Role of Caustic in Bitumen-Air Bubble Attachment and Slime Coating

by

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Abstract

Caustic is the most commonly used process aid to improve processability of mineable oil sands ores in the Athabasca region. The addition of caustic adjusts the pH of the extraction process, disperses clays, and acts as a water softener. Understanding how these changes affect the fundamental steps of extraction is important to improve current knowledge on the processability of oil sands ores by the addition of caustic. Understanding these effects enables the enhancement of bitumen recovery and improvement of froth quality in the extraction process.

In this study, the aeration (bitumen-air bubble attachment) process was shown to be negatively impacted by caustic addition to the system. On the other hand, caustic addition reduces slime coating (bitumen-fines heterocoagulation). While the hindrance of aeration negatively impacts the extraction process, a reduction in slime coating positively impacts bitumen recovery. For aeration, the release of carboxylic surfactant, and a decrease in divalent cation concentration led to increases in the induction time of bitumen-bubble attachment. The release of carboxylic surfactant, decrease in divalent cation concentration and increase in humic acid concentration by caustic addition all hindered slime coating of fines on bitumen droplets. The types of fines/clays present in the oil sands also affect the slime coating.

The processability of ores changes with these modifications to the aeration and slime coating processes. Aeration and slime coating, along with bitumen liberation, create a balance that governs the processability of each ore. Both bitumen liberation and slime coating are positively affected by increased caustic dosage, while the aeration process is hindered. The difference in recovery and froth quality between two ores processed using a batch extraction unit were explained by the differences in their bitumen liberation and slime coating behaviour, as the induction time of bitumen-air bubble attachment measured in the tailings water from these ores was quite similar.

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1 Introduction

1.1 Froth Flotation

Conventional mineral processing by froth flotation has been around for over 100 years with its introduction in 1877 (Fuerstenau, et al., 2007). Since then it has been a long journey and new and more sophisticated technologies have been developed. The specialized froth flotation of bitumen (a thick, viscous petroleum fluid) in the oil sand industry has been developed. After Karl Clark and coworkers' pioneering work of bitumen froth flotation in the 1920-30s (Clark & Blair, 1927); (Clark, 1929); (Clark & Pasternack, 1932), the first commercially successful application of bitumen froth flotation was achieved by Great Canadian Oil Sands , now Suncor Energy Inc., in 1967 (Masliyah, et al., 2004). All initial processing of oil sands was achieved using the Clark Hot Water Extraction (CHWE) process which adds steam and caustic to crushed ore and to separate bitumen from sand grains by mechanically mixing (Clark & Pasternack, 1932). Even in Dr. Clark's early studies on recovery of bitumen from oil sands, the clay content of the ore, pH of the ore-water slurry and cationic concentration in the process water were considered of great importance. The original CHWE process was performed at around 80°C where the process was very robust with relatively low fine/clay ores being utilized. There is currently a decreasing feed ore quality (higher fines and lower bitumen content), with environmental/economic factors that led to lower temperature extraction processes such as the warm slurry extraction process with an increased amount of water recycle. These factors all lead to an increased importance on understanding how various controllable/uncontrollable parameters affect the oil sand extraction process.

Conventional mineral processing utilizes surface active chemicals to maximize the recovery of valuable minerals and expulsion of gangue (waste) material from its flotation facilities (Fuerstenau, et al., 2007). Frothers aid in the creation of small air bubbles and stabilize them to minimize their coalescence. Collectors increase the hydrophobicity of the minerals that are to be recovered, which improves the mineral-air attachment and leads to higher/faster recovery of these minerals. Depressants are used to make the unwanted gangue minerals more hydrophilic (less likely to attach to air bubbles). This depression in the gangue's attachment to air bubbles decreases gangue flotation and improves the quality of froth produced. In the oil sand industry, the nature of bitumen allows all of the aids of conventional flotation to be realized with only the addition of caustic. The bitumen in oil sand releases natural surfactants at increased caustic dosage, which has the dual effect of creating/stabilizing small bubbles and increasing fines' surface charge. The latter leads to a decrease in their floatability (Schramm, et al., 2003). These naturally occurring surfactants therefore act as both frothers and depressants in the system. The bitumen is also hydrophobic and attaches to air naturally, requiring no specific collector to be added in most cases (Moran, et al., 2000).

1.2 Oil Sand Processing

Currently, about 47% of oil sand is processed using the surface mining technique (Holly, et al., 2016). In 2014, over 1 million barrels per day (bpd) of crude oil was produced using surface mining technology. The three other oil sand extraction technologies (known as in situ methods) are primary/enhanced oil recovery (EOR), cyclic steam stimulation (CSS), and steam assisted gravity drainage (SAGD). These methods make up the remaining almost 1.2 million bpd of crude oil produced from oil sand. Even though a majority of oil sand is only recoverable using these in situ technologies, the use of surface mining to recovery bitumen from oil sands is expected to continue to be a key extraction process for years to come (Masliyah, et al., 2011) and will be the focus in this study.

Figure 1.1 shows the generalized flowsheet for a commercial surface mining oil sand operation. Utilities and bitumen upgrading are outside the scope of this work and will not be discussed. More information on this topic can be found is reported by Masliyah, et al. (2011). The oil sands are first mined using trucks and shovels from an open-pit mine. The oil sand lumps are crushed and oversize material is rejected from the system. This mined oil sand is then mixed with warm water and process aids in devices such as tumblers, rotary breakers, cyclofeeders or mix boxes. In the next step, the oil sand must be properly conditioned to allow bitumen liberation, coalescence, and aeration processes to begin (Masliyah, et al., 2004). This is performed historically in rotating tumblers, but more recently in hydrotransport pipelines. At this stage, the conditioned slurry as well as flood water (used to achieve optimum density for separation) is introduced into large gravity separation vessels for the primary separation of aerated bitumen. The entrained air that attaches to the liberated bitumen surface floats to the top of these vessels and forms a froth bed that overflows to become primary froth. Coarse tailings fall to the bottom of the vessel and are sent to tailings ponds as coarse tailings. A middlings stream is withdrawn from the vessel and flows to a secondary recovery stage that utilizes mechanical flotation cells (Tyler, et al., 2009). The lean froth collected from the secondary flotation is returned to the primary flotation while the tailings are sent to tailings ponds as fine tailings and this completes the extraction portion of oil sand processing.

Froth treatment is the next stage, where a majority of the solids and water are removed from the froth. The primary froth (comprised of approximately 60% bitumen, 30% water and 10% solids) is first deaerated and screened. The froth is then treated using either the "Syncrude Process" or "Albian Process" (Romanova, et al., 2006). The "Syncrude Process" involves diluting the froth with naphtha, while paraffinic solvent is used in the "Albian Process". The solids and water are separated by centrifuges or a three-stage gravity settling process. The water and solids are rejected as froth treatment tailings and the naphtha or paraffinic solvent is recovered for reuse. In the naphtha based process, the bitumen product is sent to upgrading where fluid coking, delayed coking or hydrotreating occur to create a product that can then be sent to refineries to create products such as gasoline, jet and diesel fuel, and heating oil.

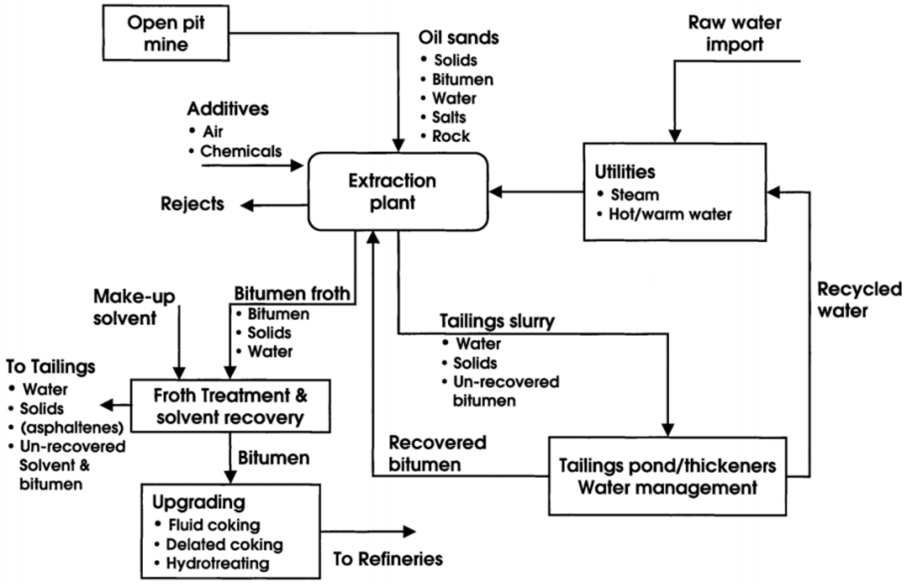

Figure 1.1: Flowsheet of a commercial oil sand extraction process using water based extraction (Masliyah, et al., 2011)

The coarse, fine, and froth treatment tailings collected are all sent to various tailings treatment facilities and eventually are sent to tailings ponds. Typical schematics of an oil sand tailings pond is shown in Figure 1.2. The coarse solids settle quickly and form the beach sand at the bottom of the pond, while a layer of mature fine tailings (MFT), comprised of about 30% fine solids and 70% water, forms above this layer. The top layer consists of water that is available for recycle back to the extraction process. MFT is the troublesome layer in tailings management, as it is very stable and does not settle, even after years of sitting. The MFT traps a significant amount of water that could otherwise be used for recycle and slows reclamation efforts. The technologies developed to improve MFT settling include physical/mechanical processes, natural processes, chemical/biological amendments, mixtures/co-disposal, and permanent storage (BGC Engineering Inc., 2010). Permanent storage of MFT is undesirable as it leads to increased land disturbance. The reduction of current tailings inventory to expedite land reclamation/decrease land disturbance and to maximize water recycle that minimizes fresh water requirements is of paramount importance in tailings research. A few key processes that are currently in use are consolidated (composite) tailings (CT), and thickened tailings (TT). The CT process involves the addition of gypsum to mature fine tailings (stable mixtures of ~30% clays and 70% water that do not readily separate) to consolidate the clays into non-segregating mixtures (Cymerman, et al., 1999). The TT process, also known as paste technology, involves rapid settling and sedimentation of suspended fines. The TT process occurs within a thickener with the addition of chemicals that aid in flocculation of fines and produces warm water that can be recycled back to the process with little reheat required (BGC Engineering Inc., 2010).

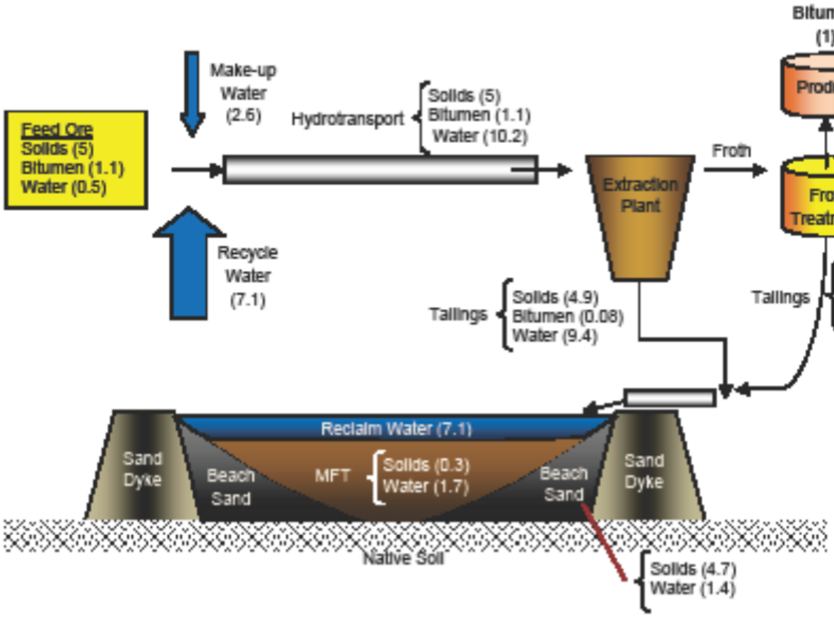

Figure 1.2: Schematics of oil sand tailings deposition (BGC Engineering Inc., 2010)

1.3 Thesis Outline

The focus of this thesis is to study the effect of caustic (sodium hydroxide) dosage on bitumen aeration and slime coating (bitumen-fines heterocoagulation) involved in oil sands extraction. The bitumen aeration and slime coating of bitumen by fines will be discussed in detail in the next section. The bitumen aeration process is important as increased efficiency of air bubbles attaching to bitumen leads to increased bitumen recovery. The slime coating of fines on the bitumen surface is also vitally important as it can be detrimental to the bitumen aeration process and would lead to a decrease in bitumen recovery and froth quality. The hypothesis evaluated is that caustic releases natural surfactants and changes water chemistry such that it improves aeration and/or slime coating of bitumen. This thesis focuses on understanding the effects caustic has on bitumen aeration and slime coating of bitumen by fines that enables the enhancement of bitumen recovery and improvement of froth quality in the oil sands extraction process. The thesis is separated into six distinct chapters and a brief overview is as follows:

Chapter 1: An introduction into the oil sand industry, discussing current bitumen extraction technology and processes being commercially used.

Chapter 2: A review of current literature, focusing on the role of caustic addition in the bitumen flotation process with emphasis on the fundamental flotation steps. A brief summary of the role of natural surfactant concentration, water chemistry, and oil sand composition in the bitumen recovery process is given.

Chapter 3: Experimental procedures as well as equipment descriptions are provided.

Chapter 4: The role of caustic addition in determining the effectiveness of the fundamental steps (aeration and slime coating) in bitumen flotation for seven ores is provided. Induction time and zeta potential measurements are performed using tailings water obtained from extractions with different dosages of caustic. Selected water chemistry parameters are varied to determine the effect of calcium, pH, carboxylic surfactant and humic acid.

Chapter 5: The flotation data obtained from a batch extraction unit (BEU) for two of the ores is discussed. The trends in recovery and froth quality are illuminated upon using the aeration and slime coating data provided in chapter 4.

Chapter 6: An overview of the key learnings of this work is provided. Some future work that would help to further this research is also proposed.

2 Literature Review

2.1 Alberta Oil Sands

Alberta oil sands contain between 4-14% bitumen, 2-15% water and 80-85% solids by weight. The bitumen grade and fines content (solid fraction less than 44 μm) greatly affect the maximum recovery of bitumen from oil sands (Sanford, 1983). Higher bitumen grade and lower fines content generally lead to a higher recovery of bitumen. To improve the recovery of bitumen from low grade and/or high fines ores, more caustic is added to the process to maximize recovery. The definition of fines (i.e. < 44 μm) is still quite a coarse fraction of solids, and it is more likely that the clay fraction found in oil sands (e.g. kaolinite, illite, montmorillonite, etc.) cause the decrease in recovery. There appears to be a correlation between fines content and the clay content of ores (< 2-5 μm) and therefore fines content can be used as an indicating factor to ore's processability (Sanford, 1983).

It has been proposed that a thin aqueous film (~10 nm thick) exists between the bitumen phase and solids in Athabasca oil sands (Czarnecki, et al., 2005); (Takamura, 1982). Figure 2.1 shows the hypothetical microscopic structure of the Athabasca oil sands suggested by Takamura (1982). It shows that the oil sand is a mixture of bitumen, water, quartz sand and clays. There is a thin layer of water between the quartz or clay minerals and bitumen that leads to the belief the Athabasca oil sand solids are water-wet/hydrophilic in nature. The presence of this water film and the hydrophilic nature of the solids make the hot/warm water extraction process possible. Electrostatic forces arising from oil-water and water-sand electrical double layers stabilize the water film (Takamura, 1982). The existence of this thin water layer has yet to be experimentally verified and therefore its presence used to interpret other results can potentially be dangerous.

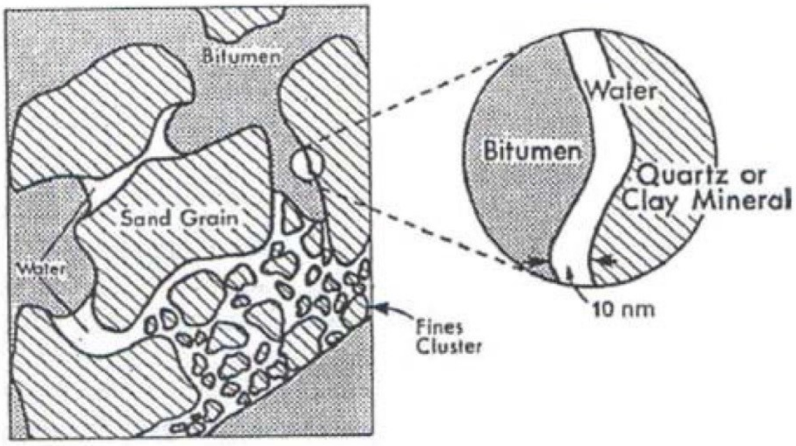

Figure 2.1: Hypothetical structure of Athabasca oil sands (Takamura, 1982)

Oil sand processing involves multiple steps that together culminate in effective separation and recovery of bitumen. They are: bitumen liberation (bitumen-solid detachment) and coalescence (bitumen-bitumen attachment), bitumen aeration (bitumen-air attachment) and subsequent flotation. The optimization of all of these fundamental steps enables the maximum amount of bitumen to be recovered. Slime coating (bitumen-solids heterocoagulation) is another important factor that can negatively impact flotation and froth product quality. The addition of caustic to the system modifies all of these processes and causes changes to the water chemistry of the system that can either benefit or hinder flotation. These elemental steps of extraction will be discussed in the next section.

2.2 Elemental Steps of Bitumen Extraction

2.2.1 Bitumen Liberation and Coalescence

The liberation process starts with the thinning and rupture of the bitumen film on the sand grain, and the displacement of the three-phase (bitumen-water-sand) contact line of this ruptured film. This thinning, rupture and displacement leads to recessed bitumen droplets on the sand grain surface that eventually detaches from it (Basu, et al., 1997). A simplified diagram of the bitumen liberation process is shown in Figure 2.2. The expected hydrophilic nature of the solids in Athabasca oil sands aids in the bitumen liberation process which occurs in the hydrotransport pipeline in commercial oil sand processing operations. The hydrotransport pipeline is a few kilometers long and makes the oil sand subject to mechanical shear that aids the liberation process (Masliyah, et al., 2004). It has been proposed that the addition of either hydrophobic or hydrophilic clays has little impact on bitumen displacement/detachment from a glass surface. It was therefore suggested that the decrease in recovery for high clay content ores discussed above was due to decreases in bitumen coalescence and poor bitumen aeration (Basu, et al., 1998).

Many methods have been used to study the bitumen liberation process/bitumen-solid interactions in oil sands processing. Basu, et al. (1997) studied the liberation process by coating a film of bitumen on a glass slide. The effect of adding water with different pHs was investigated. A pH cycle for optimal bitumen liberation was suggested, as it was noted that a higher rate of bitumen film thinning and rupture occurred at higher pH of 11 and then a change to low pH of 3 resulted in faster three phase contact line movement. Increasing the pH to 11 again would then create bitumen droplets with low static contact angles that would easily detach from the sand grains.

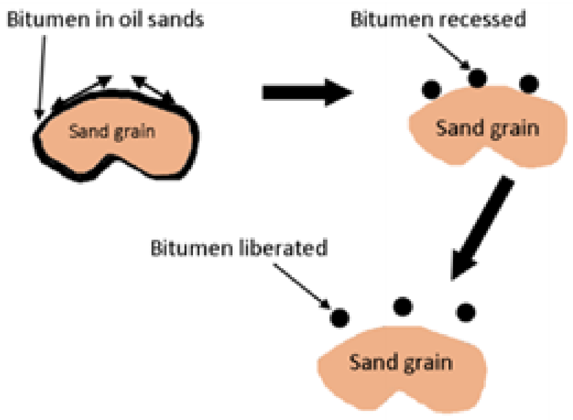

Figure 2.2: Detachment (liberation) process of bitumen from solids (Zhao, et al., 2009)

An online image analysis technique has also been used to evaluate degree of bitumen liberation using a laboratory hydrotransport extraction system (LHES) (Wallwork, et al., 2004). Oil sand slurry is circulated through an extraction loop and pictures of the process are collected using a charge-coupled device (CCD) camera. An open slot at the top also allows aerated bitumen to be collected as froth from the top of the loop, allowing bitumen recovery to be studied simultaneously. The collected pictures are sent to a PC where real-time analysis occurs. By analysing the relative darkness of the pictures collected, degree of bitumen liberation data is obtained. It was found using this method that increasing temperature resulted in an increase in bitumen liberation.

More recently, Srinivasa et al. (2012) developed a novel liberation setup called bitumen liberation flow visualization cell (BLFVC). This device uses a low level vacuum to hold oil sand in place as water is flowed over its top surface. A microscope with a CCD camera attached allows images of the liberation process to be collected and sent to a PC at a 10 frames per second rate. The degree of bitumen liberation in the system was determined based on the percentage of clear sand within the view. It was found that temperature, solution pH, and kerosene addition increased the rate of bitumen liberation as well as the final degree of liberation. The positive effect of pH increase (addition of caustic) was hypothesized to be due to increase in the acid-type surfactant concentration, negatively charging the bitumen/solids that leads to repulsion between them. It was also found that ore weathering, increasing salt (NaCl) concentration and high fines ores had a negative impact on the bitumen liberation process.

A change to the data analysis procedure of this system recently allows high fines ores (where counting the number of sand grains present on the screen is impractical) to be tested (Chen, 2015). This recent development utilizes a method similar to that used by Wallwork, et al. (2004). The images are converted to greyscale and a unique threshold greyscale value is determined for each ore. The image is then converted to black and white based on this threshold value and all white area is considered to be bitumen liberated, while all black is not.

The atomic force microscope (AFM) has also been proven to be an excellent tool to study bitumen-sand interactions. Zhao, et al. (2006) used AFM to study the effect of surfactant and divalent cation concentration on the long range repulsive and adhesion forces between silica and bitumen. It was shown that calcium and magnesium ions decrease bitumen liberation by increasing the adhesion force between bitumen and silica. The increase in surfactant concentration decreased the adhesion force and therefore was able to alleviate the negative impact of increasing divalent cation concentration on decreasing bitumen liberation. The presence of anionic surfactants at the bitumen-water interface and increased charge of the silica surface due to ionization of surface silanol groups leads to negatively charged bitumen and silica surfaces at alkaline pH as shown in Figure 2.3. The divalent cations can then bind these surfaces together, while increased surfactant concentration decreases the free divalent cation concentration, which decreases the adhesion force between bitumen and silica (Zhao, et al., 2006).

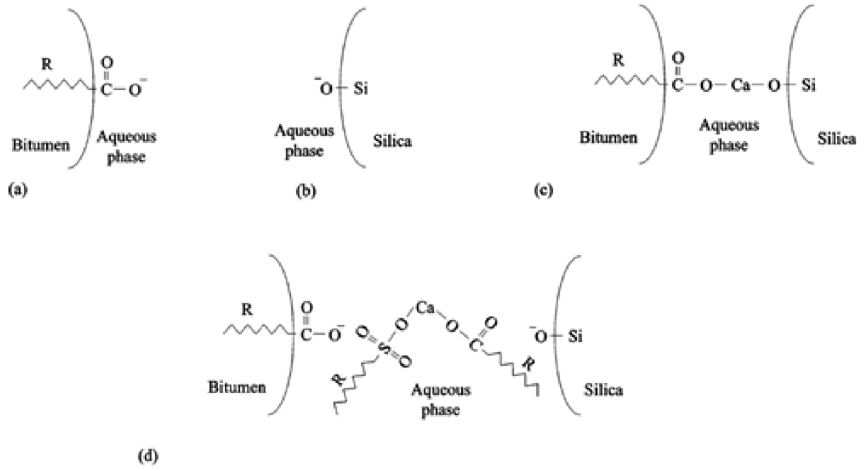

Figure 2.3: Schematics showing the effect of calcium and surfactants on bitumen-silica interactions: a) bitumen surface; b) silica surface; c) calcium binding silica and bitumen; and d) possible combination of calcium and surfactants in solution (Zhao, et al., 2006)

AFM was also used to show that electrical double layer forces dominate in bitumen-silica systems for good processing ores, while electrical double layer forces as well as hydrophobic forces are important for poor processing ores (Liu, et al., 2005b). The classical DLVO theory, first introduced by Derjaguin, Landau, Verwey, and Overbeek, considers only van der Waals (VDW) and electrostatic double layer forces which is sufficient to describe the interactions for good processing ores (Berg, 2009). The more complex extended DLVO, which also accounts for hydration forces, hydrophobic forces, repulsive steric forces, and attractive bridging forces, is required when poor processing ores are discussed. Liu, et al. (2005b) also showed that increasing calcium concentration led to an increase in adhesion force between bitumen-silica and an increase in pH was shown to weaken the attractive force. The bitumen-bitumen interactions were also studied with the results showing the similar behaviour to the bitumen-silica systems. The study on bitumen-bitumen interactions provides insights into the bitumen coalescence. The coalescence is important to allow bitumen droplets to grow to a critical size (> 1 mm) that result in maximum recovery (Wik, et al., 2008). The increase of pH and divalent cation concentration has similar impacts on bitumen-bitumen and bitumen-silica interactions. This increase of pH and divalent cation concentration leads to a hindering of the coalescence process (decreased bitumen coalescence), while the bitumen liberation process would be positively impacted by decreased bitumen-solids attachment. A balance between these flotation parameters must therefore be made to obtain a maximum bitumen recovery.

The bitumen coalescence has been shown to be negatively impacted by the addition of montmorillonite into the system (Liu, et al., 2005a). An AFM study showed that montmorillonite led to a strong repulsion between bitumen droplets as well as weaker adhesion forces. The addition of calcium increased this effect. Montmorillonite only loosely binds to the bitumen droplets without calcium in the system, while it strongly attaches to the bitumen when calcium is present. An increase in salt and calcium concentration decreased both attractive and repulsive forces between bitumen droplets. The higher salinity reduced the repulsive barrier and diminished the adhesion force. The calcium adsorbs on the bitumen surface, leading to decreased surface hydrophobicity, leading to decreases in adhesion force while also reducing bitumen surface charge density that reduces the repulsive force. This would allow the droplets to coalesce more, but it would also mean that it would be easier to break the droplets apart.

2.2.2 Bitumen Aeration

The aeration step involves the attachment of the liberated bitumen to air bubbles in the system as depicted in Figure 2.4. The bitumen is expected to engulf the air bubble at higher temperatures and to attach without engulfing at lower temperatures (Zhao, et al., 2009). This necessary step occurs in the hydrotransport line and allows the bitumen (that has a similar density to water) to decrease in density by the formation of bitumen-air aggregates that are able float to the top of the separation vessel. Bitumen-air aggregates have been shown to be larger for higher quality ores than poor processing ores (Ng, et al., 2000). The aggregate size of the poor processing ores were able to increase with the addition of caustic to the flotation system, and the increase in aggregate size was beneficial to bitumen recovery.

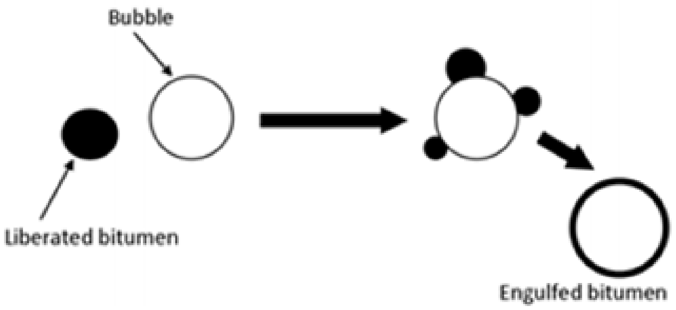

Figure 2.4: Bitumen-air attachment (aeration) process (Zhao, et al., 2009)

The aeration process can also be studied using a single bitumen droplet and an air bubble. A micropipette technique that involved contacting small bitumen droplets with air to quantify the probability of bitumen aeration has been used (Moran, et al., 2000). It was found that aeration had a strong dependence on the solution ionic strength, with higher ion concentrations leading to increased bitumen aeration. This corresponds to a depressed repulsive electric double layer at increased ionic strength (Israelachvili, 1991). The addition of fine particles into the system decreased the probability of bitumen-air attachment because of a steric barrier. This steric barrier between the bitumen and air hinders the aeration process.

The induction time is also used as a quantitative measure of the aeration process. The induction time has been defined as a three step process involving the time for i) the intervening liquid film between bitumen-air to thin to a critical thickness, ii) the rupture of the intervening liquid film, and iii) the development of a stable attachment (Najafi, et al., 2008). Interactions between gas bubbles and flat surfaces were investigated using a single micro-bubble that was allowed to vertically approach an inclined solid surface (Najafi, et al., 2008). A high-speed CCD camera was used to collect images, which alows the sliding velocity and induction time to be measured. Physical parameters, such as temperature, terminal velocity, bubble size, type of gas, and the presence of dissolved gases, were all found to affect the sliding velocities and induction time of bitumen-air bubble attachment. It was also noted that the presence of surfactant decreased the bubble rise velocity and increased the induction time, hindering the aeration process.

Another novel induction apparatus was used to study the attachment of hydrogen bubbles to bitumen (Gu, et al., 2004). Individual hydrogen bubbles were generated and released to make contact with a suspended bitumen droplet. In this study, the induction time was equated to the slide time of the hydrogen bubble on the bitumen surface. This study used very small diameter bubbles (>10 μm), that for the first time allowed the fundamentals of small bubble aeration to be studied (small bubbles had been shown to decrease induction time and improve flotation efficiency). It was shown that larger bubbles had higher terminal rise velocities, but also longer induction times. Critical bubble diameters, which were dependent on water chemistry and bubble rise velocity, were determined and any bubbles larger than this diameter would not attach to the bitumen surface. Increasing the temperature of the system aided the aeration process by increasing the critical diameter and decreasing the induction time. An increase in rise velocity was found to decrease the induction time. This was explained by an increase in pressure applied to the water film with an increase in velocity, which is theoretically expected to be inversely proportional to the induction time (Gu, et al., 2004).

The induction timer, described by Gu et al., used a speaker to contact an air bubble with a bitumen surface (2003). Increasing approach velocity was found to decrease induction time as was noted above. This was again attributed to an increase in pressure applied to the water film between the bitumen and air surfaces. One thing to note about this result was that at high velocity, bubbles have been noted to bounce away from the bitumen surface (Gu, et al., 2004). In this system, the surfaces were not allowed to separate and therefore were able to attach. In a real system, high mechanical shear could lead the bubbles and bitumen to just bounce off each other without attachment due to high velocities in the system. This must be considered when extrapolating fundamental studies to real commercial operations. Deionized water was found to have the lowest induction time, followed by process water and process water with 0.5% fines added. The addition of calcium to the process water in the absence of fines was found to decrease the induction time, while a large increase in induction time was found when fines and calcium were added into the system. Both bitumen and air bubbles are naturally negatively charged in an aqueous environment (Masliyah, et al., 2004) and therefore a scheme similar to that shown in Figure 2.3 occurs with the addition of both calcium and fines. The calcium is able to bind the negatively charged bitumen and air bubbles with the fines present in solution. This leads to steric repulsion between the two surfaces and a subsequent increase in induction time.

2.2.3 Bitumen Flotation

Once the bitumen liberation/coalescence and aeration processes have been successfully completed, the flotation of the bitumen-air bubble aggregates takes place in a large gravity separation vessel. In this separation vessel, the aerated bitumen floats while coarse sand settles through the middlings zone (Schramm, 1989). The large gravity separation vessel is kept under quiescent conditions that decrease mixing to promote plug flow in the vessel and increase ultimate separation efficiency. The middlings zone is typically high in quartz and clays such as kaolinite and illite, which can impede the flotation of aerated bitumen. A pilot scale study showed that higher process aid (NaOH) concentration led to lower viscosity in the middlings zone. The Stokes terminal rise velocity of spherical particles rising in laminar flow is:

$$v_t = \frac{(\rho_s - \rho) g D_p^2}{18\eta}$$

where ρ_s is the bitumen-air aggregate density, ρ the middlings density, g the force of gravity, D_p the bitumen-air aggregate diameter, and η the viscosity of the middlings (Schramm, 1989). Since the viscosity of the middlings is inversely proportional to the rise velocity, its decrease with the addition of caustic is expected to increase the rise velocity and therefore improve the flotation process.

The formation of colloidal clay gels in the primary flotation stage can occur when increased levels of ultrafines (phyllosilicate clays with diameters < 0.3 μm) in the primary separator (Mercier, et al., 2012). Even at low levels, ultrafines can form thixotropic gels that have the double detrimental effect of increasing the middlings viscosity as well as slime coating the liberated bitumen surface (to be discussed in the next section). The addition of divalent cations enhances the gel forming properties of ultrafines and allows formation of such gels at even lower concentrations of ultrafines.

2.3 Slime Coating

Slime coating of liberated bitumen droplets by fines/clays is an important factor affecting bitumen extraction. The attachment of solids to bitumen has a profound negative effect on both the recovery and froth quality of bitumen (Masliyah, et al., 2004). Kasongo et al. (2000) studied the role of calcium concentration and clay content in bitumen extraction using a modified Denver cell. It was found that the addition of any calcium, kaolinite, illite and montmorillonite alone did not have a strong effect on the overall bitumen recovery. Similarly, when calcium was added along with either kaolinite or illite, the recovery was again not affected significantly. Conversely, when calcium was added with montmorillonite, a negative impact on recovery was observed (especially above 30 ppm calcium). Calcium was found to be taken up by montmorillonite, allowing the calcium covered montmorillonite to interact with carboxylic surfactants on the bitumen surface, leading to slime coating of the bitumen droplets. The type of clays present in the oil sand are therefore expected to impact the slime coating of bitumen by fines. The slime coating leads to steric repulsion of bitumen to air and directly decreasing the froth quality produced during the extraction process.

A novel method for studying the slime coating of clays on bitumen in aqueous solution was developed based on the measurement of zeta potential distributions (Liu, et al., 2002). Single component suspensions exhibited a zeta potential distribution with a single peak, while bitumen mixed with fines exhibited different distributions, depending on the nature of slime coating in the system. The montmorillonite-bitumen system with the addition of calcium was confirmed to cause montmorillonite coating of the bitumen surface, while kaolinite did not. Montmorillonite was suggested to bind strongly with calcium due to a cation exchange mechanism, while kaolinite only binds through weak electrostatic adsorption. This strong binding of montmorillonite leads to slime coating of montmorillonite in contrast to the absence of slime coating by kaolinite. This method depends on the particles of interest having different electrophoretic mobilities, and is not helpful if there is a strong overlap in the particles' zeta potentials.

Recently, a quartz crystal microbalance with dissipation monitoring (QCM-D) method was developed to study bitumen-clay interactions (Bakhtiari, et al., 2015). In this method, a thin layer of bitumen was spin-coated on a quartz piezoelectric sensor. Solutions were then passed through the QCM-D and changes in frequency and dissipation were monitored. An example of a non-slime coated (a) and a slime coated (b) system is shown in Figure 2.5. When montmorillonite was passed through the quartz cell, no change in frequency or dissipation was observed. Conversely, when calcium was added along with the montmorillonite, a large decrease in frequency and increase in dissipation occurred, corresponding to montmorillonite deposition on the bitumen surface. Using this method, it was found the illite has the ability to slime coat bitumen surfaces at low caustic dosages. This illite-bitumen interaction was decreased by the increase in humic acid concentration (released at high caustic addition levels). This led to humic acids being studied in this thesis as potential aids to decrease bitumen slime coating by fines and improve bitumen aeration. Humic acids are large macromolecules, some of which are based on aromatic structures with phenolic and carboxylic substituents, linked together. They lead to steric repulsion between bitumen and fines that decreased the coating of illite on a bitumen surface.

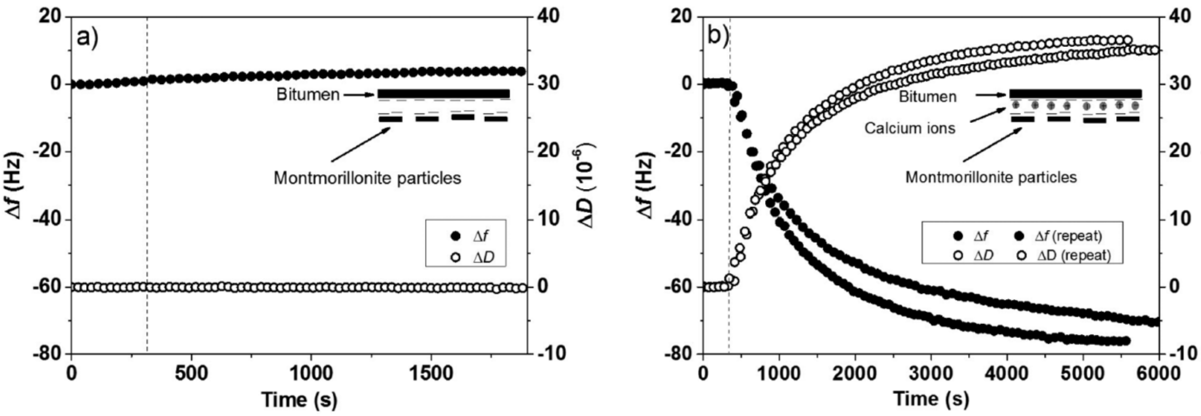

Figure 2.5: Interaction of montmorillonite clay with bitumen in 1 mM KCl solution at pH 8.5 a) without the addition of calcium and b) in the presence of 40 ppm calcium (Bakhtiari, et al., 2015)

2.4 Effect of Caustic on Water Chemistry

The addition of caustic plays many important roles in the oil sand extraction process. It acts as a pH adjusting chemical, clay dispersing agent, and a water softener. As caustic is added, natural surfactants from bitumen are released that affect all surface properties in the system. It is important to understand how the addition of caustic into the extraction process affects the chemistry of the system and how this in turn affects the oil sand processability.

The addition of caustic into the bitumen extraction process releases natural surfactants contained in the bitumen phase. The surfactants produced are primarily carboxylates and sulphates/sulphonates (Schramm & Smith, 1987a); (Schramm & Smith, 1987b). It has been suggested that an optimal concentration of carboxylic ($12 \cdot 10^{-5}$ N) and sulphate/sulphonate ($15 \cdot 10^{-5}$ N) surfactants exists that corresponds to maximum recovery, no matter the grade or fines content of the ore (Schramm & Smith, 1987a); (Schramm & Smith, 1987b). The decrease in recovery after this concentration has been proposed to be linked to the formation of hemimicelles that hinder the extraction process (Schramm, et al., 1983). At this maximum recovery point, the carboxylic surfactants are expected to impart maximum charge on the bitumen/solids surfaces as well as lower bitumen-water interfacial tension (Schramm, et al., 2003). To quantitatively understand the role of natural surfactant released, the spreading coefficient, S, is given by:

$$S = \gamma_W - \gamma_{BW} - \gamma_B$$

where γ_W is the water surface tension, γ_{BW} is the bitumen-water interfacial tension, and γ_B is the bitumen surface tension. When $S > 0$, spreading of bitumen over the bubble surface is favoured, as was shown in Figure 2.4. A decrease in bitumen-water interfacial tension makes the spreading coefficient more positive and therefore promotes spreading. Such conditions lead to a more stable attachment of bitumen to air, requiring significantly more energy to detach bitumen from the air bubble (Schramm, et al., 2003).

With the addition of caustic, only a small portion of the caustic added is expected to be used to release natural surfactants from bitumen (Schramm, et al., 1983); (Smith & Schramm, 1992); (Schramm, et al., 2003). The rest is consumed by polyvalent metal carbonates, sulphates and clays (Smith & Schramm, 1992); (Schramm, et al., 2003); (Wik, et al., 2008). This finding suggests that ores higher in these types of minerals would require higher dosages of caustic to release the same concentration of surfactants. It has also been noted that a majority of carboxylic acids contained in bitumen contain 20-25 carbon atoms, whose sodium salts are insoluble in water. The natural surfactants that are found in the aqueous phase would contain 13-18 carbon atoms and only about 2% of acids present in bitumen are expected to be in this range (Masliyah, et al., 2004). Although all bitumen carboxylic acids are not expected to migrate into the water phase, they would still react with the alkaline water, contributing to the surface charge. The natural surfactants released to the aqueous phase help to stabilize bitumen droplets, air bubbles, fines, and froth (Schramm, et al., 2003); (Zhou, et al., 2000); (Wik, et al., 2008); (Choung, et al., 2004).

The addition of caustic also has a water softening role that is important to remove divalent cations, such as calcium and magnesium, especially for the water from the CT process (Cymerman, et al., 1999). The CT process uses gypsum ($CaSO_4$) to aid fine solids settling in tailings ponds. With the introduction of this gypsum, the concentration of calcium in the tailings/recycle water increases and therefore can impact the extraction process. To understand how caustic reduces the calcium content of recycle water, the alkalinity of the aqueous phase is important and depends on the equilibrium of numerous species. Carbon dioxide (CO_2) enters the (open) system through equilibrium with the atmosphere, which can then form carbonic acid (H_2CO_3). This results in a pH dependent system made up of H_2CO_3, bicarbonate (HCO_3^-), and carbonate (CO_3^{2-}) (Zhao, et al., 2009)

$$CO_2(aq) + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^{2-}$$

As the pH increases, the above equilibrium shifts to the right and more carbonate is produced. The carbonate/bicarbonate buffers the system and has been found to disperse the solids and decrease the concentration of calcium in solution, which in turn leads to a reduction in bitumen-solid adhesion, all benefitting the extraction process (Zhao, et al., 2009). For the divalent cations in an alkali environment, the calcium precipitates out as $CaCO_3$ and magnesium as $Mg(OH)_2$ (Dai, et al., 1992); (Wik, et al., 2008). As discussed above, caustic releases carboxylic surfactants into the aqueous phase that is also expected to precipitate calcium as calcium carboxylates (Smith & Schramm, 1992); (Zhao, et al., 2009); (Masliyah, et al., 2011). High concentrations of calcium are especially detrimental when montmorillonite is present in the ore, due to strong heterocoagulation of bitumen and montmorillonite (Kasongo, et al., 2000); (Liu, et al., 2002); (Bakhtiari, et al., 2015).

The addition of caustic increases the pH of the system which leads to all of the above stated changes in water chemistry. The use of a different pH modifying process aid leads to different flotation water chemistry at the same flotation pH (Flury, et al., 2014). Ammonium hydroxide (NH_4OH) and NaOH were compared as process aids at two pHs (8.5 and 11.3). It was found that NaOH produced significantly more carboxylic surfactants than NH_4OH. This in turn created differences in the processability of ores based on the process aid used. Significantly more NH_4OH was required to increase the pH to the same degree. Due to low surfactant release, it did not exhibit the same inhibition of aeration, decrease in bitumen hydrophobicity, and decrease in negative charge on bitumen/air surfaces (Flury, et al., 2014).

The addition of caustic also increases the salinity of recycled process water, and the concentration of sodium increases as repeated recycle of process water is performed (Chen, 2015). Added salt has been shown to stabilize air bubbles (Kirkpatrick & Lockett, 1974); (Del Castillo, et al., 2011), hinder aeration (Chen, 2015) and liberation (Srinivasa, et al., 2012) due to suppression of repulsive electric double layer forces of air-bitumen-solids surfaces, and favours bitumen coalescence again due to electrostatic double layer compression, but also with a decrease in adhesion force, facilitating bitumen breaking apart (Liu, et al., 2005a).

The addition of caustic also has significant implications to tailings disposal. As NaOH is beneficial in the extraction process by dispersing the clays (Schramm, 1989), it negatively impacts the required settling of tailings. The dispersion of clays leads to MFT (Mercier, et al., 2012) being created and therefore other technologies are required to enhance settling of tailings quickly that enables maximum water recycle and minimum reclamation time. The release of carboxylic surfactants by NaOH addition mentioned above also has environmental impacts on tailings. A group of carboxylic acids released with caustic addition, known as naphthenic acids, have been found to be acutely toxic to a range of organisms (Scott, et al., 2008). These naphthenates are of cyclic, branched hydrocarbon chains that have lower biodegradability. Due to their toxicity, the release of naphthenates should be minimized.

3 Materials and Methods

3.1 Ore Characterization

Seven oil sand ores used in this study were provided by Syncrude Canada Ltd. The samples were homogenised using a Comil, followed by hand mixing. The ores were then separated into 600 g portions to be used for testing and stored in a freezer at ~ -20 °C to minimise aging/oxidation until 2 hours prior to their use (Schramm & Smith, 1987a).

3.1.1 Dean Stark Analysis

Dean Stark analysis was used to determine the oil-water-solids (OWS) content in the oil sand ores as well as the froth (Starr & Bulmer, 1979). The set up consisted of four distillation units. Fisher Scientific ACS grade toluene was used as the reflux solvent.

Approximately 200 mL of toluene was added into each of the four round bottom reflux flasks. 50 g of thawed oil sand ore or froth from flotation was added into a Whatman cellulose extraction thimble and placed into a metal basket which was hung from the adaptor. A screen was placed over the extraction thimble to minimise overflow and equally distribute the reflux solvent over the sample. The adaptor was connected to both the flask and the distillation trap with condenser. The condenser cooling water was turned on and adequate flow of cooling water was ensured. The heating mantles were then turned to 250°C. Bitumen entered the toluene phase as hot toluene vapours refluxed through the system because of its high boiling point and soluble nature in toluene. The bitumen and toluene dripped into the bottom of the flask. Water, insoluble in toluene, condensed in the bottom of the distillation trap due to its higher density than the toluene phase. The solids remained in the thimble throughout the process.

The heating mantles were left on until the toluene dripping through the extraction thimble ran clear and were periodically checked to make sure sufficient reflux solvent was available. Once the dripping toluene became clear, the mantle was turned off and the distillation unit was allowed to cool down to room temperature. The distillation unit was then dismantled and the toluene/bitumen mixture was diluted with toluene to 250 mL in a volumetric flask. A 5 mL aliquot was taken and pipetted onto a pre-weighed glass microfiber filter paper. The filter paper was then hung in a fumehood to evaporate all toluene over 20 minutes, and weighed once more to obtain the mass of bitumen. Water from the distillation trap was collected and weighed. The thimble containing all solids was put in a vacuum oven at 80°C overnight to evaporate toluene and weighed the next day. All equations used are given below:

$$Bitumen\ content\ (wt\%\ of\ ore) = \frac{Bitumen\ mass\ from\ filter\ (g) \cdot 50}{Mass\ of\ oil\ sand\ used\ (g)} \cdot 100\%$$

$$Solids\ content\ (wt\%\ of\ ore) = \frac{Mass\ of\ dried\ solids\ (g)}{Mass\ of\ oil\ sand\ used\ (g)} \cdot 100\%$$

$$Water\ content\ (wt\%\ of\ ore) = \frac{Mass\ of\ water\ (g)}{Mass\ of\ oil\ sand\ used\ (g)} \cdot 100\%$$

If the sample being run was froth from bitumen extraction, then the denominator of all these equations becomes “Mass of froth collected”. The water content of the oil sand was calculated in two ways: one using the actual weight of water collected from Dean Stark analysis and one from a mass balance on the system. If more than a 2%

difference between the two methods was found, the run was discarded. The mass balance equation values were used for all further calculations.

3.1.2 Fines Separation

The solids from the oil sand thimble recovered from Dean Stark Analysis were sieved to determine the fines content (< 45 µm). A sieve (mesh 325) was cleaned and dried before sieving. The solids were deaggregated using a rolling pin on kraft paper. The weight of the empty sieve was recorded, and the weighed solid sample was then added to the sieve. The sieve was put in a ROTOtap for 15 minutes and the fines were collected in a collection tray below the sieve. The sample was then wet sieved with tap water to remove any additional fines until the water ran clear. All the water with clay solids was collected and dried in the oven at 70 ºC overnight to obtain additional fine solids. These were added to the fines obtained using the ROTOtap and used for fines characterization and zetaphoremeter slime coating experiments.

$$Fines\ content\ (wt\%) = \frac{All\ solids\ (g) - Coarse\ solids\ (g)}{All\ solids\ (g)} \cdot 100\%$$

3.2 Water Characterization

All process water used in this study was from the Aurora plant at Syncrude Canada Ltd. All process water pails were shaken before use to ensure a homogeneous solution. In order to use the tailings water after each extraction test, it 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. This solid free water was used for all further testing. All tailings water that was used for induction time and zeta potential measurement was obtained from Denver cell flotation tests as discussed in appendix A.1.

3.2.1 Water Chemistry Characterization

Atomic absorption spectroscopy (AAS) or inductively coupled plasma optical emission spectrometry (ICP-OES) was used to analyze the concentration of cations in tailings water. Mr. Shiraz Merali performed all AAS measurements for this study and Dr. Mingsheng Ma performed all the measurements using ICP-OES.

3.2.2 Carboxylic Surfactant Concentration

All carboxylic surfactant concentration analyses were performed by Marjan Tamiz Bakhitiari. A detailed procedure and all results can be found in appendix C.1.

3.3 Aeration

The aeration was studied by determining the attachment of a single air bubble to bitumen surface using a unique induction time apparatus. Induction time measurement has been proven to be a powerful tool to study the aeration process in flotation systems. All tests were performed at 45 ± 0.2°C (same as the extraction temperature used).

3.3.1 Induction Timer

Tailings water obtained at different caustic loadings was prepared for induction time testing as described in section 3.2 above. The tailings water with 0, 0.03 and 0.1 wt% of caustic addition in terms of mass of ore during extraction runs was used for induction time measurement. In this work, induction time was measured using an in-house built induction time apparatus (Gu, et al., 2003). Figure 3.1 shows the schematics of the system used. A 40-watt speaker was used as the power driver. An amplifier interfaced with a computer was used as a power source to drive the speaker and move the air bubble that is attached to the capillary tube (OD=1.3 mm). A fresh air bubble (1.5 mm diameter) was generated at the end of the capillary tube by a Gilmont microsyringe. A lens and a CCD camera were used to assist precise positioning and viewing the contacting process between the air bubble and bitumen surface.

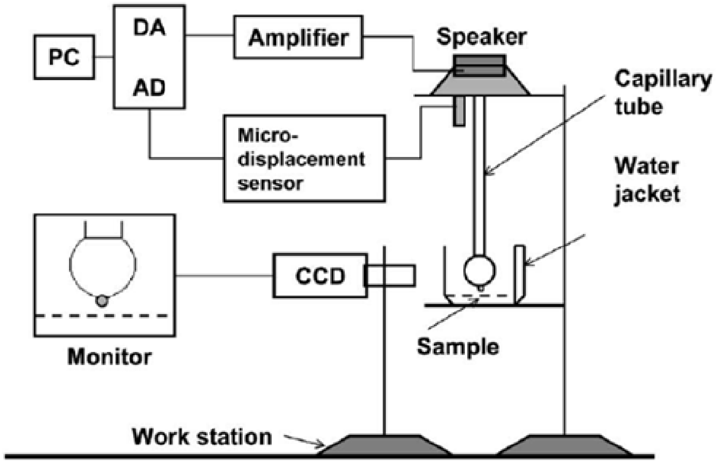

Figure 3.1: Schematics of novel in-house built induction timer (Gu, et al., 2003)

The bitumen surface was prepared by coating vacuum distillation unit (VDU) bitumen obtained from Syncrude on a 7mm diameter Teflon disc. The Teflon disc was washed with toluene and then de-ionized water between runs to remove organic contaminants. The bitumen surface was allowed to sit in a covered container for about 10 minutes to obtain a smooth bitumen surface. It has been recognized that the presence of natural surfactants at the oil-water interface reduces the interfacial tension and the interfacial tension reduces with aging time (Isaacs & Smolek, 1983); (Wang, et al., 2014). Therefore, the bitumen was allowed to equilibrate in the tailings water (free of solids) for thirty minutes to allow the surface active species to migrate from bulk bitumen to the bitumen-water interface. The temperature was checked prior to each test and at 5 minute intervals during testing. Three Teflon discs with a thin bitumen layer were used in each solution, and 20 spots were picked to measure the induction time on each Teflon disc.

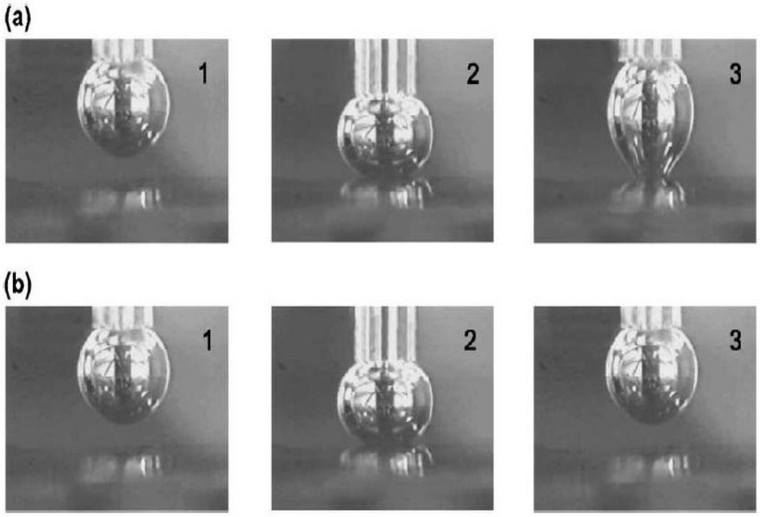

Figure 3.2: Induction timer view of: a) attachment between air bubble and surface; and b) no attachment between air bubble and surface (Gu, et al., 2003)

In each measurement, a fresh air bubble was generated and moved towards the bitumen surface at 40 mm/s approaching velocity. This bubble was kept in contact with the bitumen surface for increasing amounts of time (from ~ 300 ms to 2000 ms) with 20 data points collected at each time. Figure 3.2 shows the induction timer view of the case when the bubble attaches to the surface (a), and when it does not (b). From these data points, a probability of attachment at each time is calculated. This probability data was then analyzed using OriginPro 8.0 and a Boltzmann distribution to calculate the induction time, defined as the time with 50% probability of attachment (Yoon & Zhou, 2002). A shorter induction time corresponds to better aeration or bubble-bitumen attachment at that condition.

3.4 Slime Coating

The electrophoretic mobility of bitumen droplets and fine particles is measured to study the slime coating in oil sand extraction. Since bitumen and fine solids from the ore have different mobilities in the tailings water of interest, their zeta potential distributions can be used to provide a qualitative measurement of the slime coating of the system. All zeta potential distribution measurements were performed at room temperatures (the zetaphoremeter does not have a heating device).

3.4.1 Zetaphoremeter

A Zetaphoremeter III (SEPHY/CAD) was used to determine zeta potential distributions. The instrument was equipped with laser illuminating and video-viewing systems which enable the researcher to trace the movement of particles at the stationary layer. The captured images were analyzed by built-in image processing software and were then converted to zeta potential using the electrophoretic mobility and the Smoluchowski equation (Hunter, 2001).

To prepare the bitumen or fines suspensions, 0.01-0.1 wt% (higher pH required higher dilution due to increased number of bitumen droplets/fines dispersion) of bitumen or fines were emulsified/suspended in the required tailings water using an ultrasonic dismembrator for 10 minutes. The tailings water with the same caustic loading as the induction time measurements was also used for slime coating tests. Fine solids were obtained from each oil sand after Dean Stark analysis of the ore and sieving. The bitumen used was Syncrude VDU bitumen. About 50 mL of each suspension is prepared in a beaker and drawn into the zetaphoremeter cell using a plastic syringe. Three measurements were performed. More solution was then drawn into the cell for three additional measurements. A total of nine measurements were performed. The average of all these measurements was reported in this thesis. Once the zeta potential distributions of individual components were measured, a 1:1 mixture of bitumen emulsion and fines suspension was made for further zeta potential distribution measurements.

The zeta potential of bitumen is generally more negative than the fines in the tailings waters of interest. Heterocoagulation can be determined by comparing the zeta potential distribution of a 1:1 bitumen emulsion and fine solids suspension mixture with zeta potential distributions of individual components. Figure 3.3 shows the peaks of individual components (a) and suspension mixture possible zeta potential distribution patterns for no slime coating (b), slime coating (c) and partial slime coating (d). In the case of heterocoagulation (slime coating), only one zeta potential distribution peak is detected that is in between the individual zeta potential distribution peaks of bitumen and clays. This single zeta potential distribution peak moves closer and closer to the clay peak when excessive amounts of clay are present, indicating full coverage of the bitumen surface by clays. A bimodal zeta potential distribution where each peak corresponds closely to the individual zeta potential distribution peaks of bitumen and clays is detected when there is no heterocoagulation (no slime coating). A bimodal zeta potential distribution is also detected in the case of partial slime coating. In this case, one peak corresponds to the individual clay peak, while the other peak is a broader peak in between the individual bitumen and clay peaks. These distribution characteristics indicate partial coverage of the bitumen surface by clays, making the bitumen surface less negative, while some other clays remain dispersed to show their own zeta potential distribution peak centered around the zeta potential distribution peak for individual clay particles (Liu, et al., 2002).

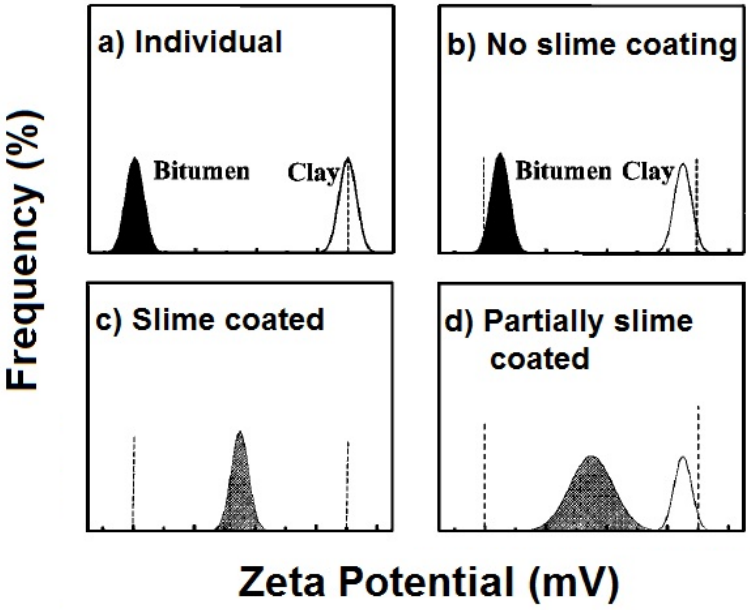

Figure 3.3: Zeta potential distribution for a bitumen-clay system of: a) individual peaks of bitumen and clay; b) no slime coating in a binary mixture; c) a slime coated system in a binary mixture; and d) a partially slime coated system in a binary mixture (Liu, et al., 2002)

3.5 Flotation

The batch extraction unit (BEU) has long been used for small scale oil sand processability tests. It allows for quick and efficient testing of different process variables such as process temperature, oil sand type or type/concentration of process aid (in this case, caustic) using a minimal amount of ore. Although there is some variation between this bench scale testing and pilot/commercial scale production, the results obtained can be compared with each other to determine useful trends (Sanford, 1983). In this study, all tests were performed at 45°C to imitate a warm slurry extraction process (Cymbalisty, et al., 1995). Two other extraction methods were also tested (Denver and modified Denver cells) and the results of these tests are found in appendix A.

3.5.1 Batch Extraction Unit (BEU)

A one litre BEU as shown in Figure 3.4 was used to study the effect of caustic addition on bitumen extraction. The temperature of the cell and its contents were kept constant by a water jacket connected to a thermal bath. For each test, 500 g of oil sands was added to 150 g of ~90°C process water with the required sodium hydroxide dosage. The sodium hydroxide (Fisher Scientific, Certified ACS Grade) to oil sand mass ratio was varied from 0 to 0.1 wt% of ore. The temperature was checked to be within 1°C of 45°C before slurrying was initiated. The slurry was mechanically agitated at 600 RPM and air was added at a flow rate of 150 mL/min for five minutes in this conditioning stage. After the conditioning of the slurry, 900 g of 45°C flood water was poured carefully into the cell and primary froth began to float to the top of the vessel. While the froth floated during the primary flotation period, no air was added into the cell and the mixing speed remained at 600 RPM. After 10 minutes of primary flotation the mixer was turned off and all froth was collected into a Whatman extraction thimble using a froth skimmer. Secondary flotation then began with the addition of 50 mL/min of air and an increase in mixing speed to 800 RPM. Secondary froth was collected after five minutes of secondary flotation in the same manner as the primary froth. Both froth samples were weighed and then the oil-water-solids (OWS) composition was determined using Dean Stark analysis, as described in section 3.1.1.

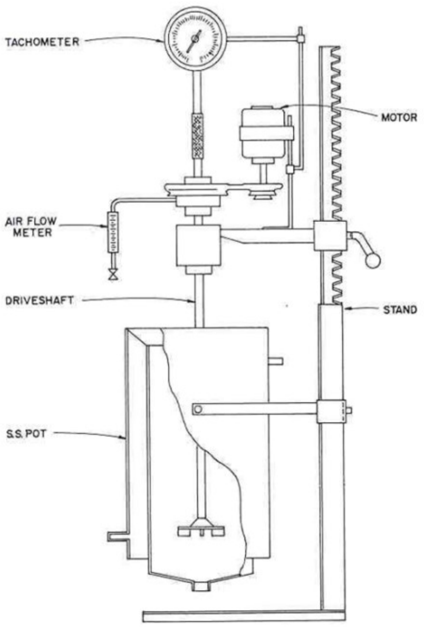

Figure 3.4: Schematics of batch extraction unit (BEU) (Sanford & Seyer, 1979)

4 Effect of Caustic Addition on Aeration and Slime Coating

4.1 Oil Sand Ores and Process/Tailings Water

Table 4.1 summarizes the results of the OWS characterization of the seven ores tested in this study. The following classification was used to organise the ores tested: <10 wt% fines - low fines ores, 10-20 wt% fines – average fines ores, 20-40 wt% fines – high fines ores, and >40 wt% fines – ultra high fines ores. Since this study is focused on how caustic is able to improve bitumen recovery, no low fines ores were tested as these are normally good processing ores that typically do not require any caustic addition to reach their maximum recovery (Schramm, et al., 1983). The study was therefore focused on high fines ores (five ores) and also included an average and an ultra high fines ore.

Table 4.1: OWS characterization of ores tested

Classification	Name	Composition of Ores, wt%			
		Bitumen	Water	Solids	Fines*
Average fines	AO	10.8	4.0	85.1	18
High fines	AE	6.5	9.5	83.9	22
	AS08	8.9	7.1	83.9	25
	AR	8.9	5.7	85.4	26
	AN	10.5	2.2	87.3	33
	AE13	8.3	4.9	86.8	35
Ultra high fines	AL	9.1	3.9	87.0	46

*Fines are defined as particles of sizes less than 44 μm and are expressed as percentage of total solids

These ores were all extracted using a Denver flotation cell. The results of tailings water characterization for caustic dosages of (0, 0.03 and 0.1) wt% of ore are given in Table 4.2. For comparison, the water chemistry of typical process water used is also given in Table 4.2. As expected, the pH of the tailings water collected increased as the amount of caustic added increased. It has been suggested that only a small portion of caustic produces natural surfactants and that most of it is consumed by polyvalent metal carbonates, clays and sulphates (Smith & Schramm, 1992). This would lead to the expectation that higher fines ores would consume more caustic than lower fines ores, and higher concentrations of NaOH would be required for high fines ores to maximize the recovery. If this is the case, the higher fines ores would be expected to have a lower tailings water pH than lower fines ores. Figure 4.1 shows the pH of the tailings water as a function of caustic dosage. The average fines ore is shown with a triangular marker, while the high fines ores are shown by square markers and the ultra high fines ore by a circular marker. The ultra high fines AL ore is of the lowest tailings pH with caustic addition, so is the high fines AR ore, especially at low caustic addition levels. All other ores exhibit very similar pH and no separation is evident between the average fines ore and other high fines ores. This result may mean that the composition of the fines/clays rather than the total amount in the oil sands would be a better indication of whether caustic is consumed by the clays. AL and AR ores might contain more caustic consuming minerals that performing detailed mineralogy would illuminate on.

The divalent cation concentrations decreased in the tailings water as the caustic dosage increased, as can be seen in Table 4.2. The two ores that had the lowest tailings pH with caustic addition also had the highest calcium concentrations. Both AR and AL actually had a higher concentration of calcium in their tailings water with zero caustic addition than that of process water. The concentration of calcium ions in the tailings water of AR and AL ores at 0.03 wt% caustic dosage was almost the same as the process water. This finding means the AR and AL ores released calcium into the process water during the extraction process, which is most likely due to cation exchange. This release of calcium leads to the observed decrease in pH as the calcium consumes more carboxylic surfactants which are precipitated out as calcium carboxylates (Smith & Schramm, 1992), consuming more NaOH. Similar trends were obtained for magnesium, which showed a higher magnesium concentration in the tailings water of both AR and AL ores than in the process water. This would lead to a direct consumption of NaOH as magnesium is precipitated out as magnesium hydroxide (Dai, et al., 1992). As the caustic dosage was increased to 0.1 wt% only small amounts of divalent cations remained in the tailings water for all the ores. As expected, for most ores an increase in sodium concentration occurred with NaOH addition while the potassium concentration appeared to decrease with NaOH addition.

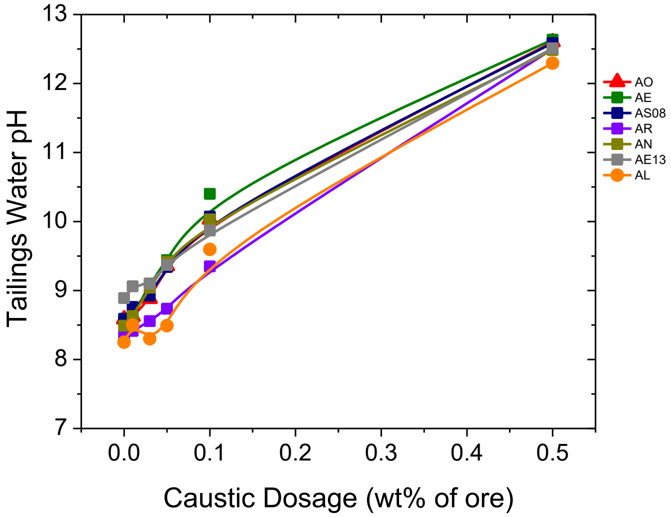

Figure 4.1: pH of oil sand extraction tailings water at different caustic dosages

Table 4.2: Characterization of typical process and tailings water

Ore	Caustic, wt% of ore	pH	[Carboxylic Surfactant], 10^{-5} mol/L	Concentration of ions, ppm			
				Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}
PW	n/a	8.2	25	40	17	570	19
AO	0	8.5	33	30	20	891	26
	0.03	8.9	39	20	10	634	22
	0.1	10.0	50	4.2	0.9	878	17
AE	0	8.5	42	25	21	652	23
	0.03	9.0	47	10	10	720	23
	0.1	10.4	54	0.9	0.9	870	20
AS08	0	8.6	33	23	15	465	31
	0.03	8.9	34	18	9.1	509	28
	0.1	10.1	47	4.8	0.9	863	21
AR	0	8.0	57	46	28	1025	27
	0.03	8.5	64	38	17	1095	22
	0.1	9.4	88	3.0	1.6	1130	20
AN	0	8.5	38	28	17	873	32
	0.03	9.0	45	18	11	642	30
	0.1	10.0	56	5.3	1.1	1156	23
AE13	0	8.8	32	13	17	669	28
	0.03	9.0	36	10	10	734	23
	0.1	9.8	50	2.6	1.4	992	22
AL	0	8.3	29	54	33	555	30
	0.03	8.5	32	40	30	773	33
	0.1	9.3	40	9.8	5.3	781	24

4.2 Aeration

As an example, 50% probability of bitumen-air attachment (induction time) curves measured in tailings water of AE13 ore are shown in Figure 4.2. An increase in induction time with increasing caustic dosage is observed. Based on repeatability tests, the uncertainty in induction time of bitumen-bubble attachments was shown to be ~ 30 ms. The induction time of bitumen-air bubble attachment in tailings water with increasing tailings water pH are shown in Figure 4.3. As expected, an increase in induction time with increasing caustic dosage (as was obtained with AE13) was observed for all ores. As the pH increases, different induction time values were obtained for different ores. The induction time for most ores starts out at ~600-750 ms at zero caustic addition and increases to 1000-1100 ms at the 0.1 wt% caustic addition. The induction time of AR (an increase from 910 to 1350 ms from 0-0.1 wt% caustic) is slightly higher than the other ores tested. The induction time of bitumen-bubble attachment in tailings water of AL ore at lower caustic dosages appears to also be slightly higher (810 to 980 ms from 0-0.03 wt% caustic). The induction time then did not significantly change from 0.03-0.1 wt% caustic (1080 ms). To explain the differences in induction time measurements the water chemistry of the system is considered.

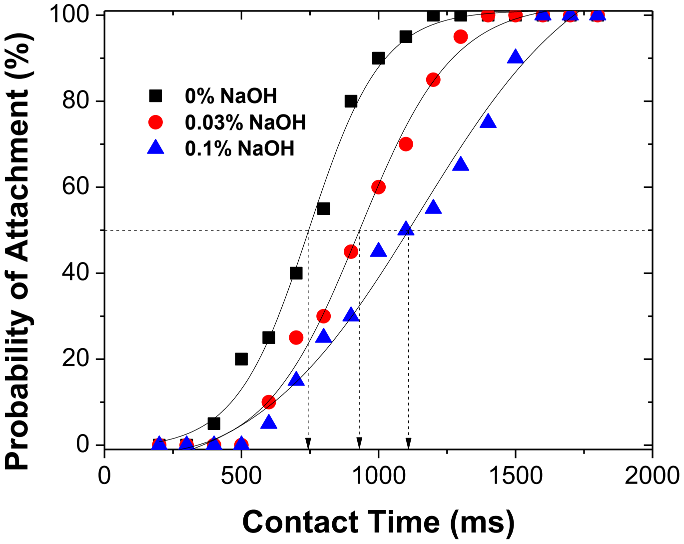

Figure 4.2: Probability curves of bubble-bitumen attachment for AE13 ore

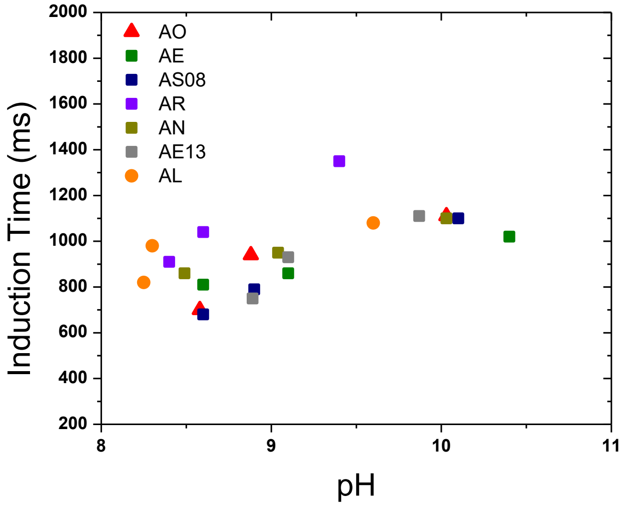

Figure 4.3: Induction time of bitumen-bubble attachment in tailings water for all ores as a function of pH

The addition of caustic is known to increase concentration of carboxylic surfactants. The concentration of carboxylic surfactants in the tailings waters obtained by Fourier transform infrared spectroscopy (FTIR) is shown in Figure 4.4 (more detailed information can be found in appendix C.1). As expected, the concentration of carboxylic surfactants increases with increasing pH. Most ores start at a concentration of ~30-40$\cdot 10^{-5}$ mol/L with zero caustic addition and increase to ~40-60$\cdot 10^{-5}$ mol/L at 0.5 wt% NaOH addition. The only outlier is AR, which has a significantly higher concentration of carboxylic surfactant (ranging from 57-107$\cdot 10^{-5}$ mol/L). This explains why AR has a higher induction time than the other ores. The carboxylic surfactants increased concentration in the aqueous phase can adsorb on both the bitumen and bubble surface, thus leading to increased repulsion between the two surfaces. Although this explains the increased induction time for AR tailings water, AL does not have a higher concentration of carboxylic surfactants in its tailings water. It appears that other phenomena may also play a role to hinder bitumen aeration.

As mentioned previously, not all carboxylic surfactants are water soluble. Larger acids (> C20) still ionize on the surface of bitumen-alkaline aqueous interfaces that can still contribute bitumen surface charge. As will be discussed in more detail later, the zeta potential for AL went from -52 mV at 0 wt% caustic to -71 mV at both 0.03 and 0.1 wt% NaOH addition. These values were more negative than that for other ores at similar pHs which could explain why the induction time of bitumen-bubble attachment in tailings water from AL ore was higher than the other ores. The increased charge on the bitumen surface leads to increased electrostatic repulsion between the bitumen and air bubble. It also explains why the induction time of bitumen-bubble attachment in tailings water for AL ore did not increase significantly as the caustic dosage was increased from 0.03 to 0.1 wt%, as the surface charge of bitumen did not increase over this range. The bitumen chemistry affects the bitumen surface charge.

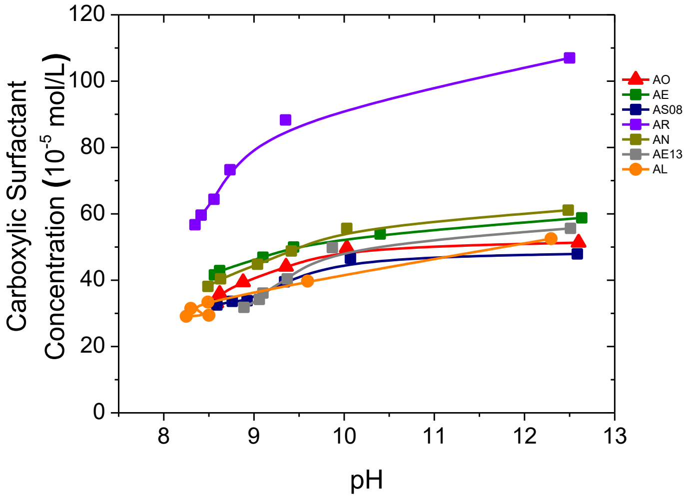

Figure 4.4: Carboxylic surfactant concentration in tailings water as a function of pH from (Bakhtiari, 2015)

4.2.1 Role of Water Chemistry

The water chemistry has been shown to play an important role in the aeration process and is further studied in this section. The effect of carboxylic surfactant/pH, calcium, and humic acid concentration on the induction time is examined here. The role of carboxylic surfactant concentration/pH was studied by adjusting the pH of the tailings water obtained with 0.1 wt% caustic addition (the highest carboxylic surfactant concentration) to the pH without caustic addition (the lowest carboxylic surfactant concentration). Dilute hydrochloric acid and sodium hydroxide (both from Fisher Scientific, certified ACS grade) were used to adjust the pH of the tailings water. The results are shown in Figure 4.5 for ore AE13. The induction time of bitumen-bubble attachment in the 0.1 wt% tailings water was the same whether it was at its original pH (9.9) or pH 8.9 corresponding to the case without caustic loading. It should be noted that the concentration of calcium also decreased as the caustic dosage increased and therefore it could be either increased carboxylic surfactant or decreased calcium content that increased the induction time from 0 to 0.1 wt% NaOH. To separate these effects, an additional test was performed by measuring the induction time in process water with and without removal of the carboxylic surfactant from this process water (Bakhtiari, 2015). The results of this test are presented in Table 4.3. The induction time in deionized water (pH adjusted to 8.6 using NaOH) was also included for comparison. The process water with the carboxylic acid removed had the fastest induction time, followed by the deionized water and then the process water. The significant decrease in induction time from 680 ms in process water to 370 ms in process water without carboxylic surfactant indicates that it is the increase in carboxylic acid concentration not the increase in pH or decrease in calcium concentration that hinders the aeration process. The decrease of induction time from process water to deionized water arises from the same mechanism. The decrease of induction time from deionized water to process water without carboxylic surfactant can be explained by the increased concentration of divalent cations and salinity of the process water. Since both bitumen and air bubbles are negatively charged in alkaline solutions, the presence of divalent cationic species would be expected to bridge the bitumen-air bubble surfaces. The increase in salt concentration is anticipated to depress the electric double layer, decreasing repulsion and increasing attraction forces between the two surfaces (Berg, 2009).

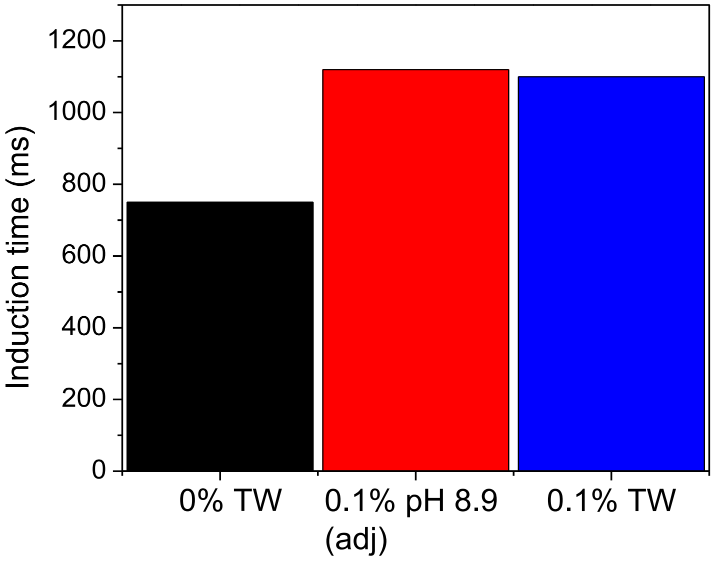

Figure 4.5: Effect of pH on induction time for ore AE13

Table 4.3: Induction time of bitumen-bubble attachment in deionized and process water

Sample	Deionized Water	Process Water	Process Water with Carboxylic Surfactant Removed	
pH	8.6	8.6	7.6	8.6
Induction Time, ms	520	680	400	370

The positive role of divalent cations in the aeration process (in this case calcium) was confirmed by doping the 0.1 wt% caustic loaded tailings water (lowest calcium concentration) with 60 ppm calcium (calcium chloride, Fisher Scientific ACS grade). Figure 4.6 shows that the addition of calcium to the tailings water led to a decrease of about 100 ms in induction time, confirming that the addition of divalent cations is beneficial to the aeration process. One thing to note is that all of these tests were performed in the absence of solids. It has been shown before that when both calcium and fines are present, slime coating of fines on the bitumen surface increases, which leads to steric repulsion between air and bitumen (Gu, et al., 2003). An expected reduction in bitumen aeration efficiency would result.

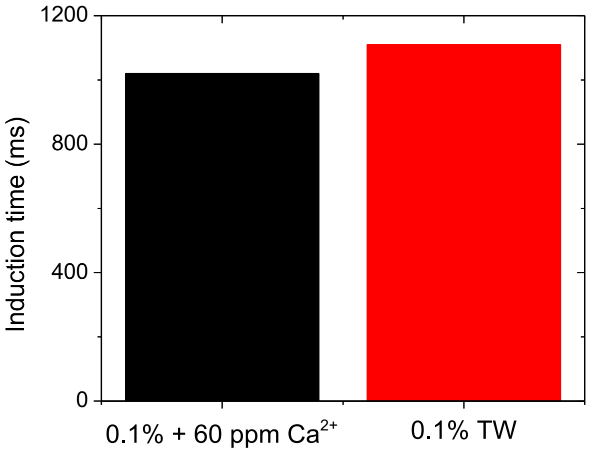

Figure 4.6: Effect of calcium concentration on induction time for AE13 ore

The presence of humic acids (which are released at high caustic dosages) has recently been proposed to decrease the uptake of illite by bitumen (decreasing slime coating) (Bakhtiari, et al., 2015). The addition of 30 ppm humic acid (MP Biomedicals) to the tailings water without caustic addition (tailings water with no humic acid) was performed to see if aeration could also be improved with this additive. Humic acid changes the colour of the water to a light brown at low concentrations and darker brown as its concentration increases. The tailings water obtained without caustic addition but with 30 ppm humic acid added qualitatively looked similar in colour to the tailings water with 0.1 wt% NaOH addition, and therefore was used for this study. The humic acid was found to have no effect on the induction time as can be seen in Figure 4.7. Although humic acids were shown to adsorb on the bitumen surface in the presence of carboxylic surfactants (Bakhtiari, et al., 2015), this does not appear to hinder or aid the aeration process.

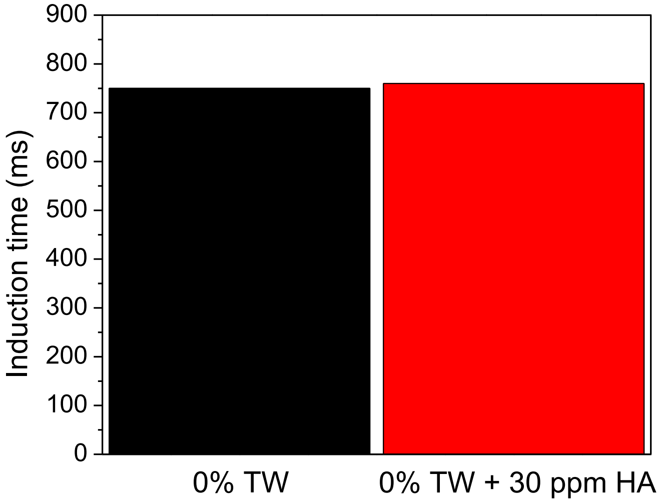

Figure 4.7: Effect of humic acid concentration on induction time

4.2.2 Induction Time Generalization

Both the concentration of calcium and carboxylic surfactant has been shown to be important in the aeration process. In the current simplified system with no fine solids present, the addition of calcium ions decreases the induction time while adding carboxylic surfactant increases the induction time. These two parameters were therefore used to see if any generalizations could be made. Since calcium decreases the induction time while carboxylic surfactant increases it, it is conceivable that the induction time can be normalized by the ratio of surfactant concentration to calcium concentration. This can be accomplished by calculating this ratio (with both calcium and carboxylic surfactant concentrations in mol/L) and plotting it as the y-axis. The resultant curve, as shown in Figure 4.8, was fit using an exponential decay (ExpDecay2) in OriginPro 8.0. A good fit with an R^2_{adj} of 0.9204 was obtained. This generalization was then extended to some data collected on the same piece of equipment by a different researcher, as shown in Figure 4.9 (Zhu, 2013). The data is a bit more spread out in this case, but decent fit with an R^2_{adj} of 0.6680 was obtained. This normalization indeed points to the fact that induction time is highly dependent on the concentration of divalent cations as well as carboxylic surfactants.

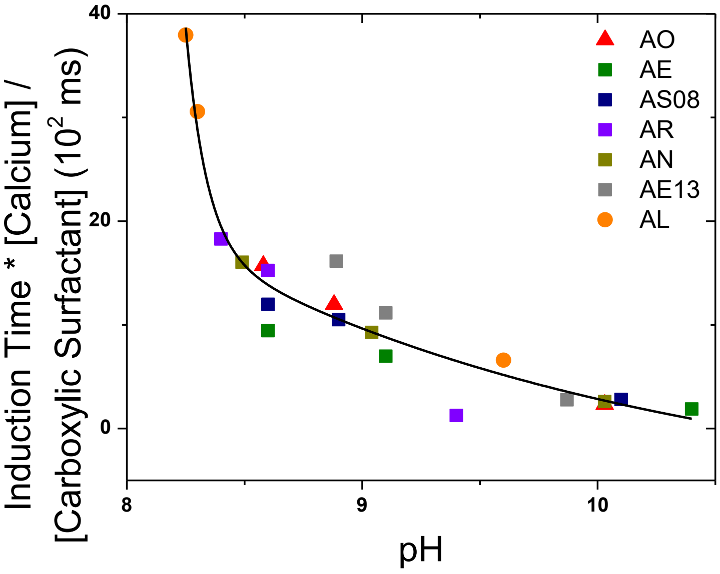

Figure 4.8: Induction time*calcium concentration/carboxylic surfactant concentration as a function of pH for current study

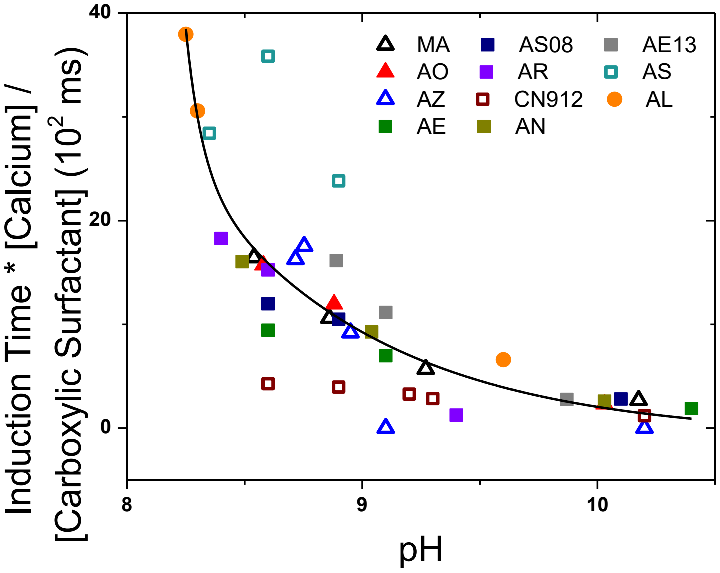

Figure 4.9: Induction time*calcium concentration/carboxylic surfactant concentration as a function of pH including data from (Zhu, 2013)

4.3 Slime Coating

The bitumen-fines interactions or slime coating is also extremely important in the flotation system. The fines coated on the bitumen has many detrimental effects on flotation process by: i) adding steric repulsion of bitumen from air bubbles, decreasing aeration efficiency; ii) decreasing bitumen coalescence due to the same steric repulsion; and iii) increasing the weight of bitumen-air bubble aggregates due to fines coated on the bitumen surface, leading to a decreased flotation efficiency. Slime coating also has a profound impact on froth quality. Fines-coating on the bitumen surface increases the solids content in the froth that will need to be dealt with in the froth treatment stage.

The slime coating data obtained through zeta potential distribution data is shown in Figure 4.10-Figure 4.12 for three ores. The data for all ores are shown in appendix B.2. In all graphs, the zeta potential distribution of fines is in the top graph, the zeta potential distribution of bitumen in the middle graph, and the zeta potential distribution of a 1:1 bitumen and fines mixture is in the bottom graph. The caustic dosage of the tailings water system tested increases from left to right. Figure 4.10 shows the slime coating data of bitumen-fines system for AO in 0, 0.03, and 0.1 wt% caustic tailings water. For this average fines ore, the ore exhibits partial slime coating when no caustic was used, showing a single but broad zeta potential distribution peak for the mixture. The system is no longer slime coated with 0.03 and 0.1 wt% caustic addition, clearly showing bimodal distribution peaks centred at the individual bitumen/fines peaks for the mixture. The system with 0.03 wt% caustic addition does show a slight overlap of the two peaks, but this is due to overlap of the bitumen/fines peaks, not slime coating.

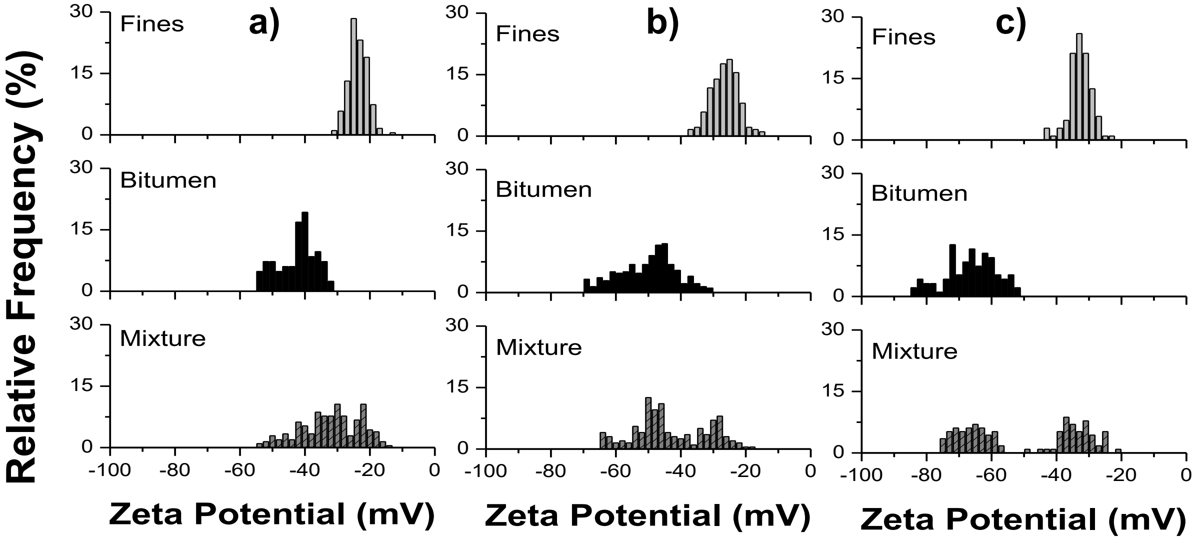

Figure 4.10: Slime coating of fines from AO ore at: a) 0% NaOH (pH 8.6); b) 0.03% NaOH (pH 8.9); and c) 0.1% NaOH (pH 10.0)

The AE and AE13 ores were chosen due to the availability of their extraction performance data. Figure 4.11 shows the slime coating of bitumen by fines of AE ore in its tailings water. The bitumen is partially slime coated by fines from this ore in tailings water at 0 and 0.03 wt% caustic addition during extraction, but a bimodal zeta potential distribution was obtained at the highest caustic addition level. The zeta potential peak of bitumen in the mixture has increased significantly from about -75 mV to -55 mV, indicating that the surface is still partially coated with fines. Figure 4.12 shows the slime coating of bitumen by fines from AE13 ore in its tailings water. This system appears to be partially slime coated when no caustic was added. At 0.03 wt% caustic addition, a reduced slime coating of bitumen by fines, if there is any, was observable showen by a clear split of broad zeta potential distribution peaks. Two peaks are observed at the

0.1 wt% NaOH condition that correspond to the zeta potential distribution peaks of individual bitumen and fines, indicating the absence of slime coating. It should be noted that the zeta potential distribution method is not applicable for systems of overlapping bitumen and fines distributions in the single component systems. In future studies, other methods such as AFM or QCM-D should be employed as a complementary method to study slime coating when such overlap exists. The same general trend of less slime coating with increased caustic dosage was observed for all ores, but the level at which slime coating ceased was different for different oil sand ores. AO ore displayed no slime coating of bitumen by fines at 0.03 wt% NaOH, while for the other two ores, at least partial slime coating of bitumen by their fines was observed until 0.1 wt% caustic was added. For AE ore, at least partial slime coating was observed up to 0.1 wt% NaOH and for AE13 ore, slime coating was absent at this same caustic dosage. This will be further investigated in the following sections.

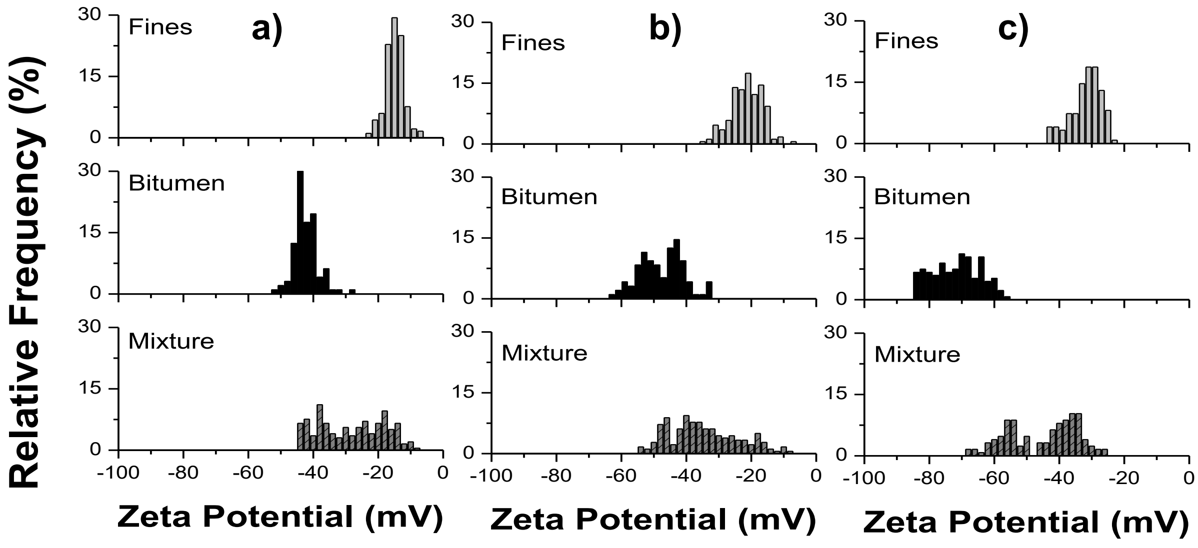

Figure 4.11: Slime coating of fines from AE ore at: a) 0% NaOH (pH 8.6); b) 0.03% NaOH (pH 9.1); and c) 0.1% NaOH (pH 10.4)

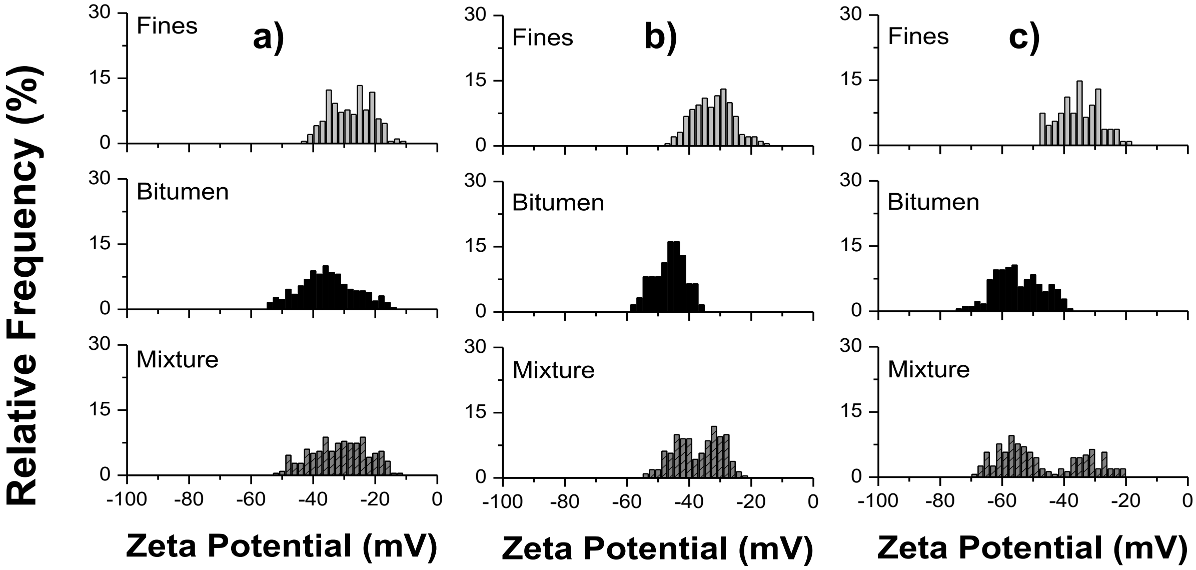

Figure 4.12: Slime coating of fines from AE13 ore at: a) 0% NaOH (pH 8.9); b) 0.03% NaOH (pH 9.1); and c) 0.1% NaOH (pH 9.9)

4.3.1 Zeta potential of Bitumen and Fines

The average zeta potential of the bitumen and fines obtained from the zetaphoremeter measurements are shown in Figure 4.13. The zeta potentials of both the fines and bitumen are negative at all pHs tested, and they become more negative with increasing pH/caustic dosage. The bitumen zeta potentials had a maximum deviation of 2 mV while the fines were all within 0.5 mV. The bitumen zeta potential is more negative than the fines zeta potential. The negative charge on these surfaces lead to electrostatic repulsion between bitumen and fines surfaces. Since AO ore bitumen was not slime coated by fines at 0.03 wt% caustic addition, a high bitumen and/or fines surface charge might explain the decreased bitumen-fines interactions. The zeta potentials as a function of pH for both bitumen and fines were quite similar for all ores, except the bitumen zeta potentials of AN and AL ores. For a majority of the ores, the bitumen zeta potentials were around -45 mV at pH 8.5 and decreased to -70 mV at pH 10. Both AN and AL start at about -55 mV in tailings water without caustic addition and increased to around -70 mV at 0.03 wt% caustic addition. The fines were slightly less negative and started at about -20 mV at pH 8.5 and decreased to -30 mV at pH 10 for all ores.

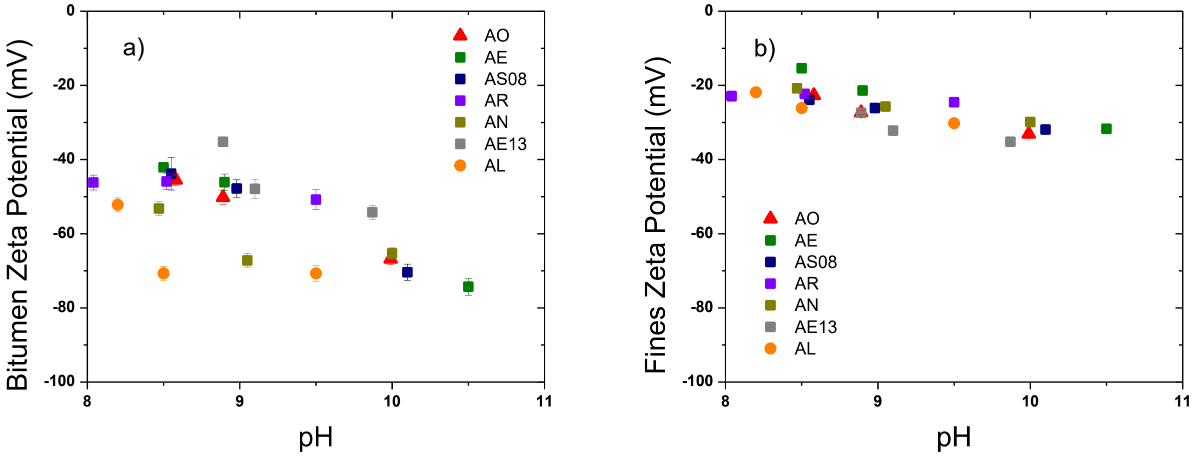

Figure 4.13: Zeta potential of: a) bitumen in tailings water; and b) fines in tailings water

AO ore has similar bitumen/fines surface charge, calcium concentration (Table 4.2), and carboxylic surfactant concentration (Figure 4.4) that is similar to the majority of other ores tested, therefore some other reason must exist for its decreased bitumen-fines interaction. The fines/clay characterizations were performed on a few ores and the results are shown in Bakhtiari (2015). It can be seen that AO ore contained the lowest concentration of montmorillonite (1.01% of the <2 μm fraction), that is notorious as a slime coating clay (Kasongo, et al., 2000); (Liu, et al., 2002). It also has a similar concentration of illite as the other ores (12.97% of the <2 μm fraction), which has recently been identified as a possible slime coating clay (Bakhtiari, et al., 2015). The low montmorillonite concentration and average illite concentration could be the reason for the decreased slime coating of bitumen by fines. The types of clays present in an oil sand is therefore a significant factor in bitumen-clay interactions.

4.3.2 Role of Water Chemistry

As with the induction time, the effect of the same water chemistry effects was tested (Section 4.2.1 above). Since AE13 ore had significant overlap of the bitumen and fines zeta potential distributions, the AE ore slime coating of bitumen by fines water chemistry data is presented here and the AE13 data can be found in appendix B.2. The pH of the 0.1 wt% NaOH addition tailings water was adjusted to the tailings water pH when no caustic was added and the results are shown in Figure 4.14. The adjustment of the 0.1 wt% caustic tailings water resulted in a slightly less negative bitumen surface (~ -70 mV to -60 mV). It is likely that the less alkaline tailings water leads to less ionization of the larger (> C20) carboxylic surfactants at the bitumen-tailings water interface. The bitumen surface is significantly less negative than when the tailings water with no caustic addition was used (-42 mV). The water soluble surfactants (C13-18) present in the higher caustic tailings water move from the aqueous phase to the bitumen-water interface, increasing the negative bitumen surface charge as compared to when the tailings water with no caustic addition was used. This produces a bitumen zeta potential that is in between the no caustic and 0.1 wt% NaOH addition tailings water. The increased water-soluble carboxylic surfactant concentration in the pH adjusted 0.1 wt% caustic addition tailings water lead to more negative fines' zeta potentials. The additional carboxylic surfactants in the aqueous phase adsorb on the fines' surface resulting in a similar surface charge from the 0.1 wt% caustic addition tailings water and the pH adjusted tailings water(~ -35 mV). The higher carboxylic surfactant concentration of the pH adjusted 0.1 wt% NaOH tailings water decreased the interaction between the bitumen and fines, resulting in fines not slime coating the bitumen. The tailings water without caustic mixture displayed slime coating of bitumen by fines and therefore the addition of carboxylic surfactants is expected to contribute to a decrease in bitumen-fines heterocoagulation. The concentration of calcium in the 0.1 wt% caustic addition tailings water is much lower than the tailings water without caustic, which could also contribute to decreased bitumen-fines interactions. The effect of calcium concentration is therefore studied next.

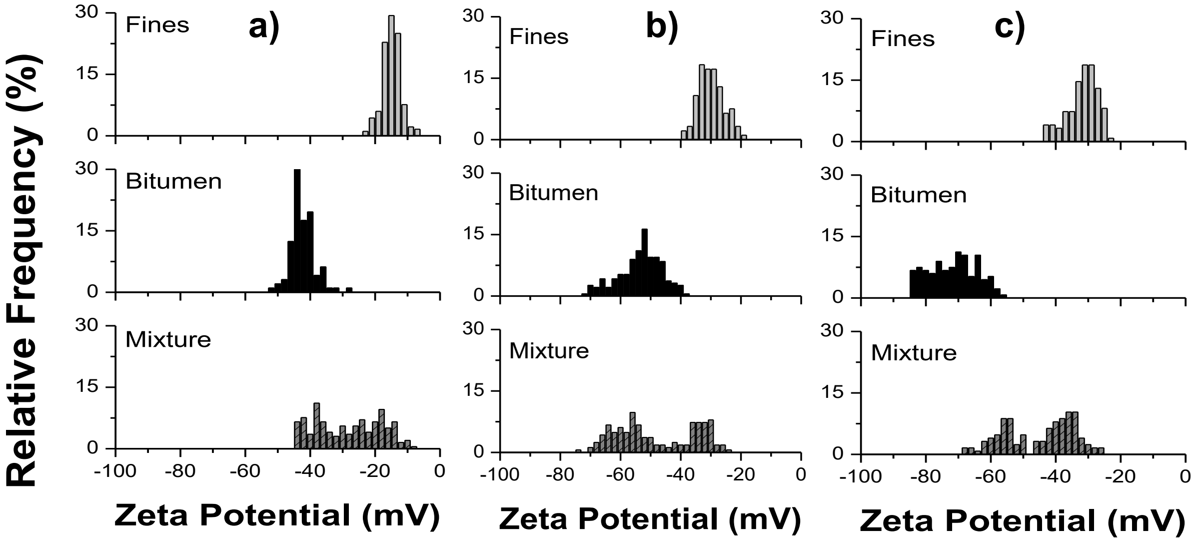

Figure 4.14: Effect of pH adjustment on slime coating of fines from AE ore at: a) 0% NaOH (pH 8.6); b) 0.1% NaOH adjusted (pH 8.6); and c) 0.1% NaOH (pH 10.4)

Figure 4.15 shows the effect of adding 40 ppm calcium to 0.1 wt% NaOH addition tailings water. The addition of calcium is shown to increase the interactions between bitumen and fines and leads to slime coating of fines on bitumen. The addition of calcium leads to less negative zeta potential distributions for both the fines suspension and bitumen emulsion. The fines' zeta potential increased from -32 to -27 mV and the bitumen's zeta potential increased from -74 to -63 mV. This increase in zeta potential is due to the positively charged calcium ions attaching to the bitumen and fines surfaces, leading to charge neutralization of the negatively charged carboxylic surfactants at the bitumen-tailings water and fines-tailings water interfaces. This promotes bitumen-air attachment in the aeration process, and promotes the attachment of fines to bitumen here. The ability of calcium to bridge the negatively charged bitumen and fines causes an increase in their interaction. This aids the bitumen aeration process, but is detrimental here as the 0.1 wt% NaOH addition tailings water is no longer bimodal and fines are now slime coating the bitumen surface.

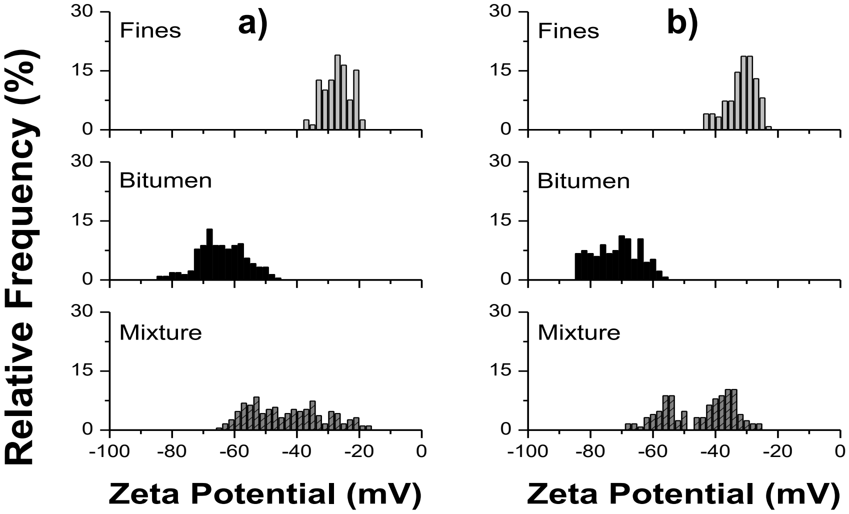

Figure 4.15: Effect of calcium concentration on slime coating of fines from AE ore at: a) 0.1% NaOH plus 40 ppm calcium (pH 10.4); and b) 0.1% NaOH (pH 10.4)

The addition of humic acid to the caustic free tailings water is shown in Figure 4.16. Originally the 0 wt% NaOH addition tailings water system showed fines slime coating on the bitumen, but with the addition of commercial humic acid, no such attachment is observed. The surface charge of the bitumen and fines remained the same with and without humic acid addition, but a bimodal mixture zeta potential distribution peak was obtained when humic acid was present. Bakhtiari, et al. (2015) showed that humic acid adsorbs on the surface of bitumen when carboxylic surfactants are present in the system. Humic acids are mixtures of aromatic and aliphatic macromolecules, containing phenolic OH and COOH groups, bridged by nitrogen and oxygen (Bakhtiari, 2015). These large macromolecules lead to steric repulsion between the bitumen and fines' surfaces, thus decreasing their interaction. This leads to the decrease in slime coating of bitumen by fines as is observed in Figure 4.16.

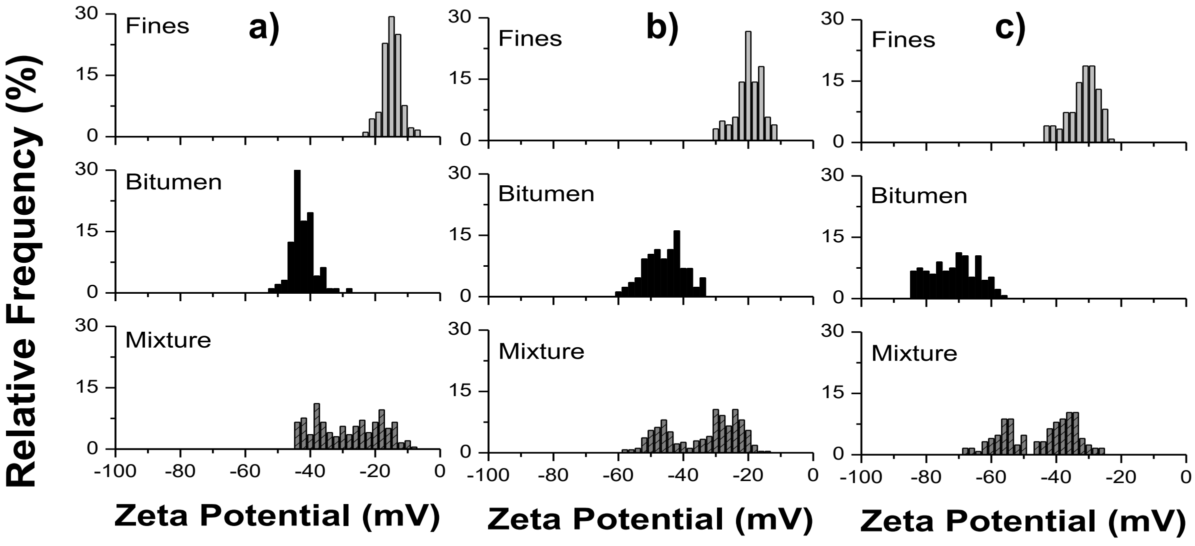

Figure 4.16: Effect of humic acid concentration on slime coating of fines from AE ore at: a) 0% NaOH (pH 8.6); b) 0% NaOH plus 30 ppm humic acids pH 8.6; and c) 0.1% NaOH (pH 10.4)

5 Effect of Aeration and Slime Coating on Oil Sand Processability

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The fundamental steps of extraction are an important indication of how an oil sand processes. The bitumen aeration and slime coating of bitumen by fines data from the previous section is linked to batch extraction unit (BEU) data here. The primary and overall recoveries as well as froth quality for two ores are compared and linked to the individual steps of extraction to help explain their different processabilities. All of the bitumen aeration and slime coating of bitumen by fines tests were performed in tailings water obtained from Denver cell (DC) extraction tests (appendix A.1). In this chapter, those results are compared to BEU test results, as the flotation parameters used in the BEU procedure appear to be more sensitive to the addition of caustic. The tailings water chemistry for the two methods is shown in Table 5.1 for AE13 ore. The concentration of ions in the tailings water were very similar for both BEU and DC tests. The carboxylic surfactant concentrations were slightly lower at the 0 and 0.03 wt% caustic dosages for the DC, but the trend is the same as the BEU. The DC tailings water is therefore expected to be representative of the BEU tailings water and is used as a substitute.

Table 5.1: Tailings water chemistry of AE13 ore extraction using batch extraction unit (BEU) and Denver cell (DC)

Caustic, wt% of ore	Extraction Method	[Carboxylic Surfactant], 10^{-5} mol/L	Concentration of ions, ppm			
			Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}
0.00	BEU	38	25	19	649	25
	DC	32	27	15	669	28
0.03	BEU	43	11	11	855	24
	DC	36	10	10	734	23
0.10	BEU	51	5	4	931	20
	DC	50	3	1	992	22

5.1 Bitumen Recovery

Figure 5.1 shows the BEU recovery during primary flotation (a) and the overall recovery (b). Caustic affects the recovery of AE and AE13 ores in different ways and different trends between primary flotation and overall flotation were observed. Duplicate runs were performed at four caustic dosages for oil sand AE13 ore (0, 0.03, 0.06, and 0.07 wt% NaOH) and the maximum standard deviation was found to be <1% during primary flotation and 2.3% for the overall recovery. There was more variability in the secondary flotation, leading to increases in overall recovery error (most froth was collected during primary flotation). The primary recovery for AE13 ore continually increased as more caustic was added (15-75% recovery), while the overall recovery increased with increasing caustic dosage until 0.06 wt% NaOH, and then remained constant at around 90% (from 30% recovery with no caustic). AE ore reached a maximum recovery at 0.03 wt% NaOH in both the primary and overall recovery and then decreased slightly as more caustic was added. The maximum recovery was also much lower than the AE13 ore recovery with maximum values of 18% for primary flotation and 35% recovery overall.

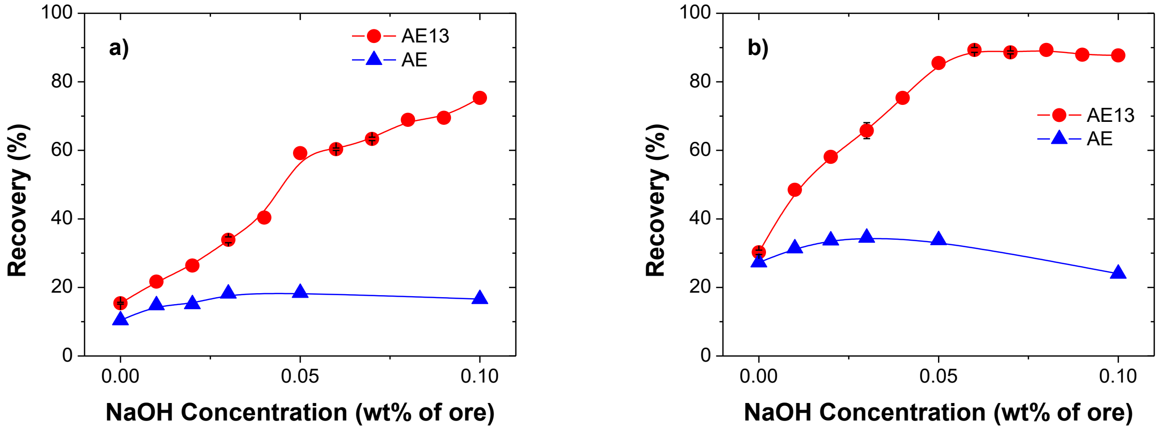

Figure 5.1: BEU bitumen recovery for: a) primary flotation; and b) overall

The induction time of bubble-bitumen attachment measurements for these two ores were quite similar with AE13 ore increasing from 750-1110 ms when no caustic was added to the 0.1 wt% caustic addition system and AE ore increased from 810-1020 ms. These values are quite similar and don't account for the changes in bitumen recovery observed, but again fines concentration and mineralogy are not accounted for in this simplified induction time system. The slime coating of bitumen by fines for these ores were slightly different. AE13 ore was observed to have fines partially slime coating bitumen in 0 and 0.03 wt% NaOH addition tailings water, but no slime coating of bitumen by fines was observed for 0.1 wt% NaOH addition tailings water. In contrast, AE ore was observed to have fines partially slime coating bitumen at all caustic levels tested. This accounts for some of the differences in the ores' recovery. Slime coating of fines on bitumen for AE ore would lead to steric repulsion between these bitumen-fines aggregates and air. This would be detrimental to the aeration process, also leading to heavier bitumen-air aggregates that are harder to float, decreasing froth quality.

The liberation data for these two ores is shown in appendix C.2. AE ore had extremely fast liberation as the thin layer of bitumen was removed almost instantaneously reaching its final liberation of ~60% with no caustic tailings water and ~70% with both 0.03 and 0.1 wt% NaOH added tailings water. AE13 ore, by contrast, had slower liberation that increased from ~50% with tailings water without caustic addition to ~80% when 0.03 and 0.1 wt% NaOH addition tailings water was used. The improvement in liberation favours improved recovery for AE13 ore more than AE ore. The liberation of AE ore increased slightly for 0 to 0.03 wt% NaOH addition tailings water, where its maximum recovery was obtained. No further improvements in bitumen liberation were found at increased caustic dosages. The liberation of AE13 ore had a much larger increase in final degree of liberation using the tailings water with no caustic addition to the 0.03 and 0.1 wt% NaOH addition system. The final degree of liberation for AE13 ore was also higher than was obtained for AE ore. One other thing to note is that AE ore contained only 6.5% bitumen and this is an extremely low bitumen content. This means that very little bitumen was on the surface of solids and as mentioned it reached its final degree of liberation after the initial pass of water over it. This indicates that it may just be the initial mechanical shear of water over the small oil sand surface used in this test that is liberating the bitumen so quickly. This could lead to errors in the liberation measurement, as the effects of process water chemistry are not able to be as effectively studied with this method.

The differences in liberation and slime coating behaviour of these two ores led to differences in their recovery. AE13 ore had a higher degree of liberation at high pH that improved more with increased caustic addition than AE ore, which would be beneficial to the extraction process. AE13 ore also went from fines partially slime coating the bitumen at low caustic levels to no slime coating of bitumen by fines in 0.1 wt% NaOH addition tailings water. This is beneficial and would lead to improved recovery. AE ore remained at partial slime coating of bitumen by fines all the way up to 0.1 wt% NaOH addition tailings water. The coating of fines on the bitumen would lead to decreased bitumen coalescence and bitumen-air bubble attachment and therefore hinder the recovery of bitumen. The induction time of bubble-bitumen attachment measurements conducted in the absence of fines were similar for both ores, and this fundamental step was always hindered by increased caustic in the system. This leads to the decrease in recovery that was observed from AE ore after 0.03 wt% NaOH addition tailings water was used. A balance of all of these steps lead to the final successful or unsuccessful flotation of bitumen in the oil sand extraction system.

One more note on the lower recovery of AE ore: the low bitumen content in AE ore would also have other implications on the recovery, since fewer bitumen droplets would be in the system. This would decrease the likelihood of bitumen-bitumen collision and decreased coalescence that would lead to fewer bitumen droplets attaining their critical size. Also bitumen-air bubble collisions would be less likely to occur, hindering the bitumen aeration process. This could account for the much lower recovery obtained for AE ore than AE13 ore.

5.2 Froth Quality

Figure 5.2 contains the bitumen to solids ratio of the primary (a) and overall froth (b). The bitumen to solids ratio is a good indication of the froth quality and is used to compare AE and AE13 ores' froth. Both ores exhibited the same increasing froth quality trend with increasing caustic dosage, but the froth quality of AE13 ore was significantly higher than AE ore. The bitumen to solids ratio increased from 1.6 to 6.6 during primary flotation and 1.4 to 3.8 overall. On the other hand, AE ore increased from 0.7 to 1.9 during primary flotation and 0.5 to 1.2 overall. The primary froth quality was also noted to be higher than the overall froth quality. The secondary froth has a lower froth quality as air is added to the system and mechanical energy input is increased to force flotation of bitumen not captured during primary flotation. This harder to float bitumen could contain more fines rendering it unable to float during primary flotation. When additional air and mechanical energy is added in secondary flotation, the bitumen is now able to float, but solid content would increase leading to decreased froth quality.

The lower froth quality obtained for AE ore was expected based on the findings from section 5.1. It was noted the AE ore had more bitumen-fines attachment than AE13 ore, which was shown as fines partially slime coating the bitumen at all caustic dosages. This increased attachment of fines on the bitumen surface means that more fines would float with the bitumen and a decrease in froth quality would occur. The increased bitumen and fines' surface charge as carboxylic surfactant concentration increased as a result of NaOH addition, decreased calcium concentration that could bridge the fines to the bitumen surface, and small amounts of humic acids that induce steric repulsion between the bitumen and solids lead to higher froth quality.

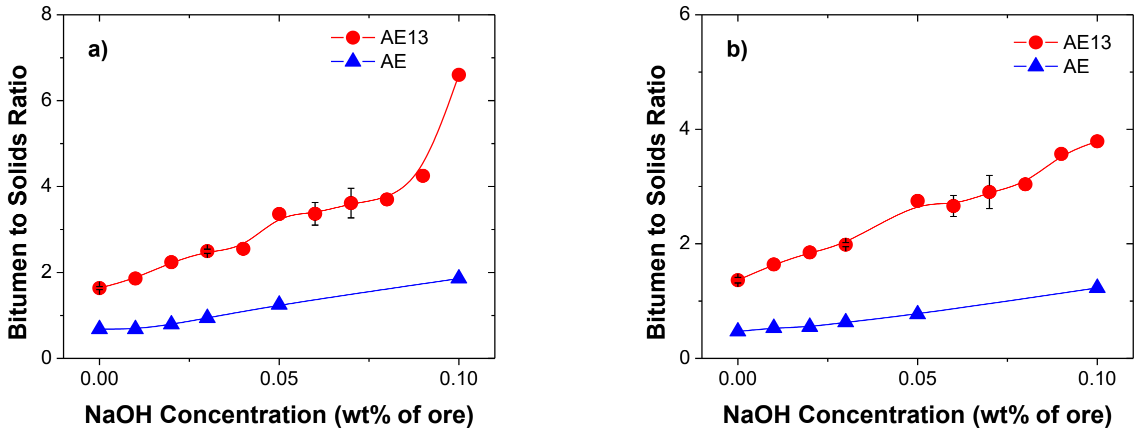

Figure 5.2: BEU bitumen to solids ratio for: a) primary flotation; and b) overall

Figure 5.3 shows the primary flotation froth composition for AE and AE13 ores. More froth was collected for AE13 ore than from AE ore. As expected from the recovery results, the weight of bitumen continually increased for AE13 ore as caustic dosage increased and maximized at 0.03 wt% NaOH addition for AE ore. The weight of solids collected increased slightly with caustic addition until 0.05 wt% NaOH addition for AE13 ore, remained constant and then started to decrease again. Even though the weight of solids was increasing slightly at lower caustic loadings, the bitumen to solids ratio was still increasing due to increased bitumen-fines repulsion. This led to a decreased weight of solids at the higher caustic concentrations as bitumen weight increases were small. The weight of solids for AE ore remained quite constant until 0.03 wt% NaOH addition when the solids started to decrease in weight, leading to improved froth quality. The water weight for both ores remained relatively constant at about 12 g for AE ore and 25 g for AE13 ore at all caustic addition levels. This may suggest that most water in the froth is due to entrainment and not a function of the chemistry of the system.

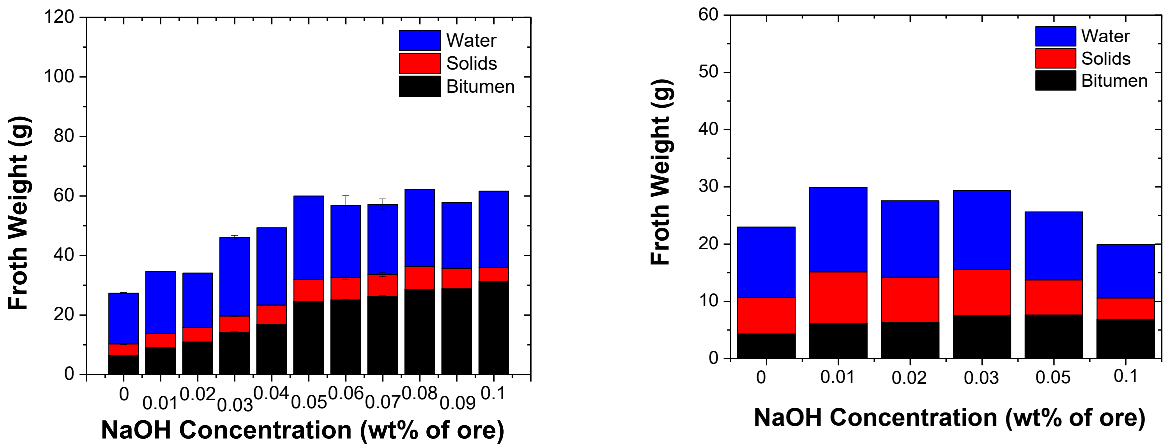

Figure 5.3: Primary BEU froth composition for: a) AE13; and b) AE

To maximize bitumen recovery, it is suggested that the minimum caustic dosage that leads to minimal bitumen-fines attachment be used. An increase in caustic addition beyond this level leads to decreased bitumen-air attachment. For AE ore, an increase in caustic addition from 0.03 to 0.1 wt% caustic addition still produced a partial slime coating of fines on bitumen, not showing a significant decrease in bitumen-fines attachment with additional caustic. However, the bitumen-bubble attachment was detrimentally affected as the caustic addition increased in the same range, which would be detrimental to bitumen flotation. This led to a maximum in recovery at the 0.03 wt% caustic dosage being observed. AE13 ore, on the other hand, displayed partial slime coating with the 0.03 wt% caustic addition tailings water and no slime coating of bitumen by fines with the 0.1 wt% caustic tailings water. The fines stopped coating the bitumen surface at a caustic dosage in between 0.03 and 0.1 wt%, where a maximum in bitumen recovery was observed (at 0.06 wt% caustic addition). The addition of caustic beyond this level did not improve the recovery as the bitumen-air attachment was hindered, just as it was for AE ore. This balance between maximizing bitumen aeration and minimizing slime coating of bitumen by fines led to no further improvement in recovery past 0.06 wt% caustic addition. An additional slime coating test with the 0.06 wt% caustic addition tailings water to verify that this is where fines stop coating the bitumen surface is recommended (using AFM or QCM-D).

6 Conclusions and Future Work

6.1 Conclusions

In this thesis, seven ores were used to study the effect of caustic addition on the bitumen aeration and slime coating of bitumen by fines that determine the efficiency of bitumen recovery by flotation. The addition of caustic to the extraction system results in many changes to the water chemistry of the system, such as the concentration of carboxylic surfactant, divalent cations, and humic acids in the process water. All of these changes in water chemistry impact the fundamental steps of bitumen extraction and affect the processability of oil sand ores.

The aeration (bitumen-air attachment) process was shown to be negatively impacted by the addition of caustic to the system, hindering the bitumen extraction process. Induction time measurements were performed in the absence of fines in this study. The increase in carboxylic surfactant concentration increases bitumen surface charge which in turn increases repulsion between bitumen and air bubbles leading to increased repulsion and longer induction times. A decrease in calcium concentration, which can bridge the negatively charged bitumen and air bubble surfaces, also leads to an increase in induction time of the system. The addition of humic acids did not impact the induction time.

The slime coating (bitumen-fines heterocoagulation) was decreased by the addition of caustic, benefitting the bitumen extraction process. Zeta potential distribution measurements showed that an increase in bitumen-fines repulsion occurred as carboxylic surfactant concentration increased. The increased charge on the bitumen and fines surfaces as well as decreased calcium bridging of the two surfaces were responsible for the decrease in bitumen-fines attachment and less slime coating. The addition of humic acids was shown to decrease bitumen-fines interaction, leading to less slime coating. The humic acid adsorbs on the surface of bitumen in the presence of carboxylic surfactant and leads to steric repulsion between the two surfaces. The composition of the fines/clays (mineralogy or clay chemistry) present in an oil sand also plays a significant role in whether a system is slime coated or not.

Based on these fundamental steps of extraction, the processability of oil sands changes. Caustic causes an improvement in bitumen liberation and decrease of slime coating of bitumen by fines, which in turn leads to an improvement in processability. However, increased caustic dosage hinders bitumen-air bubble attachment and leads to a deterioration in processability. A balance between all of these steps governs the processability of oil sand ores. Understanding of these fundamental mechanisms leads to increases in bitumen recovery and froth quality in oil sand operations.

A proposition from the current work is the idea that the minimum concentration of caustic that leads to minimal bitumen-fines attachment be used as the optimal dosage in oil sands processing. At caustic addition higher than this optimal dosage, bitumen-air attachment is detrimentally affected and balances out the positive impact that caustic has on slime coating (i.e. decrease in fines attaching on bitumen). The decrease in slime coating, balanced by decrease in bitumen-bubble attachment, leads to a maximum recovery being achieved at this optimal caustic dosage.

This thesis introduced a normalization of the induction time using the ratio of concentration of calcium and concentration of carboxylic surfactant. This new normalization shows that the concentrations of calcium and carboxylic surfactant greatly affect bitumen-air attachment in the absence of fines. It has also been shown for the first time that humic acids (shown to decrease slime coating of bitumen by illite/fines) do not negatively impact the bitumen aeration process in the absence of fines.

6.2 Future Work

A list of recommended future work is as follows:

1. It is known that the presence of fines significantly impact bitumen-air bubble attachment. Therefore, the complexity of the induction time measurement (with addition of fines) should be increased to obtain a more complete view of the aeration process. It is expected that increased clay content and certain types of clays will increase the induction time.
2. A more detailed study on the type of fines/clays in the system should be conducted to see how the mineralogy of solids affects the fundamental steps of extraction. Certain minerals have more impact on the processability of oil sand ores (such as montmorillonite) and increasing their concentration is expected to negatively impact oil sand processability.
3. Fresh extracted bitumen from the oil sand ores should be used in place of Syncrude VDU bitumen to study the effects of different types of bitumen on the fundamental steps of bitumen extraction. Bitumen with a higher concentration of larger carboxylic surfactant (>C20) is anticipated to have a higher bitumen surface charge that would affect both bitumen aeration and slime coating of bitumen by fines.
4. A complementary slime coating method (AFM/QCM-D) should be used for oil sands with overlapping individual fines/bitumen zeta potential peaks to better understand the slime coating process.

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Appendix A

A.1 Additional Flotation Methods

A.1.1 Denver Cell (DC) Experimental Procedure

A one litre DC was used for flotation tests. The temperature was kept constant by a water jacket connected to a thermal bath at 45°C. For each test, 500 g of oil sand was added to 900 g of 45°C process water with the required sodium hydroxide dosage added. The sodium hydroxide (Fisher Scientific, Certified ACS Grade) to oil sand ratio was varied from 0 to 0.5 wt% of ore. The temperature was checked to be within 1°C of 45°C before slurrying was initiated. The slurry was mechanically agitated at 1500 RPM for five minutes in the conditioning stage. Froth was collected into the first thimble after this 5 minute conditioning stage. For flotation, air was added at a flow rate of 150 mL/min and froth floated to the top of the vessel. Froth was collected at the 2, 5 and 10 minute intervals into separate thimbles. All four froth samples (conditioning, 2 minute, 5 minute and 10 minute) were weighed and then the oil-water-solids (OWS) composition was determined using Dean Stark analysis.

A.1.2 Denver Cell Results

Table A1 shows the composition of all of the ores that were run on the Denver cell. The compositions were obtained from the Dean Stark apparatus. Table A2 shows the Denver cell recovery results for all ores tested and Table A3 provides the froth quality in terms of bitumen to solids ratio. Only the overall recovery and froth quality are provided as the DC method does not include a true primary recovery stage. The recovery curve obtained is different from the BEU results in section 5.1 for AE and

AE13. Both ores display a small maximum at 0.01 wt% NaOH and then the recovery starts to decrease as the caustic dosage increases. The froth quality obtained is also significantly lower than for the froth obtained from the BEU tests (section 5.2). All ores had similar recovery and froth quality trends that indicate that this method is potentially not the best for testing how caustic affects the processability of different ores.

Table A1. Denver cell recovery results

Class	**Ore**	***Composition of Ores, wt%*** **Bitumen**	**Water**	**Solids**	**Fines (<44 μm)**
Average Fines	AO	10.8	4.0	85.1	18
High Fines	AJ	9.5	3.3	87.2	23
	AE	6.5	9.5	83.9	22
	AS08	8.9	7.1	83.9	25
	AR	8.9	5.7	85.4	26
	AB	9.5	6.8	83.6	35
	AN	10.5	2.2	87.3	33
	AA	9.7	6.3	84.0	33
	AE13	8.3	4.9	86.8	35
Ultra High Fines	AB08	9.2	5.6	85.2	40
	AL	9.1	3.9	87.0	46

Table A2. Denver cell recovery results

Class	**Ore**	***NaOH Concentration, wt% of ore*** **0**	**0.01**	**0.03**	**0.05**	**0.1**	**0.5**
Average Fines	AO	88.5	87.0	87.4	85.8	79.4	85.1
High Fines	AJ	72.3	71.7	72.4	70.4	63.3	63.8
	AE	67.5	71.8	69.1	61.2	54.4	41.5
	AS08	78.5	77.7	76.9	74.1	70.7	64.9
	AR	82.5	83.3	82.1	79.0	73.8	48.8
	AB	67.7	66.0	61.9	61.3	57.0	56.8
	AN	72.6	71.9	69.5	71.9	71.8	65.9
	AA	62.9	61.5	57.5	55.6	55.4	44.9
	AE13	71.3	73.7	70.6	71.1	61.9	39.7
Ultra High Fines	AB08	65.5	70.6	70.2	69.3	65.5	51.7
	AL	41.1	42.4	42.5	40.1	36.9	39.3

Table A3. Denver cell bitumen to solids ratio results

Class	**Ore**	***NaOH Concentration, wt% of ore***					
		0	**0.01**	**0.03**	**0.05**	**0.1**	**0.5**
Average Fines	AO	2.02	1.81	2.25	2.72	3.61	4.51
High Fines	AJ	0.79	0.83	1.31	1.60	2.41	2.00
	AE	0.58	0.53	0.59	0.60	0.87	1.02
	AS08	1.05	1.12	1.36	1.67	2.35	3.18
	AR	0.66	0.69	0.96	1.25	1.77	2.17
	AB	0.72	0.76	0.87	0.93	1.26	1.55
	AN	0.43	0.48	0.59	0.72	1.14	1.58
	AA	0.40	0.43	0.44	0.51	0.72	1.36
	AE13	0.60	0.62	0.70	0.84	1.25	1.60
Ultra High Fines	AB08	0.27	0.30	0.33	0.39	0.61	0.97
	AL	0.34	0.41	0.38	0.39	0.48	1.45

A few tests were conducted using 0.1 wt% caustic dosage tailings water recycled to perform additional DC extractions. The purpose of these tests were to see if the increased carboxylic surfactant concentration found in high caustic loading tailings water would improve the processability of ores without additional caustic. To better study the effect of carboxylic surfactant concentration, the pH of the tailings water was adjusted to the pH of the original process water (~ 8.7) using dilute hydrochloric acid (Fisher Scientific, Certified ACS grade). Three ores (AE, AR, and AE13) had two runs of 0.1 wt% caustic dosage runs performed. The tailings water from these tests were centrifuged and filtered as described in section 3.2. The pH was adjusted and then a DC extraction was performed using this water as the process water using the same ore. Table A4 shows the recovery results and Table A5 shows the froth quality results for these water recycle tests. It can be seen that the recovery improved from the 0.1 wt% NaOH level when the tailings water was recycled and the pH was lowered. They are within error of the recoveries obtained at the no caustic condition tests and therefore an increase in carboxylic surfactant concentration did not improve the recovery of these ores. There was a slight increase in froth quality for the high carboxylic surfactant concentration recycled water. Although it was increased from the no caustic loading tests, it was still significantly lower than the froth quality of 0.1 wt% caustic dosage extraction.

Table A4. Denver cell recovery results for water recycle tests

Class	**Ore**	***NaOH Concentration, wt% of ore***		
		0	**0.1 recycled**	**0.1**
High Fines	AE	62.6	65.1	47.0
	AR	81.5	80.3	68.7
	AE13	70.2	73.7	59.0

Table A5. Denver cell bitumen to solids ratio results for water recycle tests

Class	**Ore**	***NaOH Concentration, wt% of ore***		
		0	**0.1 recycled**	**0.1**
High Fines	AE	0.56	0.66	0.92
	AR	0.83	0.92	1.62
	AE13	0.54	0.73	1.29

Humic acids (HAs) have been shown to decrease the slime coating of illite on bitumen (Bakhtiari, 2015). It was therefore decided to dope process water with commercial humic acids (MP Biomedicals) at 1000 ppm to see if the froth quality using no caustic could be improved. One ore (AS08) was chosen to perform this test. Table A6 shows the recovery data and Table A7 shows the froth quality data. From Table A6, it can be seen that the addition of HA significantly decreased the bitumen recovery. There was a slight increase in bitumen to solids ratio, as seen in Table A7, but this does not compensate for the lowered bitumen recovery. An overdose of the system with the addition of 1000 ppm HA might be affecting the results and lower concentrations could be tested in subsequent experiments.

Table A6. Denver cell recovery results for humic acid doping test

Class	Ore	*NaOH Concentration, wt% of ore* 0	 0 + 1000 ppm HA	 0.1
High Fines	AS08	78.5	70.7	63.2

Table A7. Denver cell bitumen to solids ratio results for humic acid doping test

Class	Ore	*NaOH Concentration, wt% of ore* 0	 0 + 1000 ppm HA	 0.1
High Fines	AS08	1.05	1.41	2.35

A.1.3 Modified Denver Cell (MDC) Experimental Procedure

A two litre circular “shell”-type Denver cell was used to study the effect of caustic on bitumen extraction for one ore to compare extraction methods. The temperature was kept constant at 45°C by a water jacket connected to a thermal bath. For each test, 500 g of oil sand was added to 150 g of ~47°C process water with the required sodium hydroxide dosage added. The sodium hydroxide (Fisher Scientific) to oil sand ratio was varied from 0 to 0.1 wt% of ore. The agitator was raised and lowered 5 or 6 times to break up any clumps in the oil sand. The slurry was mechanically agitated at 850 RPM and air addition flow rate of 420 mL/min was added for ten minutes in this conditioning stage. After the conditioning stage, 450 g of 47°C flood water was poured carefully into the cell and primary froth began to float to the top of the vessel. No air was added into the cell and the mixing speed was maintained at 850 RPM during the primary flotation period. During the 10 minutes of primary flotation, all froth was collected into a Whatman extraction thimble using a froth skimmer. Secondary flotation then started by carefully adding 350 g of 47°C flood water and the addition of 230 mL/min of air. Secondary froth was collected for five minutes of secondary flotation in the same manner as the primary froth. Both froth samples were weighed and then the oil-water-solids (OWS) composition was determined using Dean Stark analysis.

A.1.4 Modified Denver Cell Results

One ore was chosen to be run on the MDC at five different caustic dosages between 0 and 0.1 wt% NaOH. Table A8 contains all the recovery data and Table A9 shows the froth quality data. The primary recovery shows an increasing recovery trend while the overall recovery shows a slight decrease in recovery with increasing caustic dosage. The primary recovery trend is the same as the BEU (but with much lower recovery), while the overall recovery trend is close to the overall recovery obtained using the DC. The bitumen to solids ratios obtained were much lower than obtained using the BEU, but quite similar to the regular DC results. All extraction methods displayed the same increasing froth quality trend with increasing caustic dosage, but the bitumen to solids ratios of the DC and MDC were both lower than obtained from the BEU.

Table A8. Modified Denver cell recovery results

Class	**Ore**	**Stage**	***NaOH Concentration, wt% of ore***				
			0	**0.01**	**0.03**	**0.05**	**0.1**
High Fines	AE13	*Primary*	7.1	7.8	9.2	12.3	25.7
		Overall	72.9	68.8	73.8	70.1	68.6

Table A9. Modified Denver cell bitumen to solids ratio results

Class	**Ore**	**Stage**	***NaOH Concentration, wt% of ore***				
			0	**0.01**	**0.03**	**0.05**	**0.1**
High Fines	AE13	*Primary*	0.32	0.22	0.32	0.34	0.48
		Overall	0.54	0.57	0.66	0.71	0.79

Appendix B

B.1 Additional Induction Time Measurements

The induction time measurement using fresh extracted bitumen from the ore in place of Syncrude VDU bitumen was performed. The bitumen was extracted freshly from each ore using a Rotana 460R centrifuge. The centrifugation was performed at 50°C and 18 000 G (11 500 rpm). Bitumen separated from the sands and was scooped out of the top of the centrifuge tubes after 2 hours of centrifuging. This was performed until sufficient bitumen had been obtained. This process was performed by a summer student, Sahil Bangar. Figure B1 shows the results obtained for the no caustic tailings water using both fresh and VDU bitumen for oil sand AR. The induction time increased just over 200 ms when fresh extracted bitumen was used. This suggests that bitumen chemistry is also important and should be investigated further in future studies.

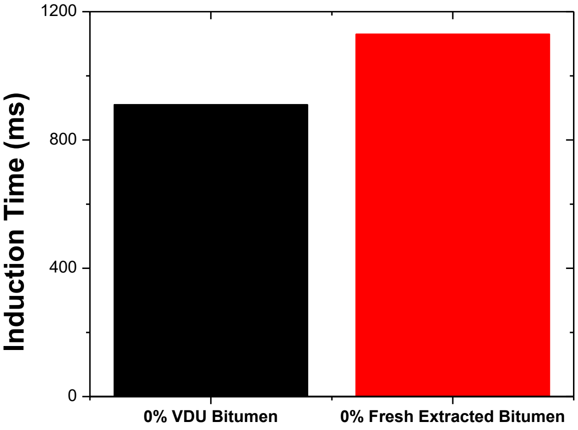

Figure B1. Induction times using both fresh and VDU bitumen for AR ore

B.2 Additional Zetaphoremeter Measurements

B.2.1 Regular slime coating results

The slime coating zetaphoremeter data for all ores not shown in the main text (AS08, AR, AN, and AL) can be found in Figure B2 to Figure B5. The slime coating of fines on bitumen for all of these ores decreased with increasing caustic dosage. They all start with high interaction between the bitumen and fines at low pH/caustic level (slime coated system) and end with lower interactions at higher pH/caustic level (partial slime coating to no slime coating). As with AE13, AS08 zeta potential peaks for bitumen and fines are overlapped at the 0 and 0.03 wt% caustic dosages, and an additional method (such as QCM-D) would be beneficial in such cases.

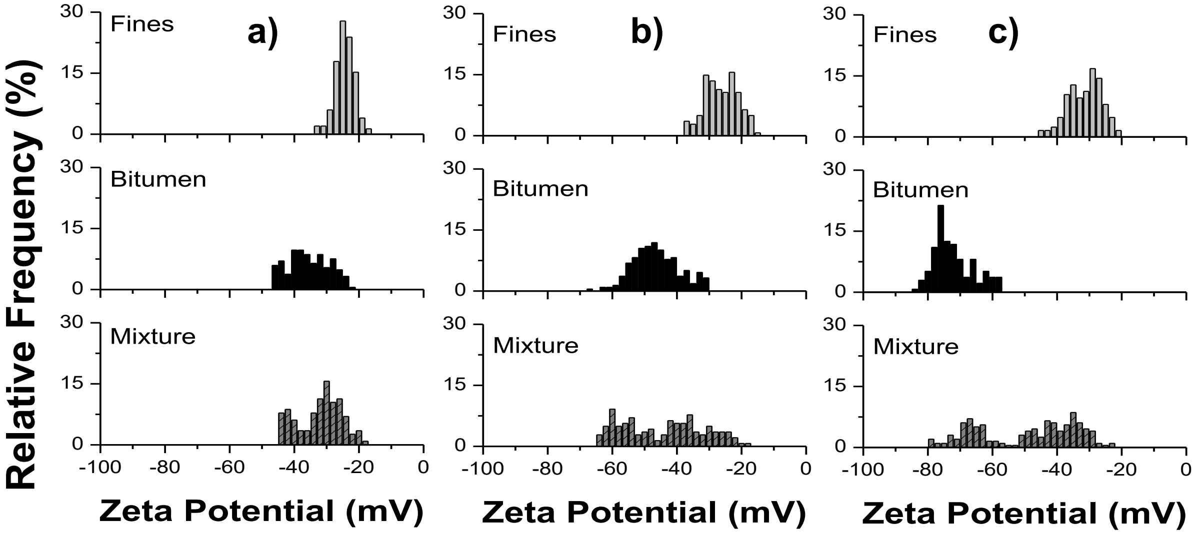

Figure B2: Effect of caustic addition on slime coating behaviour of AS08 ore at a) 0% NaOH (pH 8.6), b) 0.03% NaOH (pH 8.9), c) 0.1% NaOH (pH 10.1)

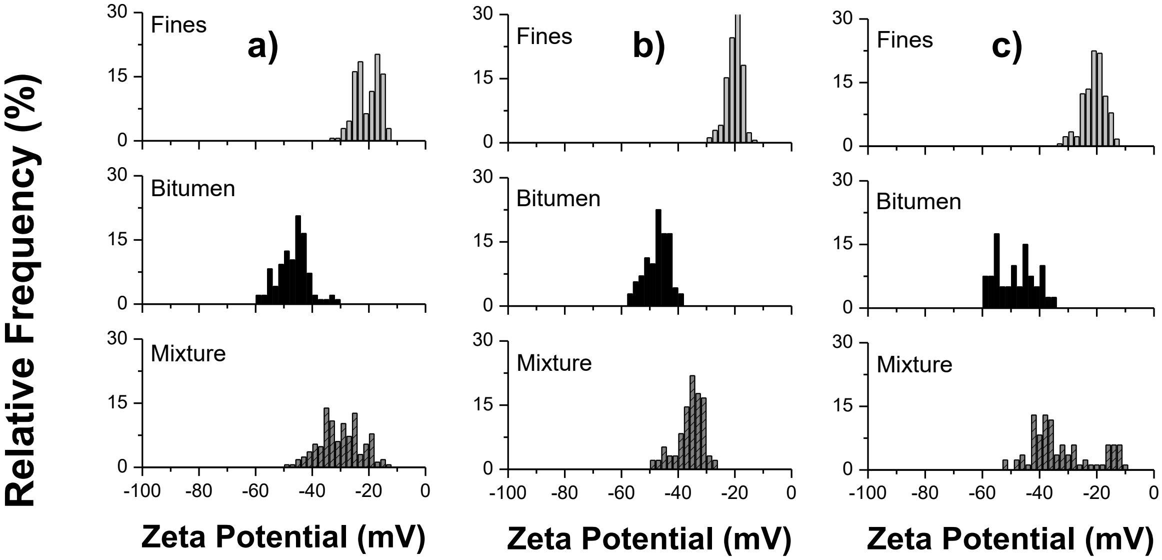

Figure B3: Effect of caustic addition on slime coating behaviour of AR ore at a) 0% NaOH (pH 8.4), b) 0.03% NaOH (pH 8.6), c) 0.1% NaOH (pH 9.4)

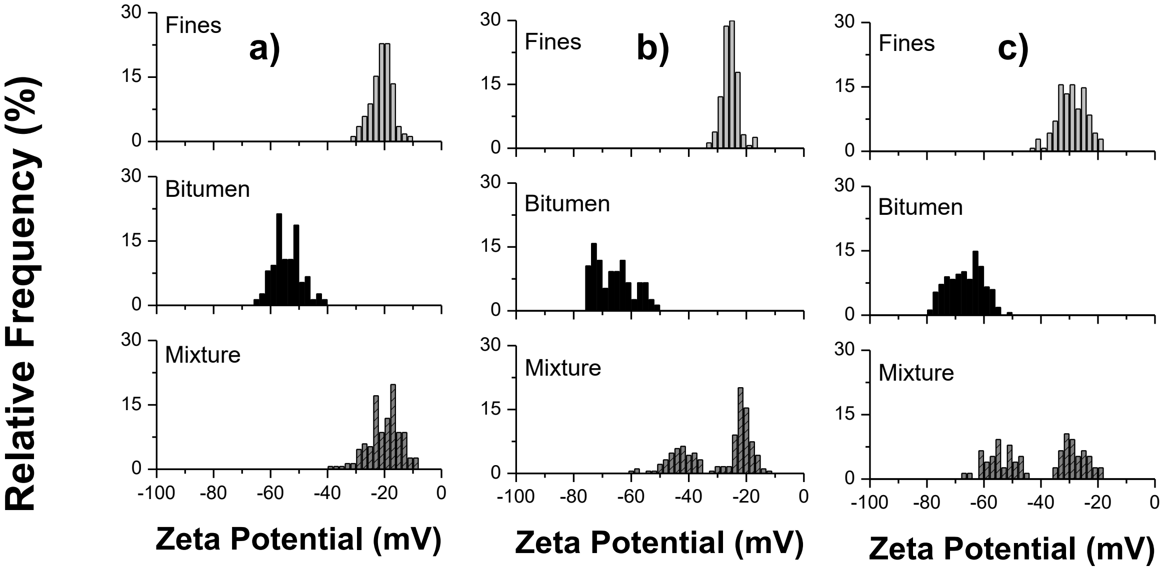

Figure B4: Effect of caustic addition on slime coating behaviour of AN ore at a) 0% NaOH (pH 8.5), b) 0.03% NaOH (pH 9.0), c) 0.1% NaOH (pH 10.0)

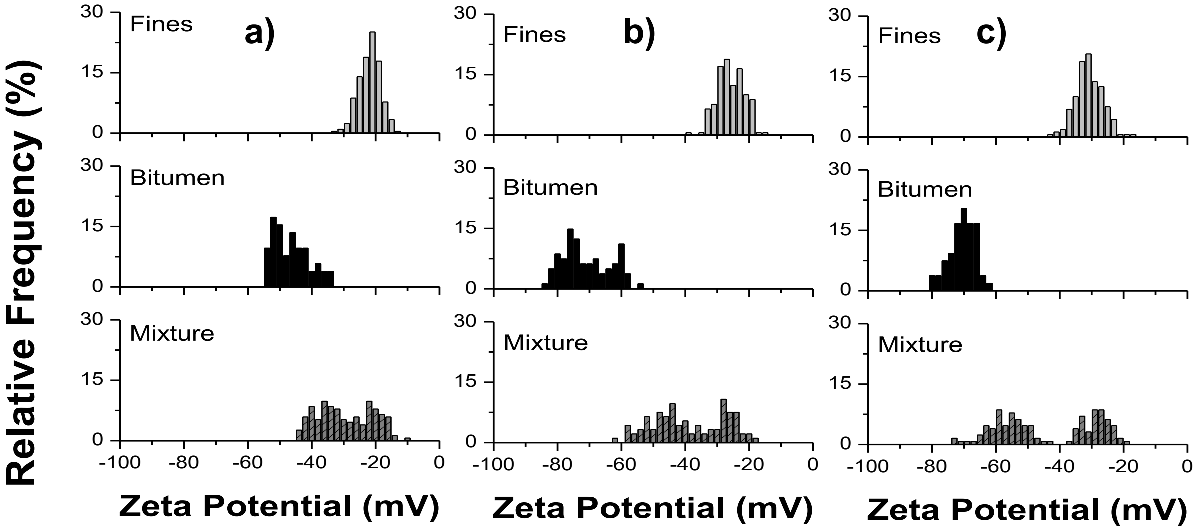

Figure B5: Effect of caustic addition on slime coating behaviour of AL ore at a) 0% NaOH (pH 8.2), b) 0.03% NaOH (pH 8.3), c) 0.1% NaOH (pH 9.6)

B.2.2 Water chemistry slime coating results for AE13

The effect of water chemistry results for AE13 are contained in Figures B6 to B8. The effect of pH is shown in Figure B6, calcium concentration in Figure B7, and humic acid concentration in Figure B8. The pH was adjusted using dilute hydrochloric acid (Fisher Scientific, ACS grade), the calcium concentration increased using calcium chloride (Fisher Scientific, ACS grade), and commercial humic acids from MP Biomedicals. As was noted in the body of this thesis, the bitumen/fines zeta potential peaks for this ore are strongly overlapped and it is difficult to determine the slime coating data based on this data.

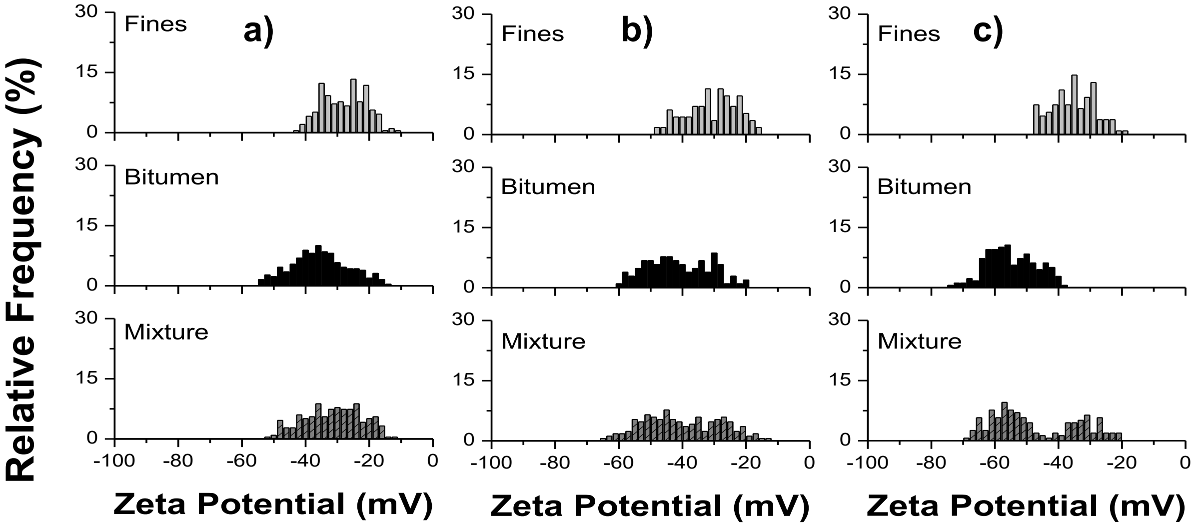

Figure B6: Effect of pH adjustment on slime coating behaviour of AE13 ore at a) 0% NaOH (pH 8.9), b) 0.1% pH adjusted NaOH (pH 8.9), c) 0.1% NaOH (pH 9.9)

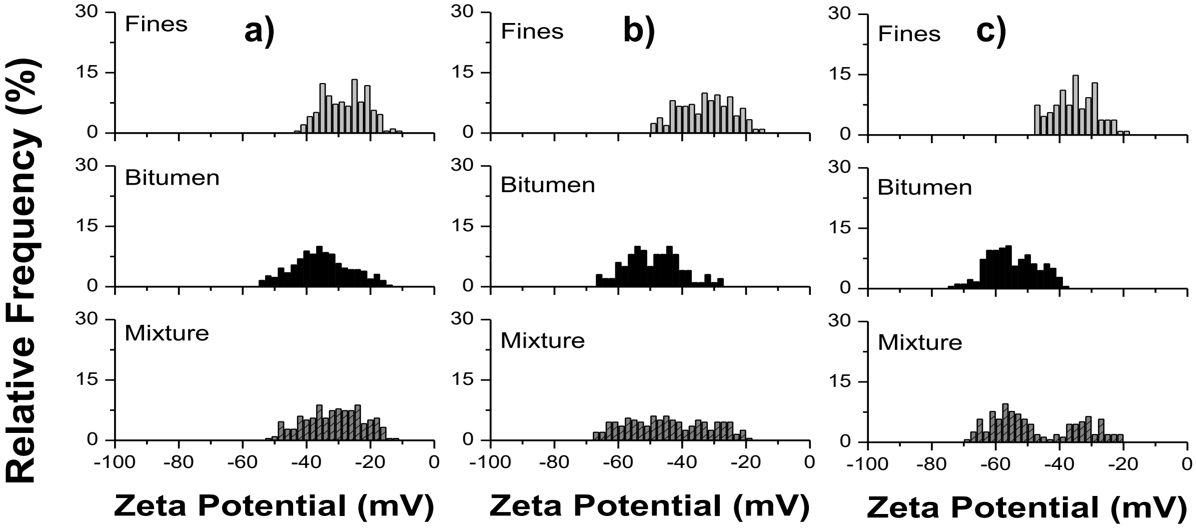

Figure B7: Effect of calcium addition on slime coating behaviour of AE13 ore at a) 0% NaOH (pH 8.9), b) 0.1% NaOH + 60 ppm Ca^{2+} (pH 9.9), c) 0.1% NaOH (pH 9.9)

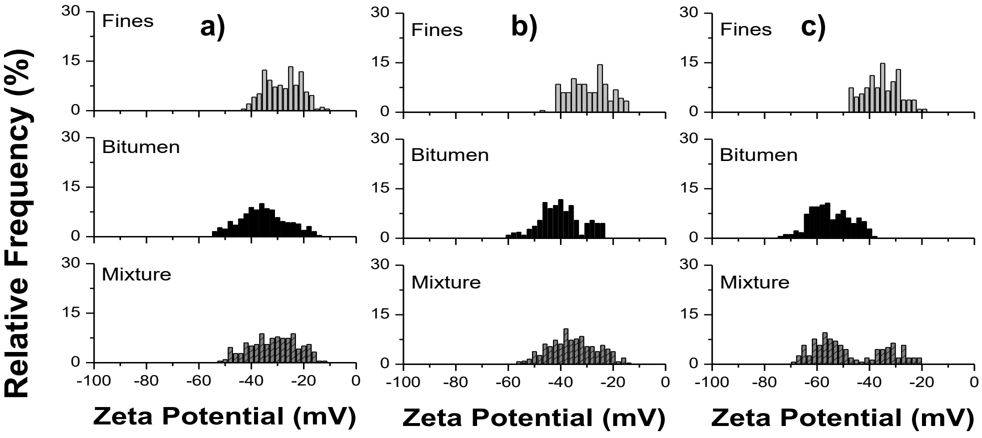

Figure B8: Effect of humic acid addition on slime coating behaviour of AE13 ore at a) 0% NaOH (pH 8.9), b) 0% NaOH + 30 ppm HA (pH 8.9), c) 0.1% NaOH (pH 9.9)

B.2.3 Fresh bitumen slime coating results for AR

Figure B9 shows the effect of using fresh extracted bitumen instead of Syncrude VDU bitumen for AR. The curves are slightly different, but not significantly. More studies need to be performed to determine if bitumen source has an impact on these slime coating tests.

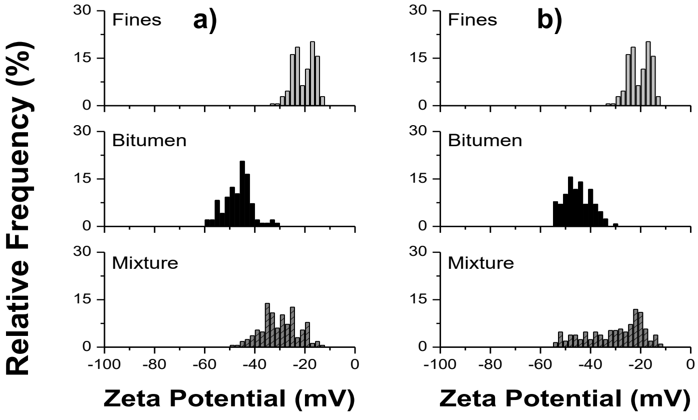

Figure B9: Effect of fresh vs VDU bitumen on slime coating behaviour of AR ore with a) 0% NaOH VDU bitumen (pH 8.4), b) 0% NaOH fresh bitumen (pH 8.4)

Appendix C

C.1 Carboxylic Surfactant

C.1.1 Experimental Procedure

All carboxylic surfactant measurements were performed by Marjan Tamiz Bakhtiari and further details can be found in Bakhtiari (2015). To quantify the concentration of carboxylic surfactants in tailings water, 50 g of tailings water was acidified to pH=2.3 using reagent grade hydrochloric acid (Fisher Scientific). The sample was then extracted using 30 g of Optima dichloromethane (DCM) (Fisher Scientific). The extraction step was repeated two to three times to remove all surface active material from the aqueous phase. Figure C1 shows the absorbance measured by FTIR on the aqueous phase after one DCM wash, two DCM washes and three DCM washes. After the third DCM wash almost all carboxyl functional group containing species had been removed and minimal absorbance was detected at the wavelengths of interest. Combined DCM extracts were collected in a glass bottle. It was dried under filtered air (45 μm filter) and then dissolved in 20 mL of fresh DCM. The sample was then analyzed by FTIR. Carboxyl functional groups absorb IR at ~1743 cm-1 (monomer) and ~1706 cm-1 (dimers). The overall absorbance intensities at these two wavenumbers was used to quantify the concentration of carboxylic surfactants based on the standard curve, which was prepared using standard model compounds.

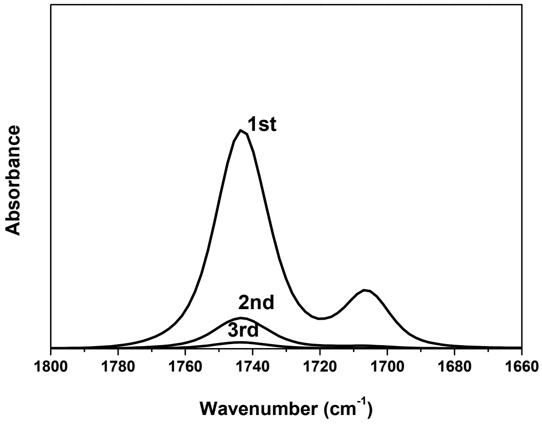

Figure C1. Three step extraction of carboxylic surfactants from tailings water

The instrument used for FTIR analysis was a Bio-Rad FTS 6000 (Cambridge, MA, USA). Varian Resolution Pro software was used to collect the spectra. KBr super sealed liquid cell with 3 mm path length (International Crystal Laboratories, ICL) was used to place the sample in the instrument. The sample compartment was continuously purged with dry air and the detector used was DTGS type. The spectra were acquired in the range of 4000-400 cm^{-1}. DCM was used as the background.

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 a standard curve. A stock solution of each of these standards was first prepared in DCM. Diluted solutions at different concentrations were then made using the stock solution. The peak heights of absorbance for each standard solution at 1743 and 1706 cm^{-1} were then summed and plotted versus concentration of the solution. Figure C2 shows the standard curve that was used.

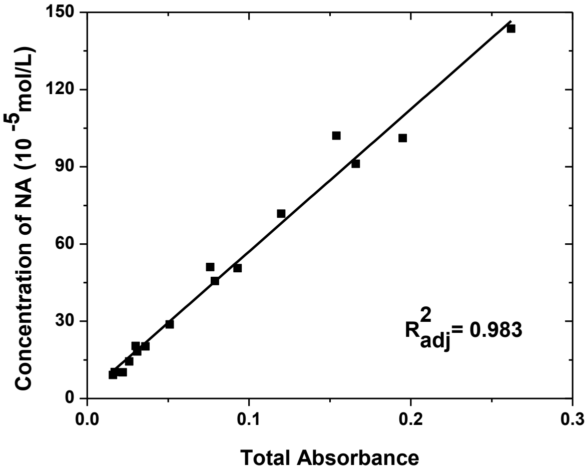

Figure C2. Standard curve prepared with 4 standard model compounds of carboxylic acids

C.1.2 Results

The carboxylic surfactant concentration in the DC tailings water is found in Table C1. The carboxylic surfactant concentration in the tailings water increases with increasing caustic dosage.

Table C1. Carboxylic Surfactant Concentration in DC Tailings Water

Class	**Ore**	***NaOH Concentration, wt% of ore***					
		0	**0.01**	**0.03**	**0.05**	**0.1**	**0.5**
Average Fines	AO	33.1	35.9	39.4	44.1	49.7	51.3
High Fines	AJ	32.2	36.7	40.3	45.2	48.3	54.1
	AE	41.6	42.9	46.9	50.0	53.9	58.8
	AS08	32.5	33.6	33.8	39.5	46.6	47.9
	AR	56.7	59.6	64.4	73.3	88.3	107.0
	AB	36.7	40.1	44.3	45.1	51.3	57.9
	AN	38.1	40.4	44.8	48.8	55.6	61.1
	AA	44.3	46.2	48.8	55.2	62.7	70.1
	AE13	31.8	34.2	36.1	40.4	49.8	55.6
Ultra High Fines	AB08	29.8	30.3	32.0	33.9	40.2	49.2
	AL	29.1	29.4	31.5	33.4	39.7	52.5

C.2 Liberation Data

C.2.1 Experimental Procedure

All liberation tests were performed by Tong Chen and further details can be found in Chen (2015). The oil sand was thawed in a sealed container for two hours prior to each run. A thin layer of bitumen was put on a circular filter paper and then placed on a cylindrical glass frit. Approximately 2 g of oil sand ore was put on the glass frit in a sample holder and hand pressed. A flat surface was created using a knife on the top and side surfaces. Two removable aluminum blocks were placed in the cell, allowing increased velocity of feed water through the channel. A glass slide was used to seal the cell with four screws used to fasten it in place. A beaker containing approximately 100 mL of the desired feed water was placed on a magnetically stirred heating plate and heated to 45ºC. A Masterflex C/L peristaltic pump cycled the water for the eight minute test at a constant rate of 10 mL/min.

For each run, the images were captured in real time using an optical stereomicroscope (SZX10, Olympus) equipped with a DP-72 digital camera (Olympus). The digital images were transferred to a computer which displayed and recorded them and analysed by a computer program, Image-Pro Plus (IPP).

A greyscale 8 threshold value was determined by selecting 30 points which were clearly fully liberated and 30 points which were still covered by bitumen. The images were converted by IPP to greyscale 8 images. Figure C3 shows an image used to determine the threshold values. The rectangles represent the liberated sand grains and the ovals are unliberated sand grains (bitumen covered). The average greyscale value of the liberated sand grains and greyscale value of the unliberated sand grains were determined. The threshold between liberated and unliberated bitumen was then defined as the mean of these two averages. The images were then converted into black and white images, as shown in Figure C4, using this threshold greyscale value. The fraction of the sand grains that were clear or the fraction of white in the whole picture was used to determine the degree of liberation for each image.

Frames were extracted at predetermined intervals during the runs. The selected intervals began at 5s, and continued at 10s, 20s, 30s, 50s, 70s, 100s, and then at 100s intervals until 400s. Each of these images were analysed to determine the degree of liberation as a function of time.

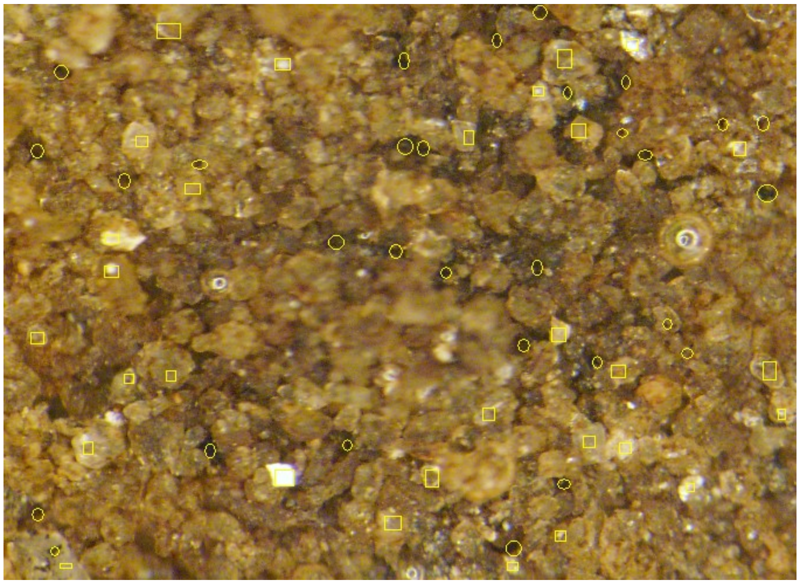

Figure C3. Liberation threshold determination: Rectangles – liberated sand grains, Ovals – bitumen covered sand grains (unliberated)

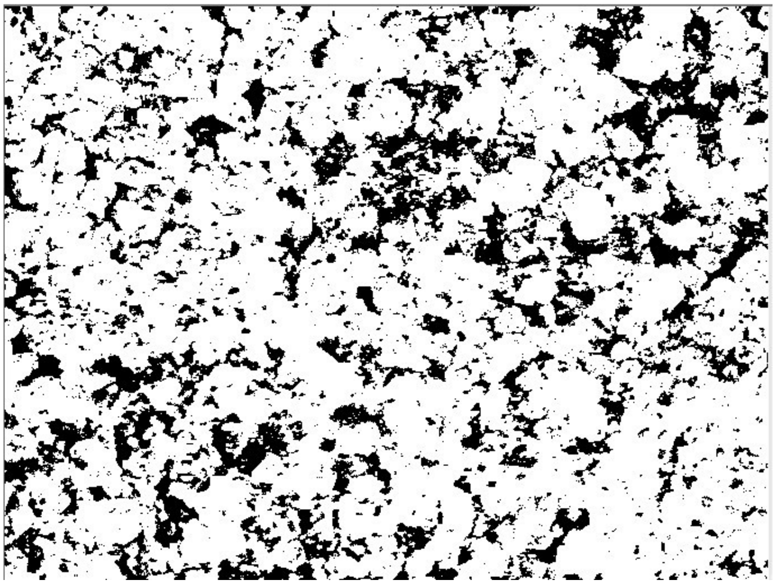

Figure C4. Liberation threshold figure converted to black and white using Image-Pro Plus software

C.2.2 Results

Figure C5 and C6 show the change in pixel intensity over the course of the eight minute liberation runs for AE13 and AE ores, respectively. Figure C5 shows that there is a significant difference in the pixel intensity as the oil sand is subjected to the tailings water for longer periods of time. The tailings water caustic dosage increases from right to left in the figure. It can be seen that as the caustic dosage increases, the pixel intensity at 400s gets closer and closer to the clean sand centered around 170 for pixel intensity. This indicates that the addition of caustic facilitates the liberation of bitumen from sand grains for this ore. This can also be seen from the left side (a) of Figure C7 where total percent of bitumen liberated is plotted. The liberation increased from about 50% liberated when no caustic was added and increased to ~80% for the 0.03 and 0.1 wt% NaOH addition runs. In contrast, AE ore liberates immediately as can be seen in Figure C6 and doesn't change much with increasing caustic dosage. The pixel intensity curves overlap each other and all of the bitumen liberation occurred after the initial flow of water over the oil sand surface. The right side (b) of Figure C7 also shows this and it is noted that the increase in percent liberation is much smaller with AE ore than AE13 ore with it changing from ~60% liberated with no caustic and ~70% with 0.03 and 0.1 wt% NaOH addition.

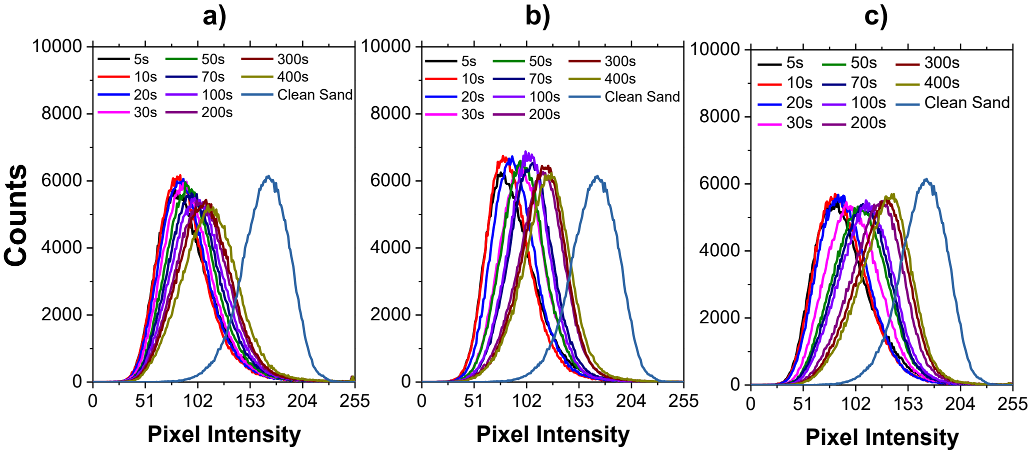

Figure C5. Change in pixel intensity with time for AE13 ore for a) 0% NaOH, b) 0.03% NaOH, and c) 0.1% NaOH

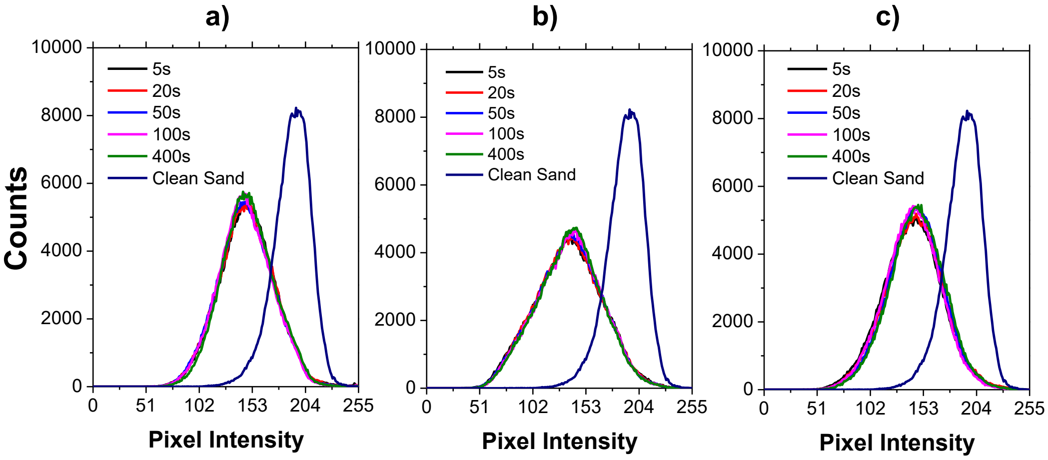

Figure C6. Change in pixel intensity with time for AE for a) 0% NaOH, b) 0.03% NaOH, and c) 0.1% NaOH

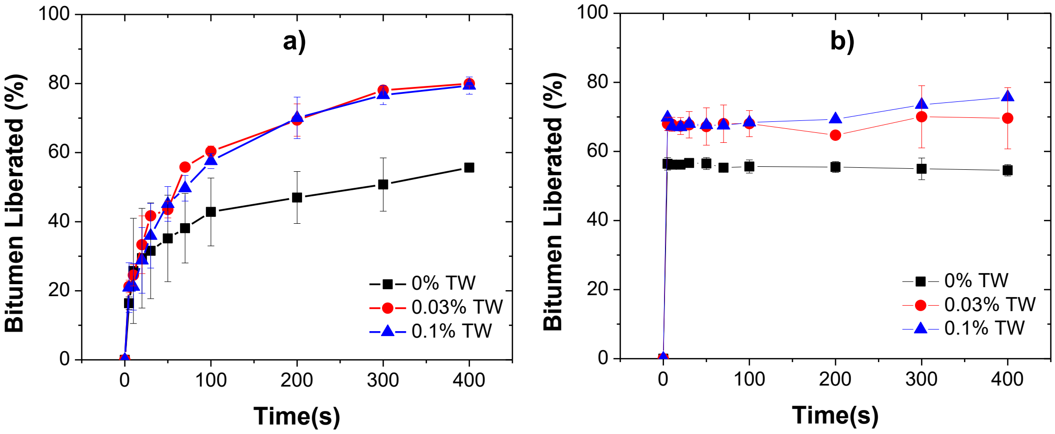

Figure C7. Amount of bitumen liberated as a function of time at different caustic loadings for a) AE13 and b) AE