University of Alberta

Understanding the Role of Caustic Addition: A Comparison of Sodium Hydroxide and Ammonium Hydroxide

by

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A thesis submitted to the Faculty of Graduate Studies and Research

in partial fulfillment of the requirements for the degree of

Master of Science

in

Chemical Engineering

Chemical and Materials Engineering

Spring 2012

Edmonton, Alberta

This thesis is dedicated to my parents **Mr. Gary Flury** *and* **Mrs. Leslie Flury** *and the rest of my wonderful family. I would never have achieved this goal without their immense support and love.*

Abstract

To understand the role of caustic addition and its effect on the bitumen extraction process, a novel flow cell and a Denver Cell extraction unit were utilized. This allowed for the comparison of sodium hydroxide and ammonium hydroxides effect on real oil sands ores. Several ores (A1, C-ore, SunP210) were tested at various pH levels in process water that was adjusted by either the sodium hydroxide or ammonium hydroxide.

The novel flow cell allowed for viewing of the liberation process which showed that both caustics performed similarly in all cases. In the overall recovery, ammonium hydroxide increased the percent recovered greatly at the high pH of 11.3. This was due to several factors such as smaller induction times, a more hydrophobic bitumen surface, less negative zeta potentials and a decrease in the release of natural surfactants in ammonium hydroxide solutions. Overall, ammonium hydroxide was found to be a suitable replacement for sodium hydroxide.

ACKNOWLEDGEMENTS

I would like to thank my supervisors Dr. Zhenghe Xu and Mr. Artin Afacan, for their guidance, support and the great amount of knowledge they bestowed upon me throughout the course of my research.

I would also like to extend a special thanks to Mr. Jim Skwarok, Ms. Jie Ru and Ms. Lisa Carreiro for all of their support, time and endless help. I would also like to thank the entire Oil Sands Extraction research group for their ideas and general camaraderie. As well, my gratitude extends to the great staff of the Department of Chemical and Materials Engineering.

Lastly, I would like to thank the NSERC Industrial Research Chair in Oil Sands Engineering for the funding.

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Chapter 1: INTRODUCTION

1.1 *Background*

One of the largest industries in Alberta is the oil sands. These oil sands contain the majority of Canada's proven crude oil reserves, which are second in the world only to that of Saudi Arabia. The Alberta reserves account for approximately 15% of the total reserves in the world (Masliyah 2009). While the current operations are largely situated in three main areas: the Athabasca, the Peace River and the Cold Lake areas, other deposits have recently been discovered. These three main oil sands areas are estimated to cover approximately 140,200 km^2 with reserves of 170.4 billion barrels of bitumen. The recent discoveries within the province of Alberta are just north of Grande Prairie, while deposits have also been found in northern Saskatchewan. These untapped markets leave large areas of expansion open for the oil sands industry.

The advancement in research has lead to a better understanding of oil sands extraction and continuous advances in technology. Even with the great advances there remain challenges of improving the extraction methods while keeping the process as environmentally friendly as possible. Helping improve the bitumen recovery and producing a higher froth quality within environmental boundaries, while keeping the process economically feasible, will continue to be a challenge in oil sands extraction.

From a fundamental viewpoint the water based extraction process involves the following essential steps as stated by Masilyah (2009):

i) Size reduction of the incoming ore using tumblers or hydro transport pipelines where the bitumen is sheared away from lumps.

ii) Bitumen liberation takes place from the sand grain. The forces of adherence to the sand grain and those pulling the bitumen from it determine the rate at which the bitumen is liberated. This step is influenced by the temperature, mechanical agitation, chemical additives and interfacial properties.

iii) The attachment of the liberated bitumen to an air bubble. With this step there are two occurrences: the bitumen either attaches to the bubble in low temperature processes or engulfs the bubble in the hot water processes.

iv) The aerated bitumen floats to the top of a process separation vessel (PSV), by the buoyancy force, and is recovered as froth.

It should be noted that these sub-processes are not necessarily sequential and very often occur simultaneously. The entire process of extraction is highly impacted by physical, chemical and hydrodynamic variables. Interfacial phenomena also play a significant role in bitumen recovery. Improving the knowledge of each of these fundamental steps will significantly improve the extraction process. The fundamental steps, beginning with the slurry preparation can be seen in Figure 1.

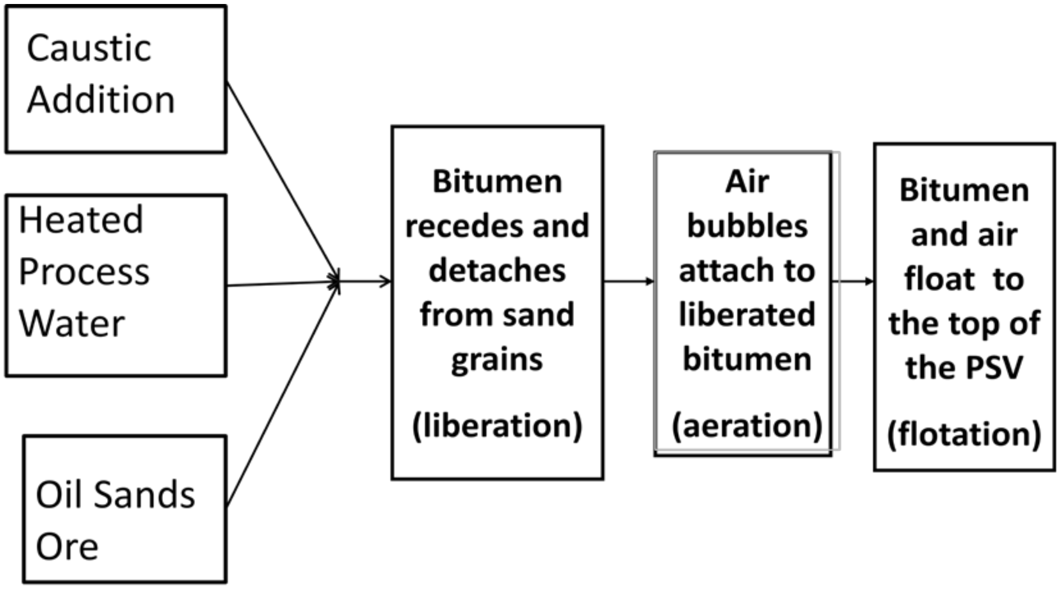


Figure 1: Fundamental steps of bitumen recovery in a mineable oil sands extraction process.

The bitumen is the desired product produced by the oil sands extraction process, but it is not the only component within the ore as stated above. Oil sands ore is also composed of water, sand and clays in addition to the bitumen. These components allow for the ores to be seen as an unconsolidated mineral sand matrix which contains bitumen. The mineral sand (solids) makes up a majority of the mined ore, approximately 82 – 85 wt% by weight in the Athabasca region. The bitumen content in an ore ranges from 1 – 18 wt%. As well, the ore contains small amounts of water occurring naturally within it. Economically it is not feasible to extract an ore where less than 6 wt% of its mass is bitumen. This, however, is considered a poor ore. The clays, which are also known as fines, are an undesirable component of the ore, and an increase in fines usually correlates to a lower quality ore. These poor ores can be occasionally found mixed with an ore of higher grade. A transition or average grade ore contains 8 – 10% bitumen by weight, while a high grade ore contains greater than 10% bitumen by weight. Elementally bitumen is composed mainly of carbon and hydrogen, with a limited amount of oxygen and sulphur. In bitumen the average percentage of each element is approximately 83% carbon, 10% hydrogen, 1% oxygen and 5% sulphur.

To help recover this bitumen a caustic is added during the slurry preparation. The caustic is mixed with the ore and hot water and serves several purposes as the mixture travels along the hydro transport pipeline. These purposes include: adjusting the solution pH, working as a water softener, as a clay dispersing agent and, also, as an aid in releasing natural surfactants from the bitumen. Caustics adjust the pH by increasing the amount of hydroxide ions in the solution. The caustics also help precipitate out divalent cations, such as calcium (Ca^{2+}) and magnesium (Mg^{2+}). The precipitation of these ions reduces the hardness of the solution and helps reduce the deposition of the precipitates that these ions would form further down the line. The addition of the hydroxide ions increases the negative charge of bitumen and solids within the solution, which in turn increases the electrical repulsion between the negatively charged particles. An increased electrical repulsion helps create a stable clay in water suspension and therefore reduces viscosity of the slurry. The additional hydroxide ions help release the natural surfactants from the bitumen, which alters several aspects of the solution. The release of the surfactants reduces the water surface tension, as well as creating a more negative charge on the bitumen surface.

The main caustic that provides all of these benefits in oil sands industry is sodium hydroxide (NaOH). This caustic is a strong base, and it fully dissociates in solution, which allows for easier adjustment of solution pH. Sodium hydroxide provides all of the benefits listed above, but it does create problems downstream in the settling of the tailings. This opens the opportunity to find an alternative caustic for oil sands extraction.

One such alternative is ammonium hydroxide (NH_4OH). This caustic would give all of the same benefits as sodium hydroxide, yet it would also add a new cationic ion (ammonium, NH_4^+) into the solution. Ammonium, as a weak base, dissociates into ammonia (NH_3) which would decrease the amount of cations in solution. Ammonium hydroxide could also be a beneficial process aid in the steam assisted gravity drainage (SAGD) process. This is due to the fact that it is gaseous in nature and can be injected with high temperature steam into the oil sands underground. This would help alter the pH of the steam, which is something that cannot be done with sodium hydroxide. One other benefit of ammonium hydroxide is that it is fairly readily available with ammonia being created in upgrading facilities. When added to water ammonia becomes ammonium hydroxide. All of these factors make NH_4OH a viable option to replace NaOH as the caustic used in the bitumen extraction process.

Liberation is the first step in bitumen recovery, after the slurry has been prepared. It is the act of the bitumen/water interface being displaced along the sand grain. The interface moving along the sand grain creates bitumen droplets on the sand surface. This displacement can be seen in Figure 2.

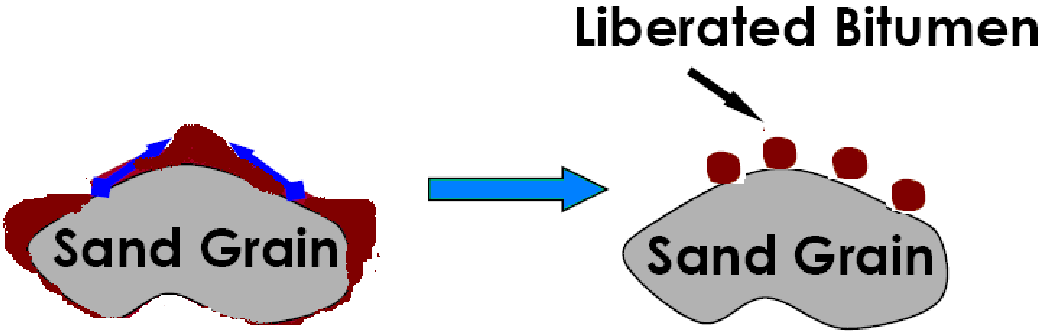


Figure 2: A schematic representation of the bitumen liberation process.

Most of the studies on bitumen liberation have been done on model systems with very few on real ores. Using model systems allows for certain parameters and experiments to be tested in ways that may not be possible with real ore. The drawback of using with model systems is that they may never represent interactions encountered in oil sands extraction of real ores.

The effect of pH on the bitumen film thinning and rupture process was studied by Basu et al. (1997). These experiments were carried out by placing a layer of bitumen on a glass microscope slide to simulate the silica in oil sands ores. In their study, the temperature was kept constant so that only the effect of pH was studied. It was found that at higher pH a greater rate of bitumen film thinning and rupture occurred, while at lower pH level a faster displacement of the triple phase point occurred. Thus a sequential changing of the pH would be beneficial to bitumen liberation. Since no fines were present in their study, the validity of the results in a real life oil sands extraction process remains questionable.

The film thinning and rupturing were tested on various model surfaces at several conditions. It was found by Basu et al. (1996) that the bitumen thins and ruptures on a glass surface while it remains stable on a polytetrafluoroethylene (PTFE). The difference between these surfaces is that the glass (silica) surface is hydrophilic, while the PTFE surface is hydrophobic. This study also confirmed that at higher pH a greater level of film thinning/rupture occurs, while a lower pH increases the rate of displacement on the glass surface. The higher the pH level, the larger contact angle of bitumen on solids allowed for easy detachment of the bitumen droplets. These results were compared with existing models for predicting dynamic contact angles. The models predicted the data quite well.

Instabilities of the modulated contact line in the bitumen liberation process were studied by Basu et al. (2000). These instabilities were studied by visualzing bitumen recession on a rectangular glass plate under various conditions. These conditions include pH levels and temperatures. They found that increasing the temperature and pH leads to a larger number of daughter droplets forming on the glass surface. The number of droplets decreases with increasing strip width. These results correlate well with previous contact line instability analysis.

Another bitumen coated glass surface was used to test the displacement of bitumen under certain saline conditions and with the addition of kerosene. Basu et al (1998) found that exposing bitumen to aqueous environments allowed for the formation of a droplet of bitumen on the glass surface. The static and dynamic contact angles were recorded in this process. It was found that increasing saline level decreased the contact angle. Adding kerosene into these solutions was able to restore the contact angle. The results were predicted quite well by the displacement model discussed in their paper. They also concluded that the amount of NaCl does not affect the bitumen displacement rate during the conditioning stage.

A liberation study was done on real ores by Srinivasa (2009). It was completed in de-ionized water at various conditions using a novel flow cell apparatus. He found that increasing both the temperature and pH helps the liberation process, while a high salt and fines content is detrimental to liberation. It is also stated that the weathering of oil sands ores decreases liberation, while adding kerosene to the same weathered ores helps increase the liberation. The method of analysis used in his thesis was highly subjective but helps show the trend of the liberation. Also, the use of de-ionized water does not represent the real world process and cannot be compared with the industrial process water as encountered in industry. This was the first time a study was done on real ore and provided insight into how a non-simulated ore reacts to the process conditions and bitumen liberation modes.

The fines are made of several different clays and each type has a different effect on the ore processability. As well, the percentage of these fines within the ore affects the processability, i.e. bitumen recovery and froth quality. A high grade ore usually contains a small percentage of clays, while a high percentage of clays leads to a poorer grade. This has been statistically proven (Masliyah 2000). There are three common types of clays present in the Athabasca oil sands ores. They types are kaolinite, illite and smectite (montmorillonite).

Basu et al. (1998) also studied the effect of hydrophobic and hydrophilic clays on bitumen displacement. This was carried out in a jacketed vessel containing the water with the bitumen placed on a glass surface (to mimic the silica in oil sands ores). A prism was placed under the vessel and a camcorder was used to record the images reflected off the prism. The wettability of clays' was modified using asphaltenes. It was found that both the hydrophobic and hydrophilic clays did not significantly impact the dynamic contact angle. This implies that the low recovery in the presence of clays cannot be attributed to bitumen displacement. This study was done on a model system using glass to replace silica and only one type of clay was studied. The results therefore may not translate to real ores.

The roles of these fine clays in bitumen extraction were studied by Liu et al (2004). They tested kaolinite and montmorillonite in KCl solutions under varying aqueous conditions. It was shown, using several different methods, that these two clays have very different surface properties. Montmorillonite was shown to have a much greater affinity to adsorb calcium. Montmorillonite may adsorb more calcium, but the kaolinite clays show some degree of specific adsorption of calcium ions. For the montmorillonite-bitumen interactions Liu et al. (2004) found that the presence of calcium ions can enhance the adhesion forces, causing slime coating of clays on the bitumen surface. In the presence of calcium for the kaolinite clays no noticeable increase in adhesive forces was found. Therefore, in the kaolinite-bitumen interactions the clays can only weakly attach to the bitumen. With both clays tested the addition of calcium ions depressed the electrical double layer. It was concluded, by Liu et al. (2004), that the strong attachment of montmorillonite presents a barrier for bitumen-air attachment, which leads to a poor overall bitumen recovery.

A novel approach to studying the effect of clays and calcium on bitumen extraction was developed by Kasongo et al. (2000). In this study they doped rich estuarine oil sands with calcium and/or clays. These additives were placed into a modified Denver flotation cell with a high grade ore during the conditioning stage. The modified Denver cell allowed the bitumen flotation kinetics to be examined for the first time. Calcium addition was studied up to 40 ppm in slurry and the fine clays were added up to a value of one percent by weight of the ore. From this study it was concluded that kaolinite and illite did not have the same adverse impact on bitumen recovery from this high grade ore, while a significant decrease in bitumen recovery was determined with montmorillonite in the presence of calcium ions. This impact was attributed to the high uptake of calcium ions by montmorillonite and the interaction of calcium with the carboxylic groups in the bitumen. This calcium carboxylate bridging causes clay deposition on the bitumen.

Dai and Chung (1995) studied the bitumen-sand interactions in oil sand processing. They found that bitumen attachment to sands is particle size dependent. They discovered that the smaller the fines the stronger the attachment. The coarse particles can have the bitumen removed by increasing the alkalinity, while this is not the case for the smaller fines. They also found that electrostatic forces play an important role, and these forces are greatly altered by increasing temperature.

All ores have at least a small amount of moisture content within them. A small percentage of this water has been speculated to be in the form of a thin layer between the bitumen and the sand grain (Takamura 1982). It is predicted that this layer is stabilized due to the electrostatic double layer forces at the interface (Takamura 1982, Anderson 1986, Hall et al. 1983). This hypothesis has not been proven experimentally, yet it is widely accepted. The presence of this water later may be one of the most important parameters in the extraction of the oil sands of northern Alberta. The sand grains are of a hydrophilic nature which allows extraction to be economically feasible using current water based methods. If the sand grains were of the hydrophobic nature, as those found in the oil sands deposits of Utah, a water based extraction method could not be utilized (Sepulveda and Miller 1978, Miller and Misra 1982). A solvent based method has been suggested for these oil sands deposits of hydrophobic sand grains, but none have been proven economically feasible to date. The water present within an ore is referred to as connate water. This connate water has been observed to contain salts of different types. These salts are the sources of various inorganic ions such as sodium, potassium, calcium and magnesium in the ore. The type and amount of ions present have a significant effect on the processability of ores. High quality ores usually have a low salt content, while poor ores usually have a high connate salt content (Masliyah 2009). The loss of connate water is credited with the poor processability and bitumen recovery of weathered ores. This work was done by Ali (1975) who attributed the failure of the structures within the ore to connate water loss from the oil sands matrix to.

Oil Sands ores have many different characteristics that require fine tuning of the processing conditions to effectively recover the bitumen from the ore. These conditions range from the temperature of the slurry to the amount of natural surfactants released from the bitumen. The slury velocity, pH, ion content and other chemical additives are, also, factors affecting the extraction process.

The temperature appears to play a big role, as it affects many of the oil sands properties. It alters the bitumen viscosity. Bitumen recovery appears to be greatly hindered under a processing temperature of 35°C. At temperatures above 50°C there seems to be little change in bitumen recovery with a further increase in temperature (Long et al. 2007). Based on processing temperature two different extraction methods are proposed: Clark’s hot water extraction and a low temperature extraction method.

The high temperature process needs a large amount of energy to heat the water, which leads to high operating costs. A low temperature process would help reduce the operating costs and cut energy use greatly. This process was researched by Sury (1990) and Hepler and Smith (1994), who studied a range of temperatures starting at 2°C and getting as high as 15°C. These researchers added a conditioning agent into the slurry to encourage the liberation of bitumen. The conditioning agent was an agent having the characteristics of either kerosene, or diesel or both. Some form of mechanical shear would need to be present, but it is interdependent of slurry temperature. For optimum recovery one may be replaced by the other as long as a minimum energy of each is maintained.

The pH levels are altered by the addition of caustics. In industry the caustic most commonly used is sodium hydroxide. The hydroxide ion works as a base and encourages the release of natural surfactants within the bitumen. A high pH level ($pH > 8.5$) promotes bitumen liberation, but increasing pH hinders attachment of air bubble to the bitumen.

In a study highlighting that NaOH improves bitumen recovery in hot water extraction, Sanford and Seyer (1979) attributed the observed effect of caustic addition to surfactant release. They indicated that the ionization of organic acids by NaOH allowed for the release of natural surfactants, which played an important role in bitumen recovery. A later paper by Sanford (1983) further studied other processing aids. Sanford also indicated that there is an optimal amount of NaOH addition, and adding more NaOH proves to be detrimental to the recovery process. He found that this optimal amount is a function of weathering of the ore and the fines content, while a sufficient level of shear force is necessary to help maximize bitumen recovery. Dai and Chung (1995) also proposed a mechanism for hot water extraction. In their study, model oil sands were used. They added NaOH to the slurry/connate water and believed that the caustic aided high recovery. They also suggested that a reduction in bitumen liberation from sand was due to the deficiency in caustic addition, while an emulsification was created due to an overdose.

Ammonium hydroxide (NH_4OH) has been suggested as a caustic in several patents. It was suggested by Choules (1981) that ammonium hydroxide or another lyotropic salt be added to the process. The ammonium was referred to as the floating agent. He recommended use of an ammonium phosphate salt which can be utilized at lower concentrations as an effective recovery agent. He went on to say that mixing combinations of various salts containing the lyoptropic ions can lead to the same results. These results were both qualitative and quantitative with a high recovery rate around 78% by using a phosphate fertilizer as a process aid.

In another patent, Myers et al (1976) recommended mixing of ammonium hydroxide with tannic acid in solution. This was proposed to help increase bitumen recovery. There were several problems noted in the patent though, with the largest problem being the separation of the bitumen from the solution. It was also suggested that the solution could be recycled and re-used without much further addition necessary. All of the results were qualitative in their patent, viewing how much bitumen was in the solution and off the sand.

Hart et al. (2011) published a patent, on behalf of Baker-Hughes Inc., regarding the use of volatile amines in the recovery of heavy hydrocarbons inside the SAGD process. They used ammonia and other short chain amines to determine their effects, relative to sodium hydroxide, on bitumen recovery. Using a Soxhlet extraction apparatus with a Dean-Stark trap they found that as the materials being added to the steam become less volatile, more hydrophobic and weaker bases the recovery decreases. They also suggested that high quality steam be used with ammonia as it will allow it to stay in a vapour state during the injection.

Wang et al. (2009) examined the effect of adding short chain amines on oil sand ore processing and discovered that adding short chain amines into the solution made the bitumen surface more hydrophobic, decreased the induction time of bitumen-air attachment and facilitated bitumen liberation. They proposed that the short chain amine becomes dissociated in water into the ammonium ion, which would also affect the surface properties of the air bubbles.

There are two main types of natural surfactants in the Athabasca oil sands that are released during the bitumen extraction process. They are carboxylates and sulfonates surfactants. Both types were found to be aliphatic and were studied by Schramm et al. (1985). They predicted that these surfactants could alter the interfacial tensions and the electrical properties of the surfaces. The surfactants adsorb onto the surfaces and interfaces, and are known to affect the electrophoretic mobility of bitumen droplets, air bubbles and the sand and fine particles. Hupka and Miller (1991) proved that the ionization and adsorption of charged surfactants can lead to an increased electrostatic repulsion. This increase in repulsion creates a larger force helping to separate the bitumen and the solid particles.

The effect of natural surfactants released from oil sands on air hold up was studied by Zhou et al. (2000). They found that in a water column de-ionized water had a lower holdup in the resultant supernatant than the water from the conditioned slurry. It was also noted that increasing the caustic addition increased the air hold up. These tests were correlated back to a greater release in natural surfactants as the cause of a greater air hold up.

Zhou et al. (1999) attempted to explore the effect of surfactants on bitumen/silica coagulation. They developed a model system and found that at acidic conditions silica coagulation was favored. Yet, the addition of calcium ions into the system decreased coagulation. In this model system they found that electrostatic force could not account for these observations, and that thermodynamics must also play a role. Only when both anionic and cationic surfactants were present was good coagulation observed. With both types of surfactants being necessary, it points towards both surfactants working together to produce the effects observed. It must be noted that it was done on a model system but may provide good insight into the complex surfactant system within bitumen.

Bitumen liberation is the first step in the extraction process with the next step being the aeration of the liberated bitumen to recover the bitumen. The aeration requires the attachment of the bitumen droplets to air bubbles. Once attached the air bubbles float to the surface. The aeration of the liberated bitumen can be seen in Figure 3.

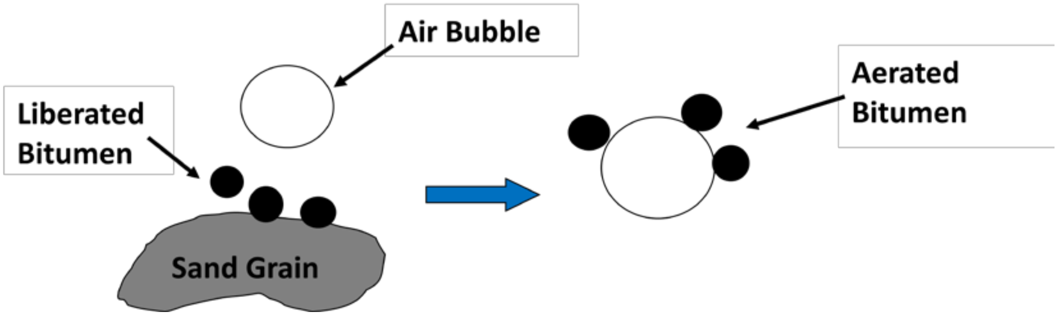


Figure 3: A schematic representation of the bitumen aeration process.

The studies on bitumen recovery have been conducted systematically under various conditions. These conditions include variable temperatures, chemical additions and ore samples. Yamazaki et al (1989) tested the recovery of bitumen using steam and various chemicals. They tested such chemicals as benzene, hexane and halide. They found that bitumen recovery increased with the addition of solvents to the stream and was directly proportional to the rate at which the solvent was injected. It was also found that the steam-alkaline not only improved recovery but also allowed the operating temperature to be lowered. Therefore, other chemicals can be used to help increase bitumen recovery.

Wang et al. (2009) studied the effect of short chain amines, specifically *n*-butylamine, on bitumen recovery in a Denver cell batch extraction unit. It was determined that at pH 8.5 short chain amines increased the recovery by 20% on a weathered ore. This increased recovery was correlated well with a shorter induction time.

One of the goals in oil sands research and development is to develop a process to extract and recover bitumen efficiently in both open pit mining and SAGD operations. Since these studies have been performed on the extraction process using the Denver cell or other flotation techniques, it is hard to tell which aspect, liberation or flotation, is affecting the recovery. It is therefore critical to study bitumen liberation and aeration independently to maximize both. A majority of previous bitumen liberation studies have been conducted on simulated oil sands ores. Fines contents were mimicked using one type of clay in solution (Kasongo et al 2000) to determine the effects of clays on bitumen liberation. The accuracy of using these simulated ores to represent real ores is always a concern. Studying liberation oil sands ores in their natural state will be very beneficial in understanding the liberation process under varying conditions. One such study was completed, by Srinivasa (2009), on real ores. This study used a novel liberation setup, but a very subjective quantification of analysis was used to determine the amount of bitumen liberation.

1.2 *Thesis Objective*

The main objective of this study is to understand the fundamentals of caustic addition in the oil sands extraction process, with emphasis on bitumen liberation. A custom designed novel in-situ bitumen liberation flow visualization cell (FIBLVC) is to be altered so that bitumen liberation kinetics can be more easily studied. A new quantification procedure will be developed to help extract information from the liberation tests using the modified visualization cell. The tests will be completed on real oil sands ore samples. Two different caustics, sodium hydroxide (NaOH) and ammonium hydroxide (NH_4OH), at various addition levels will be tested. The caustic levels will be changed using two different chemicals.

The results from the liberation study will be linked with Denver cell flotation tests to illustrate the role of bitumen liberation with caustic addition in bitumen recovery.

Chapter 2: EXPERIMENTAL SETUP AND PROCEDURES

2.1 *Materials*:

Three different ores were used in this research. The characteristics of these ores are given in Table 1. These ores were provided from several sources. They were similar in most characteristics with the biggest difference being found in the fines content. All of the ore samples were kept wrapped tightly in plastic bags in a deep freeze to minimize the oxidation of the ore. Prior to its use in any experiment, the ore was thawed at room temperature for a minimum of two hours.

Table 1: Composition of oil sands ores used in this study

	Composition (wt%)			
Ore Name	Solids	Bitumen	Water	Fines
A1	83.3	12.3	3.2	0.7
C-ore	85.4	12.6	1.2	12.1
SunP210	86.8	10.6	2.6	25.0

The process feed water was prepared using process water from Syncrude Canada. The initial cation ion concentrations for the two barrels of processs water used are given in Table 2. The pH of the water was altered using 1M sodium hydroxide (NaOH) and hydrochloric acid (HCl) solutions. As well, the pH was adjusted using an ammonium hydroxide (NH_4OH) solution.

Table 2: Cation concentration of process water from Syncrude.

	Concentration (ppm)			
Ion	Ca^{2+}	Mg^{2+}	Na^+	K^+
Pail 1	56.0	20.1	743.1	20.6
Pail 2	55.0	20.2	764.2	20.8

2.2 *Bitumen Liberation Experimental Setup*:

The liberation of bitumen from oil sands ores were examined using a novel flow visualization technique. A schematic of this novel experimental setup can be seen in Figure 4 (Sundeep 2009). The feed water temperature was controlled using a water bath (Neslab, Thermo RTE7 Digital 1). This water bath filled with tap water was set at a certain temperature. A one litre glass jar containing the process feed water was placed in the water bath and was allowed to heat for one hour to create a uniform temperature throughout the feed water. The process feed water heated to the desired temperature was pumped into the novel FIBLVC using a Masterflex C/L peristaltic pump model, from Cole-Parmer. The flow rate of the process feed water was held constant throughout the tests, unless otherwise stated. The water flowing through the cell was either returned to the original one litre glass jar or to a separate waste container. A close up view of the visualization cell used in this study is shown in Figure 5.

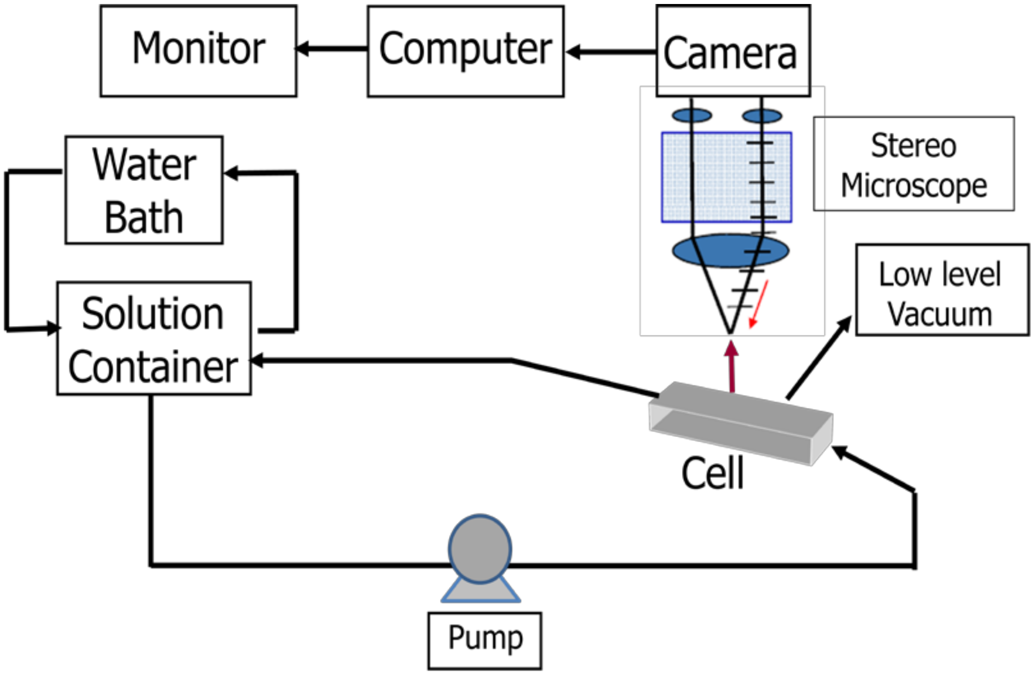


Figure 4: A schematic diagram of the novel bitumen liberation setup (Sundeep 2009)

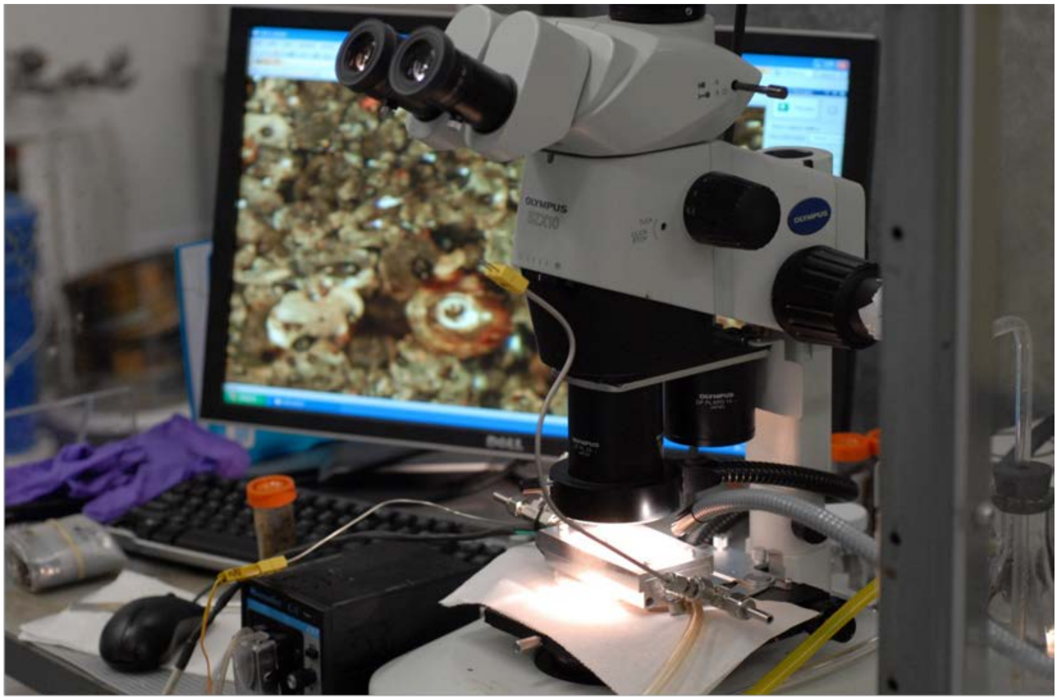


Figure 5: A photo of the bitumen liberation cell used in this study.

The process occurring within the cell was observed in real time using an optical stereo microscope (SZX10, Olympus). The microscope was equipped with a DP-72 digital camera, also from Olympus. This digital camera allowed the capture of high resolution and quality images at a rate of ten frames per second. These images were transferred to the computer where they were displayed using the software that came with the camera. An example of the high quality images produced by this system in a liberation test is shown in Figure 6.

The process required a custom built FIBLVC to be designed so that the liberation process could be observed. The cell was built out of aluminum with an inlet/outlet on each side. In the middle of the flow channel a hole was made so that a low level vacuum line could be fitted in. The vacuum held the sample placed on a glass frit. The frit had a porosity of 40-100 um and was fused into a solid glass ring. Once the frit and sample were in place, a plate with a circle cut in the middle was placed over the frit with the sample and fastened in place. Two methods were used to hold the metal plate in place: one having a small tab on each side which was tightened by a screw in each, or the other having an aluminum block on each side. The aluminum blocks were inserted to decrease the size of the flow channel, allowing increasing velocity of the process feed water through the cell.

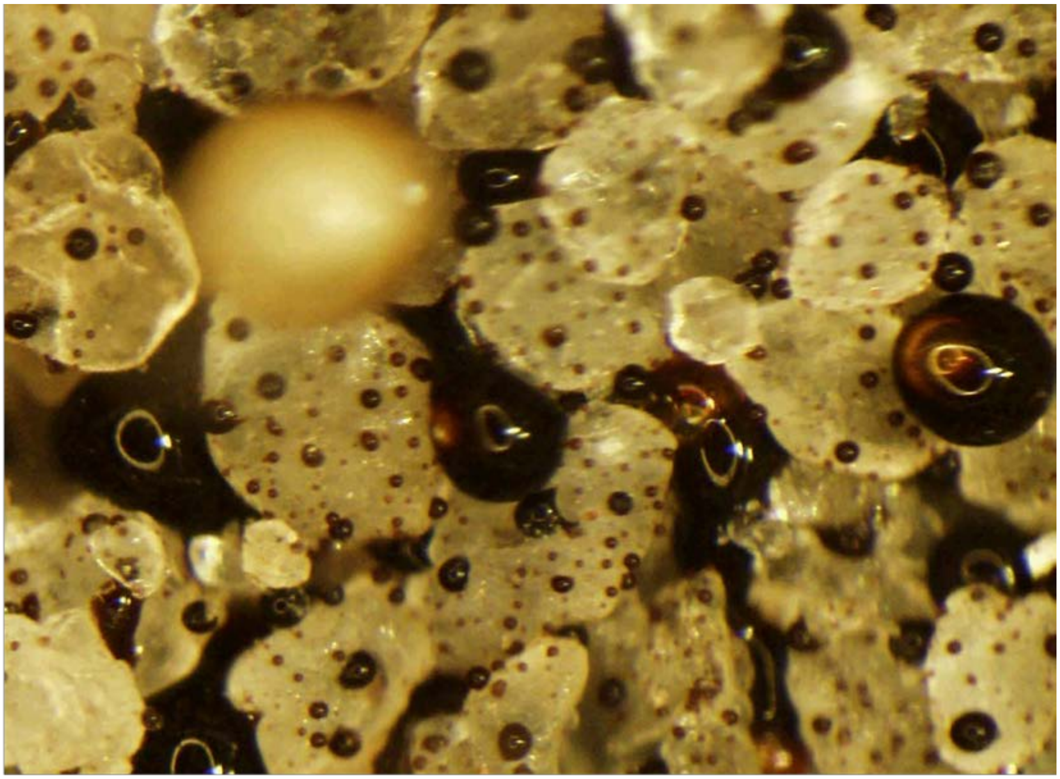


Figure 6: A high quality image captured using the stereomicroscope

It was necessary to monitor the temperature of the cell and process water. For this purpose three thermocouples were mounted to the cell. The thermocouples used were K-type. Two of the thermocouples were placed into the inlet and outlet to determine the temperature of the process water, while the third was fitted into the cell. The third thermocouple was used for measuring the temperature of the body of the cell, which was heated by two cylindrical heating elements. The outputs from each of these heaters were maintained by a controller attached to the thermocouple within the cell. The other temperatures were read using a hand held meter which could be attached to the inlet and outlet thermocouples. The schematic diagrams for the FIBLVC is shown in Figure 7.

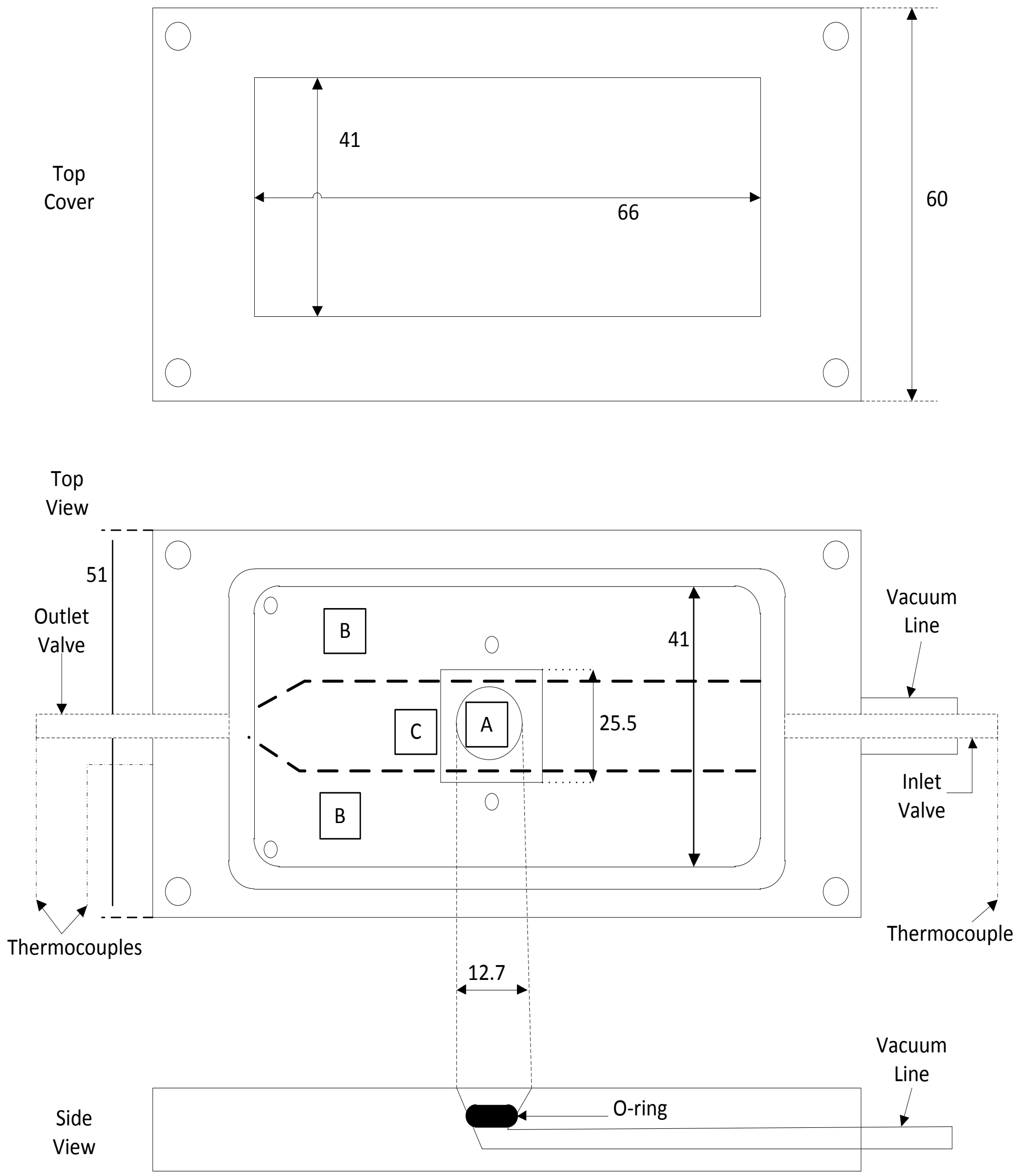


Figure 7: A schematic diagram of the novel FIBLVC.
A: Sample Holder, B: Removable aluminum blocks, C: Steel sealing plate

Note: All measurement values are in mm

2.3 Bitumen Liberation Experimental Procedure:

The ore that was used in the experiments was kept in a frozen state until 2 hours prior to its use. The sample was left at room temperature for 2 hours to thaw in a sealed container. At the beginning of each run a thin layer of bitumen (vacuum distillation unit feed) was spread on a piece of filter paper. A small portion of the thawed oil sands ore, approximately 3 grams in weight, as placed on the filter paper, which was cut to the dimensions of the glass frit. The filter paper with the oil sands sample was then placed onto the sample holder of the glass frit and the excess of oil sands sample was sheared off until the sides of the ore were even with the sides of the frit and the top was flat. This allowed the untouched ore as a top layer. The frit was then placed into the vacuum hole of the cell and sealed with a rubber oval ring and plate. The plate was then held in place and further sealed with either the aluminum blocks, which reduced the cross section area of the flow channel, or by a set of clamps that were tightened down by a set of screws. A glass slide, 75 mm by 50 mm, was placed over the top of the cell and held in place using a custom designed top cover. The top was sealed with four screws.

Once the top was sealed in place the process feed water was fed through the cell. The feed water was prepared using process water provided by Syncrude. Any alterations to the desired pH levels were done prior to this. The adjustments of pH were achieved by 1N NaOH or 14N NH_4OH and 1N HCl. Approximately 750 mL of the desired process feed water was placed into the water bath and heated to the desired temperature for one hour. The water was then passed through the cell, and upon exit the feed water either returned to the original feed jar or flowed to a separate container. A separate container was used to avoid the change of process feed water with experimental time, while return to the original container would promote recycling. The flow rate was kept constant at 32 mL/min for all runs, unless otherwise stated.

Several runs were, also, conducted at varying flow rates. These flow rates ranged from 8 mL/min to 32 mL/min while all other conditions were kept constant. The varying flow rate allowed for a change in fluid velocity. To evaluate the effect of shear (fluid flow velocity) on bitumen liberation the Peclet number was calculated using the following equation:

$$Pe = \frac{V * L}{D} \tag{1.1}$$

where V is the fluid velocity, L is the characteristic length (12.7 mm) and D is the diffusion coefficient.

The diffusion coefficient was determined using the Wilke-Chang correlation as found in Properties of Gas and Liquids by Reid et al. (1977). This correlation is as follows:

$$D_{BW} = \frac{7.4 * 10^{-8} (\phi_W M_W)^{1/2} * T}{\eta_W * V_1^{0.6}} \tag{1.2}$$

where φ_w is the association factor of the water, M_w is the molar mass of the water, T is the temperature (in K), η_w is the viscosity of the water and V_1 is the molar volume of the bitumen.

For each run the images were captured in real time using a stereo-microscope equipped with a digital camera. The digital images were transferred to a computer which displays and records them. Each run was captured for a period of 10 minutes and saved as an avi file. Images were extracted at specific times during each run for later analysis. This analysis was done using a computer program, Gnu Image Manipulation Program (G.I.M.P), which allowed custom specified threshold of a certain color.

2.4 *Quantitative Analysis*:

During the ten minute runs frames were extracted, at predetermined intervals, for analysis. The selected intervals began at 50s, the next was at 100s and then at 100 second intervals until the run was completed.

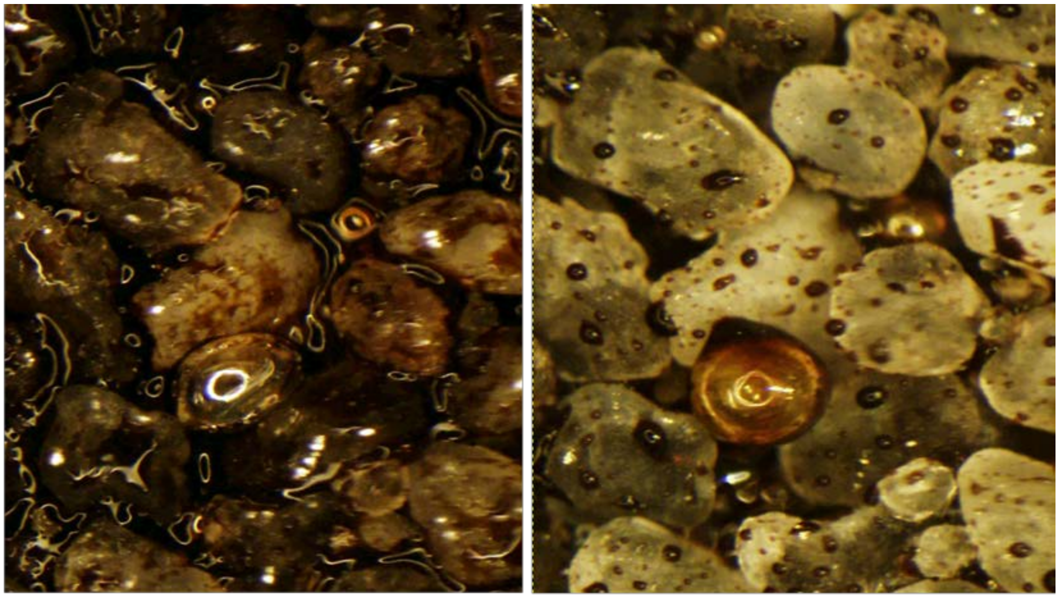
The extracted images were then opened with a Photoshop program and analyzed individually. For each image each individual sand grain was selected manually.

When a sand grain was selected it was subjected to a comparison with the thresholding value, in which the bitumen was converted to black and the sand to white. A histogram was then used to determine the fraction of the sand grain that was clear (fraction of white on the grain). This was done for every grain in the image and once all were completed an average was taken to determine the average percentage of clear grains using the equation given below:

$$Average\ Percent\ Cleared\ (DBL) = \frac{\sum \text{Percent cleared on each grain}}{\text{\# of Grains}} \qquad (1.3)$$

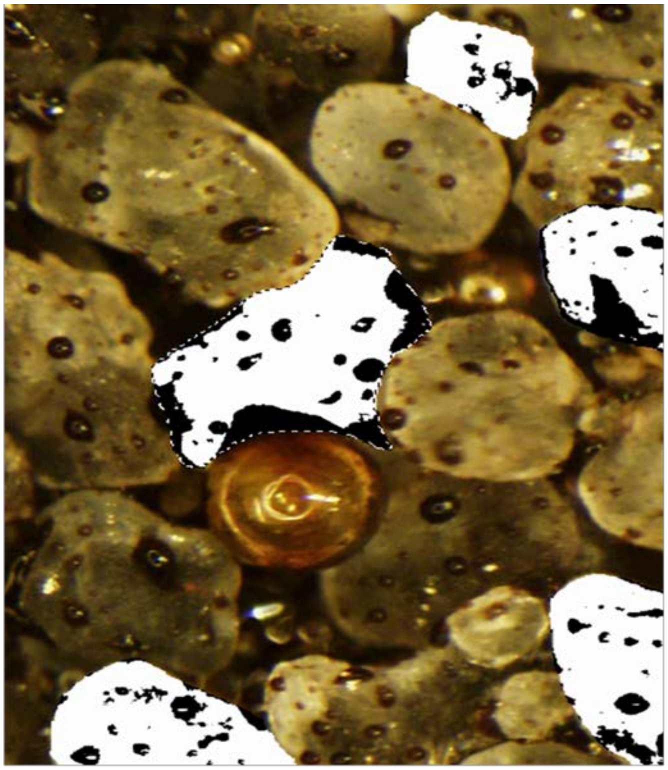
This average percentage of clear grains measures the degree of displacement of bitumen along the sand grain surface, and is referred to as degree of bitumen liberation (DBL) in this thesis.

The liberation of bitumen along the sand to form small bitumen droplets on the sand surface is shown in Figure 8. This figure shows images taken at 20 s into the run, where it is very dark and still covered with a lot of bitumen film, and 300 s into the run, showing the bitumen forming spherical droplets on the sand surface. The image taken at 300 s into the run is much lighter in color with a majority of the grains being clear. This displacement of bitumen along the sand grain allows the quantification of bitumen liberation. An example of the analysis is shown in Figure 9, with several grains selected and analyzed for calculating the percentage cleared. It can be seen in this figure that the bitumen can be easily distinguished from the lighter sand grain to which it is attached. Once the analysis was completed for an entire run the data points were plotted and a typical liberation curve can be seen in Figure 10.



t = 20s t = 300s

Figure 8: Video images of bitumen liberation on A1 ore



A1 Ore
t = 300s

Figure 9: Contrast image for quantitative bitumen liberation analysis

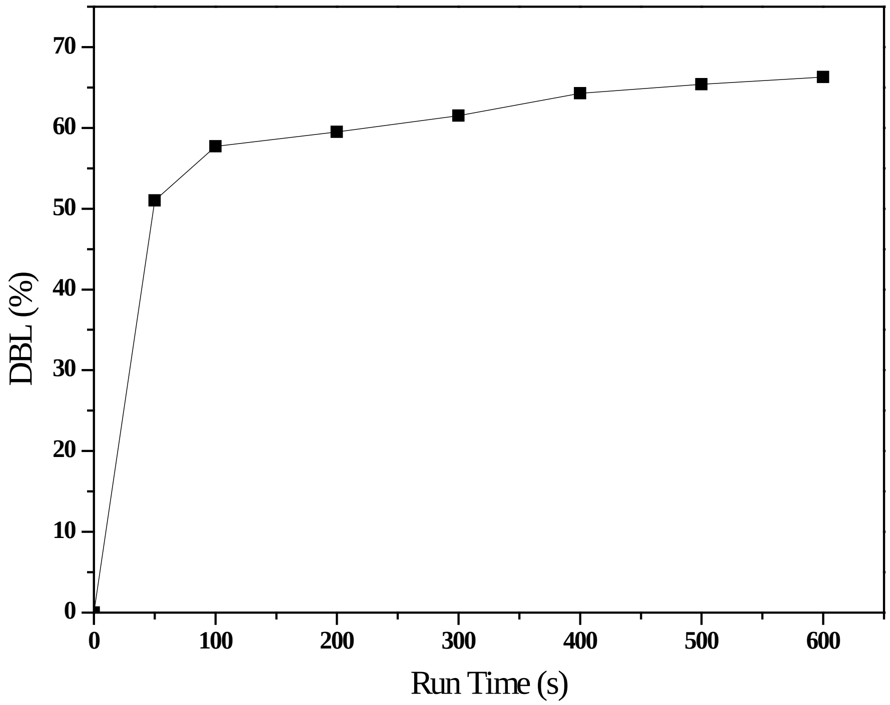


Figure 10: A typical bitumen liberation curve of A1 ore at pH 8.5 and 35°C

To understand the critical role of bitumen liberation in bitumen recovery from oil sands, several other types of tests were conducted. These tests include flotation (in a Denver cell) and Dean Stark analysis, zeta potential measurements of the bitumen in various solutions, surface tension measurements, induction time measurements and infrared spectroscopy analysis. In addition, the bitumen wettability was measured using contact angle measurements.

2.5 *Denver Cell Recovery:*

The main apparatus for bitumen flotation tests was the Denver flotation cell. The Denver flotation cell consisted of a modified 1L stainless steel cell and an impeller attached to a 1/2 HP Baldor Industrial Motor. The modified cell was enclosed in a water jacket that kept the cell at a constant temperature with water being recycled through a water bath (Neslab, EX-111). The impeller speed, was measured using a tachometer. Air was allowed to pass through the impeller shaft at a constant flow rate with the aid of a calibrated gas flow meter (Matheson).

The flotation tests were conducted at the following conditions: temperature of 35°C, rotor speed of 1500rpm and an air flow rate of 150mL/min. These conditions were kept constant unless otherwise stated. To start, the ore, either A1 or C-ore, was left to thaw for two hours. The cell was heated to a uniform temperature, and the process feed water temperature was raised to a uniform temperature of 35°C. The process feed water was prepared using industrial process water with sodium hydroxide or ammonium hydroxide to adjust the pH. The ore was weighed out to 300 g and placed into the heated cell with the process feed water to begin the conditioning stage. The conditioning stage was achieved by agitation for 10 minutes with no air flow. Once the conditioning stage was completed the air was turned on to allow the aeration to occur. The froth was collected at five minute intervals into a special thimble, which was pre-weighed. The thimble was then weighed again, after the froth was collected, and placed into the Dean Stark apparatus. The Dean Stark analysis allowed for the determination of bitumen recovery and the overall froth quality.

The cumulative bitumen recovery as a function of time, R(t), is defined as the percentage of bitumen recovered from the feed ore after a given flotation period and is calculated by:

$$R(t) = \frac{Bitumen\ in\ froth\ (g)}{Bitumen\ in\ feedstock\ (g)} * 100 \tag{1.4}$$

The froth quality is evaluated by the bitumen to solids ratio (BSR), which is a measure of the solids collected in the froth and is calculated by:

$$BSR = \frac{Cumulative\ Bitumen\ Recovered\ (g)}{Cumulative\ Solids\ in\ Froth\ (g)} \tag{1.5}$$

The cumulative recovery and bitumen to solids ratio were studied under batch conditions at several pH values. The pH was adjusted by either NaOH or NH_4OH to levels between 8.5 and 11.3.

2.6 *Froth Analysis*

The bitumen froth collected in Whatman extraction thimbles was analyzed in a Dean Stark apparatus. This is the most common method for determining not only the bitumen content but also the froth quality after flotation experiments. The special thimbles were placed in steel wire holders and a mesh lid was placed over the top. The assembly was then placed in large extraction flasks containing approximately 200mL of toluene. Dean Stark condenser and trap were then fitted into the tops of the flasks so that the water could be captured. Once the thimbles and traps were in place the apparatus was turned on and run until the toluene dripping from the base of the thimble became clear in color. The water collected in the trap was released into a pre-weighed tube. The collected water was then weighed and the percent of water in the froth was calculated. The thimble was then placed in a vacuum oven and allowed to dry at 80°C overnight. After drying, the thimble with solids was weighed again and the solids content was then calculated. The bitumen rich toluene solution left in the Dean Stark flasks was transferred to 250 mL volumetric flasks. Additional toluene was added until the 250mL flask was filled to the mark. Once the flask was full it was inverted several times to ensure uniform diluted bitumen in the toluene. After mixing a weighed filter paper (Whatman 934-AH Glass Fiber Filter Paper) was covered with 5mL of the diluted bitumen solution and allowed to dry for 20 minutes at room temperature in a well vented fume hood. After drying, the filter paper was weighed again and the bitumen content was calculated using a factor of 50:1 (to account for the 5mL removed from the 250mL flask).

2.7 *Induction Time Measurements*

To determine the effect of sodium and ammonium hydroxide addition on the air bubble and bitumen attachment induction time measurements were conducted. An induction time apparatus was used to measure the minimum amount of time required for the air bubble to attach to the bitumen surface. The faster the attachment occurs, the shorter the induction time.

The induction time measurements were carried out on a novel induction timer. The rectangular cell containing the solution and bitumen sample was placed on a three-axial translation stage. Inside the stage was a built-in heater and thermocouple that allowed the stage to be kept at a constant temperature. Above this stage was a speaker attached with a capillary tube. The speaker was connected to a charge amplifier driven by a computer program controlled the movement of the capillary tube, such as the displacement, speed and duration of the tube at the maximum displacement. The capillary held air bubbles generated using a microsyringe. These bubbles were made in contact to the bitumen surface. A light source was placed on either side of the sample to help illuminate the cell so that each trial could be captured. The capture of the attachment process was accomplished by a charge-coupled device (CCD) camera which was also connected to the computer. This visualization allowed for the determination of a successful attachment.

The bitumen used in the induction time measurements was vacuum feed distillation bitumen. This bitumen was removed from a larger barrel and placed on a circular Teflon disk. The Teflon disk was slightly hollowed out to form a half sphere shape that the bitumen could fill. Once the bitumen had filled the hollow space, the surface was made even by a razor blade. After the surface had been scraped the sample was allowed to sit for approximately 30 minutes in a covered dish so that the bitumen surface could settle and become smoother. The sample, now flat to the naked eye, was transferred into a small rectangular glass cell that had been filled with the testing solution. The solution was made from process water, from the Syncrude Aurora process plant, and the pH of the water was adjusted to 8.5 or 11.3 using 1N NaOH or 14N NH_4OH solutions. Several solutions made by either sodium or ammonium hydroxide at each pH value were used in this measurement. Again, the sample was allowed to equilibrate in the solution for 30 minutes prior to each measurement.

The rectangular cell containing the solution and bitumen sample was placed on a three-axial translation stage. The experiments were conducted by bringing an air bubble, attached to the end of the glass capillary tube, in contact with the bitumen surface for a given period and then retracting it. With the aid of a microsyringe an air bubble with a diameter of 1.5 mm was created at the free end of the capillary tube. The bubble created was brought down to the surface at a speed of 40 mm/s. After contact for a given period of time, the bubble was retracted at the same speed. This process was captured on a charge-coupled device (CCD) camera. The camera allowed clear visualization of the process and the accurate judgement whether the bubble attached to the bitumen surface or not. This process was repeated 20 times per contact time so that a percent attachment, defined as the number of attachments over total number of trials, could be obtained. The contact time with an attachment percentage of 50% was considered as the induction time.

All the measurements were carried out at 35°C. This was done with the aid of a heating element attached to the three-axial stage. This heating element, which was controlled by a thermocouple attached to a controller box, kept the stage and solutions at a constant temperature. All other conditions were ambient to the surroundings. The distance between the air bubble and surface were kept constant at 0.25mm, while the bubble displacement was kept constant at 0.4 mm.

2.8 *Contact Angle Measurements*

Contact angle measurements were conducted to test the surface wettability of the bitumen. A larger contact angle in the presence of water shows a more hydrophobic surface. The contact angle measurements were performed on a Kruss Drop Shape Analyzer (DSA). The DSA consisted of a movable sample tray, a charge-coupled device (CCD) camera, a syringe holder and a light source. The camera sent black and white images of the sample and bubble to a computer where it was displayed on the screen using a DSA program. The syringe was filled with either air or the solution depending on the experiment that was being conducted.

The static contact angle measurements were conducted using the Drop Shape Analyzer. Two different contact angle measurement experiments were performed on this apparatus. For contact angle measurement, bitumen was spread onto a circular Teflon disc and placed in a rectangular glass container. Different solutions were prepared, using sodium hydroxide or ammonium hydroxide in process water, as mentioned above. As well, the filtered tailings water from the Denver cell flotation experiments was used.

For the first experiment several drops of the prepared solutions were placed around the bottom of the rectangular glass container so that evaporation of probing liquid would not be a factor. Once the drops were in place a single drop was placed onto the bitumen and a video was recorded using Drop Shape Analyzer. Once the video was collected for, approximately 180 seconds, it was analyzed using the DSA software. The program calculated the contact angle for each frame and recorded it. This allowed for the analysis of the dynamic contact angle for the water on bitumen surface.

The second contact angle measurement was conducted using the same setup, except instead of one drop of solution on the bitumen the rectangular cell was filled with the solution. Once the bitumen filled Teflon disc was in the solution it was allowed to sit for 20 minutes to equilibrate. The cell was then placed on the stand and a micro-syringe was used to create an air bubble. This air bubble was placed onto the bitumen surface and held there until it attached to the bitumen. When the attachment occurred the syringe was quickly pulled back and the contact angle was recorded using the DSA software and analyzed.

2.9 *Zeta Potential Measurement*

The zeta potential was measured to determine the surface charge of particles in solution. The particles in this study were small bitumen droplets and air bubbles in a process feed water. All of the zeta potential measurements were carried out using a Malvern Zetasizer Nano ZS. This instrument was again attached to a computer which displayed the results. The machine required a dip cell to be placed in a small amount of the sample. Once the dip cell and sample were placed in this instrument, a phase analysis light scattering technique was used to determine the zeta potential of the sample.

In this study zeta potential of two different samples were measured using the same zeta potential instrument. The first sample was bitumen emulsions. The emulsions were created using a sonic dismembrator (Model, Maker). A small amount of vacuum distilled bitumen, approximately 1g, was placed in the bottom of a beaker and then the beaker was filled with the testing solution. In this case the solution was either the tailings water from the bitumen recovery experiments or the freshly adjusted process feed water. Once the solution was in the beaker it was placed under the sonic dismembrator tip in such a way that the tip was just above the bitumen. The sonic dismembrator was then started at a setting of 35% for 20 minutes. This caused dispersion of the bitumen into the solution forming an emulsion. Once completed the emulsion was transferred into a 125mL sample bottle and allowed to sit for 30 minutes to cool down the sample. After it was cooled to room temperature, a small amount of the emulsion, approximately 1.5mL, was transferred into a glass cuvette. A dip cell, with Pd electrodes, was then placed into the cuvette. The cuvette was placed into the zeta potential machine. A computer program (Malvern DTS Nano) was run using a standard operating procedure set up specifically for a bitumen emulsion. The program ran five consecutive measurements on each sample and all the results were recorded. A minimum of ten tests, two runs through the zeta potential analysis, were completed for each sample and an average value from these ten measurements was taken.

The second sample was bubble suspensions. To generate bubble suspensions approximately 1.5mL of solution was placed into a glass cuvette. The dip cell then was placed into the cuvette and any solution that leaked out of the top of the cuvette was thoroughly cleaned off. The cuvette was then transferred to an ultrasonic bath where it was sonicated for 15 minutes before it was placed into the zeta potential instrument. The computer program (Malvern DTS Nano) was run again using the standard operating procedure, for air bubbles instead of bitumen. The instrument completed five measurements per sample. These five measurements were done twice for each sample. The zeta potential recorded was an average of these ten measurements for all samples tested.

2.10 *Surface Tension Measurements*

Surface tension is a measure of how a surface of a solution resists an external force. In flotation a smaller surface tension allows for the creation of smaller air bubbles and also means a greater release of natural surfactants. In this study, the surface tension of process water or tailings water was measured using a Kruss K12 Processor Tensiometer. This machine consisted of a measurement unit and a separate cell in which the sample was placed. The measurement unit allowed for the input of parameters, such as air and solution density, and the selection of the measurement type that was to take place. The cell contained a moveable stand on which the sample was situated. Above the sample was a holder for the Du-Nouy ring, and all of this was enclosed by two clear plastic doors.

Various solutions were placed in a cylindrical glass cell and placed onto the metal stand. The measurement was conducted on the tailings water from the Denver cell flotation experiments at pH 8.5 and 11.3, as well as freshly adjusted process water at pH 11.3. The Du-Nouy ring was inserted into the holder, connected to an electronic balance, and the solution was brought up to a position so that the surface was just below the ring. Once the sample was set in place, the measurement parameters were set into the apparatus. All the runs were done at ambient conditions and the parameters were adjusted accordingly. After the parameters were registered in the machine the run was started. Upon the completion the results were recorded. After each measurement, the sample was removed and replaced with another sample from the same solution. This was repeated four times for each solution. The average value from the four runs was taken.

2.11 *Surfactant Analysis*

Natural surfactants play a large role in bitumen recovery as they affect the surface charge of the bitumen as well as the surface tension of the solution. Surfactant release by caustic addition was analyzed. The analysis was done in two major steps. The first step was the acidification of the solution followed by the extraction of the acidified neutral surfactant by dichloromethane (DCM). This step required a flask with a valve in one end, a stand with a metal ring holder and a separation funnel. The flask is for extraction of the solution and DCM, while the separation funnel is for the phase separation and drainage of the mixture. The extracted organic phase was analyzed using an FTIR-spectrometer. The instrument used in these experiments was an FTS 6000 FTIR-spectrophotometer from BIO-RAD, equipped with a liquid cell so that liquid samples could be analyzed.

Surfactant recovery was done in several parts. The first was to weigh out 50 g of the solution or tailings water from the flotation tests, and acidify it. The solution was brought to a pH of 2.3 using hydrochloric acid (HCl). Once this was completed the solution was mixed with approximately 30mL of dichloromethane (DCM) in the flask. The mixing was done for two minutes with an occasional opening of the valve to vent the built up gases. Then the mixture was allowed to settle for 2 minutes. The DCM part, which had settled to the bottom of the mixture, was drained into a bottle. The extraction was repeated for a second time. After this two stage extraction, the bottle with the DCM was placed under a slight air flow to evaporate the DCM. This was left for approximately three hours or until all of the DCM had been evaporated. The bottle was then checked for any water. If there was none in the sample, move to the next step.

The next step was taking the dried sample and adding approximately 20g of DCM back into the bottle. The weight was recorded and the new solution was allowed to sit. The FTIR-spectrophotometer was turned on, the computer program (Varian Resolutions Pro) was started up and a background test was completed. Next the sample was loaded into the liquid sample holder and placed into the FTIR-spectrophotometer. After acquiring the spectrum of the sample, the heights of the peaks at 1743 and 1706 cm^{-1} were recorded. These heights allowed for calculation of the concentration of the surfactant in the solution. These calculations were provided to me through a fellow group member.

Chapter 3: RESULTS AND DISCUSSION

3.1 *Bitumen Liberation*

The novel setup allowed for clear visualization and analysis of how the various caustic additions affected bitumen liberation from sand grains in an ore. The images produced by the digital camera and microscope setup showed the state of bitumen on the sand grain, which allowed for calculating the clear area of the grains. The clear area was a result of preferential wetting of the sand grain by the water. Preferential wetting occurs when the free energy of the water/sand interface is less than the free energy of the bitumen/sand interface. Once recession occurred, the bitumen formed droplets on the sand surface to minimize bitumen/water interface. As a result, bitumen droplets are much easier to remove by hydrodynamic force.

In this thesis, liberation was studied at a constant temperature of 35°C and two pH levels of 8.5 and 11.3. The lower temperature was used in this study to emphasize the effect of pH modifiers on bitumen liberation. The bitumen liberation was examined on three oil sand ores, A1, C-ore and SunP210. The characteristics of these ores were given in Table 1 of the experimental section. These three ores had similar bitumen, water and solids contents, and the biggest difference was seen in the fines content. The fines content ranged from 0.7% to 25% for A1 and SunP210, respectively. Figures 11, 12 and 13 show the percentage of sand grains that are clear, i.e., degree of bitumen liberation (DBL) for A1 ore, C-ore and SunP210, respectively. The DBL was calculated using Equation (1.3). The experimental error bars in Figure 11 represent the standard deviation of five runs at the same conditions. These runs were completed on A1 ore at pH 11.3 using ammonium hydroxide as pH modifier. All three figures (11, 12 and 13) show that the recession (bitumen liberation) occurs mainly within the first 50 s and it only increases by approximately 10% in the final 500 s. The quick initial bitumen displacement on these ores is similar at a given pH, either 8.5 or 11.3 for both sodium hydroxide and ammonium hydroxide as a pH modifier. Sodium hydroxide and ammonium hydroxide appear to have a negligible difference when it comes to bitumen liberation and pH is the most dominant parameter to determine bitumen liberation for all the ores. The small difference between the two caustics on DBL can be attributed to experimental error. Both sodium hydroxide and ammonium hydroxide behave within experimental error of each other at a given pH. Sodium hydroxide and ammonium hydroxide performed similarly for all the ores and pH conditions. The similarity at pH 8.5 can be explained by the addition of a very small amount of pH modifier stock solutions, which was at most 1mL of either sodium hydroxide or ammonium hydroxide to 1000mL of the process water. The amount needed for both caustics was very small and similar that would have very little impact on the water chemistry of the solution. At pH 11.3 much larger amounts of the caustics, 12-16mL of sodium hydroxide and 30-35mL of ammonium hydroxide solutions were added to 1L of process water. A larger volume of ammonium hydroxide was needed due to the dissociation of the ammonium ions into ammonia, which would add an extra hydrogen ion. This extra hydrogen would lower the pH and bond with the hydroxide ion, making it necessary to add more ammonium hydroxide to the solution. The dissociation of the ammonium ions and binding of hydrogen ions with hydroxide ions are given below:

$$NH_4^+ \underset{H_2O}{\longleftrightarrow} NH_3 + H^+$$

$$H^+ + OH^- \leftrightarrow H_2O$$

Since the pH is a measure of the hydroxide ion concentrations in solution the total number of hydroxide ions would be similar for a given pH even though the extra ammonium hydroxide was added to reach the pH. As a result, even though the hydroxide ions would be similar for both cases there would be an excess of ammonium ions as compared with sodium ions in the solution. The hydroxide ion plays a large role in bitumen liberation by adjusting the pH and affecting the surface charge of the bitumen and sand grains. Therefore, with a similar amount of hydroxide ions in the solutions, the bitumen displacement and liberation should be similar for both sodium hydroxide and ammonium hydroxide. This was the case as both ammonium and sodium hydroxide performed similarly on all three ores (A1, C-ore and SunP210) that were studied. Figures 11, 12 and 13 show that for a given liberation time increasing pH from 8.5 to 11.3 increases the DBL. An increase in pH from 8.5 to 11.3 shows an approximate increase of 14% in the DBL. This increase in DBL shows that higher pH promotes bitumen liberation for all three ores tested. It is known that increasing pH increases bitumen displacement. This has been shown on both model surfaces by Basu et al. (1996) who used glass plates to imitate the silica of the sand grains, and real ores by Sundeep (2009). The increased bitumen displacement with pH can be explained by the attraction-repulsion model for bitumen-sand surfaces. Takamura and Chow (1983) suggested that at higher pH the bitumen and sand surfaces are more negatively charged, leading to a stronger repulsive force; while at lower pH this repulsive force decreases. A reduction in repulsive force would lead to a lower bitumen displacement along the sand grain, i.e. a lower DBL.

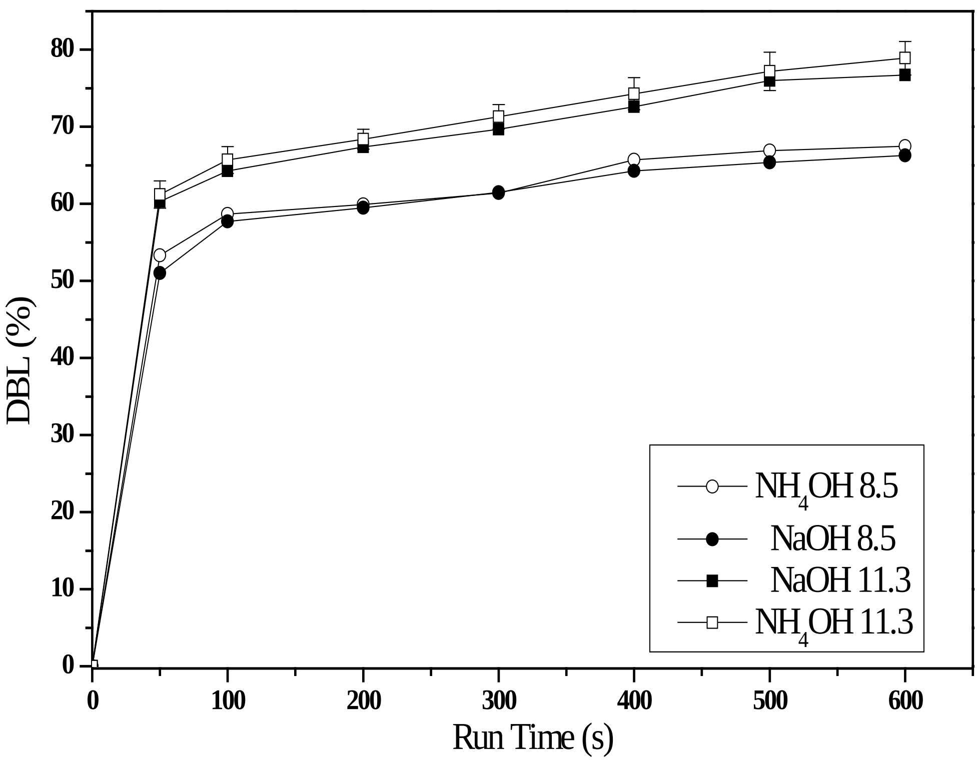


Figure 11: Bitumen liberation from A1 ore at 35°C using different caustics as pH modifiers in process water

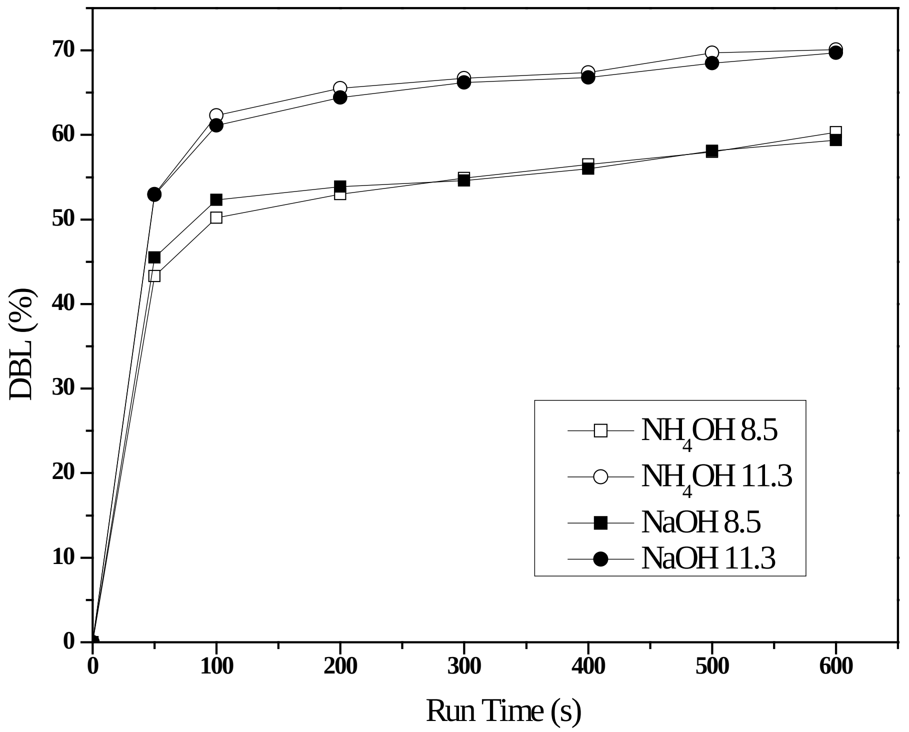


Figure 12: Bitumen Liberation from C-ore in process water at 35°C using different caustics as pH modifiers

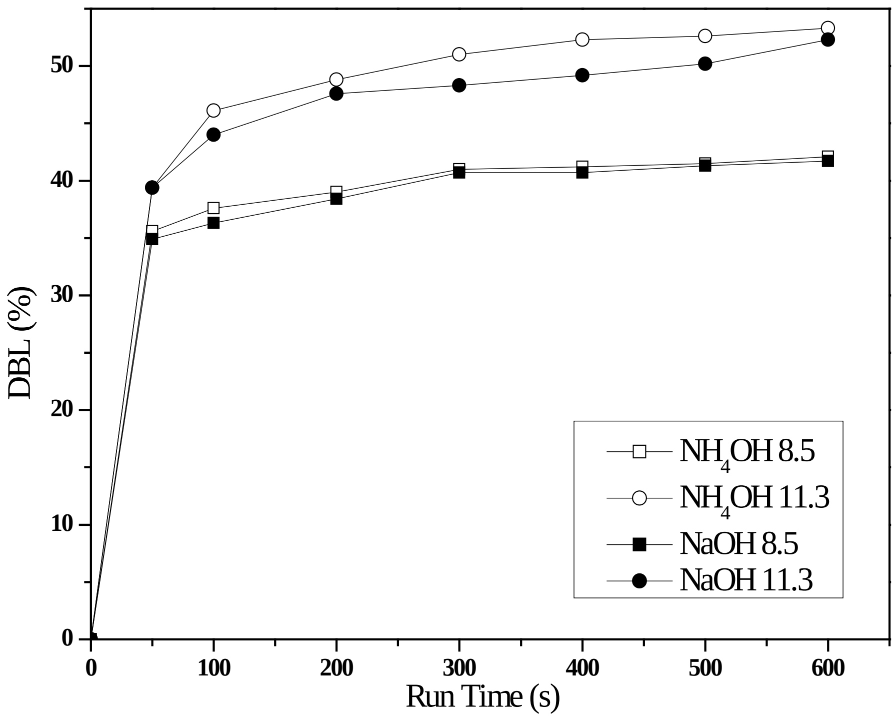


Figure 13: Bitumen liberation from SunP210 ore in process water at 35°C using different caustics as pH modifiers

The major difference in the three ores tested (A1, C-ore and SunP210) was the fines content. As can be seen in Table 1 the fines content increased from 0.7% in A1 ore to 25% in SunP210 ore with C-ore in the middle at 12%. The effect of fines on bitumen liberation was studied by testing these three ores at pH 8.5 using sodium hydroxide as the caustic. Since sodium hydroxide and ammonium hydroxide perform similarly only sodium hydroxide was selected to study the effect of fines on bitumen liberation. Also, at pH 11.3 and 8.5 showed a similar effect on bitumen liberation for all three ores, and therefore only pH 8.5 was chosen in this set of tests. The results from these tests are shown in Figure 14. It can be seen that higher fines content has a detrimental effect on bitumen liberation. As the fines content increases from 0.7% to 25%, the final DBL drops from 65% to 40%. The high fines content in the ore in the presence of calcium in the process water may lead to an increase in the "slime coating" of fines on the bitumen surface (Liu et al. 2004). Dai and Chung (1995) also stated that the smaller the particle the stronger the bitumen attachment to it. These two factors would help explain why the bitumen displacement decreases with increasing fines content, as was seen in the current study for both caustics. The decrease in bitumen displacement with increasing fines content was also observed at pH 11.3 but is not shown, decreasing the final DBL from 77% for A1 ore to 50% for SunP210 ore.

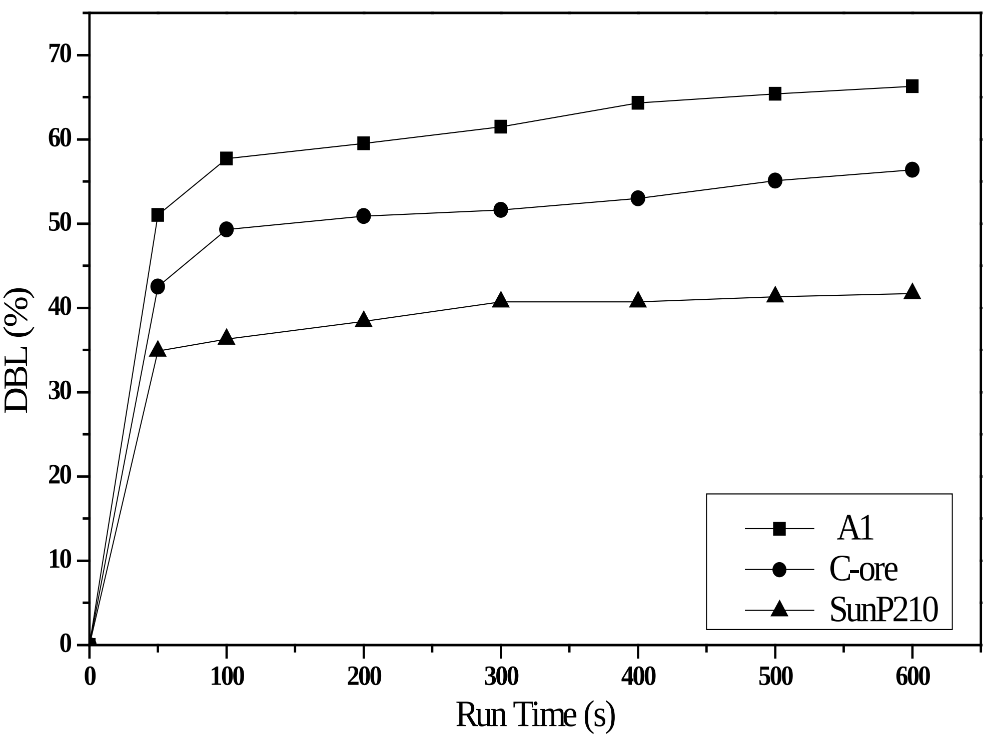


Figure 14: Effect of fines content in the ore on bitumen liberation, in process water, at 35°C and pH 8.5 using NaOH as the caustic.

The effect of process water flow rate on bitumen liberation was also examined by conducting tests at constant temperature of 35°C, and pH of 8.5. The pH was adjusted using sodium hydroxide and the tests were run for 10 minutes. The process water flow rate changed from a maximum of 32 mL/min down to 16 mL/min and 8 mL/min. The results from these runs are shown in Figure 15. It is evident that decreasing the process water flow rate, decreases the rate of bitumen displacement and the final DBL. For example, the final DBL after 600s is reduced by about 15% when the process water flow is reduced by one fourth.

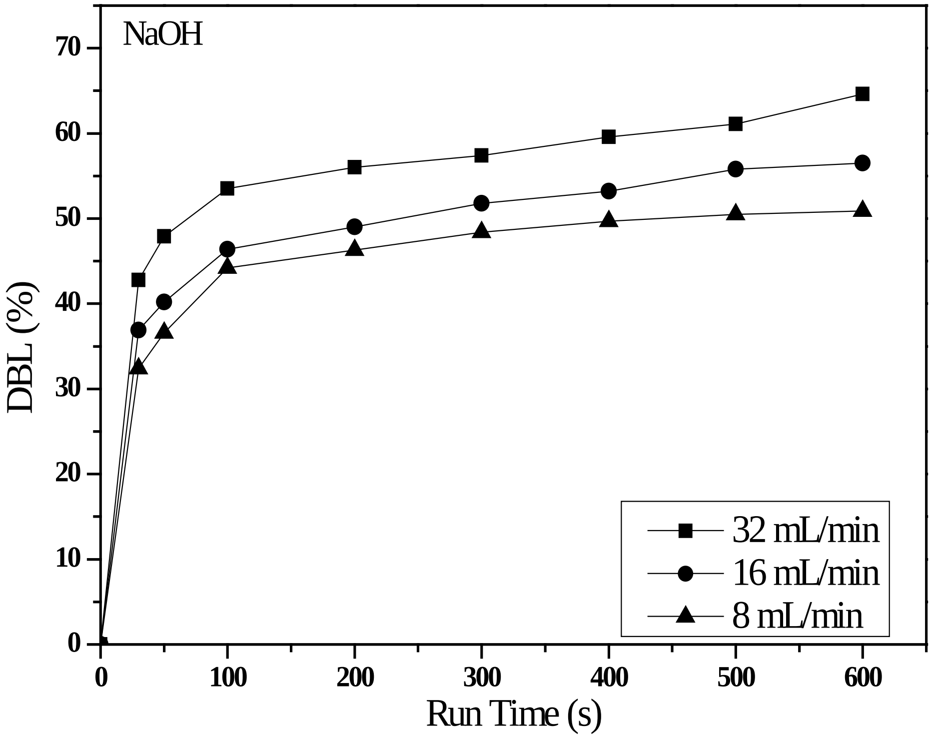


Figure 15: Effect of process water flow rate on bitumen liberation of C-ore in a pH 8.5 process water at 35°C

To better understand the role of fluid flow hydrodynamics on bitumen liberation from oil sands ores the initial rate of bitumen liberation was calculated using the results in Figure 15 and compared against the Peclet number of the system. The initial rate of bitumen liberation was calculated by taking the first DBL value and dividing by the time and the Peclet number was calculated using Equation (1.1). The velocity in the Peclet number is the velocity of the solution passing through the constant area of the flow channel and the length is the diameter of the exposed oil sands ore. The diffusion coefficient is calculated using Equation (1.2). The flow channel is a constant area. Therefore a doubling of the volumetric flow rate is equivalent to a doubling of the velocity. The results in Figure 16 show a linear increase in initial bitumen displacement rate with increasing Peclet number. For the current system, the Peclet numbers range from 2 to 26, which is considered to be large indicating that the advection rather than diffusion is the main driving force. Advection as the driving force means that the fluid flow and the shear force it produces drive bitumen displacement.

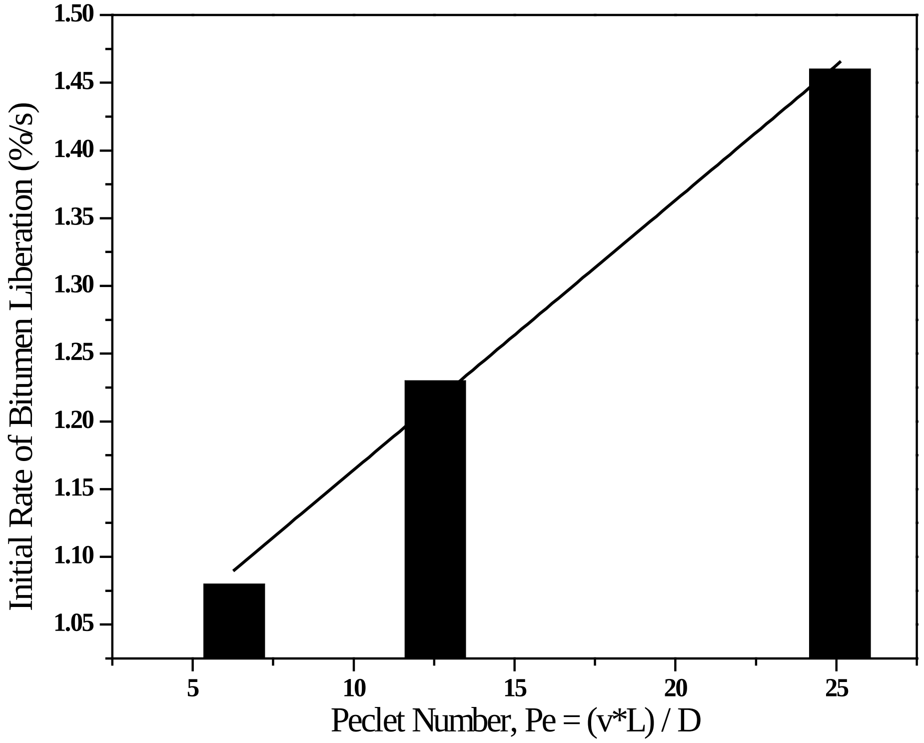


Figure 16: Peclet Number versus Initial Clearance for C-ore at 35°C

3.2 *Bitumen Recovery*

Liberation is the first step during recovery of bitumen from oil sands ores. The next step involves aeration of the liberated bitumen. Aeration, in industry, is done by entraining and/or passing air bubbles through the slurry in the hydrotransport or/and secondary bitumen recovery unit. The liberation and aeration steps allow for flotation of the bitumen and collection of bitumen froth. The bitumen recovery can be experimented using a Denver flotation cell. The Denver flotation cell adds air into the system and provides mechanical agitation, which are not present in the novel flow in-situ bitumen liberation visualization cell (FIBLVC). In the Denver cell mechanical agitation is provided by an impeller, and air is allowed to pass through the conditioned slurry at a desired rate. In the present study, the air flow rate is controlled at 150 mL/min. The combination of mechanical mixing and air addition produces froth at the top of the cell that can be collected and analyzed. The froth is separated into three components of solids, water and bitumen using Dean Stark apparatus. The quantification of these three components allows the froth quality and bitumen recovery to be calculated. The flotation tests were conducted at various pH levels adjusted by sodium hydroxide or ammonium hydroxide. The process temperature was kept constant at 35°C to determine the effect of pH and different caustics on bitumen recovery from real ores.

The bitumen recovery tests were conducted on two different ores, A1 and C-ore. Ammonium hydroxide and sodium hydroxide were used as pH modifiers to adjust the pH of the process water to the desired values. The pH values used in these experiments were 8.5 and 11.3. All the runs were completed at 35°C. The results of bitumen recovery experiments, at pH 8.5 are shown in Figures 17 and 18 for A1 ore and C-ore, respectively. The bitumen recovery was calculated using Equation (1.4) and the error bars are the typical relative error. The bitumen recovery at pH 8.5 was similar when either sodium hydroxide or ammonium hydroxide was used as pH modifier. Air bubble to bitumen attachment time (induction time), bitumen surface wettability, bitumen and air bubble surface charge and surface tension of processing fluids are known to affect the bitumen recovery process by both liberation and aeration. To understand the absence of pH modifiers at pH 8.5 on bitumen recovery these physiochemical properties are determined using these two caustics as the pH modifier and discussed in subsequent sections.

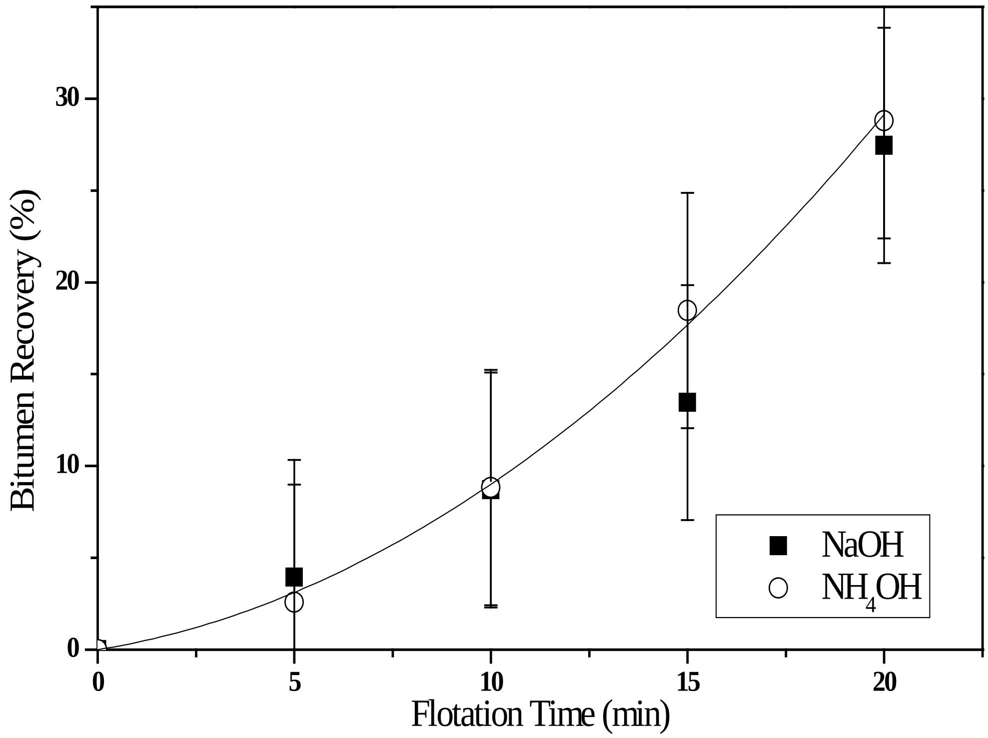


Figure 17: Effect of sodium hydroxide and ammonium hydroxide as pH modifier on bitumen recovery of A1 ore in process water at pH 8.5

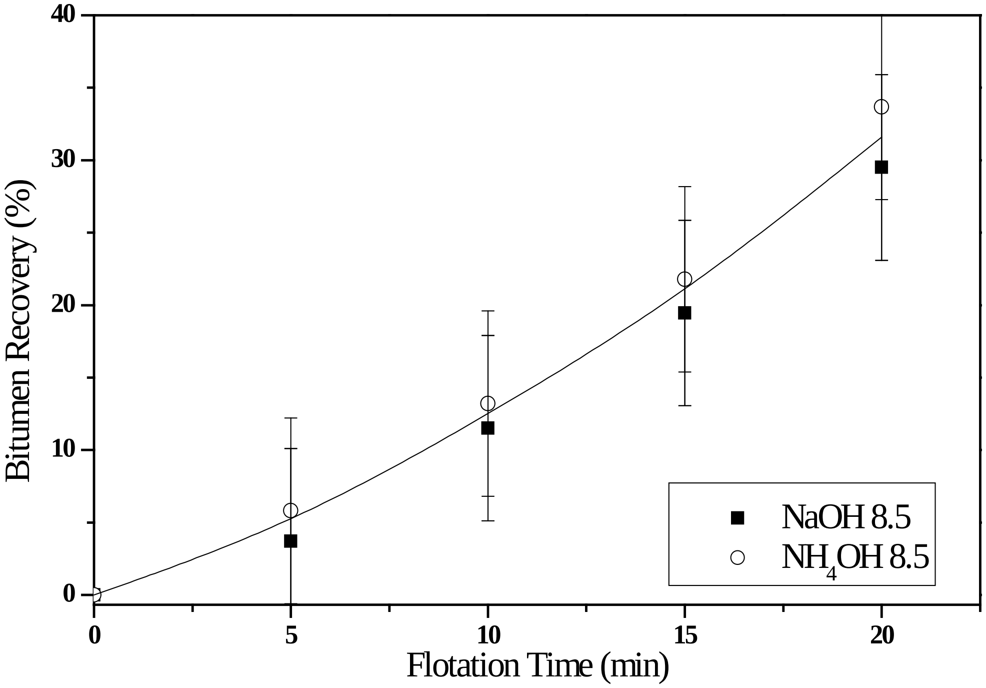


Figure 18: Effect of sodium hydroxide and ammonium hydroxide as pH modifier on bitumen recovery of C-ore in process water at pH 8.5

Although the bitumen recovery at pH 8.5 was similar for both A1 ore and C-ore, regardless of the caustic used to adjust the pH, this is not the case for pH 11.3. The results obtained at pH 11.3 are shown in Figures 19 and 20 for A1 ore and C-ore, respectively. For comparison the recovery data obtained at pH 8.5 are also included as open symbols in these figures. For both A1 and C-ore the pH change can be seen to have a very small effect on the bitumen recovery when sodium hydroxide is used as pH modifier, as they are for the most part within the experimental error. When ammonium hydroxide is used as pH modifier to raise the pH from pH 8.5 to 11.3 the bitumen recovery increases greatly. It can also be seen that the bitumen recovery obtained at pH 11.3 adjusted by ammonium hydroxide is much higher than that adjusted by sodium hydroxide. The increase in bitumen recovery when using ammonium hydroxide at pH 11.3 for both A1 and C-ore can be attributed to their effects on several physiochemical properties of flotation systems. These properties include bitumen to air bubble attachment (induction time), bitumen surface wettability, bitumen and air bubble surface charge, surface tension and natural surfactant release. These properties will be determined and discussed below.

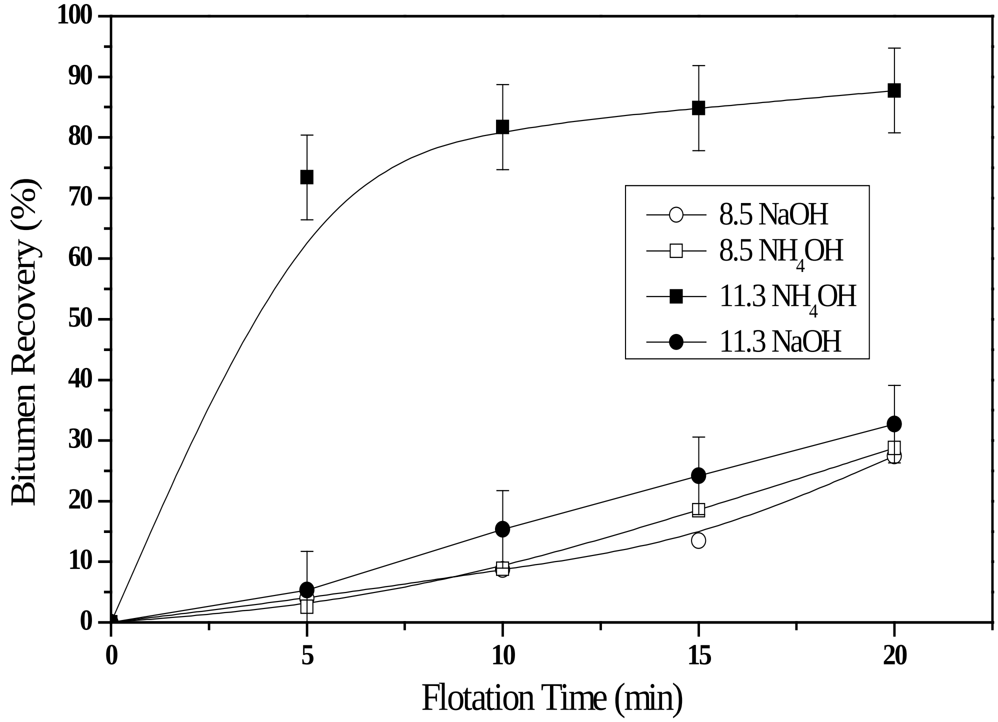


Figure 19: Effect of pH modifiers, sodium hydroxide and ammonium hydroxide, on bitumen recovery of A1 ore in process water at pH 11.3

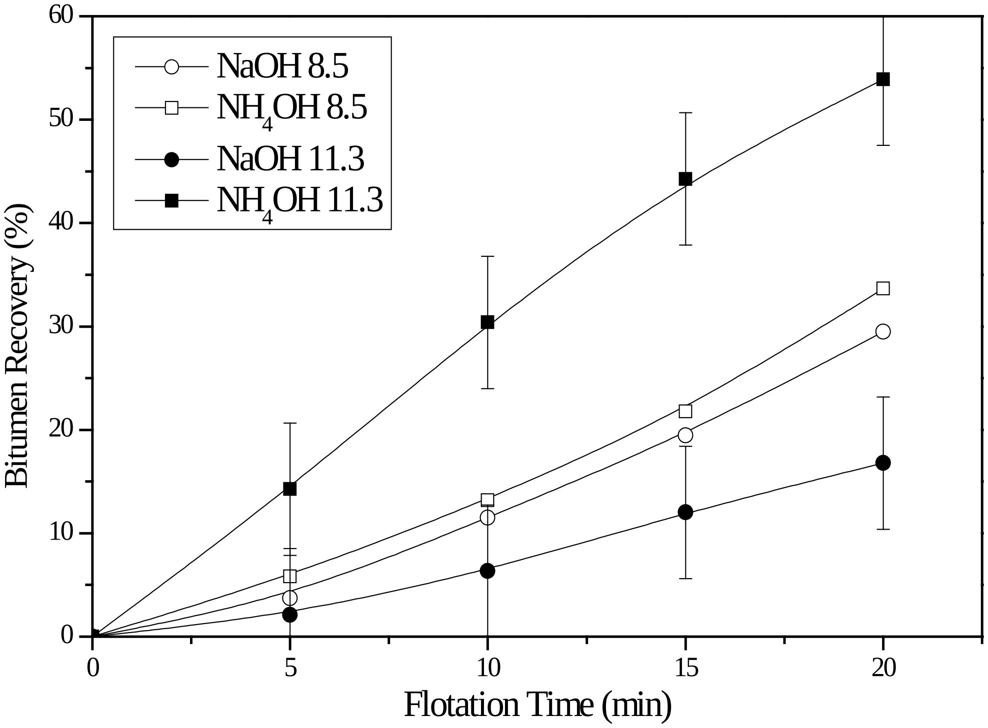


Figure 20: Effect of pH modifiers, sodium hydroxide and ammonium hydroxide on bitumen recovery of C-ore in process water at pH 11.3

3.3 *Induction Time Measurement*

To better distinguish the role of bitumen liberation and aeration in bitumen recovery, induction time was measured to see how different caustics affect the bitumen and air bubble attachment (aeration) in various process water solutions. The pH of solutions was adjusted using either sodium hydroxide or ammonium hydroxide. The results from these measurements at pH 8.5 are shown in Figure 21. At pH 8.5 the attachment curves are almost identical for these two caustics showing an induction time of 1000 ms. The similarity in induction time for these two caustics correlates well with the negligible difference in bitumen recovery at pH 8.5 adjusted with these caustics as shown in Figures 17 and 18 for both A1 and C ore.

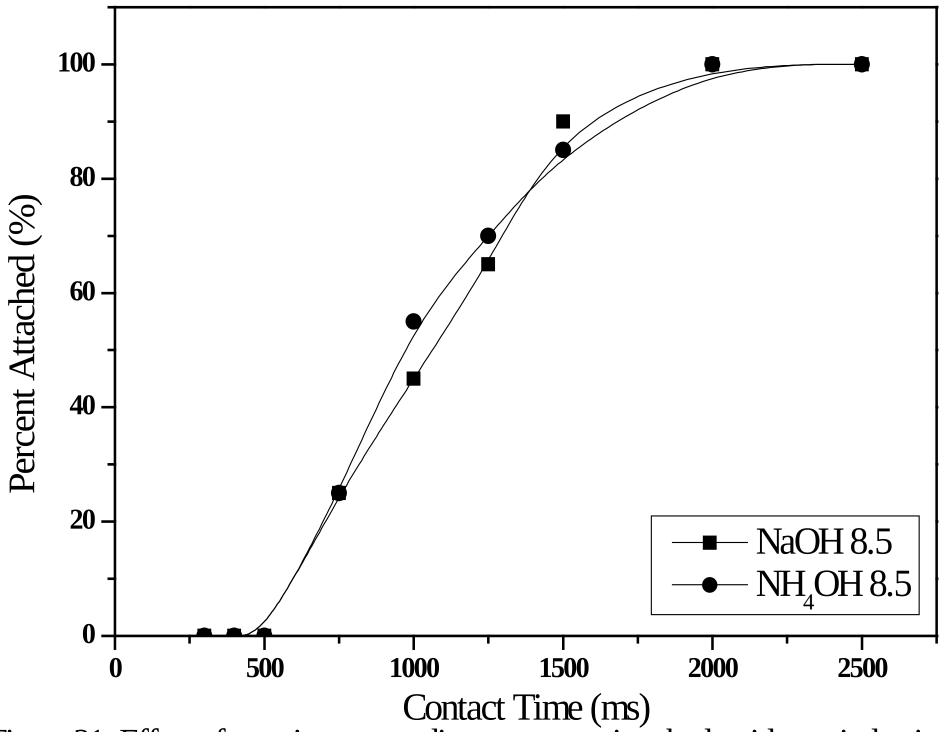


Figure 21: Effect of caustic type, sodium or ammonium hydroxide, on induction time for an air bubble to attach to a bitumen surface in process water at pH 8.5

Although there was a small difference in the induction time of air bubble attaching to a bitumen surface at pH 8.5 for two different pH modifiers, but in freshly adjusted process water at pH 11.3 this was not the case. The results of the induction time measurement using sodium hydroxide and ammonium hydroxide to adjust the pH of the process water to 11.3 are shown in Figure 22. The induction time data at pH 8.5 has also been added to the figure for comparison. For a greater chance of attachment to occur in flotation a much shorter induction time between the bitumen surface and air bubble is necessary. This greater chance of bitumen attachment to the air bubble will aid in the increase in bitumen recovery.

When compared to the induction times at pH 8.5 the ammonium hydroxide solution at pH 11.3 needed a shorter contact time to attain the attachment, i.e. shorter induction time, while the sodium hydroxide requires a double contact time to reach the attachment. The shorter induction time for ammonium hydroxide at pH 11.3 helps explain the increase in bitumen recovery with increasing pH from 8.5 to 11.3.

The induction time at pH 11.3 was also greatly reduced from 2000 ms to 600 ms when the pH modifiers were changed from sodium hydroxide to ammonium hydroxide. This shorter induction time explains the observed increase in the bitumen recovery as shown in both Figures 19 and 20.

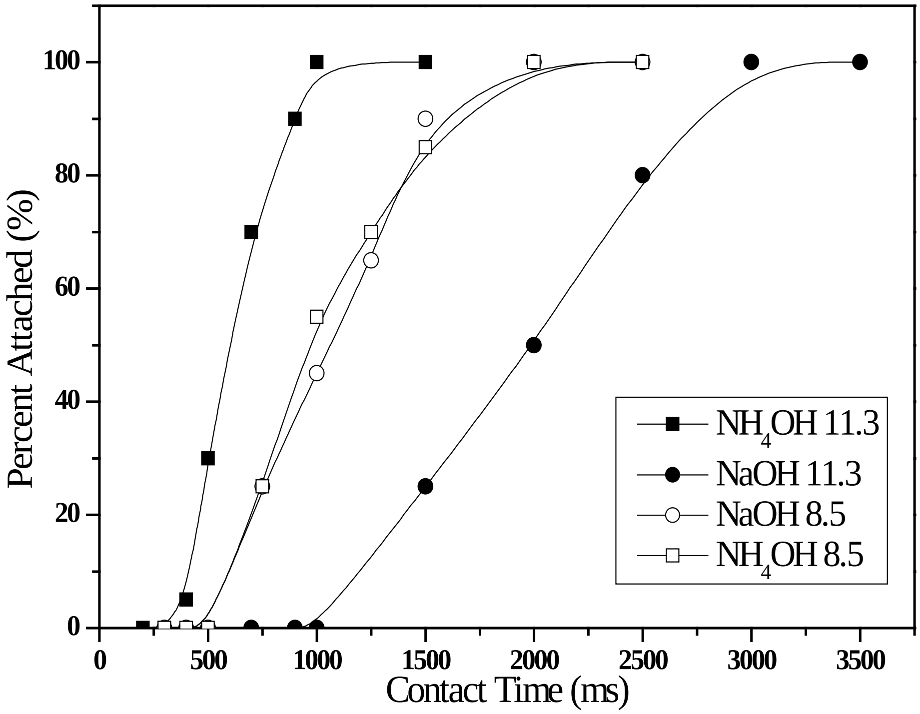


Figure 22: Effect of caustic type, sodium or ammonium hydroxide, on induction time of air bubble attaching to a bitumen surface in process water at pH 11.3

3.4 *Contact Angle Measurements*

The angle of the bubble (θ_b) attaching to the bitumen in process water was a measure of surface wettability, often used to determine how the bitumen surface is affected by solution chemistry. The angle (θ_b) was measured through the bubble using the DSA program. This angle was then subtracted from 180° to get the normal contact angle measured through the solution phase. The contact angle of bitumen in process water at pH 8.5 was found to be around 58° for both sodium hydroxide and ammonium hydroxide as pH modifier. At pH 8.5 the contact angle of 58° indicates a moderate hydrophobicity of the bitumen surface in process water, regardless of whether the pH is adjusted by either sodium hydroxide or ammonium hydroxide. The contact angle of 58° is in an excellent agreement with the value of 60° reported by Kasongo et al. (2000). The trend of similarity between sodium hydroxide and ammonium hydroxide as pH modifier again correlates well with the findings of similar bitumen recovery at pH 8.5 by either sodium hydroxide or ammonium hydroxide, as shown in Figures 17 and 18.

The contact angle was also measured at pH 11.3 with both sodium hydroxide and ammonium hydroxide as pH modifiers. The solutions used in this test were prepared from process water. The contact angle from this wettability test at pH 11.3 was found to be 38° for sodium hydroxide and 53° for the ammonium hydroxide. The bitumen surface at pH 11.3 is much less hydrophobic when compared to the surface at pH 8.5 for sodium hydroxide, while using ammonium hydroxide the contact angles are similar for both pH 8.5 and 11.3. The bitumen surfaces at pH 8.5 for both pH modifiers and at pH 11.3 the ammonium hydroxide as pH modifier possess a larger contact angle than at pH 11.3 with sodium hydroxide as pH modifier. This finding indicates that the bitumen surface is more hydrophobic in these conditions. A higher contact angle at pH 11.3 for ammonium hydroxide corresponds well with an increase in bitumen recovery. The more hydrophobic, the bitumen surface the more likely it will float to the surface of pulp, leading to a higher bitumen recovery.

3.5 *Zeta Potential Measurement*

3.5.1 *pH 8.5*

The zeta potential for both bitumen droplets and air bubbles was measured to see how the different caustics affect the surface charge and its role in bitumen liberation and aeration. The results of the zeta potential measurements at pH 8.5 adjusted using both sodium hydroxide and ammonium hydroxide solutions are shown in Table 4. The zeta potential values obtained in this study agree well with the literature values determined using sodium hydroxide as the pH modifier in both the bitumen emulsion and the air bubble suspension (Liu et al. 2002 and Elmahdy 2008). It can be seen from the results in Table 4 that the zeta potentials measured at pH 8.5 adjusted by either sodium hydroxide or ammonium hydroxide are very similar for bitumen emulsions or air bubbles. This finding suggests that the cationic counterions (Na^+ and NH_4^+) has a similar effect on the surface charges of both the bitumen droplets and air bubbles, most likely as a simple electrolyte. With the surface charges being comparable, one would anticipate similar bitumen recovery with the two caustics as pH modifiers as was seen in Figures 17 and 18.

Table 3: Zeta potential of bitumen emulsions and air bubbles in fresh process water and tailings water at pH 8.5

	Zeta Potential (mV)		
	Bitumen Emulsions		Air Bubbles
	Tailings Water		
	A1 Ore	C-ore	Process Water
pH modifier	8.5	8.5	8.5
NaOH	-37.5	-33.2	-24.7
NH4OH	-34.6	-36.3	-21.6

The zeta potential was measured at pH 11.3 to see how both the bitumen and air bubble surfaces were affected by the various tailings and process water. The results for the bitumen emulsions and air bubble suspension at pH 11.3 are summarized in Table 6. The measured zeta potential values for bitumen emulsions agree well with literature values when sodium hydroxide was used as pH modifier (Liu et al. 2002). For all the cases, the zeta potential was more negative at pH 11.3 than at pH 8.5 for the bitumen droplets. This was not the case for the air bubble suspensions. Zeta potential measured at pH 11.3 with sodium hydroxide as pH modifier was more negative than that with ammonium hydroxide as pH modifier. The zeta potential measured at pH 11.3 with ammonium hydroxide as pH modifier was very similar to that measured at pH 8.5. It can also be seen in all the cases that the zeta potential measured at pH 11.3 with ammonium hydroxide as pH modifier was less negative. A less negative zeta potential leads to a smaller electrical repulsive force. This reduced repulsive force allows for a greater chance of bitumen-air attachments. With more attachment there will be more bitumen floated to the surface, i.e. greater bitumen recovery. A less negative zeta potential, therefore, helps to show that using ammonium hydroxide will help increase bitumen recovery.

The zeta potential of the bubbles in solution also became more negative with increasing pH to 11.3 for sodium hydroxide as pH modifier. This corresponds well with literature data as more hydroxide ions in solution create a more negative environment. It can also be seen that at pH 11.3 with ammonium hydroxide as pH modifier, a much less negative zeta potential was obtained for air bubbles. Reducing this zeta potential by almost half will greatly reduce the electrical repulsion between bitumen and air bubble leading to a great chance of bitumen-air attachment. Overall, the reduction in negative zeta potential for both bitumen and air bubble at pH 11.3 with ammonium hydroxide as pH modifier leads to a greater bitumen recovery as seen in the Denver cell flotation experiments. This decrease in electrical repulsive force was responsible for the increased chance of a bitumen-air attachment. The negatively charged air bubbles attract the positively charged ammonium ions, reducing the overall surface charge. The less negative zeta potential values can also be attributed to a compressed double layer. At pH 11.3 much more ammonium hydroxide than sodium hydroxide was needed to adjust the solution pH. This greater amount of ions in the solution will cause the double layer to compress. The double layer compression reduces the effective distance of the double layer interaction forces. The effects on the double layer forces help explain the large increase in bitumen recovery seen in Figures 19 and 20.

Table 4: Zeta potential of bitumen emulsions and air bubbles in fresh process water and tailings water at pH 11.3

	Zeta Potential (mV)			
	Bitumen Emulsions			Air Bubbles
		Tailings Water		
	Process Water	C-Ore	A1 Ore	Process Water
pH	11.3	11.3	11.3	11.3
NaOH	-83.1	-80.4	-79.4	-38.8
NH_4OH	-72.8	-73.3	-71.9	-22.4

3.6 *Surface Tension Measurement*

The surface tension of the tailings water was measured to determine how the addition of different caustics affects the extraction of natural surfactants from bitumen and its role in bitumen liberation and aeration at pH 8.5 are shown in Table 5. As with all of the other results and analysis, the surface tension values at pH 8.5 are quite close to each other for tailings water from processing A1 ore and C-ore using both caustics as pH modifiers. Again, the similarity in surface tension measurements explains similar bitumen recovery shown in Figures 17 and 18.

Table 5: Surface tension of tailings water at pH 8.5.

pH modifier	Surface Tension (mN/m)	
	Tailings Water	
	A1 Ore	C-ore
NaOH	61.3	62.9
NH_4OH	61.9	61.4

The surface tension of the tailings water at pH 11.3 adjusted by either sodium hydroxide or ammonium hydroxide was measured to determine how the type of caustics affects the bitumen recovery. The results are shown in Table 7. The surface tension is much lower at pH 11.3 than the values at pH 8.5 for both pH modifiers. At pH 11.3 the surface tension of tailings water with sodium hydroxide as pH modifier is lower than that with ammonium hydroxide as pH modifier. The lower surface tensions can be attributed to a greater release of natural surfactants from the bitumen. A lower surface tension may not be a key parameter in bitumen floatability, as suggested by Kasongo et al. (2000).

Table 6: Surface tension of adjusted process water and tailings water at pH 11.3

pH modifier	Surface Tension (mN/m)		
		Tailings Water	
	Process Water 11.3	C-Ore 11.3	A1 Ore 11.3
NaOH	70.8	49.3	39.7
NH_4OH	68.6	56.8	45.2

3.7 *Surfactant Analysis*

The natural surfactants, mainly napthenic acids, which lowered the surface tension of the tailings water, were extracted from all of the tailings water from bitumen flotation tests. The results from these extraction tests at pH 11.3 are shown in Table 8. From this table it can be seen that for the all cases the sodium hydroxide released a higher concentration of surfactants into the solution. These natural surfactants carry a negative charge with them, which would lead to a more negative zeta potential of the bitumen-water and air-water interface. A more negative zeta potential increases the electrical repulsive force between bitumen and air bubble, thus reducing bitumen flotation recovery, which was seen during the bitumen recovery tests with the results in Figures 19 and 20.

Table 7: Napthenic acid concentration extracted from various tailings water using a dichloromethane extraction technique. *

	Carboxylic Acid Concentration (ppm)	
	C-ore	A1
pH modifier	11.3	11.3
NaOH	64.0	74.5
NH_4OH	52.3	54.9

*The analysis was conducted by Marjan Tamiz.

The similar bitumen recovery at pH 8.5 using either sodium hydroxide or ammonium hydroxide as pH modifier can be attributed to similar DBL characteristics and bitumen air bubble attachment. The similar DBL characteristics and bitumen recovery at pH 8.5 with either sodium hydroxide or ammonium hydroxide as pH modifier can be attributed to the small amount of the caustic at approximately 1mL of either sodium hydroxide or ammonium hydroxide added to 1L of process water needed to adjust the process water to pH 8.5, leading to similar surface wettability and surface charge of bitumen and surface tension of tailings water as if no pH modifiers were added.

The increase in bitumen recovery when using ammonium hydroxide at pH 11.3 for both A1 and C-ore can be attributed to several factors. These factors include shorter bitumen to air bubble attachment time, more hydrophobic bitumen surface, less negative surface charges, larger surface tension measurements and a decrease in the release of natural surfactants. It is noted that, more ammonium hydroxide than ammonium hydroxide is necessary to adjust the pH of the process water to pH 11.3, leading more ions in solution and a larger effect on the overall process. Clearly, ammonium hydroxide is more favorable as process aids to improve bitumen liberation and recovery from oil sands ores.

3.8 *Froth Quality*

For each of the bitumen recovery tests the froth quality was analyzed. This allowed for the bitumen to solids ratio to be calculated. These ratios are shown in Figures 23 and 24 for A1 ore and C-ore, respectively. The bitumen to solids ratio was calculated using Equation (1.5). For both ores the bitumen to solids ratio increased greatly as the pH increased using ammonium hydroxide as pH modifier. A similar trend occurs with sodium hydroxide for A1 ore, while the increase is much less in C-ore. The high bitumen to solids ratio when using A1 ore is due to the lack of fines in the ore. It appears that the coarse solids in A1 ore are more hydrophilic and harder to float. This trend in A1 ore may also be due to the lack of fines within the ore. The reason for the increasing bitumen to solids ratio when C-ore and ammonium hydroxide are utilized is that the clays may be better dispersed by ammonium hydroxide at pH 11.3. This is just a speculation as more tests would have to be completed to understand the effects of ammonium hydroxide on the clays and the settling of the tailings.

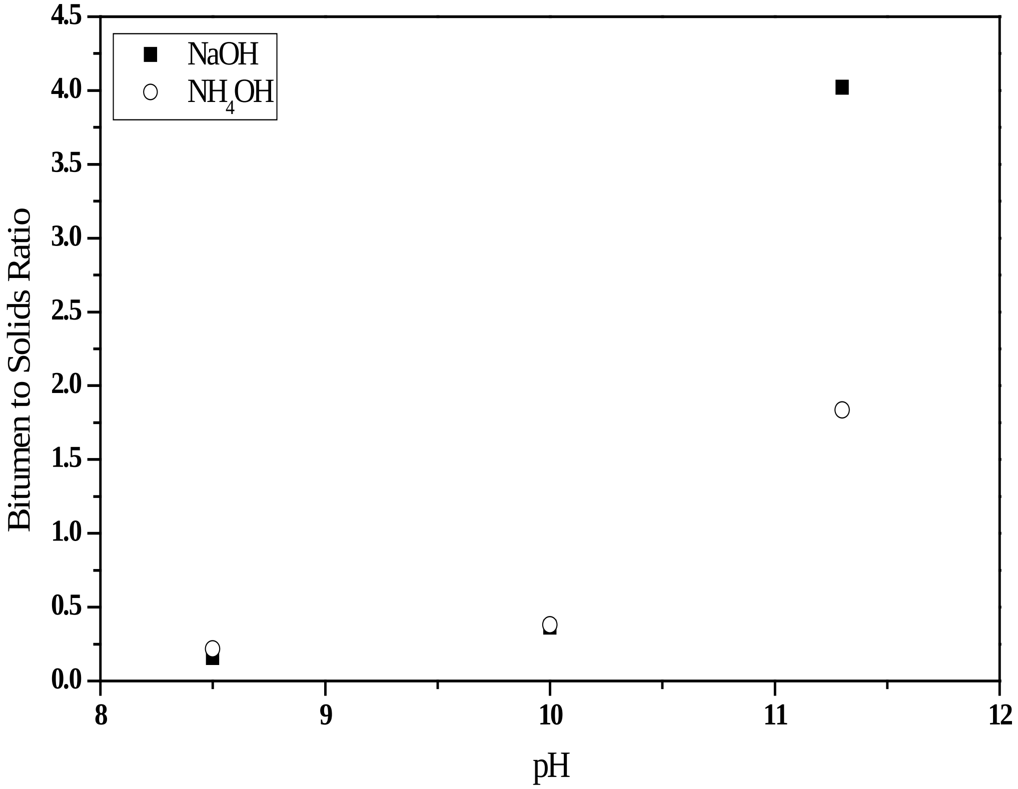


Figure 23: Bitumen to solids ratio from froth analysis of A1 ore bitumen flotation tests at various pH

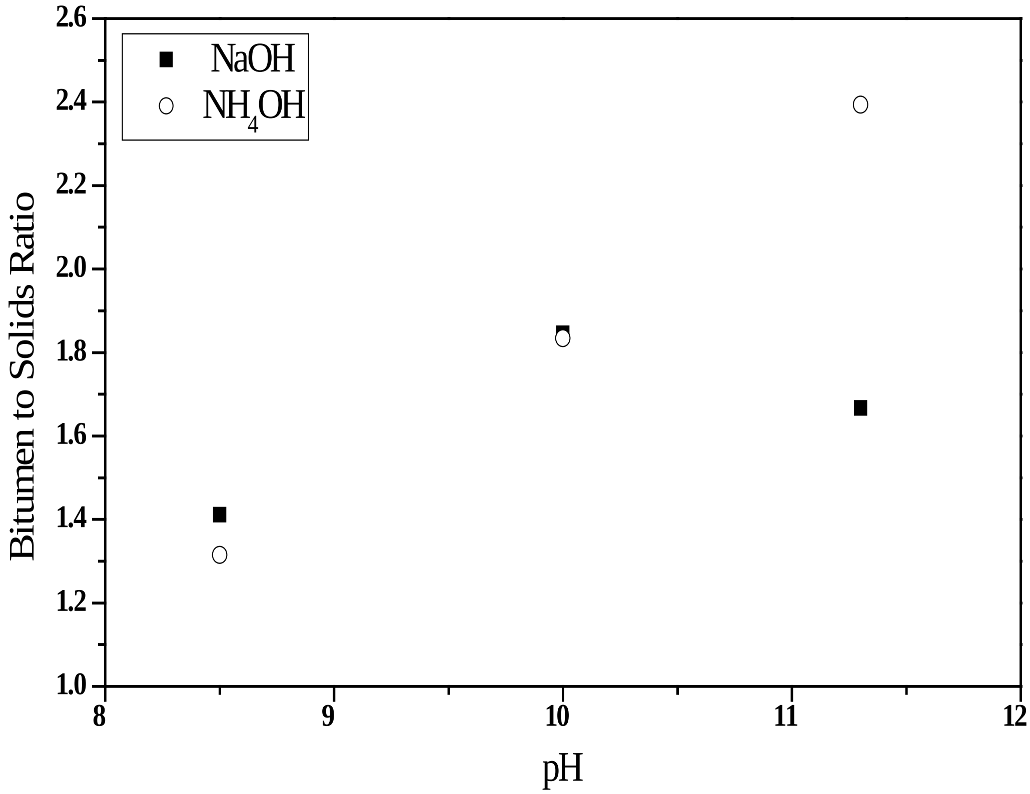


Figure 24: Bitumen to solids ratio from froth analysis of C-ore bitumen flotation tests at various pH

Chapter 4: CONCLUSIONS

The bitumen liberation in this study was done in real time on actual oil sands ore, while a majority of previous bitumen liberation studies have been conducted on simulated oil sands ores. The objectives of this study were to determine the role of two different caustics, sodium hydroxide and ammonium hydroxide, in the bitumen extraction process. This objective was carried out in two parts: the first part was the bitumen liberation and the second was the bitumen recovery. The bitumen liberation was viewed using a novel flow in-situ bitumen liberation visualization cell (FIBLVC) setup, while the bitumen recovery was completed in a Denver Cell with Dean Stark analysis completed on the froth.

The bitumen liberation, as seen in the novel FIBLVC, showed that both sodium hydroxide and ammonium hydroxide performed similarly at pH 8.5 and 11.3 on all three ores (A1, C-ore and SunP210). As well, the bitumen displacement, both rate and overall, was seen to increase with increasing pH from 8.5 to 11.3. This increased displacement was seen on all three ores. The three ores were all very similar in bitumen, water and solids content but differed greatly in fines content. The fines content increased from A1 ore to SunP210 and a decrease in bitumen displacement with increasing fines content was seen.

The bitumen recovery was shown to be very similar for both sodium hydroxide and ammonium hydroxide at pH 8.5 on both A1 ore and C-ore. A large increase in bitumen recovery was seen on both A1 ore and C-ore at pH 11.3 when ammonium hydroxide was used. This increase can be attributed to a shorter induction time, a more hydrophobic bitumen surface, a less negative surface charge of bitumen and air bubble in tailings water, a higher surface tension of tailings and a decrease in natural surfactant release. For ammonium hydroxide, the froth quality improved as pH was increased. This leads to ammonium hydroxide clearly being a more favorable process aid in the oil sands extraction process.

Chapter 5: PRECAUTIONS AND FUTURE WORK

Precautions:

Ammonium hydroxide has several attractive features including the increased recovery as seen in the results of this report. While there are these attractive qualities, there are also several drawbacks to the use of ammonium hydroxide.

The main drawback is the smell. Ammonium hydroxide dissociates into ammonia which has a very strong odour. This strong pungent smell could lead to problems in the surrounding community if it is being implemented in a plant. As well the gases can lead to damage of the throat and nasal passages after prolonged exposure without the proper safety equipment.

Another problem with ammonium hydroxide is that it has been found to be toxic to aquatic life in mid to high concentrations. This could lead to problems if it seeps into the ground water during the SAGD process.

The last drawback is the corrosive nature of ammonia. This may cause problems further down the process if precautions are not taken to protect the equipment.

Future Work:

There are several adjustments that can be recommended for the FIBLVC. The first is the addition of baffles into the flow channel to create a turbulent. This would allow for the visualization of bitumen liberation under a turbulent regime. The next modification would be the addition of a thicker viewing plate with a valve attached to it. Adding this to the cell would let the cell be filled slowly with any solution so that very initial recession can be recorded. The final suggestion is not for the cell but for the analysis of the data collected from the cell. It is recommended that a new method of analysis be created using only a computer program so that it takes all of human subjectivity out of the analysis. It would also allow for faster quantification.

It is recommended for the study of ammonium hydroxide (NH_4OH) to be completed further down the line in the extraction process. Therefore, studying the settling of the tailings and any other way the NH_4OH affects downstream processes would be crucial to completely understanding if it is a viable replacement for sodium hydroxide.

The liberation and recovery can also be subjected to other caustic additions (i.e. sodium bicarbonate). This would be to see if there are any other viable options to replace sodium hydroxide as the caustic addition. As well, various polymers can be tested to see their effects on bitumen liberation and recovery.

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APPENDIX A: Experimental Data

This appendix contains tabulated data for all experimental work completed during this research. The data here was used to create the figures and tables seen throughout the thesis.

Liberation

Table A1: Liberation data for A1 ore at 35°C, pH 8.5 and 11.3 for ammonium hydroxide

Time (s)	Number of Grains		Average Percent Cleared	
	pH 8.5	pH 11.3	pH 8.5	pH 11.3
50	28	22	53.3	61.2
100	28	22	58.7	65.7
200	28	22	59.9	68.4
300	28	22	61.4	71.3
400	28	22	65.7	74.3
500	28	22	66.9	77.2
600	28	22	67.5	78.9

Table A2: Liberation data for A1 ore at 35°C, pH 8.5 and 11.3 for sodium hydroxide

Time (s)	Number of Grains		Average Percent Cleared	
	pH 8.5	pH 11.3	pH 8.5	pH 11.3
50	31	24	51	60.3
100	31	24	57.7	64.3
200	31	24	59.5	67.4
300	31	24	61.5	69.7
400	31	24	64.3	72.6
500	31	24	65.4	76
600	31	24	66.3	76.7

Table A3: Liberation data for C- ore at 35°C, pH 8.5 and 11.3 for ammonium hydroxide

Time (s)	Number of Grains		Average Percent Cleared	
	pH 8.5	pH 11.3	pH 8.5	pH 11.3
50	44	33	43.3	53
100	44	33	50.2	62.3

200	44	33	53	65.5
300	44	33	54.9	66.7
400	44	33	56.5	67.4
500	44	33	58	69.7
600	44	33	60.3	70.1

Table A4: Liberation data for C- ore at 35°C, pH 8.5 and 11.3 for sodium hydroxide

Time (s)	Number of Grains		Average Percent Cleared	
	pH 8.5	pH 11.3	pH 8.5	pH 11.3
50	41	26	45.5	52.9
100	41	26	52.3	61.1
200	41	26	53.9	64.4
300	41	26	54.6	66.2
400	41	26	56	66.8
500	41	26	58.1	68.5
600	41	26	59.4	69.7

Table A5: Liberation data for SunP210 ore at 35°C, pH 8.5 and 11.3 for ammonium hydroxide

Time (s)	Number of Grains		Average Percent Cleared	
	pH 8.5	pH 11.3	pH 8.5	pH 11.3
50	73	69	35.6	39.4
100	73	69	37.6	46.1
200	73	69	39	48.8
300	73	69	41	51
400	73	69	41.2	52.3
500	73	69	41.5	52.6
600	73	69	42.1	53.3

Table A6: Liberation data for SunP210 ore at 35°C, pH 8.5 and 11.3 for sodium hydroxide

Time (s)	Number of Grains		Average Percent Cleared	
	pH 8.5	pH 11.3	pH 8.5	pH 11.3
50	75	61	34.9	39.4
100	75	61	36.3	44
200	75	61	38.4	47.6
300	75	61	40.7	48.3

400	75	61	40.7	49.2
500	75	61	41.3	50.2
600	75	61	41.7	52.3

Table A7: Reproducibility data for A1 ore using NH_4OH at pH 11.3

Time (s)	Average Percent Cleared		Average Percent Cleared	
	pH 11.3	pH 11.3	11.3	pH 11.3
50	58.4	60.3	56.7	59.9
100	63.5	64.3	61.2	62.3
200	66.6	67.4	65.3	65.5
300	68.3	69.7	69.6	67.1
400	70.2	72.6	71.7	68.9
500	73.1	76	74.5	70.8
600	74.8	76.7	76.6	73.1

Recovery

Table A8: Recovery data from all Denver cell runs.

Run	Date	Recovery Time (min)	Bitumen Recovered (g)	Total Recovered/Total Bitumen	Percent Recovered (%)
NaOH 8.5 Vince A1	May 11	5	1.45	1.45/36.787	3.94
		10	1.75	3.2/36.787	8.70
		15	1.75	4.95/36.787	13.46
		20	5.15	10.1/36.787	27.46
NH_4OH 8.5 Vince A1	May 12	5	0.95	0.95/36.821	2.58
		10	2.3	3.25/36.821	8.83
		15	3.55	6.8/36.821	18.47
		20	3.8	10.6/36.821	28.78
NaOH 11.3 Vince A1	May 16	5	1.95	1.95/36.820	5.30
		10	3.7	5.65/36.820	15.34
		15	3.25	8.9/36.820	24.17
		20	3.15	12.05/36.820	32.73
NH_4OH 11.3 Vince A1	May 17	5	25.7	25.7/36.822	69.80
		10	2.85	28.55/36.822	77.54
		15	1.15	29.7/36.822	80.66
		20	0.95	30.65/36.822	83.24
NH_4OH 11.3 Vince A1	May 19	5	27	27/36.778	73.41
		10	3.05	30.05/36.778	81.71
		15	1.15	31.2/36.778	84.83

		20	0.7	31.9/36.778	86.74
NaOH 11.3 C-ore	June 14	5	0.8	0.8/37.848	2.11
		10	1.6	2.4/37.848	6.34
		15	2.15	4.55/37.848	12.02
		20	1.8	6.35/37.848	16.78
NH_4OH 11.3 C-ore	June 18	5	5.4	5.4/37.844	14.27
		10	6.1	11.5/37.844	30.39
		15	5.25	16.75/37.844	44.26
		20	3.65	20.5/37.844	53.91
NH_4OH 10.0 Vince A1	August 23	5	5.3	5.3/36.817	
		10	7.0	12.3/36.817	
		15	7.35	19.65/36.817	
		20	5.15	24.8/36.817	67.36
NaOH 8.5 C-ore	August 25	5	1.4	1.4/37.801	
		10	2.95	4.35/37.801	
		15	3.2	7.55/37.801	
		20	3.6	11.15/37.801	29.50
NH_4OH 8.5 Vince A1	August 26	5	0.75	0.75/36.795	
		10	2.7	3.45/36.795	
		15	3.7	7.15/36.795	
		20	5.95	13.1/36.795	35.60
NaOH 10.0 Vince A1	August 27	5	1.7	1.7/36.833	
		10	2.5	4.2/36.833	
		15	4.05	8.25/36.833	
		20	5.8	14.05/36.833	36.37
NaOH 10.0 C-ore	Sept 1	5	0.95	0.95/37.908	
		10	1.7	2.65/37.908	
		15	2.35	5.0/37.908	
		20	3.35	8.35/37.908	22.03
NH_4OH 10.0 C-ore	Sept 2	5	1.05	1.05/37.816	
		10	2.35	3.4/37.816	
		15	4.55	8.95/37.816	
		20	5.8	13.75/37.816	36.36
NaOH 8.5 Vince A1	Sept 6	5	0.95	0.95/36.835	
		10	1.65	2.6/36.835	
		15	2.05	4.65/36.835	
		20	4.3	8.95/36.835	24.30
NH_4OH 8.5 Vince A1	Sept 8	5	0.9	0.9/36.817	
		10	1.1	2.0/36.817	
		15	3.55	5.55/36.817	
		20	4.5	10.05/36.817	27.30
NH_4OH 11.3 Vince A1	Sept 9	5	21.5	21.5/36.775	
		10	5.5	27/36.775	
		15	2.35	29.35/36.775	
		20	1.05	30.4/36.775	82.67

NH_4OH 8.5 C-ore	Sept 9	5	2.2	2.2/37.866	
		10	2.8	5.0/37.866	
		15	3.25	8.25/37.866	
		20	4.5	12.75/37.866	33.67
NaOH 11.3 Vince A1	Sept 10	5	1.75	1.75/36.794	
		10	2.9	4.65/36.794	
		15	3.65	8.3/36.794	
		20	3.85	12.15/36.794	33.02
NH_4OH 11.3 Vince A1	Sept 24	5	25.35	25.35/36.558	
		10	4.7	30.05/36.558	
		15	1.15	31.2/36.558	
		20	1.0	32.2/36.558	
NH_4OH 11.3 Vince A1	Sept 28	5	17.9	17.9/36.837	
		10	5.55	23.45/36.837	
		15	2.4	25.85/36.837	
		20	2.7	28.55/36.837	77.50

Induction Time

Table A9: Induction time results for all runs.

Run	Contact Time (ms)	# of Attachments	Percent Attached (%)
NH_4OH 11.3	300	0	0
	400	1	5
	500	6	30
	600	8	40
	700	14	70
	900	18	90
	1000	20	100
	1100	20	100
NaOH 11.3	1000	0	0
	1500	5	25
	2000	9	40
	2500	16	80
	3000	20	100
NH_4OH 8.5	500	0	0
	750	5	25
	1000	11	55
	1250	14	70
	1500	17	85
	1750	19	95
	2000	20	100
NaOH 8.5	500	0	0

	750	5	25
	1000	9	45
	1250	13	65
	1500	18	90
	2000	20	100
NaOH 8.5 (w/ kerosene)	500	0	0
	750	8	40
	1000	11	55
	1250	14	70
	1500	18	90
	2000	20	100

Contact Angle

Table A10: Drop Shape Analysis data for a process water droplet on a bitumen surface in air

pH	Static Contact Angle (°)							
	8.5				11.3			
	Run A	Run B	Run C	Average	Run A	Run B	Run C	Average
Sodium Hydroxide	97.9	92.6	95.1	95.3	98.0	95.3	95.7	96.3
Ammonium Hydroxide	97.6	95.8	97.5	97.0	94.1	93.2	97.0	94.8

Table A11: Drop Shape Analysis data for an air bubble on a bitumen surface in adjusted process water

pH	Static Contact Angle (°)							
	8.5				11.3			
	Run A	Run B	Run C	Average	Run A	Run B	Run C	Average
Sodium Hydroxide	58.5	57.9	60.6	59.0	36.8	40.1	35.0	37.7
Ammonium Hydroxide	57.5	59.3	55.7	57.5	51.1	54.0	53.3	52.8

Zeta Potential

Table A12: Zeta potential data for all process water and bitumen emulsions

Record	Sample Name	ZP (mV)	Mob (µmcm/Vs)	Cond (mS/cm)	Mean Count Rate (kcps)	Derived Count Rate (kcps)	Measured Voltage (V)
1	NH4OH 11.3 PW 1	-77.9	-6.108	1.24	60.1	42434.7	4.78
2	NH4OH 11.3 PW 2	-73.5	-5.764	1.25	93.5	65971.6	4.78
3	NH4OH 11.3 PW 3	-72.2	-5.662	1.25	139.8	98681.9	4.79
4	NH4OH 11.3 PW 4	-67.7	-5.308	1.25	79.6	56162.9	4.79
5	NH4OH 11.3 PW 5	-70.7	-5.539	1.25	81	57157.2	4.79
11	NH4OH 11.3 PW 1	-77.5	-6.074	1.24	82.8	58450.2	4.79
12	NH4OH 11.3 PW 2	-76.7	-6.011	1.25	103.8	73240.8	4.79
13	NH4OH 11.3 PW 3	-71.7	-5.617	1.24	104.5	73746.9	4.79
14	NH4OH 11.3 PW 4	-70.6	-5.532	1.24	98.4	69452.9	4.79
15	NH4OH 11.3 PW 5	-69.5	-5.452	1.24	139.9	98757.7	4.79
6	NaOH 11.3 PW 1	-75.5	-5.921	1.25	142	39266.1	4.78
7	NaOH 11.3 PW 2	-82.4	-6.459	1.25	346.4	95796.1	4.77
8	NaOH 11.3 PW 3	-84.4	-6.617	1.25	226.8	62734.3	4.77

9	NaOH 11.3 PW 4	-84.9	-6.656	1.25	254.7	70448.9	4.77
10	NaOH 11.3 PW 5	-82.7	-6.486	1.25	373.5	103294.5	4.77
26	NaOH 11.3 PW 1	-83.1	-6.516	3.89	28.4	20063.3	4.79
27	NaOH 11.3 PW 2	-86.7	-6.8	4.08	126.1	89044.5	4.79
28	NaOH 11.3 PW 3	-85.7	-6.72	4.13	80.5	56806.8	4.79
29	NaOH 11.3 PW 4	-82.5	-6.465	4.15	70.5	49760.6	4.78
30	NaOH 11.3 PW 5	-82.6	-6.475	4.17	99.8	70451.5	4.78

Table A13: Zeta potential date for all A1 ore tailings water and bitumen emulsions

Record	Sample Name	ZP (mV)	Mob (µmcm/Vs)	Cond (mS/cm)	Mean Count Rate (kcps)	Derived Count Rate (kcps)	Measured Voltage (V)
71	NaOH VA1 11.3 TW 1	-72.7	-5.703	1.26	191.3	52910.1	4.78
6	NaOH VA1 11.3 TW 1	-76.1	-5.967	4.36	549.4	43557.9	4.79
7	NaOH VA1 11.3 TW 2	-82.3	-6.452	4.95	682.7	54124.2	4.78
8	NaOH VA1 11.3 TW 3	-80.9	-6.345	4.99	714.9	56679.7	4.78
9	NaOH VA1 11.3 TW 4	-81.7	-6.404	5.01	536	42495.3	4.78

10	NaOH VA1 11.3 TW 5	-81.3	-6.374	5	518.9	41142.1	4.78
71	NaOH VA1 11.3 TW 1	-72.7	-5.703	1.26	191.3	52910.1	4.78
83	NaOH VA1 11.3 TW 1	-84.6	-6.629	4.81	289.9	80162.5	4.78
84	NaOH VA1 11.3 TW 2	-88.6	-6.948	5.04	397.7	109973.4	4.77
85	NaOH VA1 11.3 TW 3	-85.8	-6.723	5.06	237.9	65783.5	4.77
24	NaOH VA1 11.3 TW 1	-74.5	-5.84	1.26	29.2	20601.4	4.77
25	NaOH VA1 11.3 TW 2	-75.8	-5.938	1.26	107.6	75987.8	4.77
26	NaOH VA1 11.3 TW 3	-75.1	-5.891	1.26	94.6	66798.9	4.77
27	NaOH VA1 11.3 TW 4	-74.8	-5.866	1.26	93.7	66174.8	4.77
28	NaOH VA1 11.3 TW 5	-73.9	-5.795	1.26	87.4	61678.5	4.77
83	NaOH VA1 11.3 TW 1	-84.6	-6.629	4.81	289.9	80162.5	4.78
84	NaOH VA1 11.3 TW 2	-88.6	-6.948	5.04	397.7	109973.4	4.77
85	NaOH VA1 11.3 TW 3	-85.8	-6.723	5.06	237.9	65783.5	4.77
44	NaOH VA1 10.0 TW 1	-55.9	-4.385	2.72	139.2	38486.7	4.83
45	NaOH VA1 10.0 TW 2	-58.6	-4.597	2.94	387.7	107209.1	4.83
4	NaOH	-57.5	-4.505	2.96	215.6	59612.	4.83

6	VA1 10.0 TW 3 NaOH				9	
47	VA1 10.0 TW 4 NaOH	-57.1	-4.476	2.98	229.2	63383.6	4.83
48	VA1 10.0 TW 5 NaOH	-60.5	-4.742	3	147.1	40670.1	4.82
49	VA1 10.0 TW 1 NaOH	-51.3	-4.019	1.22	11.3	18801.5	4.83
50	VA1 10.0 TW 2 NaOH	-49.1	-3.852	1.21	64.3	107029.8	4.83
51	VA1 10.0 TW 3 NaOH	-48.8	-3.828	1.21	46.5	77502.6	4.83
52	VA1 10.0 TW 4 NaOH	-49.7	-3.895	1.21	40.4	67235.8	4.83
53	VA1 10.0 TW 5 NaOH	-49.1	-3.852	1.21	30.4	50680.2	4.83
54	VA1 8.5 TW 1 NaOH	-37.9	-2.973	2.65	47.5	33510.1	4.84
55	VA1 8.5 TW 1 NaOH	-40.7	-3.194	2.83	62.1	43856.8	4.84
56	VA1 8.5 TW 1 NaOH	-40.2	-3.155	2.83	64.7	45699.9	4.84
57	VA1 8.5 TW 1 NaOH	-42.1	-3.301	2.83	56.5	39877.9	4.84
58	VA1 8.5 TW 1 NaOH	-42.4	-3.324	2.83	154.4	109021.8	4.84
29	VA1 8.5 TW 1 NaOH	-34.8	-2.724	2.39	113.3	31335	4.85
30	VA1 8.5 TW 2 NaOH	-40.7	-3.189	2.66	110.8	30652	4.84
31	VA1 8.5	-38.4	-3.012	2.68	145.7	40292	4.84

	TW 3						
32	NaOH VA1 8.5 TW 4	-37.9	-2.968	2.68	105.5	29182.5	4.85
33	NaOH VA1 8.5 TW 5	-38.3	-3.003	2.7	204.6	56587	4.85
66	NaOH VA1 8.5 TW 1	-36.3	-2.843	1.21	388.2	107372.7	4.85
67	NaOH VA1 8.5 TW 2	-34.7	-2.72	1.21	148.2	40995.2	4.85
68	NaOH VA1 8.5 TW 3	-32	-2.507	1.2	73.4	20301.7	4.85
69	NaOH VA1 8.5 TW 4	-34.4	-2.693	1.21	181.4	50157.7	4.85
70	NaOH VA1 8.5 TW 5	-34.7	-2.718	1.21	90.3	24980.9	4.85
78	NH4OH VA1 11.3 TW 3	-74.9	-5.873	1.26	297.6	82296.4	4.76
79	NH4OH VA1 11.3 TW 4	-68.2	-5.348	1.26	349.1	96534.7	4.76
80	NH4OH VA1 11.3 TW 5	-66.3	-5.195	1.26	250.7	69341.4	4.76
1	NH4OH VA1 11.3 TW 1	-77	-6.038	1.26	291.9	80729.4	4.77
78	NH4OH VA1 11.3 TW 3	-74.9	-5.873	1.26	297.6	82296.4	4.76
79	NH4OH VA1 11.3 TW 4	-68.2	-5.348	1.26	349.1	96534.7	4.76
80	NH4OH VA1 11.3 TW 5	-66.3	-5.195	1.26	250.7	69341.4	4.76
104	NH4OH VA1 11.3 TW 3	-76.4	-5.99	3.21	381.9	8679.4	4.82

105	NH4OH VA1 11.3 TW 4	-74.9	-5.873	3.18	854.9	19430	4.82
106	NH4OH VA1 11.3 TW 5	-71.4	-5.596	3.17	1264.4	28736.5	4.82
107	NH4OH VA1 11.3 TW 1	-69	-5.411	3.5	23.5	16580.3	4.79
108	NH4OH VA1 11.3 TW 2	-73.6	-5.772	3.74	85.7	60511.1	4.79
109	NH4OH VA1 11.3 TW 3	-73.6	-5.769	3.75	55.1	38886.2	4.79
110	NH4OH VA1 11.3 TW 4	-71.9	-5.634	3.7	19	13444.1	4.79
111	NH4OH VA1 11.3 TW 5	-71.1	-5.57	3.76	58.4	41202.8	4.79
112	NH4OH VA1 11.3 TW 1	-65	-5.098	3.28	6.6	10967.4	4.81
113	NH4OH VA1 11.3 TW 2	-72.9	-5.718	3.5	14.8	24584.7	4.81
114	NH4OH VA1 11.3 TW 3	-69.7	-5.467	3.43	17.8	29712	4.81
115	NH4OH VA1 11.3 TW 4	-70.4	-5.518	3.4	15.6	25947.2	4.81
116	NH4OH VA1 11.3 TW 5	-66	-5.173	3.38	17.1	28487.5	4.81
125	NH4OH VA1 11.3 TW 1	-72.2	-5.662	3.34	75.1	20760.3	4.81
127	NH4OH VA1 11.3 TW 3	-78.6	-6.162	3.52	132.9	36759.2	4.81
129	NH4OH VA1 11.3 TW 5	-74.8	-5.862	3.51	178.2	49269	4.81
3	NH4OH	-53.8	-4.215	3.11	39.4	27790.	4.82

4	VA1 10.0 TW 1 NH4OH					5	
35	VA1 10.0 TW 2 NH4OH	-54.6	-4.282	3.31	66.8	47129.8	4.81
36	VA1 10.0 TW 3 NH4OH	-55.5	-4.348	3.32	125.1	88333.5	4.81
37	VA1 10.0 TW 4 NH4OH	-52.1	-4.086	3.32	52.7	37210.1	4.81
38	VA1 10.0 TW 5 NH4OH	-46.8	-3.667	3.32	51.5	36359.5	4.82
39	VA1 10.0 TW 1 NH4OH	-50.7	-3.974	3.06	79.8	22081.4	4.83
40	VA1 10.0 TW 2 NH4OH	-48	-3.759	3.35	188.1	52008.6	4.83
41	VA1 10.0 TW 3 NH4OH	-51.5	-4.036	3.37	170.5	47146.3	4.83
42	VA1 10.0 TW 4 NH4OH	-42.4	-3.324	3.38	96	26556.9	4.83
43	VA1 10.0 TW 5 NH4OH	-41	-3.216	3.39	144.1	39846.2	4.83
16	VA1 8.5 TW 1 NH4OH	-32.7	-2.565	2.54	70.3	19431.2	4.83
17	VA1 8.5 TW 2 NH4OH	-37.2	-2.919	2.85	236	65278.3	4.83
18	VA1 8.5 TW 5 NH4OH	-35.9	-2.815	2.81	94.7	26188	4.83
19	VA1 8.5 TW 1 NH4OH	-30.8	-2.415	1.22	45.3	12518.3	4.84
20	VA1 8.5 TW 2	-31.7	-2.487	1.22	167.5	46314.6	4.84
21	NH4OH VA1 8.5	-31.2	-2.445	1.22	110	30429.1	4.84

	TW 3						
22	NH4OH VA1 8.5 TW 4	-31.3	-2.456	1.22	84.6	23384.3	4.84
23	NH4OH VA1 8.5 TW 5	-32	-2.511	1.22	129.9	35930.2	4.84
59	NH4OH VA1 8.5 TW 1	-34.1	-2.676	2.78	77.5	21425.8	4.83
60	NH4OH VA1 8.5 TW 4	-35.7	-2.796	3	207.1	57264.2	4.83
61	NH4OH VA1 8.5 TW 3	-37.4	-2.932	2.85	149.9	41455.6	4.83
62	NH4OH VA1 8.5 TW 4	-36.4	-2.857	2.81	90.8	25124.2	4.83
63	NH4OH VA1 8.5 TW 2	-37.8	-2.963	2.99	217.7	60196.4	4.83
64	NH4OH VA1 8.5 TW 3	-37.2	-2.916	3	119.7	33101.2	4.83
65	NH4OH VA1 8.5 TW 5	-37.6	-2.95	3.01	91.7	25351.2	4.83

Table A14: Zeta potential data for all C-ore tailings water and bitumen emulsions

Record	Sample Name	ZP (mV)	Mob (μmcm/Vs)	Cond (mS/cm)	Mean Count Rate (kcps)	Derived Count Rate (kcps)	Measured Voltage (V)
1	NH4OH C-ore 11.3 TW 1	-76.4	-5.987	1.27	355.7	98364.7	4.73
6	NH4OH C-ore 11.3 TW 1	-75.5	-5.915	1.27	90.6	63958.9	4.75
7	NH4OH C-ore 11.3 TW 2	-78.6	-6.161	1.27	164.2	115921.6	4.74
1	NH4OH	-76.6	-6.003	1.27	66.9	47246	4.75

0	C-ore 11.3 TW 5						
71	NH4OH C-ore 11.3 TW 1	-71.3	-5.589	4.87	129.9	35932.2	4.76
72	NH4OH C-ore 11.3 TW 2	-71.7	-5.622	4.87	163.8	45298.7	4.76
73	NH4OH C-ore 11.3 TW 3	-68.1	-5.34	4.76	173.8	48066.3	4.76
74	NH4OH C-ore 11.3 TW 4	-68.1	-5.34	4.69	165.3	45715.3	4.76
75	NH4OH C-ore 11.3 TW 5	-73.4	-5.755	4.67	149.3	41284.6	4.76
51	NH4OH C-ore 10.0 TW 1	-47.4	-3.712	1.23	105	8323.5	4.82
52	NH4OH C-ore 10.0 TW 2	-46.4	-3.638	1.22	178.2	14124.6	4.82
53	NH4OH C-ore 10.0 TW 3	-44.9	-3.522	1.22	173.2	13727.8	4.82
54	NH4OH C-ore 10.0 TW 4	-44	-3.452	1.22	169.1	13410.2	4.82
55	NH4OH C-ore 10.0 TW 5	-42.1	-3.302	1.22	229.7	18207.2	4.82
56	NH4OH C-ore 10.0 TW 1	-46.5	-3.648	1.22	33	2619.5	4.84
57	NH4OH C-ore 10.0 TW 2	-44.5	-3.491	1.22	253.1	20066.1	4.84
5	NH4OH	-43.5	-3.409	1.22	361	28622.8	4.84

8	C-ore 10.0 TW 3						
59	NH4OH C-ore 10.0 TW 4	-44.1	-3.461	1.22	127.4	10102.2	4.84
60	NH4OH C-ore 10.0 TW 5	-43.7	-3.427	1.22	180.6	14314.4	4.84
21	NH4OH C-ore 8.5 TW 1	-38.9	-3.046	2.77	270.8	74902.9	4.85
23	NH4OH C-ore 8.5 TW 3	-38.7	-3.031	2.95	214.7	59375.5	4.85
26	NH4OH C-ore 8.5 TW 1	-35.7	-2.8	1.22	309.3	85551.7	4.85
27	NH4OH C-ore 8.5 TW 2	-34.7	-2.724	1.21	265.1	73322.1	4.85
28	NH4OH C-ore 8.5 TW 3	-33.1	-2.595	1.21	394	108955.5	4.85
29	NH4OH C-ore 8.5 TW 4	-34.9	-2.732	1.21	178.5	49365.8	4.85
30	NH4OH C-ore 8.5 TW 5	-35	-2.745	1.21	264.1	73029	4.85
62	NH4OH C-ore 8.5 TW 2	-37.3	-2.927	1.21	100.9	71261.6	4.85
63	NH4OH C-ore 8.5 TW 3	-38.7	-3.037	1.22	96.2	67895.6	4.85
76	NaOH C-ore 11.3 TW 1	-84.7	-6.643	3.89	177.4	125217.3	4.79
77	NaOH C-ore 11.3 TW 2	-87.1	-6.828	4.15	100.6	70982.7	4.79
78	NaOH C-ore 11.3	-87.1	-6.831	4.18	94.6	66813.5	4.79

	TW 3						
79	NaOH C-ore 11.3 TW 4	-88.4	-6.93	4.2	88.3	62328.4	4.79
80	NaOH C-ore 11.3 TW 5	-80.2	-6.291	4.2	129.6	91455.8	4.79
11	NaOH C-ore 11.3 TW 1	-81.2	-6.364	1.24	160.6	44426.9	4.81
12	NaOH C-ore 11.3 TW 2	-75.1	-5.886	1.25	364.8	100885.4	4.81
17	NaOH C-ore 11.3 TW 2	-77.3	-6.061	1.24	116.8	82473.5	4.79
18	NaOH C-ore 11.3 TW 3	-72.1	-5.654	1.25	110.1	77710.4	4.79
19	NaOH C-ore 11.3 TW 4	-71	-5.568	1.25	66.2	46702	4.79
41	NaOH C-ore 10.0 TW 1	-48	-3.764	1.2	116.5	9233.6	4.84
42	NaOH C-ore 10.0 TW 2	-44.2	-3.461	1.19	532	42173.6	4.85
43	NaOH C-ore 10.0 TW 3	-44.6	-3.497	1.2	223.9	17749.3	4.85
44	NaOH C-ore 10.0 TW 4	-41	-3.216	1.2	287.4	22787.1	4.84
45	NaOH C-ore 10.0 TW 5	-41.2	-3.23	1.2	98.6	7813.2	4.84
46	NaOH C-ore 10.0 TW 1	-48.2	-3.777	1.21	236.2	18726.6	4.86
47	NaOH C-ore 10.0 TW 2	-47.7	-3.737	1.2	483.8	38358.1	4.86
48	NaOH C-ore 10.0 TW 3	-46.1	-3.613	1.2	243.1	19269.5	4.85

49	NaOH C-ore 10.0 TW 4	-45.1	-3.533	1.2	219.8	17424	4.85
50	NaOH C-ore 10.0 TW 5	-45.5	-3.565	1.22	332.5	26360.1	4.85
31	NaOH C-ore 8.5 TW 1	-33.8	-2.646	1.22	237.4	18817.9	4.85
32	NaOH C-ore 8.5 TW 2	-33.7	-2.639	1.21	170.3	13500.2	4.85
33	NaOH C-ore 8.5 TW 3	-33.1	-2.593	1.21	176.4	13987.2	4.85
34	NaOH C-ore 8.5 TW 4	-33.3	-2.614	1.21	178.4	14141.6	4.85
35	NaOH C-ore 8.5 TW 5	-33	-2.583	1.21	200.8	15917	4.85
36	NaOH C-ore 8.5 TW 1	-35.6	-2.791	1.22	131.1	10391.6	4.85
37	NaOH C-ore 8.5 TW 2	-34.9	-2.734	1.21	398.9	31623	4.85
38	NaOH C-ore 8.5 TW 3	-30.8	-2.414	1.21	269	21330	4.85
39	NaOH C-ore 8.5 TW 4	-30.6	-2.396	1.21	642.3	50921.6	4.85

Table A15: Zeta potential data for air bubbles in solution

Record	Sample Name	ZP (mV)	Mob (µmcm/Vs)	Cond (mS/cm)	Mean Count Rate (kcps)	Derived Count Rate (kcps)	Measured Voltage (V)
3	air bubble Naoh 11.3 1	-37.1	-2.905	3.6	164.9	45616.4	4.81
4	air	-37.7	-2.952	3.79	166.4	46013.	4.81

	bubble					1	
5	Naoh 11.3 2 air bubble Naoh 11.3 3	-38	-2.981	3.78	242.8	67161.3	4.81
6	air bubble Naoh 11.3 4	-33.8	-2.648	3.79	262.3	72546	4.81
7	air bubble Naoh 11.3 5	-36.4	-2.857	3.77	214.9	59423.4	4.81
23	air bubble naoh 11.3 1	-39.2	-3.071	3.19	17.4	61.9	4.83
24	air bubble naoh 11.3 2	-41.1	-3.224	3.38	36	128.3	4.83
25	air bubble naoh 11.3 3	-41.2	-3.231	3.41	21.3	75.9	4.82
26	air bubble naoh 11.3 4	-42.7	-3.345	3.42	21.7	77.3	4.82
27	air bubble naoh 11.3 5	-41.2	-3.227	3.44	43	152.9	4.82
13	air bubble naoh 8.5 1	-24.8	-1.945	2.54	38.8	881.9	4.85
14	air bubble naoh 8.5 2	-25.3	-1.986	2.79	34.1	775.2	4.85
15	air bubble naoh	-24.5	-1.917	2.79	60.3	1369.5	4.85

	8.5 3						
16	air bubble naoh 8.5 4	-25.3	-1.981	2.79	181.5	4124.2	4.85
17	air bubble naoh 8.5 5	-23.7	-1.857	2.79	49.1	1115.9	4.85
18	air bubble NH4OH 8.5 1	-22.9	-1.792	2.89	150.7	536.1	4.85
19	air bubble NH4OH 8.5 2	-21.7	-1.698	2.93	176.6	628.4	4.85
20	air bubble NH4OH 8.5 3	-21.7	-1.7	2.93	125.7	447.4	4.84
21	air bubble NH4OH 8.5 4	-20	-1.569	2.97	99.1	352.5	4.84
22	air bubble NH4OH 8.5 5	-21.6	-1.694	2.98	50.8	180.6	4.84
28	air bubble nh4oh 11.3 1	-21.1	-1.658	3.09	29	2296.6	4.81
29	air bubble nh4oh 11.3 2	-22.3	-1.751	3.3	21	1665.4	4.8
30	air bubble nh4oh 11.3 3	-22	-1.724	3.27	14.6	1160.3	4.81

31	air bubble nh4oh 11.3 4	-21.3	-1.673	3.23	14.9	1184.2	4.81
32	air bubble nh4oh 11.3 5	-21.2	-1.664	3.2	9.5	752	4.81
8	air bubble NH4OH 11.3 1	-22.2	-1.744	3.24	6.9	4882.8	4.81
9	air bubble NH4OH 11.3 2	-23.4	-1.832	3.45	12	8476.9	4.81
10	air bubble NH4OH 11.3 3	-23.3	-1.83	3.49	25.3	17855.2	4.81
11	air bubble NH4OH 11.3 4	-23.8	-1.866	3.52	11.7	8224.7	4.81
12	air bubble NH4OH 11.3 5	-23.3	-1.824	3.52	11.8	8350.4	4.81

Surface Tension

Table A16: Surface Tension measurements of tailings water from A1 ore Denver Cell extractions

	Surface Tension (mN/m)									
	Vince A1									
pH	8.5					11.3				
	Run A	Run B	Run C	Run D	Avg.	Run A	Run B	Run C	Run D	Avg.
Sodium Hydroxide	60.07	61.33	60.69	62.95	61.26	41.13	40.14	37.76	39.88	39.73
Ammonium Hydroxide	64.17	59.37	63.15	61.23	61.98	45.55	44.33	44.75	46.05	45.17

Table A17: Surface Tension measurements of tailings water from C-ore Denver Cell extractions

	Surface Tension (mN/m)									
	C-ore									
pH	8.5					11.3				
	Run A	Run B	Run C	Run D	Avg.	Run A	Run B	Run C	Run D	Avg.
Sodium Hydroxide	64.14	62.77	61.52	63.01	62.86	50.83	47.99	48.73	49.45	49.25
Ammonium Hydroxide	60.56	62.84	61.33	60.95	61.42	57.8	56.52	55.89	57.11	56.83

Surfactant Recovery

Table A18: Surfactant recovery data from various Denver Cell extraction tailings waters

ID	H1(1743 cm-1)	H2(1706 cm-1)	Total H(cm-1)	Weight of DCM in Cell (g)	Carboxylic acids (ppm)
NH_4OH 11.3 Vince A1	0.092	0.03	0.12	20.067	54.90
NaOH 8.5 Vince A1	0.053	0.02	0.07	21.356	36.65
NaOH 11.3 Vince A1	0.123	0.052	0.175	21.094	79.23
NH_4OH 11.3 SunP210	0.092	0.036	0.128	23.111	65.08
NaOH 11.3 C-Ore	0.089	0.035	0.124	20.428	64.04
NaOH 11.3 SunP210	0.094	0.039	0.13	23.288	67.91
NH_4OH 11.3 C-Ore	0.082	0.03	0.115	20.451	52.27

APPENDIX B: Sample Calculations

This appendix contains sample calculations for all equations used. The calculations were repeated when necessary and used to create the figures throughout the thesis.

Liberation (using NH_4OH at 35°C on A1 ore at pH 11.3 and 200s of run time):

$$Percent\ Cleared = \frac{\sum \text{Percent cleared on each grain}}{\text{\# of Grains}}$$

$$\begin{aligned} Percent\ Cleared \\ = {} & \begin{matrix}(68.1 + 69.2 + 66.3 + 73.4 + 65.7 + 50.2 + 77.1 + 80.5 + 46.4 + 67.9 + 49.9 \\ +65.3 + 73.3 + 58.3 + 82.4 + 76.2 + 60.1 + 69.6 + 75.6 + 68.8 + 76.3 + 84.2)\end{matrix} \Big/ 22 \end{aligned}$$

$$= 68.4\ \%$$

Peclet Number (at a volumetric flow rate of 32mL/min):

$$Pe = \frac{V * L}{D}$$

$$V = \frac{v}{A} = \frac{32\left(\frac{mL}{\min}\right)}{(0.64 * 1.25)cm^2} * \frac{1cm^3}{1\ mL} * \frac{1min}{60s} * \frac{1m}{100cm} = 0.00667\frac{m}{s}$$

$$L = 12.7mm = .0127m$$

$$D = \frac{7.4 * 10^{-8}(\phi_w M_2)^{1/2} * T}{\eta_2 * V_1^{0.6}} = \frac{(7.4 * 10^{-8}) * \left((2.6 * 18.02)^{\frac{1}{2}} * (308)\right)}{(1.0) * (1000^{0.6})}$$

$$= 3.373 * 10^{-6}\frac{m^2}{s}$$

$$Pe = 0.00667 * \frac{0.0127}{3.373 * 10^{-6}} = 25.11$$

Recovery (after 20min using NH_4OH at pH 11.3 on A1 ore):

$$R(t) = \frac{Bitumen\ in\ froth\ (g)}{Bitumen\ in\ feedstock\ (g)} * 100$$

$$R(t) = \frac{31.9\ g}{36.75\ g} * 100 = 86.74\ \%$$

$$BSR = \frac{Cumulative\ Bitumen\ Recovered\ (g)}{Cumulative\ Solids\ in\ Froth\ (g)}$$

$$BSR = \frac{31.9\ g}{17.94\ g} = 1.78$$