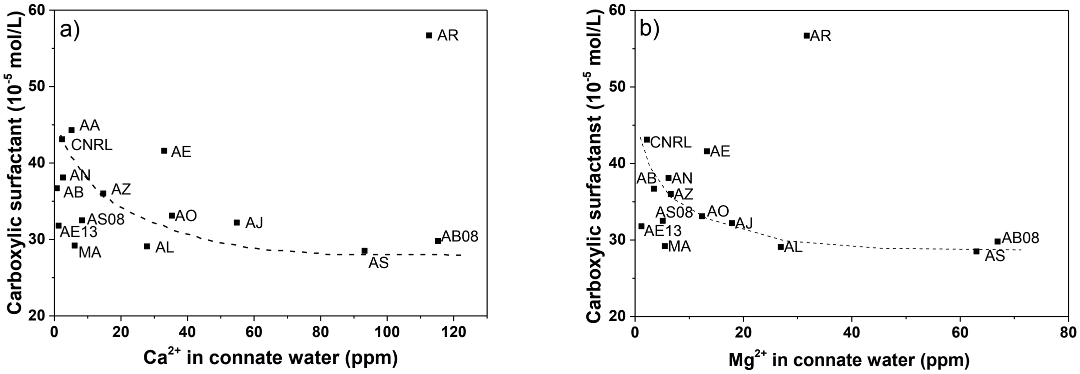

Figure 4.11. Concentration of free carboxylic surfactant in tailings water (0 wt. % NaOH) of different ores vs. concentration of: a) Ca^{2+} and b) Mg^{2+} ions in connate water.

4.3.5.2 Relationship between the concentration of divalent cations in tailings water and concentration of free carboxylic surfactant in tailings water

In performing extraction tests (using Denver cell) at different NaOH dosages, the equilibrium concentration of Ca^{2+} and Mg^{2+} ions in the tailings water is a function of different factors such as initial Ca^{2+}/Mg^{2+} concentration in the ore, process water chemistry (process water contains 40 ppm Ca^{2+} and 17 ppm Mg^{2+}), concentration of carbonate/bicarbonate ions in connate water and process water, and pH of the slurry (NaOH dosage is changing from 0 to 0.5 wt.% of ore). In this section the correlation between the equilibrium concentration of carboxylic surfactant in tailings water and the concentration of Ca^{2+} and Mg^{2+} in the corresponding tailings water was investigated.

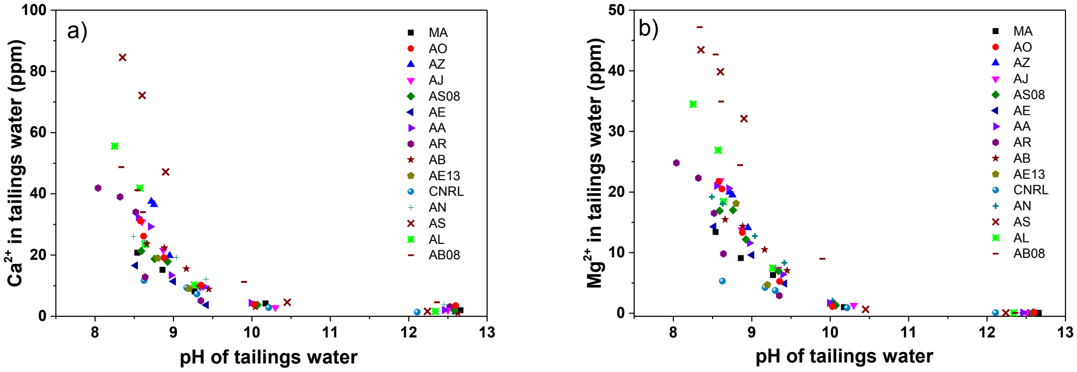

Figure 4.12. Concentration of a) Ca^{2+} and b) Mg^{2+} ions in tailings water prepared with different ores at different caustic dosages.*

To this end, the concentration of Ca^{2+} and Mg^{2+} in tailings water was measured using AAS analysis. Figure 4.12 shows that for the all ores studied, the addition of NaOH to flotation test scavenges the concentration of Ca^{2+} and Mg^{2+} in tailings water. The scavenge happens because at high pH values, the concentration of CO_3^{2-} ions increases (as shown in Figure 4.10) and Ca^{2+} and Mg^{2+} can be precipitated out in the form of calcium or magnesium carbonates (reactions 6 and 7). Also, due to the high concentration of OH^- groups, $Mg(OH)_2$ and $Ca(OH)_2$ might form as well. However, $Mg(OH)_2$ and $CaCO_3$ have smaller solubility product constant. Therefore, it is more probable that they are formed first. Ca^{2+} and Mg^{2+} can also precipitate in the form of carboxylates (reactions 2 and 3) since more carboxylate ions are generated as pH increases (reaction 1). Table 4.4 compares the measured concentrations of calcium, magnesium, carbonate, bicarbonate and carboxylate ions for MA ore at two different

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* The raw data are shown in Appendix B.6.

caustic dosages. As shown, CO_3^{2-} and $RCOO^-$ ions measured at 0.5 wt.% NaOH addition were higher than that at 0.05 wt.% NaOH addition.

Table 4.4. Water chemistry of tailings water for MA ore

Water sample	pH	Ca^{2+}	Mg^{2+}	CO_3^{2-}	HCO_3^-	$RCOO^-$
		(ppm*)				(10^{-5} mol/L)
Process water	8.2	40	17	0	580	24.0
0.05 wt.% NaOH TW	9.5	7.3	3.8	110	463	36.9
0.5 wt.% NaOH TW	12.7	1.4	0.09	2890	46	48.8

* ppm or mg/L is milligram (mg) of ion per liter (L) of tailings water.

Figure 4.13 is a plot of concentration of free carboxylic surfactant in the samples of tailings water produced with different ores as a function of equilibrium concentration of Ca^{2+} and Mg^{2+} ions in the corresponding tailings water. As shown, when the concentration of carboxylic surfactant is high, there is less divalent cations left in the tailings water. Also, from the data shown in 4.13, ion product or solubility quotient (Q_{sp}), of calcium and magnesium carboxylates in tailing water can be determined. An example of calculating Q_{sp} value for MA ore at 0 wt.% NaOH is shown below.

$[RCOO^-] = 30.60\times10^{-5}$, $[Ca^{2+}] = 0.52\ mM/L$, $[Mg^{2+}] = 0.55\ mM/L$

Q_{sp} *for* $Ca(RCOO)_2$:

$$[Ca^{2+}]\times[RCOO^-]^2 = [0.52\times10^{-3}]\times[30.60\times10^{-5}]^2 = 4.86\times10^{-11}$$

Q_{sp} *for* $Mg(RCOO)_2$:

$$[Mg^{2+}]\times[RCOO^-]^2 = [0.55\times10^{-3}]\times[30.60\times10^{-5}]^2 = 5.14\times10^{-11}$$

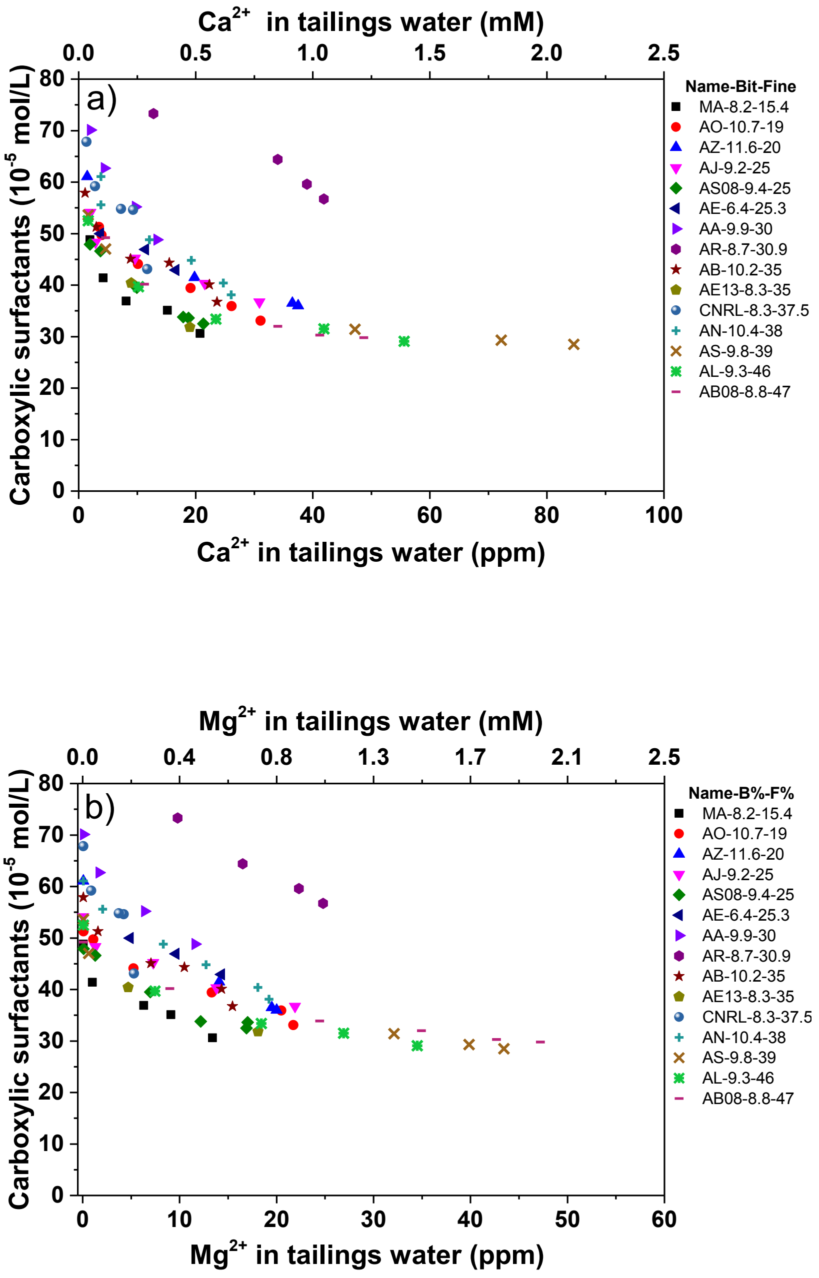

Figure 4.13. Concentration of carboxylic surfactant in tailings water samples of different ores prepared at different caustic levels as a function of a) Ca^{2+} and b) Mg^{2+} concentration in tailings water.

The plot of Q_{sp} as a function of pH (Figure 4.14) shows that the solubility of $Ca(RCOO)_2$ and Mg $(RCOO)_2$ in the tailings water samples decreases by increasing the pH. Since no precipitate exist in the tailings water samples, one can conclude that the solubility product (K_{sp}) values of $Ca(RCOO)_2$ and $Mg(RCOO)_2$ should be of a greater value than Q_{sp}.

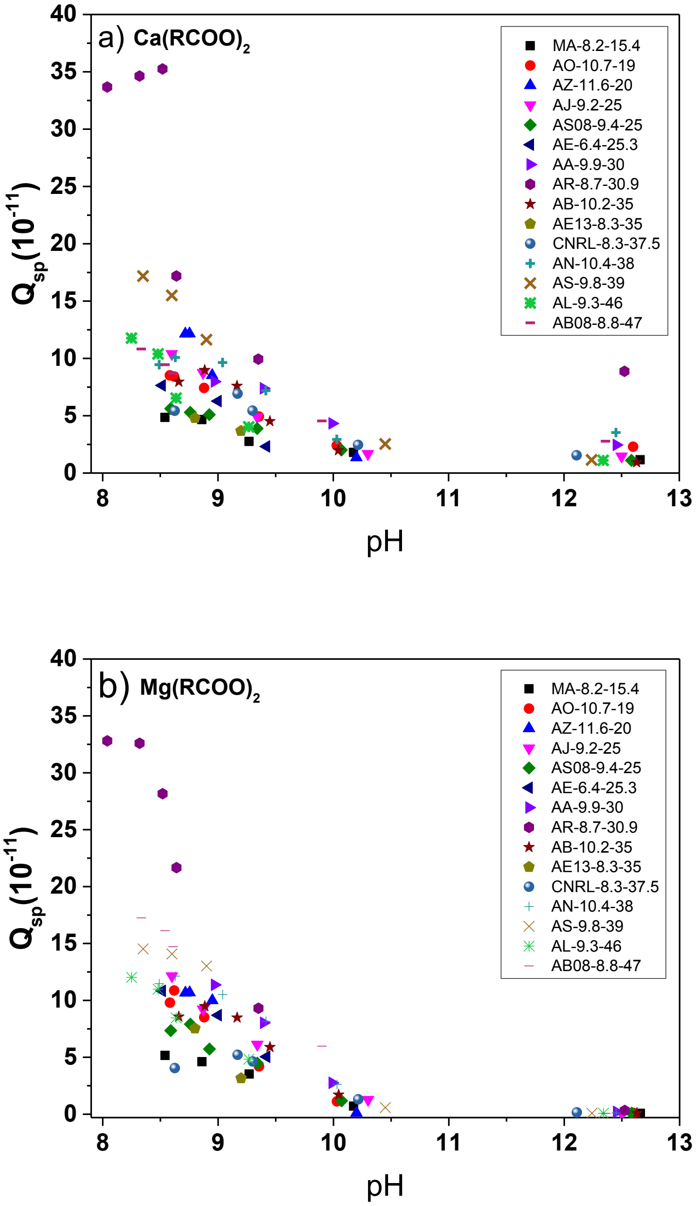

Figure 4.14.Q_{sp} values for a) $Ca(RCOO)_2$ and b) $Mg(RCOO)_2$ in tailings water prepared with different ores at different NaOH dosage.

4.3.5.3 Addition of calcium and magnesium ions to floatation test (using Denver cell)

To better understand the role of Ca^{2+} and Mg^{2+} ions in determining the processability of oil sands ores, Ca^{2+} and Mg^{2+} ions in the form of calcium chloride and magnesium chloride were added to the flotation tests of CN912 ore at different caustic levels (NaOH from 0→0.5 wt.%). As illustrated in Table 4.5, addition of 130 ppm Ca^{2+} and 60 ppm Mg^{2+} (ppm: mg of cations per liter of process water) to floatation tests increased the equilibrium concentration of Ca^{2+} and Mg^{2+} ions in the tailings water for all NaOH dosages except for the case of 0.5 wt.% NaOH addition. As a result, bitumen recovery dropped in the NaOH range of 0 to 0.1 wt.% (pH values less than 10.5) as shown in Figure 4.15a. Also, pH of the tailings water dropped and the concentration of free carboxylic surfactant in the tailings water reduced (Figure 4.15 b).

On the other hand, at the very high pH (pH 12.2, 0.5wt.% NaOH) the addition of Ca^{2+} and Mg^{2+} ions to bitumen extraction tests had a negligible effect on the tailings water pH, bitumen recovery and free carboxylic surfactant concentration.

Table 4.5. Concentration of calcium and magnesium ions in tailings water (CN912 ore)

NaOH (wt. % of ore)	Calcium (ppm*)		Magnesium (ppm*)	
	Without addition of Ca^{2+} and Mg^{2+}	With the addition of 130 ppm Ca^{2+} and 60 ppm Mg^{2+}	Without addition of Ca^{2+} and Mg^{2+}	With the addition of 130 ppm Ca^{2+} and 60 ppm Mg^{2+}
0	11.7	80.6	5.3	49.5
0.01	-	-	-	-
0.03	9.3	33.8	4.25	33.7
0.05	7.25	19.4	3.75	17.9
0.1	2.8	5.9	0.9	7.5
0.5	1.35	2.8	0.085	0.07

*ppm or mg/L is milligram (mg) of cation per liter (L) of tailings water.

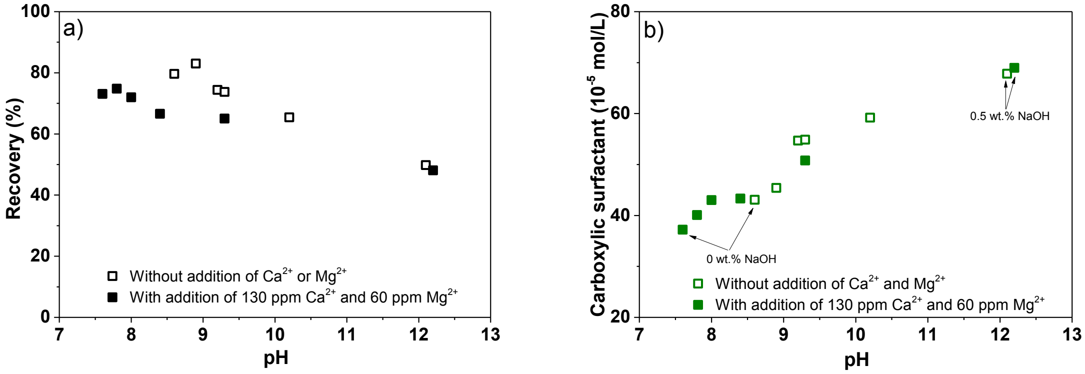

Figure 4.15. Effect of Ca^{2+} and Mg^{2+} ion addition to flotation tests on a) comparison of bitumen recovery, b) free carboxylic surfactant concentration in tailings water.

The role of Ca^{2+} and Mg^{2+} ion addition to extraction tests was studied for three different pH ranges (shown below).

pH < 8.5 (NaOH dosage of 0 and 0.01 wt.%):

For pH values bellow 8.5, concentration of CO_3^{2-} is negligible (Figure 4.10). Therefore, by increasing the concentration of Ca^{2+} and Mg^{2+} ions, balance the excess Ca^{2+} and Mg^{2+} ions form the precipitates of $Ca(RCOO)_2$ and $Mg(RCOO)_2$; thereby reducing concentration of $RCOO^-$. Reaction (1) shifts to the right direction to compensate the consumed $RCOO^-$ ions, which results in the reduction of OH^- ions in the solution and hence pH drops. Ca^{2+} and Mg^{2+} ions may also precipitate in the form of hydroxides. In addition, the reduction of bitumen recovery could result from the reduced electrostatic repulsive forces between bitumen and sands due to high concentration of Ca^{2+} and Mg^{2+} ions in the slurry. Such reduction in the electrostatic repulsive force leads to a decrease in the degree of bitumen liberation and an increase in the degree of slime coating of bitumen by fine clays.

<u>8.5 < pH < 10.5 (NaOH dosage from 0.03 to 0.1 wt.%):</u>

In this pH range, by increasing the concentration of Ca^{2+} and Mg^{2+} ions in addition to $Ca(RCOO)_2$ and $Mg(RCOO)_2$ precipitates other precipitates such as $Mg(OH)_2$ and $CaCO_3$ might form as well. Reactions 1 and 10 shift to the right to compensate the consumed $RCOO^-$ and CO_3^{2-} ions, leading to a decrease in the concentration of OH^- and the pH of the tailings water.

<u>pH > 12 (NaOH dosage 0.5 wt.%):</u>

At pH > 12, humic acids are released from oil sands ores (Reaction 11) and excess Ca^{2+} and Mg^{2+} ions react with humic acids to form calcium or magnesium humates (Reaction 12). The precipitation of humic acids is confirmed by colour comparison of the two samples of tailings water prepared with and without the addition of Ca^{2+} and Mg^{2+} ions at 0.5 wt.% NaOH, (shown in Figure 4.16). The lighter colour in Figure 4.16b indicates less humic acids due to Ca^{2+} and Mg^{2+} ion addition.

$$HA + OH^- \rightarrow HA^- + H_2O \qquad (11)$$

$$Ca^{2+} + HA^- \leftrightarrow Ca(HA^-)_2 \downarrow \qquad (12)$$

HA: humic acids, HA^-: ionized form of HA

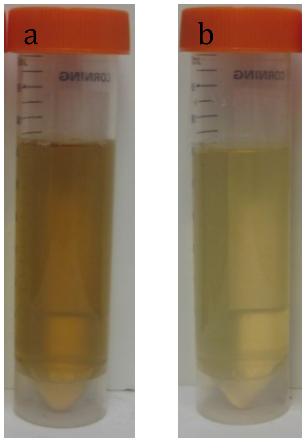

Figure 4.16. Tailings water prepared with the addition of 0.5 wt.% NaOH to flotation test, a) without addition of extra Ca^{2+} and Mg^{2+} ions b) with the addition of 130 ppm calcium and 60 ppm Ca^{2+} and Mg^{2+} ions to flotation tests.

Furthermore, concentration of CO_3^{2-} ions at this pH is very high (Figure 4.10, Table 4.4); thereby, extra Ca^{2+} and Mg^{2+} ions also precipitate in the form of carbonates (Reaction 6 and 7). High concentration of CO_3^{2-} and HA^- in the slurry counterbalances the effect of extra Ca^{2+} and Mg^{2+} ions on pH. As a result, the pH remains constant.

4.3.6 Role of clay type in the production of carboxylic surfactant from oil sands ores

Clay type and clay composition in the oil sands ores are important in determining the final concentration of carboxylic surfactant in tailings water (Smith and Schramm, 1992; Amirianshoja et al., 2013). To illustrate such an effect, eight ores were selected to perform mineralogy analysis in different size fractions of solids: > 45 µm, < 45 µm and < 2 µm. The results of quantitative mineralogy analysis are given in Table 4.6. Concentrations of free carboxylic surfactant in tailings water (0 wt.% NaOH) of the ores studied were plotted versus the percentage of different minerals in the ores at different size fractions. Among the studied minerals, only pyrite content in fines fraction (< 45 µm) showed a correlation with concentration of free carboxylic surfactant in tailings water. Figure 4.17 shows that the ores with higher pyrite content (in solids < 45 µm) produced less carboxylic surfactant.[*]

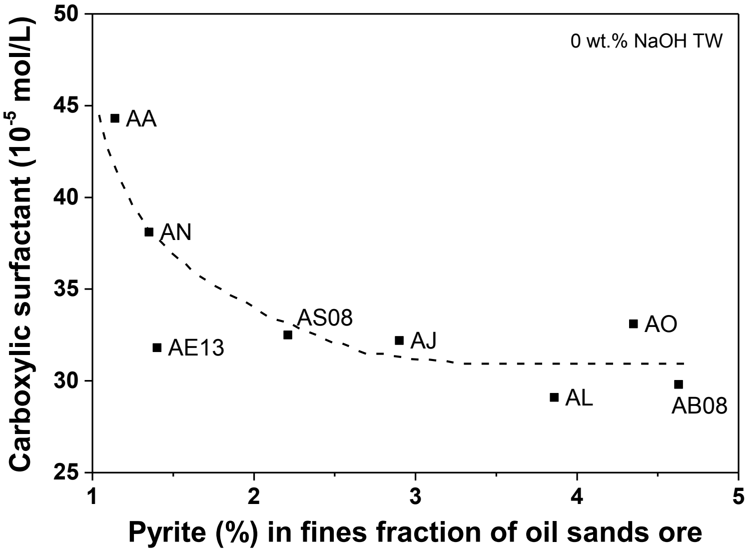

Figure 4.17. Concentration of free carboxylic surfactant in tailings water (0 wt. % NaOH) of different ores as a function of pyrite in fines fraction (<45 µm).

Pyrite can react with oxygen to form $FeSO_4$, increasing the acidity of the solution (Reaction 13), which might have detrimental effect on surfactant production (Brant and Ziemkiewicz, 1998; Schramm and Smith 1987b). Pyrite (FeS_2) has been proposed to have roles in reducing the concentration of carboxylic surfactant released from weathered/oxidized ores (Schramm and Smith, 1987b).

$$2FeS_2(s) + 7O_2(g) + 2H_2O(l) \rightarrow 2Fe^{2+}(aq) + 4SO_4^{2-}(aq) + 4H^+(aq) \qquad (13)$$

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[*] No correlation was observed between the concentration of released carboxylic surfactant and percentage of other minerals in the oil sands ores studied.

Table 4.6. Clay composition for eight oil sands ores used in this study

			Quartz	Carbonates		Pyrite	Rutile	Clays								Other
				Calcite	Siderite			Kaolinite	Muscovite	Vermiculite	Montmorillonite	Halloysite	Illite	Kaolinite - Montmorillite	Illite - Montmorillite	
Average Fines	AO	>45	92.00	0	0	0.43	0.09	1.62	2.80	0.84			1.68			0.54
		<45	51.35	1.32	0.59	4.35	1.36	5.34	13.89	1.52	3.79	1.57	8.08	2.02	3.79	1.03
		<2	30.22	2.34	1.91	4.35	1.35	21.05	4.05	5.68	1.01	3.27	12.97	3.24	5.07	3.49
High Fines	AJ	>45	90.94	0.32	0.18	0.21	0.19	1.48	2.57	1.03	-	-	2.06	-	-	1.02
		<45	51.87	2.62	2.95	2.91	2.26	9.29	7.25	2.90	4.83	2.40	3.87	1.93	2.42	2.50
		<2	41.90	0.33	5.29	4.35	1.36	12.97	7.71	1.93	3.21	3.20	10.28	1.28	1.61	3.58
	AE13	>45	90.91	0.26	0.29	0.22	0.42	1.09	1.42	1.13	-	-	3.40	-	-	0.86
		<45	62.02	1.55	1.02	1.40	2.37	7.51	5.20	2.08	1.30	0.97	6.24	1.56	3.90	2.88
		<2	25.43	1.87	2.27	4.35	1.36	18.85	4.75	8.32	-	2.58	15.45	2.38	7.43	4.96
	AS08	>45	91.18	0.41	0	0.74	0.26	2.03	0.75	0.90	-	-	3.01	-	-	0.72
		<45	51.75	1.59	1.93	2.21	2.10	9.70	5.31	7.97	1.33	1.65	6.37	1.59	3.98	2.52
		<2	20.39	3.15	3.06	3.27	2.55	13.16	4.56	16.53	2.87	3.19	13.68	3.99	7.13	2.47
	AA	>45	87	0.78	0.34	0.22	0.51	2.10	3.12	1.25			3.12	-	-	1.56
		<45	63.14	1.58	1.14	1.14	2.36	6.12	10.22	1.36	1.13	0.85	3.63	0.91	3.41	3.01
		<2	18.12	3.41	0.84	2.39	2.74	20.78	9.14	12.05	2.07	2.32	9.14	7.06	7.27	2.67
	AN	>45	90.81	0.52	0.15	0.42	0.33	1.39	0.72	1.15	-	-	4.04	-	-	0.47
		<45	52.60	1.82	1.32	1.35	2.12	5.04	10.48	2.62	2.62	2.28	7.33	3.67	5.24	1.51
		<2	27.43	3.44	1.97	2.87	2.70	13.03	8.41	3.27	1.17	2.90	6.54	3.74	17.52	5.01
Ultra High Fines	AL	>45	83.84	0.40	0.34	0.83	0.54	1.56	5.05	1.62	-	-	4.04	-	-	1.78
		<45	53.37	1.15	0.43	3.86	1.45	5.36	23.22	1.49	0.93	1.15	2.97	0.74	2.78	1.10
		<2	30.35	1.17	2.30	6.32	1.85	13.65	9.13	3.04	1.27	3.15	7.10	8.62	6.33	5.72
	AB08	>45	91.84	0	0.06	0.36	0.16	1.69	1.89	1.01	-	-	2.52	-	-	0.47
		<45	52.48	1.23	0.59	4.63	1.48	3.92	17.86	1.36	0.85	1.48	4.76	2.38	5.10	1.88
		<2	30.63	3.27	1.27	4.35	1.36	17.53	5.75	2.88	2.40	2.09	13.43	3.84	7.20	4.00

4.3.7 Pattern recognition of production of carboxylic surfactant from different oil sands ores

So far, it is shown that the generation of natural carboxylic surfactant from ores depends on different parameters such as bitumen content, bitumen chemistry, concentration of divalent cations, connate water chemistry, clay type and clay content, and pH of extraction process. In an attempt to find a pattern accounting for the concentration of released carboxylic surfactant in tailings water samples prepared with different ores, concentrations of carboxylic surfactant for each ore at different NaOH dosages were normalized by the maximum concentration of carboxylic surfactant for that ore at 0.5 wt.% NaOH. Plotting the normalized concentrations of carboxylic surfactant as a function of pH (Figure 4.18b) revealed a better correlation than NaOH dosage (Figure 4.18a) between the two parameters. The absolute relative error (%) for the fitted line in Figure 4.18.a was calculated to be 6.5 % while for the fitted line in Figure 4.18.b was 4.8 %. Figure 4.18 illustrates that although many factors can affect the concentration of released surfactant in tailings water, the fraction of the total carboxylic surfactant that can be released from each ore at the same pH value is similar.

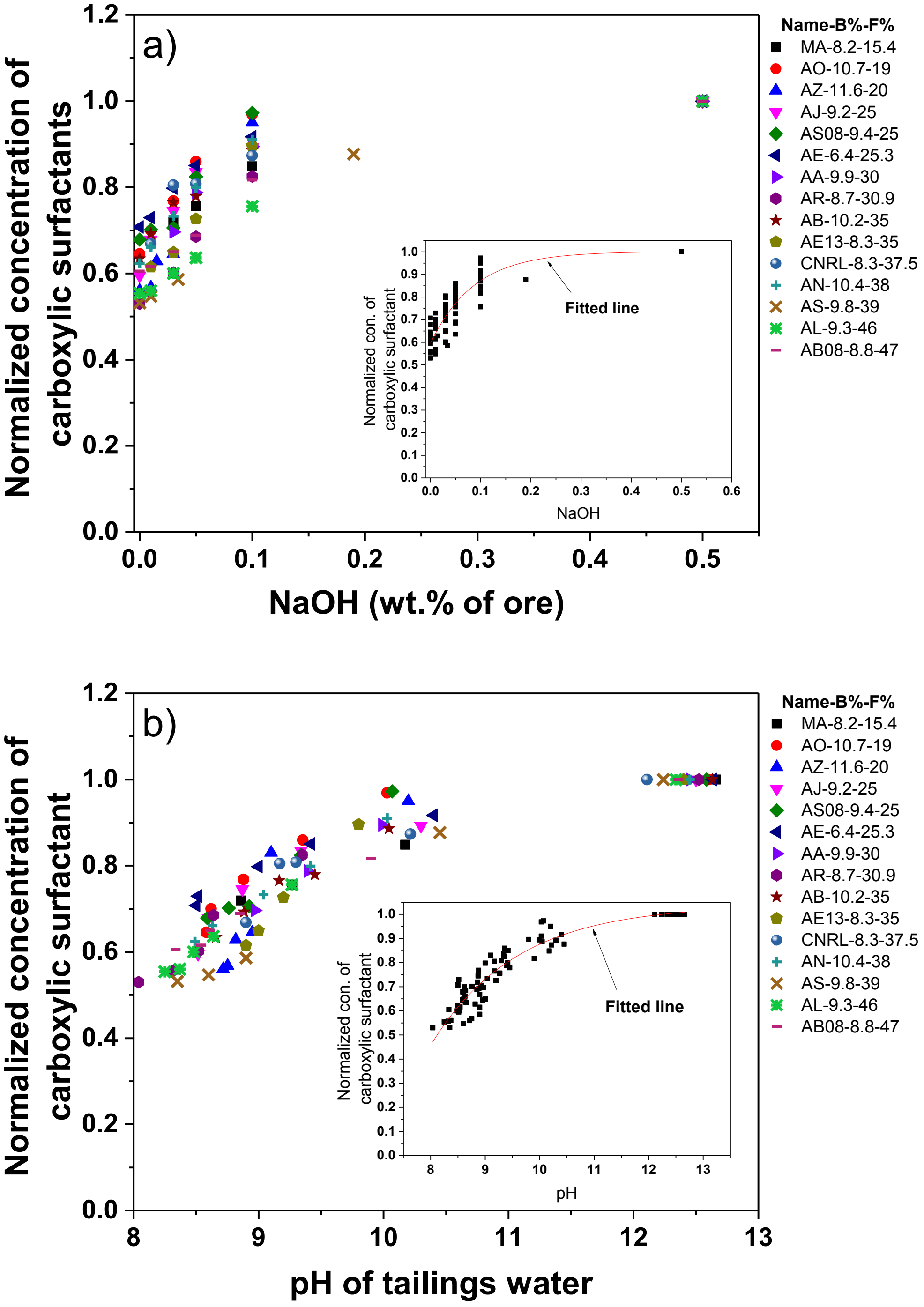

Figure 4.18. Normalized concentration of free carboxylic surfactant in tailings water of different ores prepared at different NaOH dosages. a) as a function of NaOH (wt.% of ore) added to flotation tests, and b) as a function of pH of the tailings water. Concentration of carboxylic surfactants were normalized by the maximum concentration of carboxylic surfactant released at 0.5 wt.% NaOH.

4.3.8 Ore weathering/ oxidation/aging

In a number of wreathing/aging case studies, the reduction in the generated surfactant concentration was reported as the main reason for the observed reduction in bitumen recovery (Schramm and Smith, 1987b; Schramm and Smith, 1987c; Wallace et al., 1989). To understand the role of aging in deteriorating surfactant production and hence bitumen recovery, two different ores (AE13 and AR) were artificially weathered in an oven for 2 days at 60 °C following the method established by Ren et al. (2009a). Denver flotation tests were then used for both ores at two NaOH dosages: 0 and 0.05 wt.% NaOH.

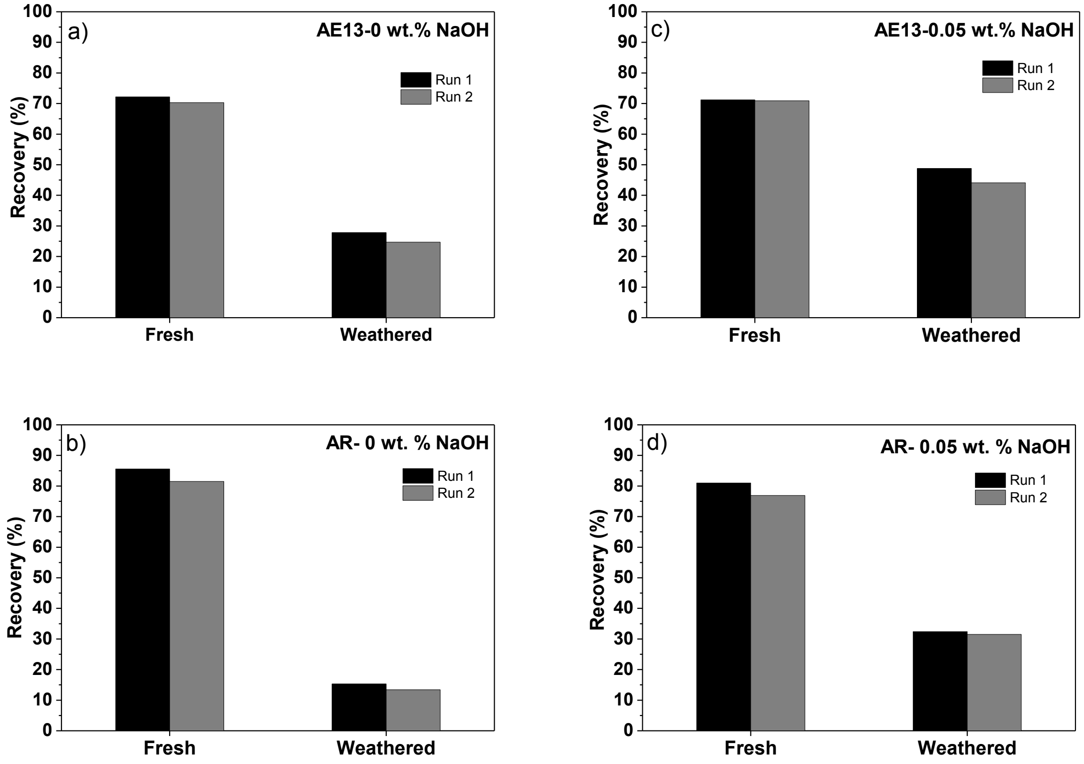

Figure 4.19. Effect of weathering on bitumen recovery. a) AE13 ore at 0 wt.% NaOH, b) AE13 ore at 0.05 wt.% NaOH, c) AR ore at 0 wt.% NaOH, d) AR ore at 0.05 wt.% NaOH.

The results of bitumen recovery and concentration of free carboxylic surfactant in tailings water are shown in Figure 4.19 and Figure 4.20, respectively. As shown, bitumen recovery for both ores at 0 wt.% NaOH decreased drastically after weathering from ~75% to ~25% for AE13 and from ~85% to ~15 % for AR. Addition of 0.05 wt.% NaOH only marginally changed the bitumen recovery of fresh ores. However, it almost doubled the bitumen recovery of weathered ores. The positive impact of NaOH addition on bitumen recovery of oxidized ores was also reported by Mikula et al. (2003).

Figure 4.20 shows that the concentration of free carboxylic surfactant in tailings water prepared with weathered ores are consistently lower that fresh ores; however the difference is not significant. Especially for AE13, the difference in the carboxylic surfactant concentrations before and after weathering is negligible (from ~32 x10^{-5} mol/L to ~29 x10^{-5} mol/L at 0 wt.% NaOH). Hence, it can be concluded that the decrease in the concentration of natural surfactant is not the main reason that causes more than 60% reduction in the bitumen recovery. According to other studies, it is most likely that the changes in the hydrophobicity of solids by losing the water layer between the bitumen and sands and the attachment of bitumen to sands cause the poor processability of weathered ores (Dang-Vu et al., 2009a; Ren et al., 2009a). Ren et al. (2009b) used atomic force microscopy (AFM) to show that weathering had a significant effect on bitumen-solid interactions. Strong repulsive forces were changed to attractive forces, which was attributed to the increased hydrophobicity of solids during weathering process. Mikula et al. (2003) revealed that changes in the bitumen chemistry are another key factor for the low bitumen recovery of degraded or oxidized ores. They reported that loss of aliphatic carbons in favour of hydroxyl groups in bitumen is the main reason for the recovery drop in weathered ores.

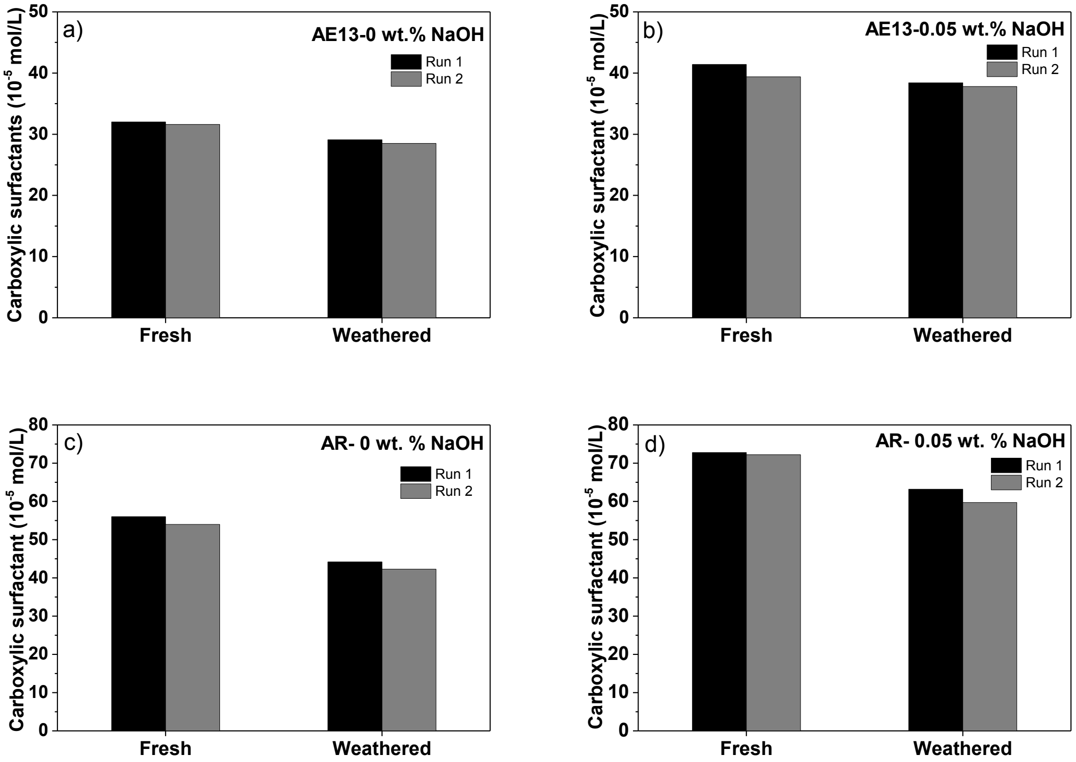

Figure 4.20. Effect of weathering on concentration of free carboxylic surfactant in tailings water. a) AE13 ore at 0 wt.% NaOH, , b) AE13 ore at 0.05 wt.% NaOH, c) AR ore at 0 wt.% NaOH d) AR ore at 0.05 wt.% NaOH

In order to examine the role of water chemistry (mainly surfactant concentration) versus the changes in the wettability of solids in reducing the bitumen recovery of weathered ores, bitumen liberation test (using image processing method) at three different conditions was conducted: i) fresh ore with tailings water prepared with fresh ore, ii) weathered ore with tailings water prepared with weathered ore and iii) weathered ore with the tailings water prepared with fresh ore, which has higher concentration of carboxylic surfactant. Degrees of bitumen liberated from fresh and weathered AE13 ore at 0 wt.% NaOH is compared in Figure 4.21.As shown, by weathering the bitumen liberation has drastically decreased (■ and ●). By substituting the tailings water of weathered ore with fresh one in performing the liberation test of weathered ore, negligible changes in the degree of bitumen liberated was observed (● and ▲), indicating that the role of surfactant concentration in changing the bitumen liberation of weathered ore is insignificant.

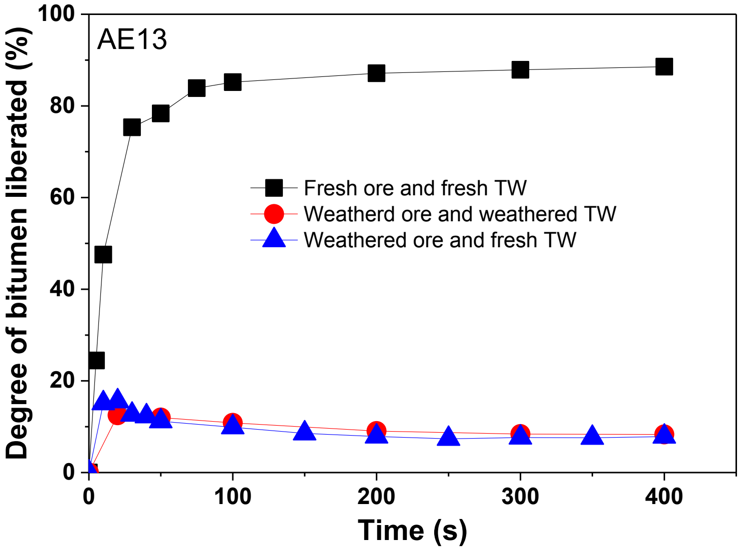

Figure 4.21. Effect of weathering on degree of bitumen liberated from AE13 ore.

4.4 Conclusions

In this chapter, the possible variables (properties) of oil sands extraction system in connection with the concentration of free carboxylic surfactant in tailings water produced after floatation test were studied.

It was found that the addition of caustic to flotation tests increased the concentration of released carboxylic surfactant in tailings water for all the ores. The variation in the pH values of the tailings water samples and concentrations of carboxylic surfactant released from different ores at the same NaOH dosage was attributed to the difference in the water chemistry (connate water and process water), bitumen chemistry, ore composition, and clay types of ores. Because of the complexity of the oil sands ores, the limited number of ores studied, and undiscovered and/or unmeasured parameters which could have impact on the generation of carboxylic surfactant, it was impossible to establish a unique pattern for the production of surfactant from all types of oil sands ores. However, some trends were observed.

It was shown that fine content in the ores can affect the pH of the tailings water. Tailings water samples prepared with average fine ores had higher pH values compared to ultra-high fines ores at the same NaOH dosage. Other than fine content, clay type also was shown to have effect on controlling the pH. It was shown that the effect of illite on reducing the pH of process water was stronger than kaolinite.

Ores with higher bitumen content and lower fines content released more carboxylic surfactant, although outliers were observed. Bitumen chemistry and clay type also play a significant role. It was found that the same weight of bitumen extracted from different ores contained different amount of carboxylic surfactant. Also it was shown that ores with higher pyrite content (in the fine fraction) produced less surfactant.

Concentration of divalent cations (calcium and magnesium) was another key factor affecting the concentration of free carboxylic surfactant in tailings water. Ores with higher calcium and magnesium contents released less carboxylic surfactant. At pH values less than 12, addition of calcium and magnesium ions to flotation tests resulted in reduction of pH and had a detrimental effect on the production of carboxylic surfactant and bitumen recovery. It is suggested that calcium and magnesium ions were precipitated mostly in the form of carbonate or hydroxides over this pH range. At pH values above 12, the added calcium and magnesium were consumed mainly by carbonate and humate ions, hence the pH of tailings water, concentration of carboxylic surfactant and bitumen recovery remained almost unchanged.

By normalizing concentrations of carboxylic surfactant for each ore by the maximum concentration of free carboxylic surfactant measured for that ore (maximum concentration was measured for tailings water prepared with 0.5 wt.% NaOH), a similar pattern for all ores between the normalized concentration of carboxylic surfactant and pH of the tailings water was observed.

Weathering diminished bitumen recovery by more than 60 %. According to several studies, the reduction of bitumen recovery was assigned to the hindrance effect of weathering on production of carboxylic surfactant. In this work, with the help of bitumen liberation test it was shown that concentration of carboxylic surfactant has a negligible effect on bitumen liberation and hence recovery of weathered ores. It was suggested that the observed depression in bitumen recovery is associated most likely with other factors, such as changes in the wettability of the solids.

CHAPTER 5

5 Role of Caustic Addition in Bitumen-Clay Interactions

A version of the following chapter has been accepted for publication by journal of Energy and Fuels. The objective of this paper was to investigate the role of clay types and water chemistry caused by NaOH addition in bitumen-clay interaction or bitumen slime coating. Additional results to this chapter are summarized in Appendix C.

5.1 Introduction

In 2013 Alberta, Canada produced an average 331.4 thousands (10^3) m^3/d of crude bitumen, of which around 47% was extracted by surface mining (Alberta government quarterly update, Spring 2014) and warm slurry extraction process. The water-based extraction process relies on the efficient detachment of bitumen from solids, namely liberation (Basu et al., 1996; Masliyah,et al., 2004; Srinivasa et al., 2012), and the subsequent attachment of bitumen to air bubbles, namely aeration. (Clark, 1929; Clark, 1944; Sanford, 1983; Flynn et al., 2001; Gu et al., 2004; Su et al., 2006 ; Wang et al., 2010). 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 (Liu et al., 2005). In this case, the fines 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 (Gu et al., 2003). The attached clays to the bitumen surface can also cause problems in bitumen froth treatment by forming a rag layer (Jiang et al., 2011a; Jiang et al., 2011b; Kiran, 2009).

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 (Liu et al., 2005; Kasongo et al., 2000; Liu et al., 2002; Liu et al., 2003; Liu et al., 2004a; Liu et al., 2004b; Zhao et al., 2006; Ding et al., 2006). While oil sands ores are a complex mixture of clays including kaolinite, illite, chlorite, montmorillonite, etc., 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 (Liu et al. 2002; Liu et al., 2004b). 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 (Liu et al., 2002). As proposed by Masliyah, et al., calcium ions can act to bridge bitumen and clays, with the level of slime coating being related to the calcium ion –

clay binding strength (Liu et al., 2002; Liu et al., 2004b). 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 (Liu et al., 2002; Wallace et al., 2004). Using AFM to study the interaction potential between bitumen and clays (montmorillonite and kaolinite) in the presence of calcium, Liu et al. (2005) 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 (Liu et al., 2004a).

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. (2006) 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^{o}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. (2000) 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.

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 (Long et al., 2007; Harjai et al., 2012). 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 (Masliyah et al., 2004), (Schramm et al., 2003), (Schramm and Smith, 1987a), (Flury et al., 2014).

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.

5.2 Materials and experimental methods

5.2.1 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 (d50) 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.

5.2.2 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 (Ivanchenco et al., 1995; Rodahl and Kasemo 1996; Notley et al., 2005; Fatisson at al., 2009; Alagha et al., 2011; Wang et al., 2011; Alagha at al., 2013; Gotoh et al., 2006). 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 (Sauerbrey, 1959), 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.

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

where, n is the overtone number, f_0 is the fundamental resonance frequency, ρ_q (2648 kg/m^3) is the density of quartz, t_q (3.3×10^{-4} m) is the thickness of the quartz crystal and c (0.177 mg/m^2·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 deposites. Frequently, the deposited film may exhibit viscoelastic properties where the frequency is influenced by the mechanical properties of the film, including the shear modules and viscosity (Cho et al., 2007). 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 (Rodahl et al., 1995), 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.

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

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 Voinova -Voigt equation (Eqs 3,4 and 5)(Cho et al., 2007; Voinova et al., 1999), by considering both the frequency and dissipation data. In the following equations indices 0, 1 and 2 represent quartz, adsorbed viscoelastic layer and Newtonian fluid, respectively.

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

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

$$\delta = \sqrt{\frac{2\eta_2}{\rho_2\omega}} \tag{5}$$

Where h is thickness, ρ *is* density, η *is* viscosity, μ is shear modulus and ω *is* the circular 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.

5.2.3 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 ^{o}C for 24 hrs 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 dropwise 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. By attaching the two data sets using stitch command in the Q-Sense software, the approximate layer thickness (DDMS + bitumen) was determined to be ~200 nm using Q-Tools software (Q-Sense analysis software). [*]

5.2.4 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 5.1) was slurried

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[*] The graph is shown in Appendix C.1

for 5 min at 1500 rpm in 900 g of process water (chemical composition shown in Table 5.2). 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. (2004). 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 5.1. 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 5.2. Chemistry of process water

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

* ppm or mg/L is milligram (mg) of ion per liter (L) of process water

5.2.5 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 to the low interfacial tension between bitumen and water which may cause emulsification of bitumen into the aqueous phase. 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 ~ pH 4.5. For all the experiments the fluid temperature was maintained at $22 \pm 0.02^{\circ} C$ 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%.

5.2.6 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 5.1, with a weak broad band around 1743 cm^{-1} of the Fourier transform infrared (FTIR) absorbance spectrum of the 3rd extraction.

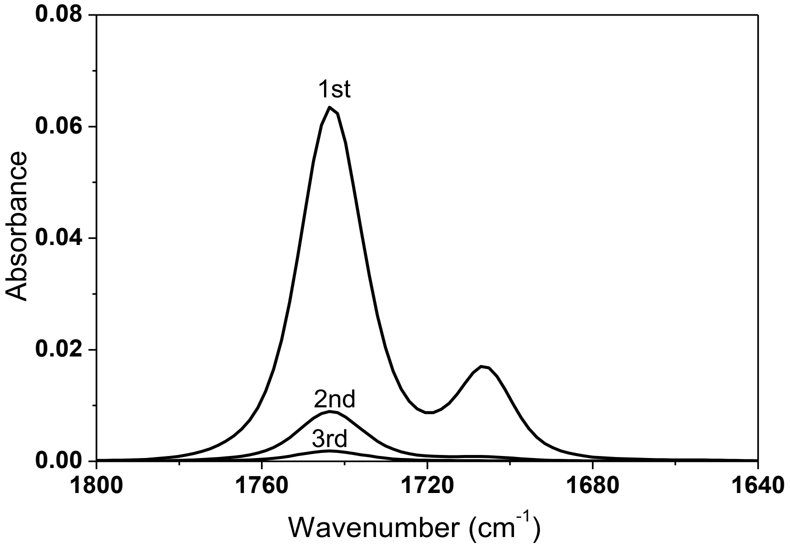

Figure 5.1. FTIR spectra of extracted carboxylic surfactants from tailings water in dichloromethane. Extraction was performed in three steps.

The three DCM extraction samples were combined and then placed in a vented fume hood to evaporate the solvent under filtered air (45 µm 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) (Clemente and Fedorak 2005; Scott et al., 2008). 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 4000-400 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 ~1706 cm^{-1} (dimmers) 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).

5.3 Results and discussion

5.3.1 QCM-D method evaluation

Frequently, slime coating phenomena have been investigated by zeta potential distribution analysis (Liu et al., 2005; Liu et al., 2002; Liu et al., 2003; Liu et al., 2004a; Liu et al., 2004b; Zhao et al., 2006; Ding et al., 2006). The technique has identified specific conditions which promote slime coating of montmorillonite on bitumen and coal in the presence of divalent cations (Liu et al., 2002; Xu et al., 2003). Therefore, the interaction between montmorillonite, with bitumen in the absence and presence of calcium was chosen to validate the QCM-D technique. Figures 5.2a 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 5.2a) 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 $(\Delta f / n \sim -65Hz)$ and positive dissipation shift $(\Delta D \sim +32 \times 10^{-6})$ 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.

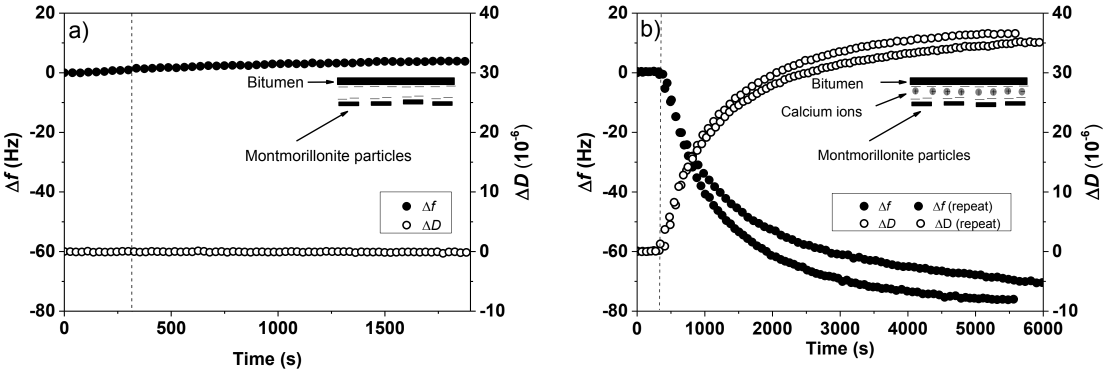

Figure 5.2. Interaction between montmorillonite clay particles and bitumen surface in 1 mM KCl solution at pH 8.5, a) without Ca^{2+} and b) with addition of 40 ppm Ca^{2+} (1 mM CaCl2). Dashed line indicates fluid switching from background (Milli-Q® water at pH 8.5) to montmorillonite suspension.

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 5.3a, a heterogeneous layer of particles was observed to be deposited on and engulfed within the bitumen layer. At lower resolution (Figure 5.3b) 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 ~2.7 g/cm3 (Mitchell, 1976), and with a sensor area of 1.21 cm2, the mass of particles deposited per unit area based on 16% surface coverage is calculated to be 6.67 µg/cm2. The apparent mass deposited (Figure 5.4) 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 $\mu g/cm^2$. Close agreement between the two approaches confirms that QCM-D is a suitable technique to assess slime coating potential.

It is worth nothing that all the QCM-D tests conducted in this work were repeated. The variation in the measurements was less than ~10 %.

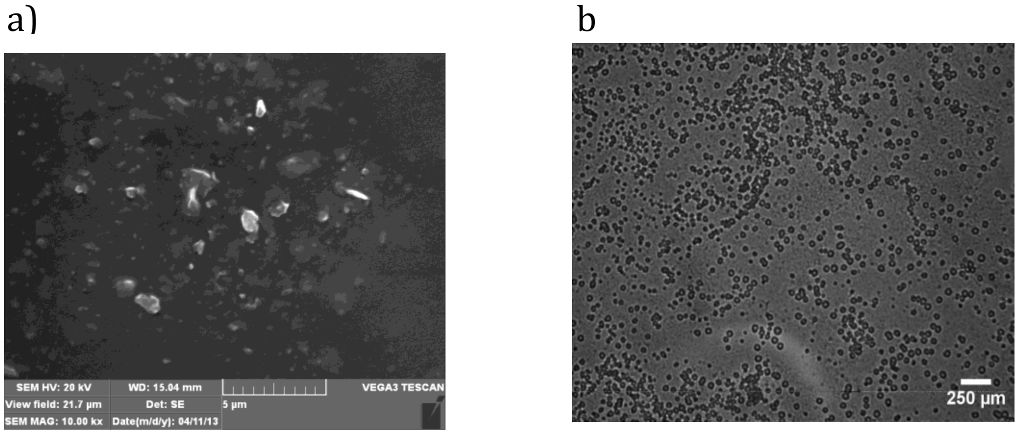

Figure 5.3. (a) SEM and (b) optical microscope images of deposited montmorillonite particles on the surface of bitumen coated sensor. Fluid conditions: 0.1 wt.% montmorillonite suspension in 1mM KCl solution with 40 ppm Ca^{2+} (1mM CaCl2) at pH 8.5.

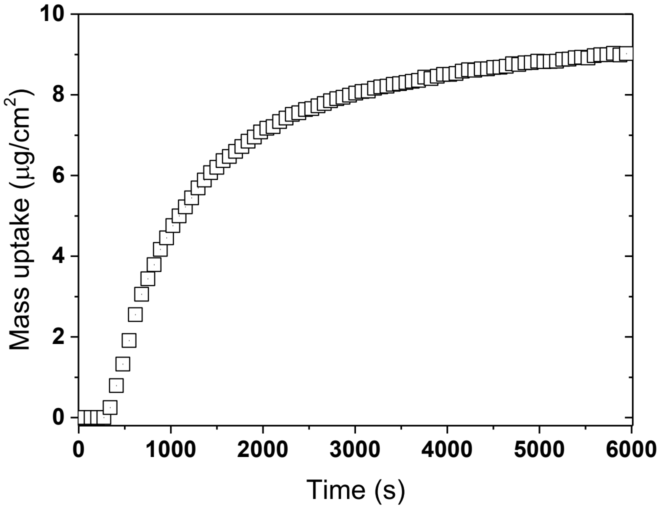

Figure 5.4. Apparent mass of montmorillonite particles deposited on bitumen coated sensor surface as determined by Voigt model (using Q-Tools software). Fluid conditions: 0.1 wt.% montmorillonite suspension in 1mM KCl solution with 40 ppm Ca^{2+} (1mM CaCl2) at pH 8.5.

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

Kaolinite: Figure 5.5 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 tgailings 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 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. The results presented in Figure 5.5 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 model particle studies (Kasongo et al., 2000; Liu et al., 2002).

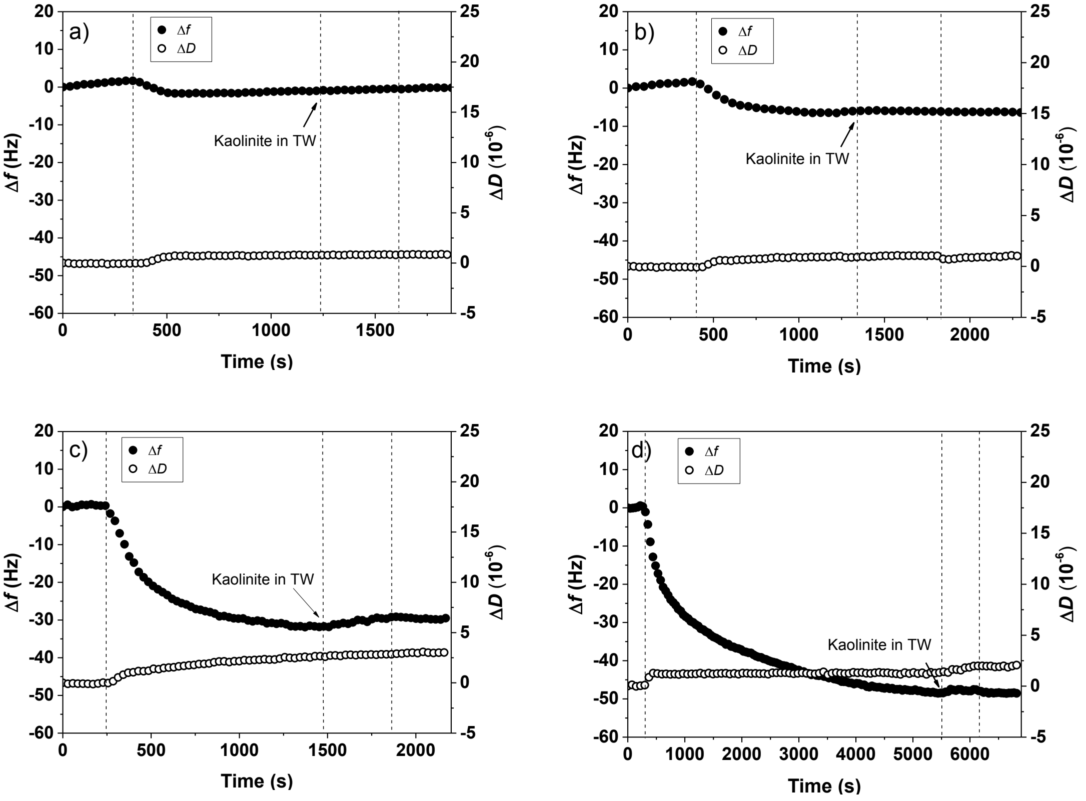

Figure 5.5. Interactions between kaolinite particles and bitumen surface in tailings water prepared with different levels of caustic additions during bitumen extraction: a) 0 wt.% NaOH, b) 0.05 wt.% NaOH, c) 0.1 wt.% NaOH and d) 0.5 wt.% NaOH with initial suspension particle concentration of 0.1 wt.%. 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

Illite: Figure 5.6 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 5.2a and 5.5a-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 (Romanova et al., 2006). 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 data provides fundamental understanding for the detrimental effect caused by ultrathin illite (<0.3 μm) particles on the overall bitumen recovery (Mercier et al., 2008; Fu et al., 2010).

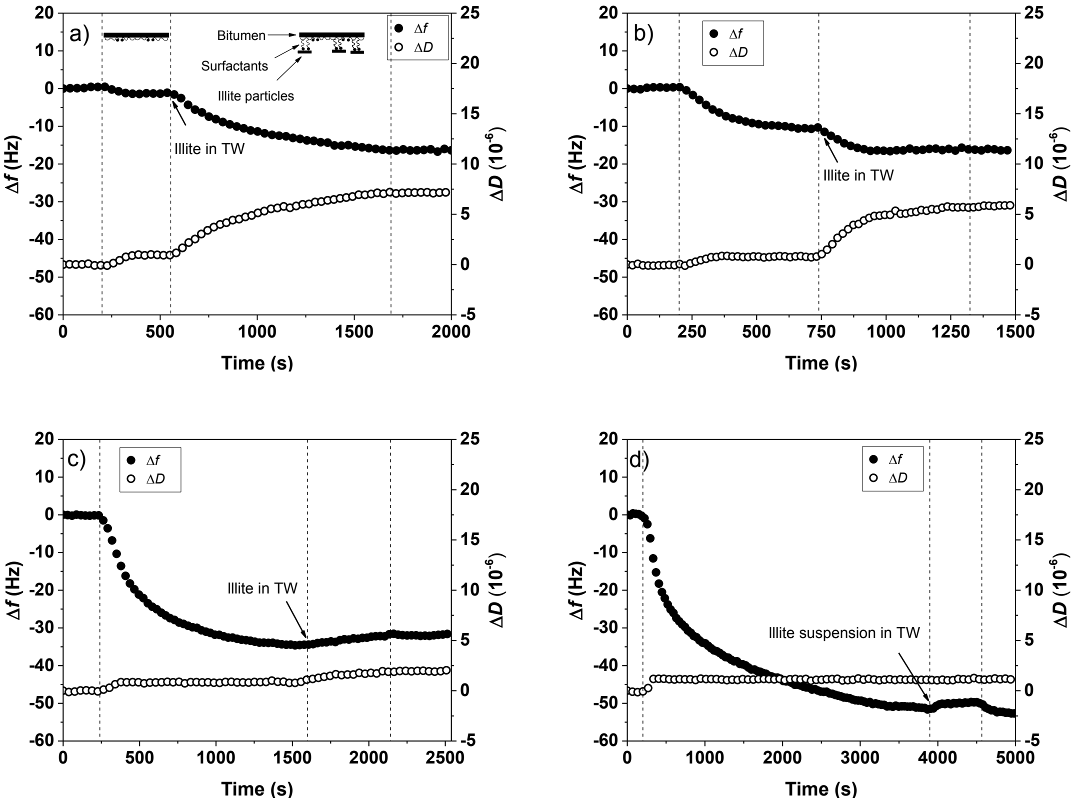

Figure 5.6. Interactions between illite particles and bitumen surface in tailings water prepared with different levels of caustic addition during bitumen extraction: a) 0 wt.% NaOH, b) 0.05 wt.% NaOH, c) 0.1 wt.% NaOH and d) 0.5 wt.% NaOH with initial illite clay particle concentration of 0.1 wt.%. Dashed lines indicate fluid switching (from left to right: background to tailings water; tailings water to illite suspension in tailings water; tailings water rinse).

Calculating the deposited particle mass by the Voigt model, the deposited mass was determined to be in the range of 0.5 – 0.6 μg/cm2 for both the 0 and 0.05 wt.% caustic samples, see Figure 5.7. 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+}.

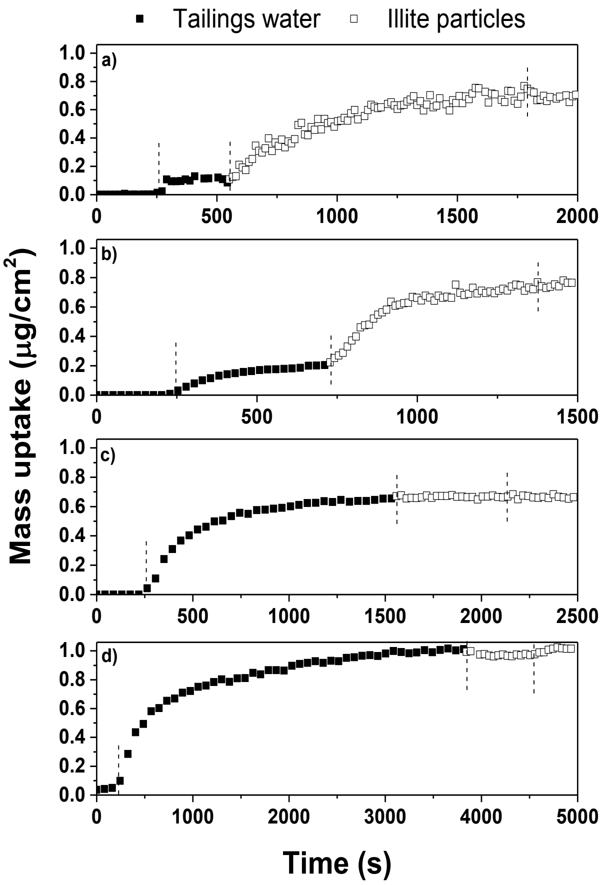

Figure 5.7. Apparent deposited mass caused by tailings water and illite clay particles on bitumen surface determined by Voigt two layers model (using Q-Tools software) at increasing caustic concentrations: a) 0 wt.% NaOH, b) 0.05 wt.% NaOH, c) 0.1 wt.% NaOH, d) 0.5 wt.% NaOH.

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 (↑ 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 (Schramm and Smith 1987a; Wik et al., 2008b).

Table 5.3. 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.
** ppm or mg/L is milligram (mg) of cation per liter (L) of tailings water.

As previously shown in Figures 5.5 and 5.6, 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 5.8. 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).

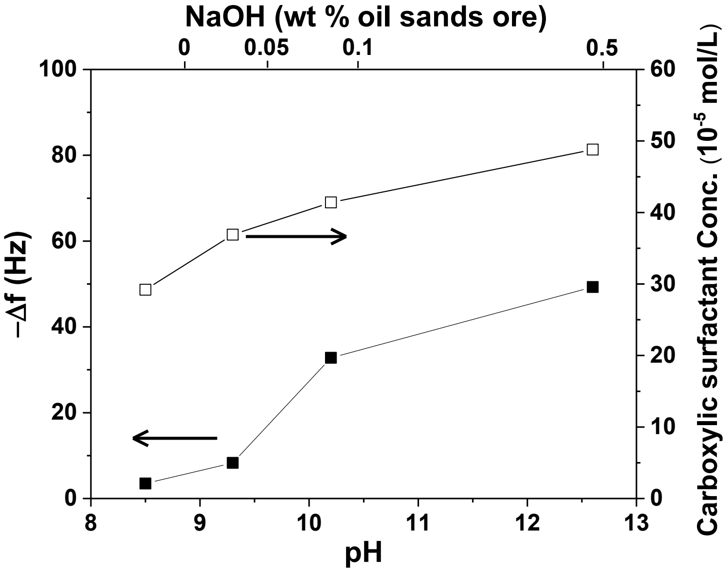

Figure 5.8. Variation in the resonance frequency of bitumen coated sensors upon switching of fluid from Milli-Q® water to tailings water without clay particles (left axis), and the corresponding tailings water carboxylic surfactants concentration (right axis) as a function of pH/caustic level.

On visual inspection of the tailings waters, a noticeable discoloration (browning) was observed with increasing caustic addition as shown in Figure 5.9. 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 (Majid and Ripmeester, 1990; Majid et al., 1992; Gutierrez and Pawlik, 2014a, Gutierrez and Pawlik, 2014b). 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 acid 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.[*]

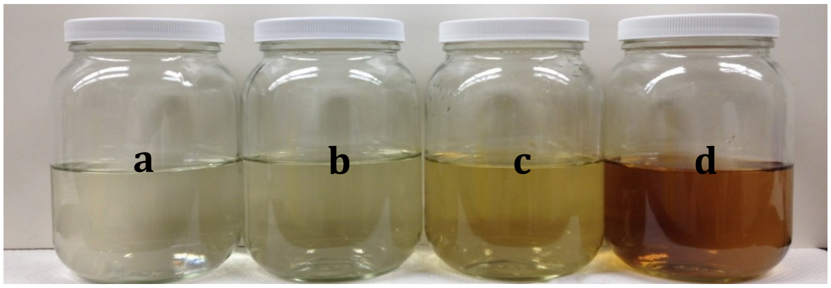

Figure 5.9. Changes in the color of laboratory extracted tailings water with increasing caustic addition during bitumen extraction :a) 0 wt.% NaOH (pH 8.5), b) 0.05 wt.% NaOH (pH 9.3), c) 0.1 wt.% NaOH (pH 10.2) and d) 0.5 wt.% NaOH (pH 12.6).

Qualitative verification by color comparison of the tailings water prepared with 0.5 wt.% NaOH and solutions of humic acids in Milli-Q water confirmed that the humic acids content in the tailings water (0.5 wt.% NaOH) should be in the range of 50 ppm. 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

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[*] Adsorption of humic acids by illite clay have been investigated in Appendix C.2

[†] ppm: mg of humic acids sample per liter (L) of water sample.

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.

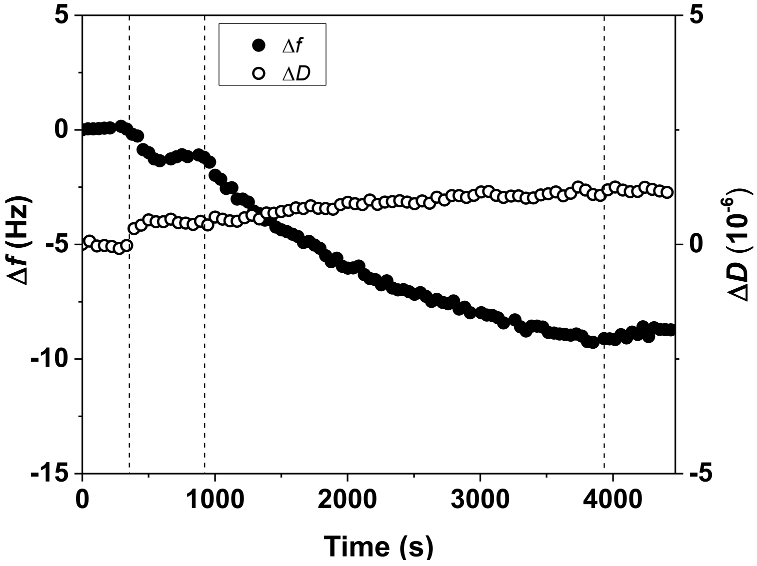

Figure 5.10. Frequency and dissipation shifts of bitumen-coated QCM-D sensor during the introduction of tailings water (0 wt. % NaOH) followed by introduction of tailings water containing humic acids of the same pH. Dashed lines indicate the switching of the fluid (from left to right: background to tailings water; tailings water to tailings water containing 50 ppm humic acids; and tailings water rinse.

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. 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 5.9 and 5.10 tend to suggest that the 'sharp decrease' in resonance frequency between pH 9.3 and pH 10.2 (shown in Figure 5.8) results from the added contribution of humic acids.

5.3.3 Effect of water chemistry on illite – bitumen slime coating

5.3.3.1 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 (Dai et al., 1992; Zhao et al., 2009; Masliyah et al., 2011). Previous research has demonstrated the pivotal role of Ca^{2+} on bitumen slime coating by montmorillonite model clay particles (Liu et al., 2002). 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 (Wik et al. 2008a; Dai et al., 1992; Masliyah et al., 2011). 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 5.11 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.

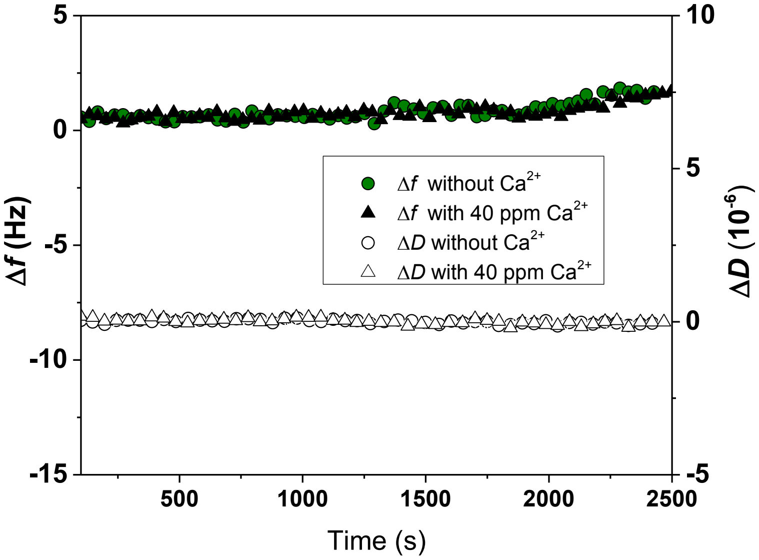

Figure 5.11. Interaction between illite particles and bitumen surface in 1 mM KCl solution at pH 8.5, with and without the addition of 40 ppm Ca2+ (1 mM CaCl2). Dashed line indicates fluid switching from background (Milli-Q® water at pH 8.5) to illite suspension.

5.3.3.2 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 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 when comparing experiments: i) 0 wt.% NaOH tailings water and iii) 0.5 wt.% NaOH tailings water with humic acids extracted. 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 (Δf ~ -14Hz) and dissipation responded rapidly to reach a new steady state condition. For the high surfactant concentration solution (0.5 wt.% NaOH tailings water with humic acids extracted), in the absence of illite particles the frequency shift is greater than the experiment conducted using 0 wt.% NaOH tailings water, with the dissipation shift being almost the same. With the addition of illite clay particles the frequency (Δf ~ -14Hz) and dissipation responded rapidly to reach a new steady state condition. For the high surfactant concentration solution (0.5 wt.% NaOH tailings water with humic acids extracted), in the absence of illite particles the frequency shift is greater than experiment performed with (0 wt.% NaOH) tailings water, with the dissipation shift being almost the same. With the addition of illite particles both the frequency (Δf ~ -11Hz) 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 (Liu et al., 2004a). The interaction strength between the clay particles and bitumen is lower as shown by the increase in frequency during tailings water wash.

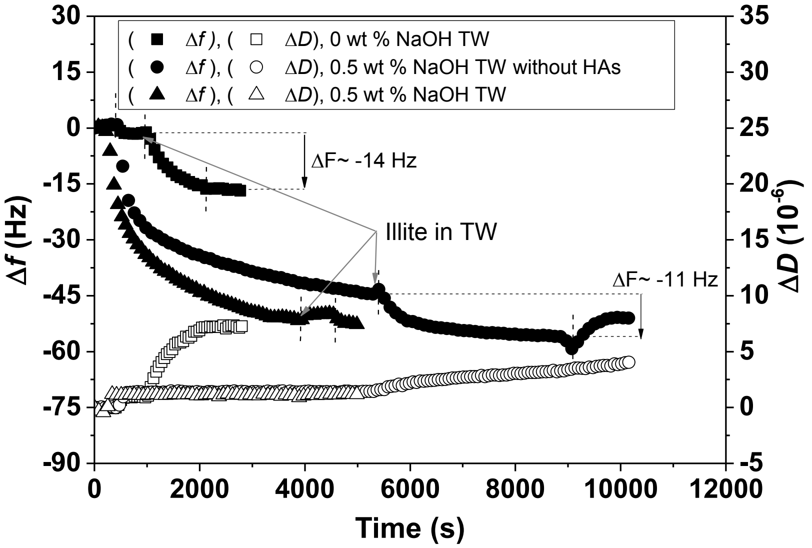

Figure 5.12. The effect of surfactant concentration (■ and ●) and humic acids concentration (▲ and ●) on the slime coating potential of illite on bitumen. Dashed lines indicate switching of the fluid (from left to right: background to tailings water; tailings water to illite suspension in tailings water (0.1 wt.%); and tailings water rinsing). HAs: humic acids.

The role of humic acids was considered by comparing experiments using 0.5 wt.% NaOH tailings water and 0.5 wt.% NaOH tailings water with humic acids extracted. While the QCM-D test performed using 0.5 wt.% NaOH tailings water with humic acids extracted confirms slime coating of bitumen by illite particles, the test conducted using 0.5 wt.% NaOH tailings water with humic acids present, shows contrasting behaviour. 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 0.5 wt.% NaOH tailings water with humic acids extracted where particle deposition was measured.

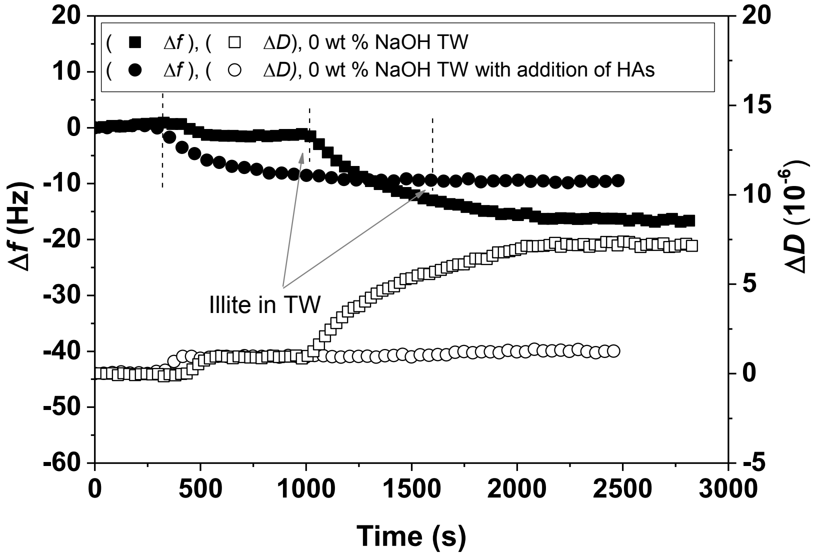

Figure 5.13. Effect of humic acids (addition) on the interaction of illite clay particles with bitumen. Dashed lines indicate fluid transitions (from left to right: background to tailings water; tailings water to illite suspension in tailings water (0.1 wt.%); tailings water rinse). HAs: humic acids.

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

5.13. 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 5.12) and addition (Figure 5.13) 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.

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 (Derjaguin and Landau, 1941; Verwey and Overbeek, 1948). A general rule of thumb for colloidal stability/instability transition is a surface/Stern potential around ± 30 mV.

Table 5.4. 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 (Churaev and Derjaguin, 1985; Xu and Yoon, 1989). To assess the hydrophobic force contribution, 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 Ca^{2+} and 0 wt.% NaOH tailings water without and with 50 ppm humic acids addition. Further details on the WDPT method can be found elsewhere (Dang-Vu et al. 2009b). 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 mm^3) 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 Ca^{2+} 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^{o}) 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 (Gutierrez and Pawlik, 2014a), the attractive hydrophobic interaction between the bitumen and illite particles weakens, potentially lowering the interaction potential between illite and bitumen. Figure 5.14 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 illite (Ksiezopolska and Pazur, 2011; Kretzschmar et al., 1997; Goodwin, 2004), 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.

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[*] Bitumen wettability in presence of humic acids was studied using micropipette in Appendix C3.

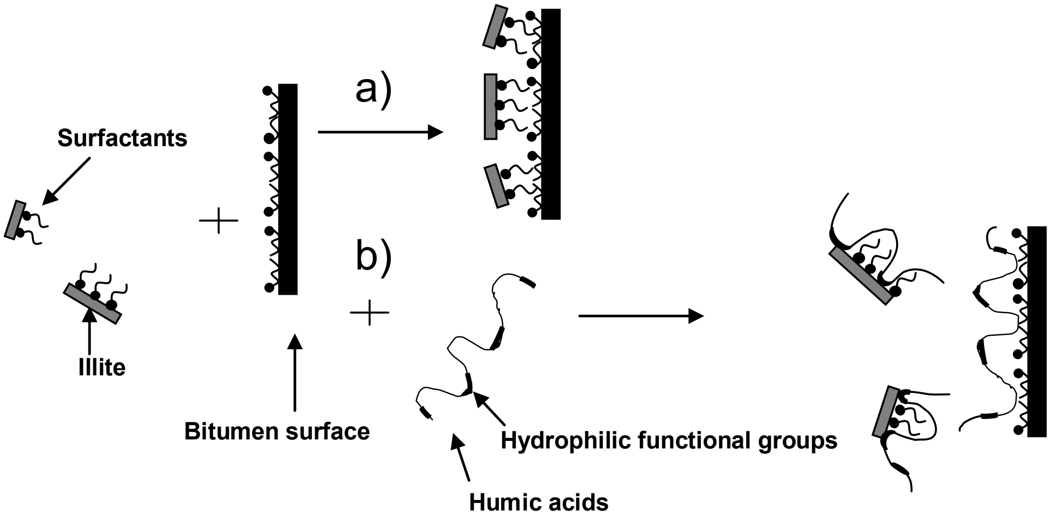

Figure 5.14. Model of interaction between illite and bitumen in tailings water without (a) and with (b) humic acids.

5.4 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.

CHAPTER 6

6 Conclusions and Future Works

6.1 Conclusions

This thesis described the studies on the role of NaOH in the bitumen extraction process. Research efforts were focused on quantifying the concentration of surfactant released during extraction process and investigating the effect of NaOH and related parameters on surfactant generation, bitumen extraction efficiency and bitumen-clay interactions.

Addition of NaOH as a process aid to water-based extraction process was to increase the alkalinity of the extraction process. In this work it was shown that the addition of the same NaOH dosage to the flotation tests, performed with different ores, resulted in production of tailings water samples with different pH values. It was found that in addition to water chemistry of the extraction process, other factors related to ore characteristics, such as fine content and clay types could also affect the pH of tailings water. It was shown that at the same caustic level, tailings water samples prepared with average fines ores had generally higher pH values than the ones prepared with ultra-high fines ores. Also, it was shown that illite clay have stronger impact on reducing the pH of the tailings water than kaolinite clays.

Addition of NaOH as a process aid to water-based extraction process was found to aid the release of natural surfactant (mainly carboxylic types) from oil sands ores. A modified version of an existing DCM extraction and FTIR technique was used to quantify the carboxylic surfactant in the tailings water. In this method, individual carboxylic compounds were used to establish a mol/L calibration curve. Compared to the original method (with mg/L calibration curve) the new method provides a more accurate reference for comparing the concentration of carboxylic surfactant from different sources. The addition of NaOH to pH above 10 was also found to liberate humic acids. Presence of humic acids and other soluble organic or inorganic matters in the tailings water had a negligible effect on quantification of carboxylic surfactant using DCM extraction and FTIR technique.

Based on surface tension measurements performed before and after the extraction of carboxylic surfactants from tailings water, it was shown that the addition of NaOH at the levels investigated had a negligible effect on the release of sulfonic surfactant from oil sands ores during the extraction process.

The comparison of measured carboxylic surfactant for different ores demonstrated that each ore responded differently to the addition of NaOH in the generation of carboxylic surfactant. However, after normalizing the concentrations of carboxylic surfactants produced from each ore at different caustic levels to the maximum concentration measured for each ore at 0.5% wt. NaOH, it was shown that the normalized concentrations as a function of pH collapsed into a single curve with a relative error of 4.8%.

Bitumen content, initial carboxylic surfactant content in the bitumen, the amount of NaOH added, concentration of divalent cations and carbonate ions, and pyrite content in the oil sands ores were investigated as important parameters in determining the concentration of carboxylic surfactant in the tailings water. In the study on the addition of calcium and magnesium to the flotation tests, it was found that the scavenging effect of calcium and magnesium on carboxylic surfactants and hence on bitumen recovery was diminished at pH greater than 12. The added calcium and magnesium were mostly precipitated in forms of calcium and magnesium carbonates or humates at such high pH. At lower pH values, the added calcium and magnesium were also partially precipitated in the form of carboxylates or hydroxides.

Artificially weathered ores were used to understand the role of weathering or oxidation on processability and surfactant production of weathered ores. A significant decrease (more than 70%) was measured in the bitumen recovery of the weathered ores, while the concentration of the released surfactant decreased only by 10-20%. The results of liberation tests before and after weathering indicated a drop in bitumen liberation by 85%. Additional liberation tests showed that the sharp reduction in the bitumen recovery of weathered ores was not due to the loss of surfactant in the weathering process, but more attributed to other factors such as changes in wettabilty of sands.

Using QCM-D to investigate bitumen-clay interactions, an excellent agreement was shown between the results of zeta potential distribution measurements and QCM-D technique when the interactions between bitumen and montmorillonite clay particles in the presence of calcium ions were studied. In using the QCM-D technique to study the role of NaOH addition in interaction of bitumen and clays, it was found that kaolinite did not exhibit any attractive interactions with bitumen. However, illite clay particles were found to coat on bitumen when tailings waters produced at weak alkaline conditions were used. Illite-bitumen interaction was diminished at strong alkaline conditions when tailings water prepared with high caustic dosages was used (pH > 10). Systematic studies, using QCM-D technique, showed that the addition of divalent cations did not activate the deposition of illite clay particles on bitumen as it did for montmorillonite. The presence of surfactants in the tailings water was found to help illite deposition on bitumen.

One of the key findings of this research was that the release of humic acids at high caustic dosages was identified as the main factor for the deactivation of bitumen-illite interaction. The major role of humic acids was found to be the reduction of the hydrophobicity of bitumen surface and increasing the steric hindrance between the bitumen and illite particles. The critical role of humic acids in preventing bitumen-illite interactions was confirmed by designing experiments in which humic acids were added or removed from the illite suspensions in the tailings water.

6.2 Future work

There are several possible extensions of the current study:

- In Chapter 3, the concentrations of carboxylic surfactants were measured in the tailings water prepared at different caustic dosages added to flotation tests. Flotation tests in this study were performed by Denver cell. However, the bitumen recovery is more sensitive to caustic addition when Batch extraction unit (BEU) is used. Using BEU or modified Denver cell instead of Denver cell to study the relationship between the bitumen recovery for different types of ores and the amount of carboxylic surfactant released in the tailings water is a part of an ongoing study.

- In this thesis, it was shown that the generation of surfactants in the tailings water is pH dependent; however, the mechanism is not fully understood and needs more investigation. One possible reason that limits the solubility of surfactants at certain pH could be reaching to the saturation point, which is affected by the common ion effect (OH^- ions can be consumed by other ions). Study the solubility of standard surfactants in water in the presence of different ions at different pH values may help to understand this part better. Another reason can be the dependency of the solubility of some surfactants to pH. Some surfactants may dissolve in water at higher pH values. It is suggested to analyze the changes in the type and structure of the produced surfactants, such as the number of carbon, hydrogen and oxygen, and surface activity as a function of pH at which the flotation test has been conducted.

- In Chapter 5, it was shown that kaolinite didn't interact with bitumen at any conditions studied, while illite deposited on bitumen in the presence of surfactants and montmorillonite interacted with bitumen in the presence of calcium ions. It is worth extending this work to understand the interaction mechanisms of the studied clays and the reasons for observing such differences at the activation conditions of different clays.

- In the Appendix C of this thesis, it is shown that montmorillonite can deposit on bitumen surface in the presence of potassium as well as calcium ions. The reduction of bitumen recovery by addition of montmorillonite to the flotation test in the presence of calcium ions has been previously studied. It is suggested to study the addition of montmorillonite to flotation tests in the presence of potassium ions and study the possible changes in the bitumen recovery.

- QCM-D was shown to be a good and sensitive method for investigating different interactions between different oil sands components. So far, only the slime coating potential of monolayer clays on bitumen has been investigated. Since mix-layer clays such as kaolinite-smectite, illite-smectite have also been reported to be present in oil sands ores, it is suggested that slime coating of bitumen by these types of clay be investigated as well.

- There are only few studies conducted on the effect of humic acids on the processability of oil sands ores. It is suggested that more research to be done to understand the role of humic acids in the bitumen extraction process, wettability of fines, bitumen characteristics and the interaction of different components of oil sands with each other.

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Appendix A: Additional Results to Chapter 3

A.1. Using fluorescence technique for measuring the concentration of carboxylic surfactant in tailings water

Fenderson et al. (2012) used this method to measure the removal efficiency of naphthenic acids by a polymeric adsorbent from OSPW and tailings water. They used Sigma commercial NAs to find the Excitation /Emission wavelength for NAs, which were found to be 230/340 (nm). Therefore, the excitation wavelength was set at 230 nm and the emitted light intensity was measured in the region of 300-400 nm. In this work the same set up was used. A Varian Cary Eclipse Fluorescence Spectrophotometer with Cary Eclipse software was used for spectrophotometric measurements. Stock solution of Sigma NAs (180 ppm) was made in Milli-Q$^{®}$ water at 50 ° C and pH=8.5 because pH can affect the emitted light intensity. Aliquots of the stock solution were diluted with Milli-Q$^{®}$ water with the same pH (8.5) to construct a calibration curve.

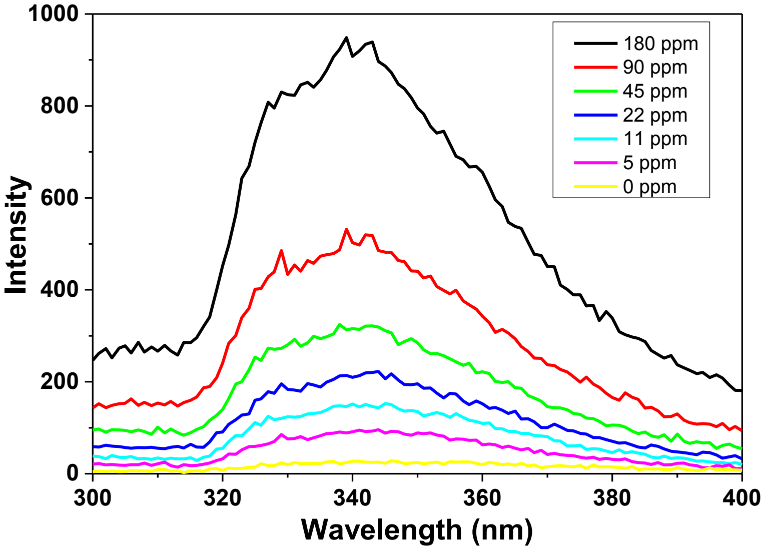


Figure A.1. Fluorescence spectra of Sigma NAs solution in Milli-Q$^{®}$ water at pH 8.5.

Figure A.1 shows the increase in emitted light intensity with the increase in NAs concentration. In the next step the fluorescence spectra of tailings water at the same instrument setup were collected for AR tailings waters prepared at different caustic levels. However, as shown in Figure A.2 the intensity of the tailings water were beyond the intensity limit except for 0.5 wt.% NaOH tailings water, which actually contained more carboxylic compounds as measured by FTIR.

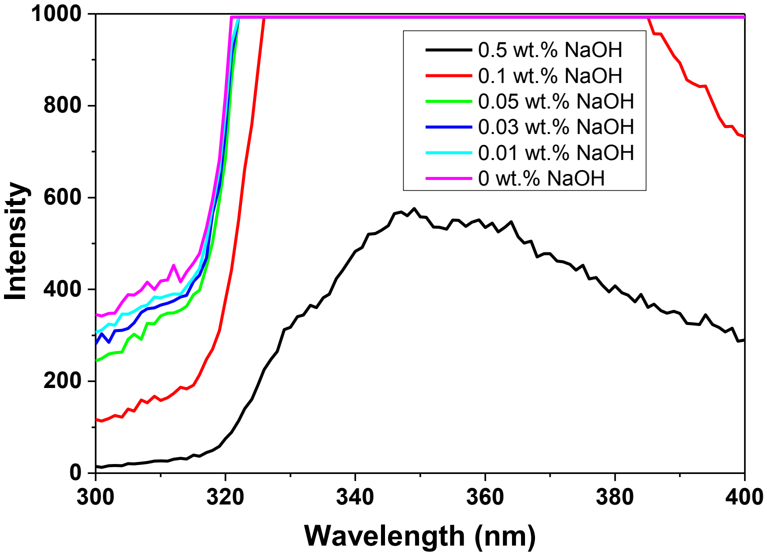


Figure A.2. Fluorescence spectra of AR tailings water prepared with the addition of different caustic dosages to flotation test.

To better understand our observations in Figure A.2, AR tailings water with 0.5 wt.% NaOH was diluted by Milli-Q$^{®}$ water and scanned at the same Ex/Em wavelength. The results are shown in Figure A.3. Increasing the dilution factor decreased the emitted light intensity until reaching to the intensity limit after 256 times of dilution. It is possible that the addition of more NaOH to flotation tests increased the solubility of the chromophore compounds which do not emit light. The chromphores are colorful compounds. As discussed in Chapter 1, increasing the concentration of NaOH added to flotation test increased the releases of humic acids which gave brownish color to the tailings water. Therefore, using fluorescence spectrometric technique for measuring carboxylic surfactants in the tailings water which have humic acids or other chromophores is ineffective.

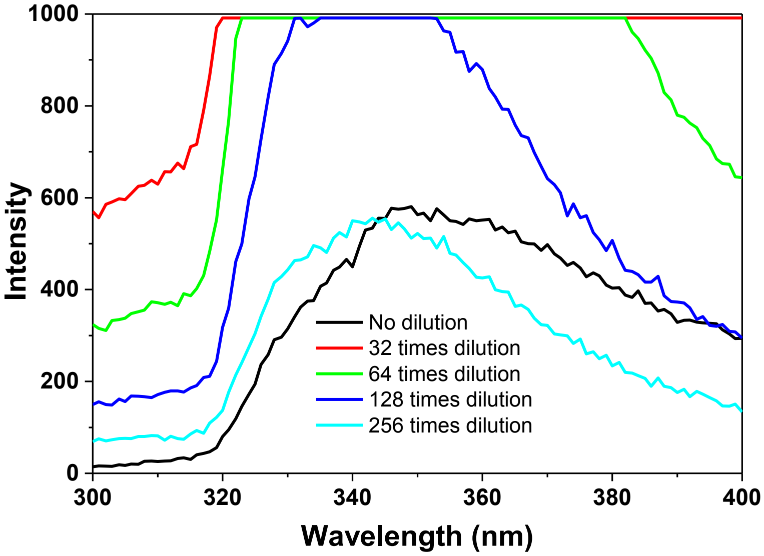
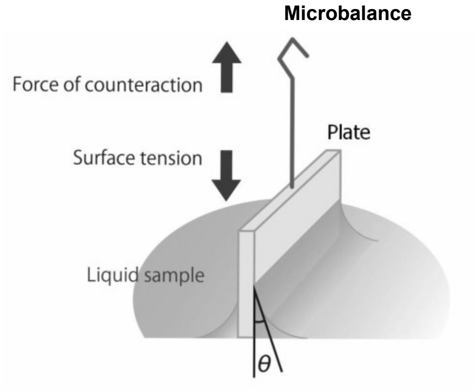


Figure A.3. Fluorescence spectra of diluted AR (0.5 wt.% NaOH) tailings water

A.2. Surface tension measurement of tailings water

Surface tensions of tailings water were measured at room temperature using Processor Tensiometer K12 (Krüss, Hamburg, Germany). Flat Wilhelmy plate method was used. Figure A.4 illustrates the Wilhelmy plate and the equations from which the surface tension is calculated.



$$p = mg + L\gamma.\cos\theta - sh\rho g$$

Balance Force = Plate weight + The total surface tension - Plate buoyancy

Where:

m: Plate mass
γ : Surface tension
s: Cross-sectional plate area
g: Gravity acceleration
θ : Contact angle of plate and liquid
h: Sinking depth of plate
L: Perimeter of plate
ρ : Liquid density

Figure A.4. Wilhelmy plate to measure surface tension

A.3. Mass spectrometry for other commercial mixtures of naphthenic acids

The mass spectrometry analysis of Fluka and Merichem commercial mixtures of NAs is shown in Figure A.5.

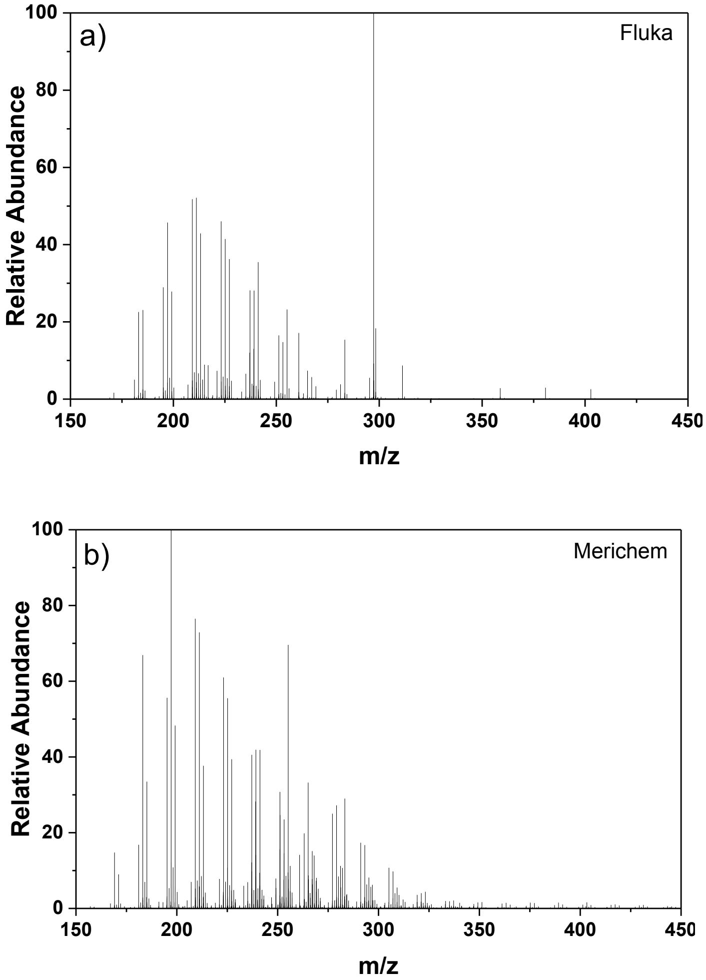


Figure A.5. ESI-FT-ICR Mass spectrometry of a) Fluka and b) Merichem commercial mixture of NAs. The graph for Merichem NAs was extracted from the work done by Grewer et al. (2010)

A.4. Surface activity of humic acids

The impact of humic acids on surface tension of Milli-Q® water was measured using Wilhelmy plate. The surface tension of the Milli-Q® water remained almost constant even after the addition of 350 ppm HAs to the solution. However, as shown in Figure A.6., addition of the same amount of Sigma NAs to Milli-Q® water decreased the surface tension of the solution drastically.

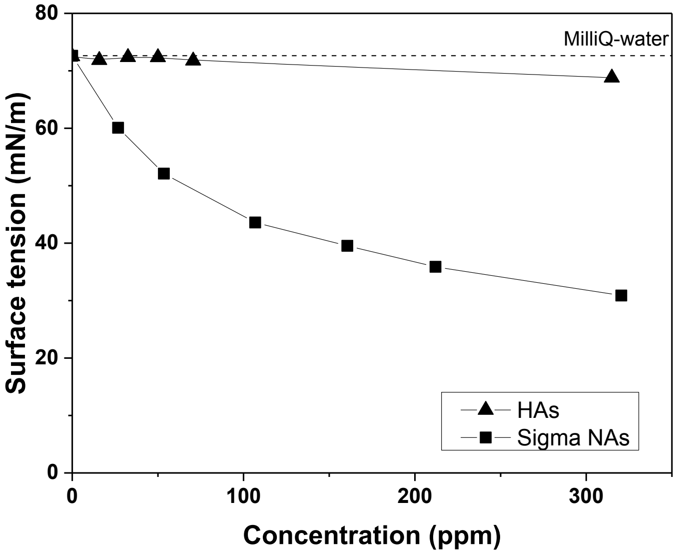


Figure A.6. Surface tension measurements of solutions of naphthenic acids and humic acids in Milli-Q® water.

A.5. Dilution of tailings water

Dilution of tailings water was initially performed in order to avoid the formation of precipitate layer (humic acids precipitation) during the acidification and DCM extraction of tailings water. Tailings water of MA ore prepared with the addition of 0.5

wt.% NaOH was diluted by 5 and 10 times. The diluted tailings water was then acidified and extracted. As shown in Figure A.7, dilution of tailings water with Milli-Q® water at the same pH did not prevent formation of precipitate (humic acids) layer.

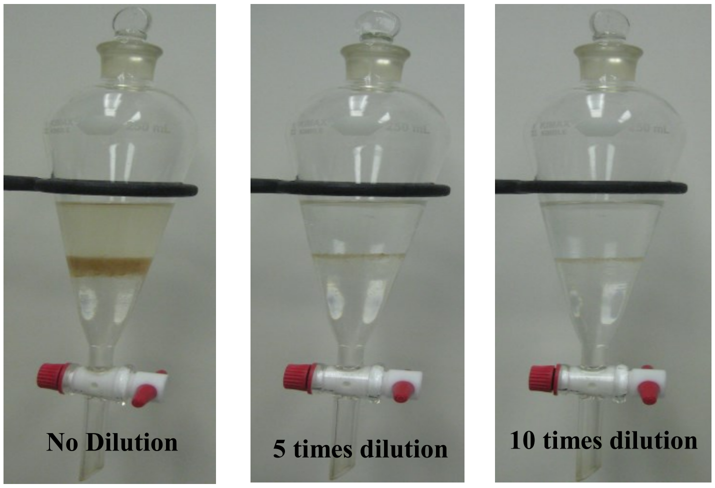


Figure A.7. Extraction step of tailings water (MA ore, 0.5 wt.% NaOH) before and after dilution with Milli-Q® water

The concentration of carboxylic surfactants in the diluted tailings water samples were measured using calibration curve prepared with 4 standard model compounds. However, it was found that the measured concentrations in the diluted samples were higher than what expected to be (Table A.1).

Table A.1. Concentration of carboxylic surfactants in tailings water samples before and after dilution

Concentration of carboxylic surfactants (10^{-5} mol/L)			
No dilution	2 times diluted	5 times diluted	10 times diluted
55.5	26.1	13.2	8.4

In order to understand the reason for this difference, the same experiments were performed by solutions of standard model compounds or commercial mixtures of NAs. Table A.2 shows that the concentration of naphthenic acids in the solutions after dilution did not increase as it did for real samples of tailings water. What causes the increase in the concentration of carboxylic surfactants in the tailings water after dilution is not known yet and needs more investigation.

Table A.2. Concentration of naphthenic acids in their solutions before and after dilution

Solution of	No dilution	2 times diluted	5 times diluted	10 times diluted
Sigma NAs (ppm)	99.3	-	21.3	10.1
	194.5	-	38.38	18.2
Model compounds (10^{-5} mol/L)	8.45	-	1.7	-
	9.67	-	1.93	-

The effect of humic acids on the quantification of naphthenic acids was studied in Chapter 3, and it was shown that addition of humic acids did not affect the naphthenic acids measurements in the standard samples. Also, using CSFTW for making standard solutions of naphthenic acids instead of Milli-Q® water did not show any interference on quantification of naphthenic acids.

A.6. Role of pH adjustment of tailings water on surface activity of surfactants

In order to understand the role of pH and surfactants concentration in bitumen extraction processes, the pH of the tailings waters with pH values higher than 8.5 were adjusted to 8.5, which was the pH of the tailings water prepared without addition of NaOH. The pH adjustment was done in order to prepare tailings waters, which have the same pH but different surfactants concentrations. The role of pH adjustment was first studied in terms of the changes that might have been applied to the surface activity of tailings water. For this purpose foaming tests with the following set up were carried out.

Foaming test

Foaming tests were carried out to qualitatively analyze the presence of surfactants in tailings water and determine the changes in the surface activity of surfactants after pH adjustment. For this purpose a graduated glass column, 40 centimeter in height and 2.54 cm (1 inch) in diameter, was used (Figure A.8).

Figure A.8. Foaming test set up

The column was open at the top. At the other end a sparger with 40-60 µm diameter holes (bottom) was placed. Nitrogen gas flows through the plastic tubing from a nitrogen cylinder; passes the sparger, and enters the column. Nitrogen gas was used in order to avoid a change in the pH of the solution due to impurities such as CO_2. Inlet pressure was set to 30 psi. For each test, a 20 ml of sample was added to the column at once as nitrogen gas was introduced through the column for 70 seconds. The sample began to form foams. After 70 seconds the nitrogen flow was stopped and the height of the foam was recorded. As shown in Figure A.9a, tailings water prepared with higher caustic dosages started to form foams at lower flow rates: 5, 70, 85 and 125 ml/min for 0.5, 0.1, 0.05 and 0 wt.% NaOH tailings water respectively. Also, at the higher NaOH concentration the foam height generated by flowing nitrogen gas through the column increased.

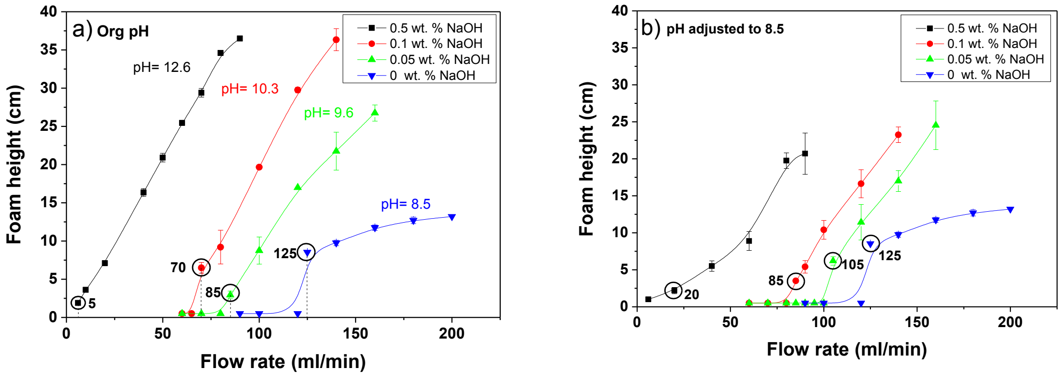


Figure A.9 Height of foams generated by flowing nitrogen gas through the tailings water in the column, a) tailings waters at original pH, b) tailings waters at pH adjusted to 8.5.

After adjusting the tailings waters' pH to 8.5 (Figure A.9 b), the height of the generated foam decreased in comparison to the tailings with the original pH. The minimum flow rates for forming the foam also increased. This observation shows that the amount of surface active materials in the tailings waters with pH adjusted to 8.5 is lower than the tailings water with the original pH. Since the total surfactants concentration in tailings water samples before and after pH adjustments has not been changed, the only thing that could have changed the surface activity of the tailings water is a neutralization process of a fraction of the existing surfactants. The portion of surfactants ionized at different pH was measured by FTIR in the next section.

Concentration of extracted surfactants at adjusted pH

Tailings waters of MA ore prepared with 0.1 and 0.5 wt.% NaOH were extracted at their original pH, pH adjusted to 8.5 and 2.3 (with DCM). The concentrations of carboxylic surfactants were then quantified by FTIR. Extraction at pH 2.3 shows the total concentration of carboxylic surfactants in the tailings water. As shown in Figure A.10a and b, there have been some surfactants extracted at pH 12.6 and 10.2. These surfactants can be either existing in neutralized form at these pHs, which allows them to transfer to organic phase or ionized form, which their transfer to organic phase is due to their solubility at these pHs. By adjusting the pH from 12.6 or 10.2 to 8.5, the amount of extracted surfactants increased indicating that some of the ionized surfactants have been neutralized at pH 8.5.

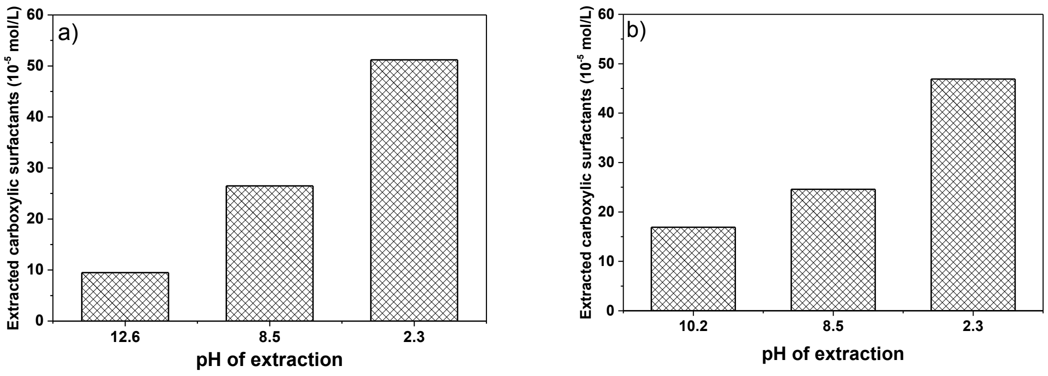


Figure A.10. Concentration of carboxylic surfactants extracted from tailings water with pH adjusted at different values. a) tailings water prepared with 0.5 wt.% NaOH, b) tailings water prepared with 0.1 wt.% NaOH.

Although the average pKa value of carboxylic acids is approximately 4.5, the relatively high concentration of carboxylic surfactants extracted at pH 8.5 as mentioned in other studies could be due to existence of some fatty acids with long carbon chain (such as palmitic acid and stearic acids), which have pKa values higher than 4.5 (Figure A.11) (Kanicky et al., 2000; Kanicky and Shah, 2003; Heikkila et al., 1970) . The presence of these types of fatty acids in oil sands tailings water was reported by Grewer et al. (2010).

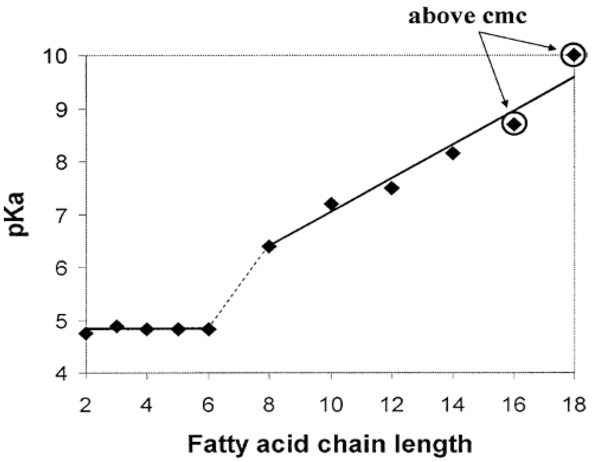


Figure A.11. Effect of chain length on the pKa of fatty acid solution (Kanicky and Shah, 2003).

The extractability and surface activity of the carboxylic surfactants at different pH intervals were investigated for 0.5 wt.% NaOH tailings water and the results are shown in Figure A.12 and Table A.3.

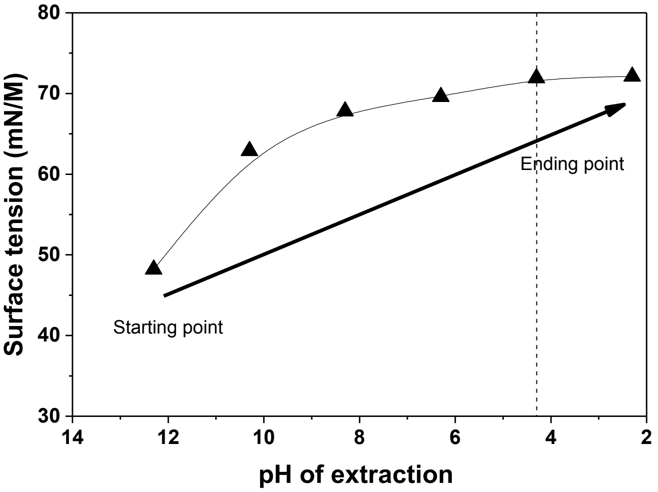


Figure A.12. Changes in the surface tension of the tailings water by decreasing the pH and extracting the surfactants.

Figure A.12 shows that surfactants extracted by adjusting the pH of tailings water from 12.3 to 10.3 were the most surface active. They had the biggest effect on the surface tension of the tailings water. The surface tension of the tailings water after extraction of these surfactants increased by 14.7 mN/m. On the other hand, the surfactants extracted by decreasing the pH from 4.3 to 2.3 were the least surface active or almost not surface active (Table A.3).

Table A.3. Changes in the surface tension of the tailings water by decreasing the pH and extracting the surfactants.

pH of extraction	Surface tension (mN/m)	pH range	Δ Surface tension (mN/m)	Δ Surfactants concentration (10^{-5} mol/L)	Surface activity
12.3	48.2	-	-	-	Surface active (80.69 %)
10.3	62.9	12.3-10.3	14.7	13.5	
8.3	67.8	10.3-8.3	4.9	10.9	
6.3	69.6	8.3-6.3	1.8	6.1	
4.3	71.9	6.3-4.3	2.3	10.9	
2.3	72.1	4.3-2.3	0.2	9.9	Not surface active (19.31%)

Effect of pH adjustment on liberation and aerarion

After studying the effect of pH adjustment on surface activity of the surfactants in the tailings water, the effect of pH adjustment was studied on bitumen liberation from sands and bitumen aeration or bitumen-air bubble attachment.

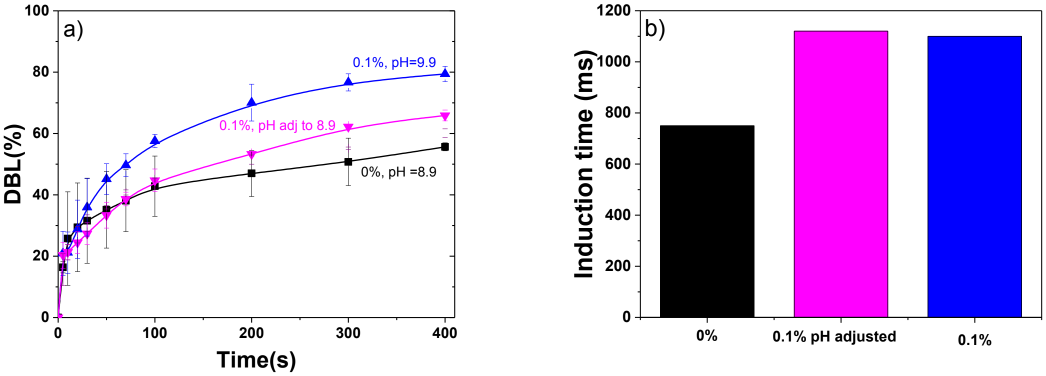


Figure A.13. Effect of pH adjustment on a) bitumen liberation and b) bitumen-air attachment for AE13 ore

As shown in Figure A.13, we observed a decrease in the degree of bitumen liberated (DBL) from sands after adjusting the pH of tailings water (0.1 wt.% NaOH) from 9.9 to 8.9, the pH of the tailings water of 0 wt.% NaOH. However, it is higher than DBL measured by using 0 wt.% NaOH TW. This observation shows that pH is an important factor in bitumen liberation process and that liberation is not solely controlled by surfactants concentration. On the other hand, insensitivity of the bitumen-air bubble attachment to the changes of the pH of the 0.1 wt.% NaOH tailings water points to the importance of the role of surfactants in controlling the bitumen aeration process.

Appendix B: Additional Results to Chapter 4

B.1. Concentration of carboxylic surfactants in tailings water prepared at different caustic dosage

Table B.1. Composition of ores and concentration of carboxylic surfactants in tailings water prepared with different caustic dosage

Ores			**Composition of ores (wt. %)**				**Concentration of CSs* (10^{-5} mol/L) in tailings water**					
#	**Class**	**Name**	**Water**	**Solid**	**Bitumen**	**Fine (wt. % of solids)**	**NaOH (wt.% of ore)**					
							0	**0.01**	**0.03**	**0.05**	**0.1**	**0.5**
1	Average fines	MA	8.3	83.5	8.2	15.4	29.2	-	35.1	36.9	41.4	48.8
2		AO	3.5	85.6	10.7	19	33.1	35.9	39.4	44.1	49.7	51.3
3		AZ	3.7	84.7	11.6	20	36	36.5	41.5	53.4	61.1	64.3
4	High fines	AJ	3	87.4	9.2	25	32.2	36.7	40.3	45.2	48.3	54.1
5		AS08	7.1	83.9	9.4	25	32.5	33.6	33.8	39.5	46.6	47.9
6		AE	9.1	84.1	6.4	25.3	41.6	42.9	46.9	50	53.9	58.8
7		AA	6.3	84	9.9	30	44.3	46.2	48.8	55.2	62.7	70.1
8		AR	5.2	85.7	8.7	30.9	56.7	59.6	64.4	73.3	88.3	107
9		AB	6.7	83.7	10.2	35	36.7	40.1	44.3	45.1	51.3	57.9
10		AE13	4.9	86.8	8.3	35	31.8	34.2	36.1	40.4	49.8	55.6
11		CN912	7.4	84.3	8.3	37.5	43.1	45.3	54.6	54.8	59.2	67.8
12		AN	2.2	87.3	10.4	38	38.1	40.4	44.8	48.8	55.6	61.1
13		AS	3.8	86.4	9.8	39	28.5	29.3	31.4	-	-	53.6
14	Ultra high fines	AL	3.9	87	9.3	46	29.1	29.4	31.5	33.4	39.7	52.5
15		AB08	5.6	85.3	8.8	47	29.8	30.3	32	33.9	40.2	49.2

***CSs: Carboxylic surfactants**

B.2. pH of tailings water prepared at different caustic dosage

Table B.2. Composition of ores and pH of tailings water prepared at different caustic dosage

Ores			Composition of ores (wt. %)				pH					
#	Class	Name	Water	Solid	Bitumen	Fine (wt. % of solids)	NaOH (wt.% of ore)					
							0	0.01	0.03	0.05	0.1	0.5
1	Average fines	MA	8.3	83.5	8.2	15.4	8.5	-	8.9	9.3	10.2	12.76
2		AO	3.5	85.6	10.7	19.0	8.5	8.6	8.9	9.4	10.0	12.6
3		AZ	3.7	84.7	11.6	20.0	8.7	8.8	8.9	9.1	10.2	12.6
4	High fines	AJ	3.0	87.4	9.2	25.0	8.5	8.6	8.9	9.3	10.3	12.5
5		AS08	7.1	83.9	9.4	25.0	8.6	8.8	8.9	9.3	10.1	12.6
6		AE	9.1	84.1	6.4	25.3	8.5	8.5	9.0	9.4	10.4	12.6
7		AA	6.3	84.0	9.9	30.0	8.6	8.7	9.0	9.4	10.0	12.6
8		AR	5.2	85.7	8.7	30.9	8.0	8.3	8.5	8.6	9.4	12.5
9		AB	6.7	83.7	10.2	35.0	8.7	8.9	9.2	9.5	10.1	12.6
10		AE13	4.9	86.8	8.3	35.0	8.8	9.0	9.0	9.2	9.8	12.4
11		CN912	7.4	84.3	8.3	37.5	8.6	8.9	9.2	9.3	10.2	12.1
12		AN	2.2	87.3	10.4	38.0	8.5	8.6	9.0	9.4	10.0	12.5
13		AS	3.8	86.4	9.8	39.0	8.3	8.6	8.9	-	-	12.2
14	Ultra high fines	AL	3.9	87.0	9.3	46.0	8.3	8.4	8.5	8.6	9.3	12.3
15		AB08	5.6	85.3	8.8	47.0	8.3	8.5	8.6	8.9	9.9	12.4

B.3. Effect of extraction method on concentration of carboxylic surfactants in tailings water

Effect of two different bitumen extraction methods on concentration of free carboxylic surfactants measured in tailings water were studied using Batch Extraction Unit (BEU) and Denver Cell (DC). Table B.2 shows that using BEU method produces more carboxylic surfactants in tailings water than DC. The observed difference could be due to the different procedure of using BEU and DC methods. In using BEU method, the added sodium hydroxide was dissolved in 150 ml of the process water, which was added to the oil sands ore in the conditioning stage. However, in using DC method, the added sodium hydroxide was dissolve in the 900 ml process. Therefore, the pH of the added process water in BEU was higher than DC when the same amount of sodium hydroxide was used and consequently more surfactants were released.

Table B.3 Concentration of free carboxylic surfactants in tailings water of AE13 ore prepared with Batch Extraction Unit (BEU) and Denver Cell (DC)

wt.% NaOH	BEU	DC
0	37.5	31.8
0.03	43.4	36.1
0.1	51.4	49.8

B.4. Relation between the pH of tailings water and NaOH dosage added to flotation test based on weight percent of fines in the ore

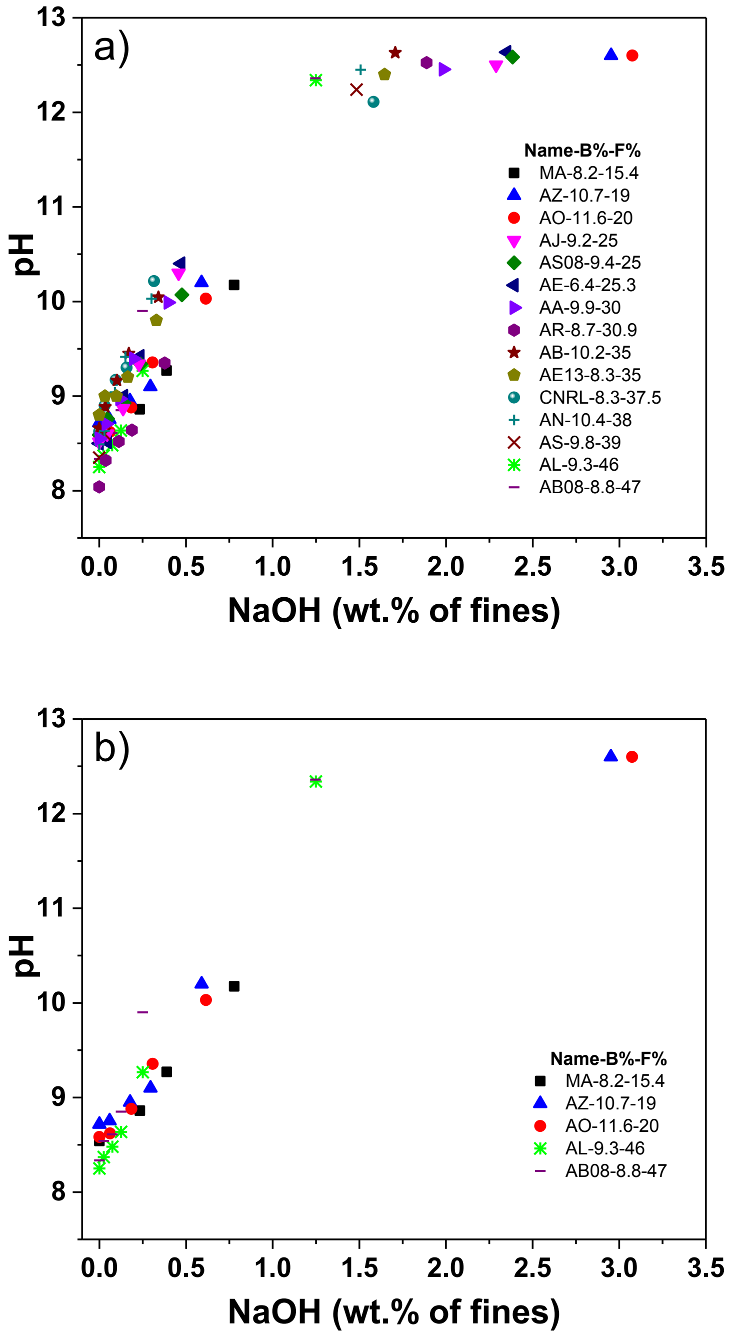


Figure B.1. pH values of tailings water as a function of NaOH dosage (based on wt.% of fines), a) all ores, b) average and ultra-high fines ores.

B.5. Viscosity of the bitumen extracted from ores

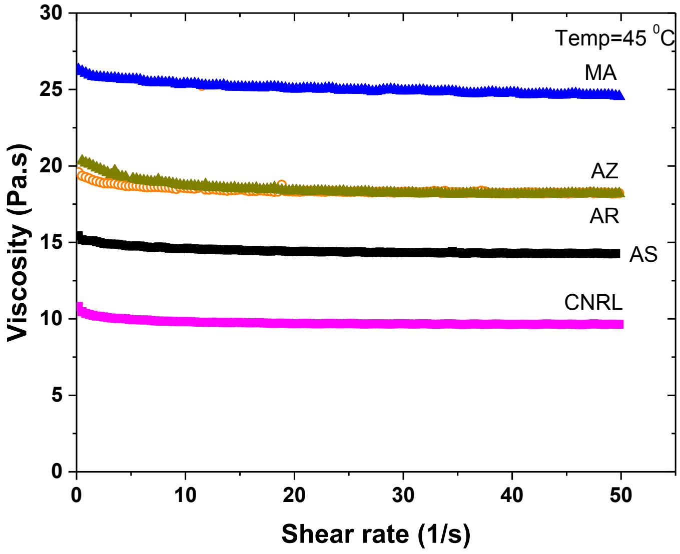


Figure B.2. Viscosity of bitumen extracted from different ores. Bitumen was extracted using centrifugation method.

B.6. pH of tailings water prepared at different caustic dosage

Table B.5. Composition of ores and concentration of divalent cations in tailings water prepared at different caustic dosage

Ores			Composition of ores (wt. %)				Concentration of Ca^{2+} and Mg^{2+} in tailings water (mg/L of tailings water)											
#	Class	Name	Water	Solid	Bitumen	Fine (wt. % of solids)	NaOH (wt.% of ore)											
							0		0.01		0.03		0.05		0.1		0.5	
							Ca^{2+}	Mg^{2+}	Ca^{2+}	Mg^{2+}	Ca^{2+}	Mg^{2+}	Ca^{2+}	Mg^{2+}	Ca^{2+}	Mg^{2+}	Ca^{2+}	Mg^{2+}
1	Ave. fines	MA	8.3	83.5	8.2	15.4	20.7	13.4	-	-	15.1	9.1	8.1	6.3	4.2	1.0	1.9	0.1
2		AO	3.5	85.6	10.7	19.0	31.1	21.7	26.2	20.5	19.1	13.3	10.1	5.3	3.9	1.1	3.5	0.1
3		AZ	3.7	84.7	11.6	20.0	37.5	20.0	36.5	19.5	-	-	19.8	14.1	-	-	1.5	0.1
4	High fines	AJ	3.0	87.4	9.2	25.0	-	-	30.9	219	21.5	13.8	9.6	7.2	2.8	1.3	2.0	0.1
5		AS08	7.1	83.9	9.4	25.0	21.3	16.9	18.7	17.0	17.8	12.2	9.9	7.0	3.7	1.3	1.9	0.1
6		AE	9.1	84.1	6.4	25.3	-	-	16.6	14.3	11.4	9.6	3.7	4.9	-	-	-	-
7		AA	6.3	84.0	9.9	30.0	32.3	21.1	29.3	20.6	13.4	11.6	9.7	6.4	4.4	1.7	2.0	0.1
8		AR	5.2	85.7	8.7	30.9	41.9	24.8	39.0	22.3	34.0	16.5	12.8	9.8	5.1	2.9	3.1	0.1
9		AB	6.7	83.7	10.2	35.0	23.6	15.5	22.3	14.3	15.5	10.5	8.9	7.0	3.0	1.6	1.1	0.1
10		AE13	4.9	86.8	8.3	35.0	19	18.1	-	-	-	-	9.0	4.7	-	-	-	-
11		CN912	7.4	84.3	8.3	37.5	11.7	5.3	-	-	9.3	4.3	7.2	3.8	2.8	0.9	1.35	0.1
12		AN	2.2	87.3	10.4	38.0	26.0	19.2	24.7	18.1	19.2	12.7	12.1	8.3	3.8	2.1	3.7	0.1
13		AS	3.8	86.4	9.8	39.0	84.6	43.5	72.2	39.9	47.2	32.1	-	-	-	-	1.6	0.1
14	Ultra high fines	AL	3.9	87.0	9.3	46.0	55.6	34.5	-	-	41.9	26.9	23.4	18.4	10.2	7.4	1.6	0.1
15		AB08	5.6	85.3	8.8	47.0	48.7	47.2	41.2	42.7	34	34.9	-	-	11.2	9.0	4.6	0.1

Appendix C: Additional Results to Chapter 5

C.1. DDMS and bitumen coating on silica sensor

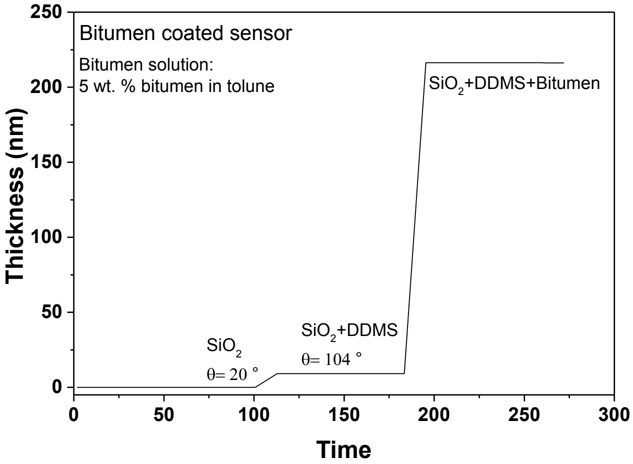


Figure C.1. Thickness of DDMS and bitumen layers coated on silica sensor using spin coater. Q-Soft and Q-Tools software were used to stitch the plots.

C.2. Adsorption of humic acids by clays

To assess the adsorption of humic acids by kaolinite and illite clays, solution of 200 ppm of humic acids in Milli-Q water was prepared at pH 8.5. Illite and kaolinite were added to the humic acids solution separately (2 wt.%). The suspension was shook for 2 hours and then filtered.

Table C.1. Dissolved organic carbons measured in the filtered humic acids solution before and after treated with kaolinite and illite clays.

Dissolved Organic Carbon (ppm)		
HAs Solution	Kaolinite	Illite
64.2	36.6	9.3

According to Figure C.2 and Table C.1, illite adsorbed more humic acids comparing to kaolinite.

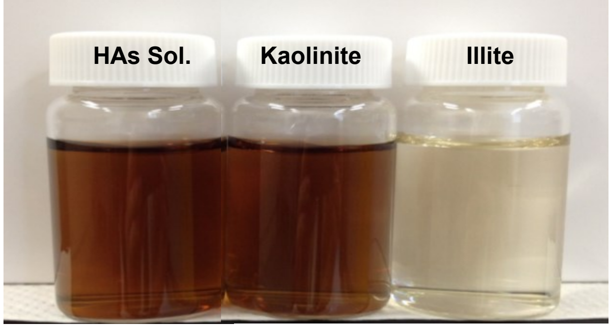


Figure C.2. From left to right: humic acids solution, filtered humic acids solution after being mixed and shook with kaolinite clays, filtered humic acids solution after being mixed and shook with illite clays.

In the next step, humic acids was added to tailings water (0 wt.% NaOH) instead of Milli-Q water. Illite was then added to the solution (2 wt.%). The suspension was then shook for 2 hours and filtered. The results are shown in Table C.2 and Figure C.3.

Table C.2. Dissolved organic carbons measured in the solution before and after treated with illite clay.

Dissolved Organic Carbon (ppm)			
TW	TW treated with illite	TW+ 50 ppm HAs	TW+ 50 ppm HAs treated with illite
73.3	60.4	90.7	65.5

Figure C.3. Left: tailings water with 50 ppm humic acids, Right: tailings water with 50 ppm humic acids after being treated with illite clay.

C.3. Effect of humic acids on bitumen wettability

Micropipette method was used to understand the effect of humic acids addition to tailings water on wettability of bitumen droplet. As shown bitumen become more hydrophilic in the presence of 50 ppm humic acids (Figure C.4). Change in the contact angle by time is shown in Figure C.5.

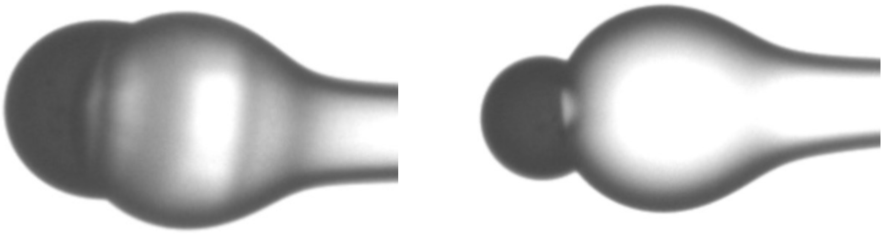


Figure C.4. Left: tailings water (0 wt.% NaOH), right: tailings water (0 wt.% NaOH) with 50 ppm humic acids.

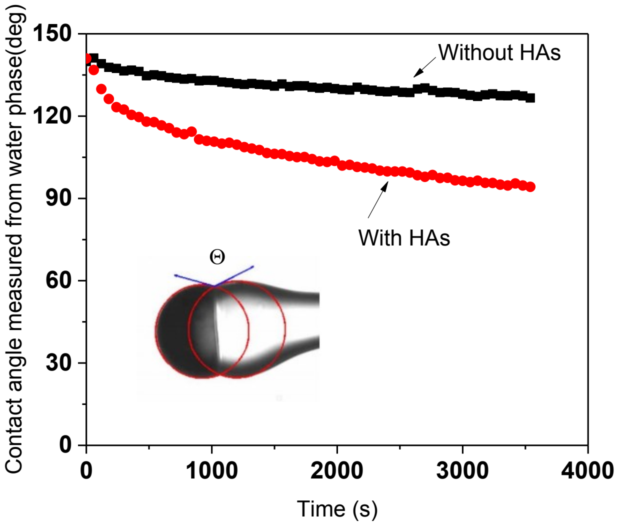


Figure C.5. Contact angle between bitumen droplet and micropipette measured in water phase.

C.4. Application of DLVO theory for bitumen-clay interaction in ansence and presence of calcium ions

The DLVO theory explains the tendency of colloids to agglomerate or remain discrete by combining the Van der Waals attraction curve with the electrostatic repulsion curve to form the net interaction energy curve as shown in Figure C.6. Classical DLVO theory was applied for bitumen-clay interactions at different conditions and the results were compared to the QCM-D observations. The following equations were used for DLVO calculations (Hogg et al., 1966).

$$V_T = V_A + V_R \qquad V_A = \frac{-Aa_1a_2}{6(a_1+a_2)x} \qquad A_{132} = (\sqrt{A_{11}} - \sqrt{A_{33}})(\sqrt{A_{22}} - \sqrt{A_{33}})$$

$$V_R = \frac{\varepsilon a_1 a_2(\varphi_{01}^2 + \varphi_{02}^2)}{4(a_1+a_2)}\left[\frac{2\varphi_{01}\varphi_{02}}{(\varphi_{01}^2+\varphi_{02}^2)}\ln(\frac{1+\exp(-Kx)}{1-\exp(-Kx)}) + \ln(1-\exp(-2Kx)\right]$$

where, V_T is the total energy, V_A is the Van der Waals energy between particles and V_R is the electrostatic repulsive energy caused by particles charges. A_{123} is the Hamaker constant for clay particles and bitumen in water. a_1 and a_2 are radii of clay particle and bitumen droplet respectively, x is the distance between the particles and bitumen, ε is permittivity, φ_{01} is the zeta potential of clay particle, and φ_{02} is the zeta potential of bitumen droplet and $(1/K)$ is the Debye length.

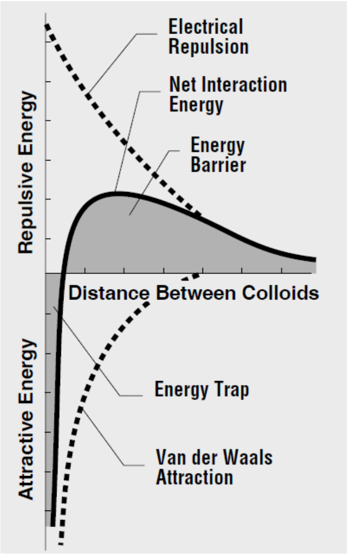


Figure C.6. Interaction of Van der Waals attractive and electrostatic repulsive energies.

The Hamaker constants and zeta potentials are shown in Table C.3

Table C.3. Parameters used for DLVO applications

Parameter	Bitumen	Illite	Montmorillonite
A (Hamaker constant, 10^{-20} J)*	6	14	13
<u>Zeta potential (mV)** in :</u>			
1 mM KCl solution	- 78	-37	-25
1 mM KCl +1mM CaCl2	- 35	-14	-10
10 mM KCl	-70	-30	-26
30 mM KCl (extrapolated)	-48	-27	-28
50 mM KCl	-38	-26	-30

* (Novich and Ring , 1984)

**(Zhao et al., 2006), (Liu et al., 2002)

The forces between the clay particles and bitumen are calculated as follows:

$$F_T = F_A + F_R \qquad F_T = -\frac{dV_T}{dx} \qquad F_A = \frac{-Aa_1a_2}{6(a_1+a_2)x^2}$$

$$F_R = \frac{\varepsilon a_1 a_2(\varphi_{01}^2+\varphi_{02}^2)}{4(a_1+a_2)}\left[\frac{2\varphi_{01}\varphi_{02}}{(\varphi_{01}^2+\varphi_{02}^2)} \times \frac{2K\exp(-Kx)}{(1-\exp(-Kx))(1+\exp(-Kx))} - \frac{2K\exp(-2Kx)}{(1-\exp(-2Kx))}\right]$$

Based on the above mentioned equations, the force diagrams as a function of distance between the montmorillonite clay particles and bitumen droplet were calculated in two different conditions, with and without 40 ppm calcium cations (Figure C.7).

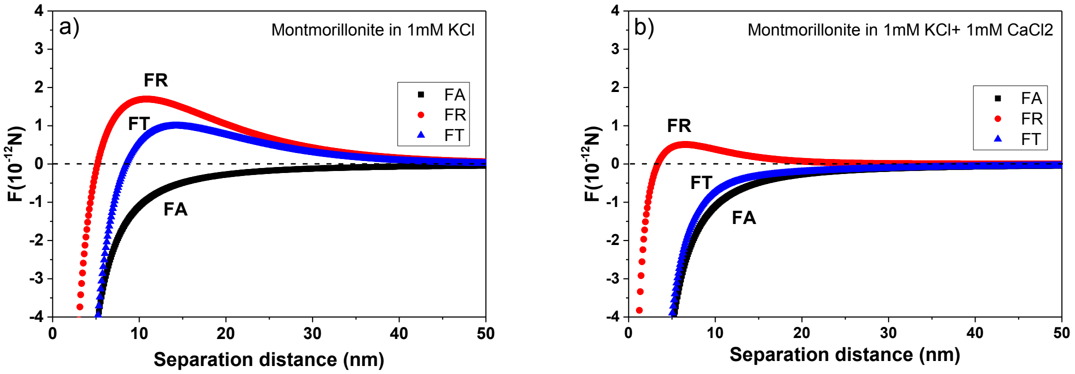


Figure C.7. DLVO for bitumen-montmorillonite clay particles. a) in 1 mM KCl solution and b) in 1 mM KCl + 1mM $CaCl_2$ solution

Positive values of F_T in Figure C.7 a (non-interacting particles) and negative values of F_T in Figure C.7 b (interacting particles) agree well with previous observations obtained by QCM-D measurements (Chapter 5, section 5.3.1), which showed bitumen-montmorillonite slime coating or interaction in the presence of calcium. On the contrary, DLVO graphs did not match well with QCM-D observations for bitumen-illite interaction. According to Figure C.8, illite particles are expected to interact with bitumen when calcium cations are added to the solution. However, QCM-D did not measure any interaction. This disagreement shows that classical DLVO theory may not be suitable for the predication or interpretation of illite-bitumen interactions

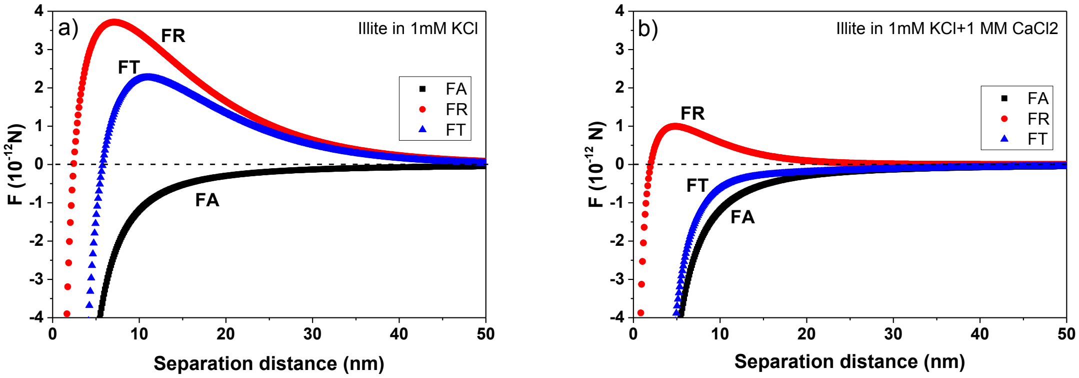


Figure C.8. DLVO for bitumen-illite clay particles. a) in 1 mM KCl solution and b) in 1 mM KCl + 1mM CaCl2 solution.

C.5. Bitumen-clay interaction and DLVO application in absence and presence of potassium ions

The ability of potassium ions for activating the montmorillonite-bitumen slime coating was investigated. For this purpose, KCl solutions in Milli-Q® water at different concentrations (10 mM, 30 mM and 50 mM) were prepared. pH was adjusted to 8.5. The baseline was collected for 5 minutes. Montmorillonite suspension in Milli-Q® water was pumped afterwards. The deposition was then washed off with background solution. Figure C.9.a shows that montmorillonite clay particles did not interact with bitumen when 10 mM KCl solution was used. Instead, they deposited on the bitumen surface in presence of 30 and 50 mM KCl. The DLVO graphs shown in Figure C.9 b, c and d also agreed well with QCM-D results. F_T value was positive (showing no interaction) at 10 mM KCl concentration and was negative at 30 and 50 mM KCl concentrations when slime coating (deposition) was measured.

In the previous studies, it was suggested that bitumen-montmorillonite interactions were due to the bridging of the negatively charged bitumen and montmorillonite clay particles surfaces by divalent cations (like calcium). However, the activation of montmorillonite deposition on bitumen by mono-valent potassium ions shows that bitumen-montmorillonite interactions can also be triggered by compression of electrical double layer.

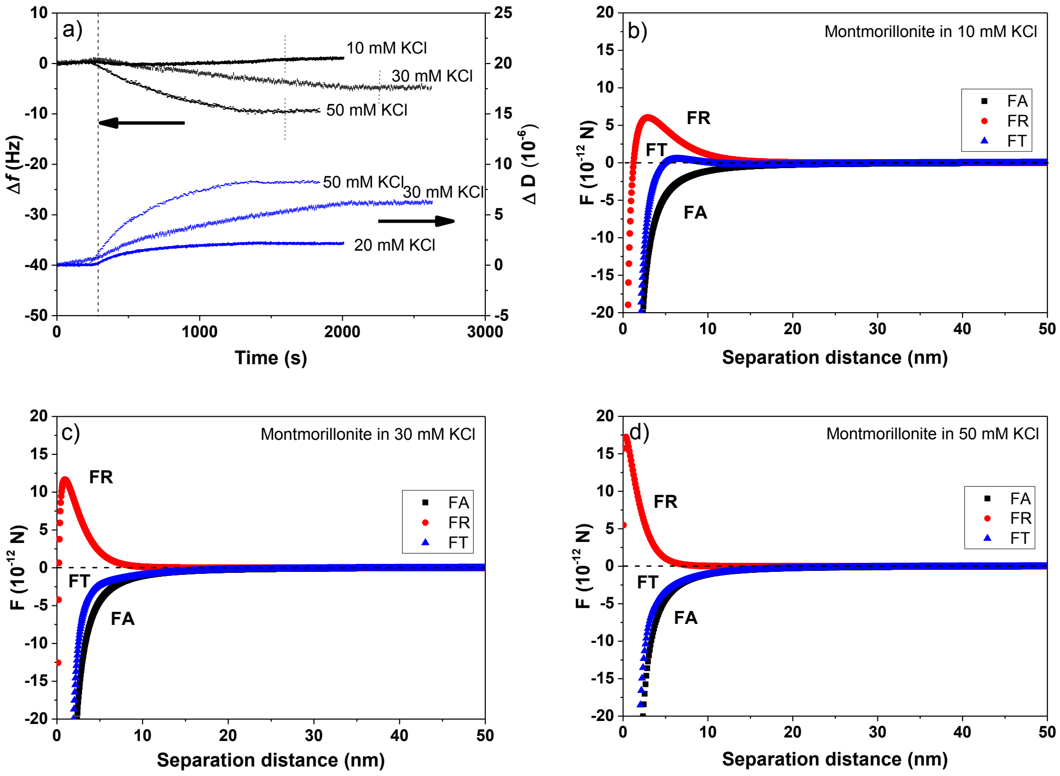


Figure C.9. Bitumen-montmorillonite clay particles interaction. a) QCM-D measurements; DLVO application in b) 10 mM KCl solution, c) 30 mM KCl solution and d) 50 mM KCl solution.

In the next part of the study, the role of potassium ions on deposition of illite clay particles on bitumen was investigated. Again 10, 30 and 50 mM KCl solutions were used to prepare the illite suspension and it was shown that none of the solutions activated the illite deposition on bitumen surface. A higher concentration of KCl solution (100 mM) was also not effective. Figure C.10a shows QCM-D measurements for illite-bitumen interactions in the presence of 50 mM KCl. Despite the fact that illite clay particles did not deposit on bitumen surface, the DLVO diagram (Figure C.10b) shows a net attractive force between illite and bitumen, which does not exist. Once again, the inapplicability of classical DLVO theory for illite-bitumen interaction is shown

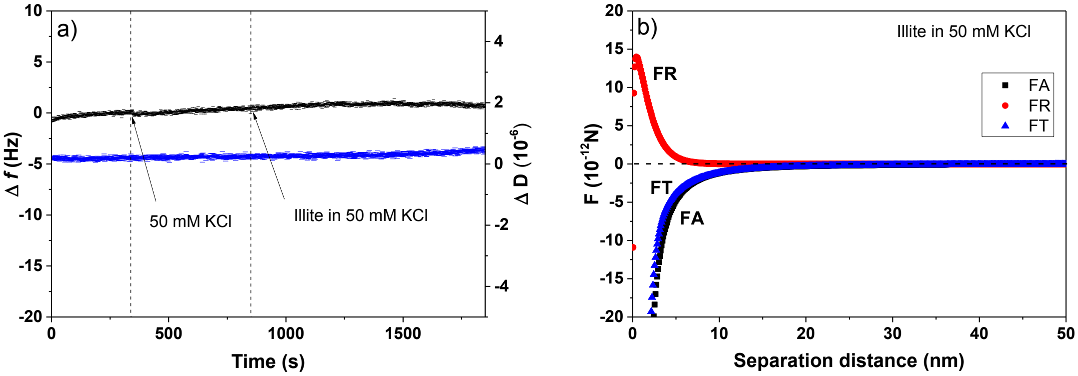


Figure C.10. Bitumen-illite clay particles interaction in 50 mM KCl solution. a) QCM-D measurement, b) DLVO application.

C.6. Application of QCM-D test to study the interaction of real clays separated from froth and bitumen surface

In addition to the tests on standard clays for investigating the bitumen-clay interaction in tailings water, additional tests with real clays extracted from oil sands ores were also performed. For this purpose, 2 wt.% suspensions of dry solids from froth fines after Dean Stark extraction were prepared in Milli-Q® water. The suspensions were sonicated and mixed completely so that all solids were completely dispersed in the water. The suspension was then centrifuged at 470 g for 20 min. The supernatant was then pipetted out and dried in a vacuum oven at 40 °C. d_{50} of the dried solids was ~130 nm. These solids were then used for QCM-D measurements. Figure C.11a shows that solids from froth fines deposited on bitumen surface in 0 wt.% NaOH tailings water. However, when tailings water prepared with 0.5 wt.% NaOH was used (Figure C.11b), by introducing the solids to the cell, the resonance frequency shift decreased, which is possibly due to the adsorption of attached humic acids or even surfactants by solids from the bitumen surface. By reintroducing tailings water (tailings water rinsing) to the cell, the resonance frequency dropped due to the adsorption of humic acids and surfactants in the tailings water on the bitumen surface.

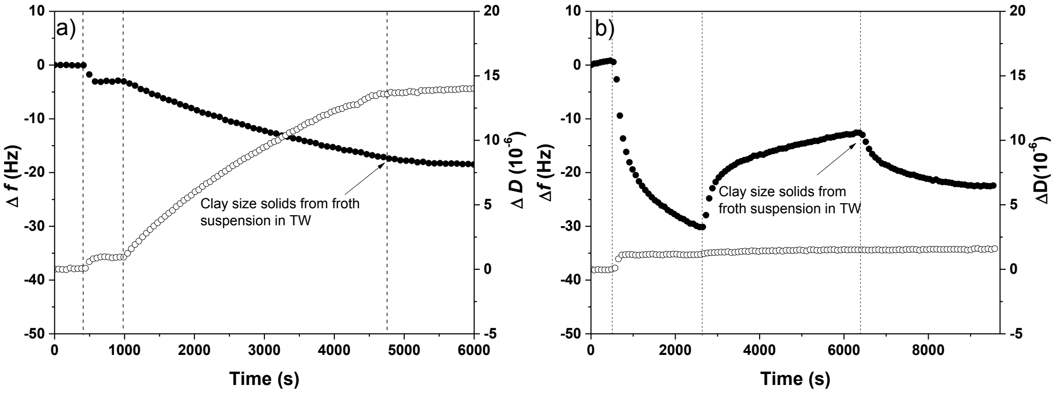


Figure C.11. Bitumen- clay particles (obtained from froth) interaction in MA tailings water. a) 0 wt. % NaOH b) 0.5wt. % NaOH. Dashed lines indicate switching of the fluid (from left to right: background to tailings water; tailings water to clay size particles from froth suspension in tailings water; and tailings water rinsing)

C.7. Addition of humic acids to flotation test using Denver cell

In order to study the effect of humic acids on extraction process, humic acids (MP Biomedical) was added to the Denver flotation test at 1000 ppm concentration. Bitumen recovery, froth quality, DOC of the tailings water in the presence and absence of humic acids were measured and compared.

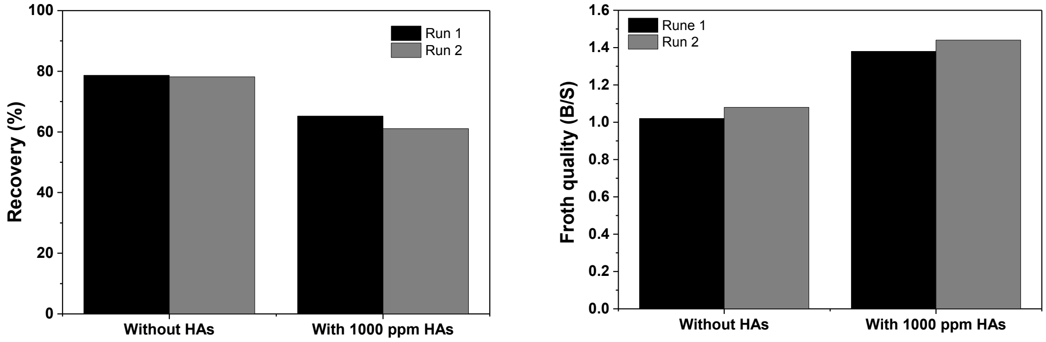


Figure C.12. a) Bitumen recovery and b) froth quality measured for AS ore at 0 wt.% NaOH with and without humic acids addition to the flotation test.

Shown in Figure C.12 is the recovery (a) and froth quality (b) measured for four flotation tests. The addition of humic acids to the floatation tests decreased the bitumen recovery whereas the froth quality increased. An increase in hydrophilicity of bitumen surface due to the adsorption of humic acids decreases bitumen-air bubble attachment, which resulted in lower bitumen recovery. Also, less hydrophobic bitumen surface lowered clay-bitumen attachment, which increased the froth quality. Figure C.13 compares the tailings water, prepared with 0 wt.% NaOH and 1000 ppm HAs with the tailings water prepared with 0.5 wt.% NaOH. Since the process water with the 1000 ppm humic acids added is completely dark brown in color (not shown), Figure C.13

confirms the adsorption of an extensive amount of the added humic acids by fine solids, clays and bitumen during the floatation tests.

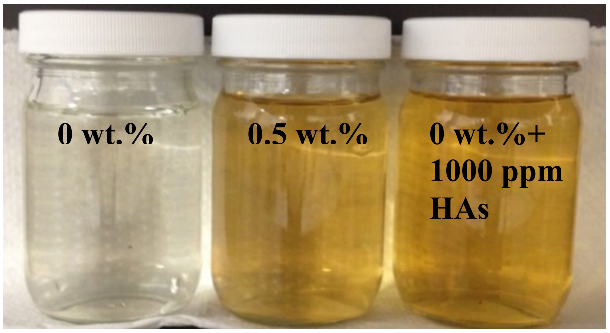


Figure C.13. From left to right: tailings water prepared with the addition of 0 wt.% NaOH, 0.5 wt.% NaOH and 0.5 wt.% NaOH with 1000 ppm HAs for AS ore.

In table C.4, the lower DOC value of the 0 wt.% NaOH with 1000 ppm HAs comparing to 0.5 % wt.% NaOH could be due to the less surfactant produced because of less sodium hydroxide added to the flotation test.

Table C.4. DOC of the tailings water prepared with the addition of 0 wt.% NaOH, 0.5 wt.% NaOH and 0.5 wt.% NaOH with 1000 ppm HAs.

Dissolved Organic Carbon (mg/L*)		
0 wt. % NaOH	0.5 wt. % NaOH	0 wt. % NaOH + 1000 ppm HAs
108.3	170.0	136.2

* milligram of carbon content per liter (L) of tailings water .