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Study of Bitumen Liberation from Oil Sands Ores

by

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This thesis is dedicated to my parents, ***Mr. S.S.Rajagopalan*** *and* ***Mrs. Sumithra Rajagopalan****, and my family. I would have never achieved this feat without their love and blessings.*

I would also like to dedicate this thesis to my grandparents, their blessings and memories will always be with me.

Last but not the least, this thesis is dedicated to God who has given me the strength to accomplish my dreams.

*"****Sarvam Krishnarpanam****", in the spirit of Abject Dedication to Him- Bhagvad Gita 3.30*

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ABSTRACT

To better understand bitumen conditioning stage in oil sands extraction process a flow cell was designed to study bitumen liberation directly from sand grains, using real oil sand ore. A high-grade oil sand ore was subjected to various water temperatures and pH values to examine the bitumen liberation. The effect of weathering of the high-grade ore and the presence of salt in the water were also examined to evaluate their effect on bitumen liberation.

Bitumen liberation was found to be critically and proportionately dependent on solution (water) temperature and pH values. A high temperature of 46°C and pH value of 11.3 promoted fast liberation with a high bitumen liberation. High salt concentration complemented with a high pH value was found to be detrimental to bitumen liberation from a high-grade ore. Overall, this novel setup provided distinct, high quality images and interesting results, which aided in understanding the critical parameters behind bitumen liberation from an oil sand ore.

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Chapter 1: INTRODUCTION

1.1. Previous studies

Oil sands are also known as tar sands or bituminous sands. The world's two largest sources of bitumen are found in Canada and Venezuela. Canada also boasts the second largest global proven crude oil reserve after Saudi Arabia and accounts for 15% of the total world reserve. Canada's bitumen resources are located almost entirely within the province of Alberta and majorly found in three locations in the province: The Athabasca, Peace River and Cold Lake regions. The total oil sands area in Alberta is estimated to be around 140,200 km^2 with proven reserves of 170.4 billion barrels. Alberta Energy: Facts and Statistics (2010).

A typical oil sand ore primarily consists of bitumen, water, sand and clays (or fines). Oil sands can be visualized as an unconsolidated mineral sand matrix with bitumen. The Athabasca deposits in which minerals form the major part of the mined oil sands approximately contain 82-85% of mineral solids. The bitumen content in the oil sand ore varies from 1% - 18% by weight. Usually, an oil sand containing less than 7% of bitumen by weight is not considered economically feasible to mine but this poor grade ore can although be blend with stock of higher grade oil sands. An Oil sand with 8% - 10% is considered an average or transition grade ore while an oil sand with bitumen content greater than 10% is considered a rich or high-grade ore. On average, the bitumen is composed of 83.2% of Carbon, 10.4% of Hydrogen, 0.94% of oxygen and 4.8% of sulphur. The hydrocarbons in bitumen can be either naphthalene type (used in making gasoline and petrochemicals) or asphaltenes type (used in making asphalt). Masliyah et al. (2004)

The most important parameter that makes the oil sands of northern Alberta economically viable to extract with the present water based extraction technology is the “hydrophilic” or “water wet” nature of the sand grains. As suggested by Takamura (1982) that each sand grain is enveloped by a thin film of water (about 10 nm), which is further surrounded by continuum bitumen layer. This aqueous film is predicted to be stabilized due to the electrostatic forces arising from the electrical double layer at the oil/water interface and water/sand grain interface (Takamura, 1982; Hall et al., 1983; Anderson, 1986). It has also been suggested that only a fraction of the total water are present as films as rest were in the form of pedular rings at the grain to grain contact area, with the clay minerals suspended in the water phase (Cameron Engineers, 1978; Takamura, 1982). However, the existence of such a water film remains to be experimentally verified. The adverse low temperature during winter in Canada freezes the water layer present in the oil sands and makes the oil sand as hard as aged concrete. While in the summer the oil sands are as soft as molasses making driving conditions on it treacherous. Alberta Energy: Facts and Statistics (2010).

The hydrophilic nature of the sand grains in Athabasca deposits is the only reason which allows for water –based extraction methods, when compared to the hydrophobic character found in the oil sand deposits of Utah in USA (Sepulveda and Miller, 1978; Miller and Misra, 1982). Consequently, for such deposits, a solvent-based extraction method is suggested, which is yet to be proven economically profitable with the present technological advancement.

Zajic et al. (1981) proposed a paradoxical description regarding the microstructure of oil sands. His analysis was based on his experimental technique, which involved electron microscopic study of freeze-fractured samples. This technique involved rapid freezing of samples, which led the water in oil sands form glassy solids rather than crystals. The glassy solid formed was fractured using a sharp object. These fractured surfaces were later coated with carbon and platinum, after which the sample was melted and removed. Finally, electron micrographs of the oil sands samples were analyzed. It was proposed that water phase was present as droplets emulsified in bitumen. The droplets were predicted to be of the order of 0.5 microns while no evidence was found for the existence of water on sand or clay surfaces.

As the oil sands ores are classified based on their bitumen content, the percentage of fines and clays in the ore also play an important role in bitumen recovery from the oil sand ore. It has been found that the particle size distribution of the mineral solids can be correlated as a function of bitumen content in the ore while usually finer solids are present in low-grade ores. Therefore, study of solid particle composition and distribution in oil sand ore becomes more evident and meaningful. The mineral composition of sand varies with 90 %- 92% of quartz with traces of feldspar, mica, chert, rutile, muscovite, pyrite and tourmaline (Carrigy and Kramers, 1973; Boon, 1977). Mineral solids smaller than 44 microns are defined as fines in oil sands mineral terminology. Clays predominantly kaolinite and illite with small fractions of montmorillonite form the main constituent of fines found in the oil sand ores. It has been experimentally proven that high-grade ores contain fewer fines in comparison with poor grade ore, which are observed to contain high amount of fines (Masliyah et al., 2004).

Oil sand matrix has also been observed to contain various salts in connate water at different concentrations. The various inorganic ions present are sodium, potassium, calcium and magnesium. Bitumen content in oil sands ore is found inversely proportional to the ion concentrations in connate water. Put differently, rich oil sands usually found to have low salt content, while poor oil sands have high salt content in the connate water (Masliyah and Gray, 2010).

Our understanding of bitumen extraction at each individual step has extended from the macroscopic scale to down to molecular level with the development and adoption of advanced analytical instrumentations. However, the task to improve bitumen recovery, achieve better bitumen froth quality from poor processing ores and extracting bitumen from oil sands ore with at most environment friendliness is still a future challenge in oil sands processing.

From the fundamental point of view, Masliyah and Gray (2010) described the bitumen recovery process from oil sands using series of steps: i) Lump size reduction of oil sands ore in tumblers or hydro-transport pipelines leading to shearing of the outer lump surface; ii) Bitumen liberation from a sand grain takes place due to bitumen recession and three phase contact angle displacement of the bitumen film. This step is highly influenced by the process temperature, interfacial properties, mechanical agitation, and chemical additives; iii) the liberated bitumen globule after disengaging itself from the surface attaches to an air bubble. The attachment of bitumen globule to air bubble is also governed by the process temperature. At a low temperature (e.g. < 35 ^{o}C) the bitumen attaches to the droplet, whereas bitumen engulfs the air bubble under hot process water conditions (75-80 ^{o}C); and iv) Finally the aerated bitumen floats to the top of the separation vessel and is consequently recovered as bitumen froth. The complex bitumen extraction method is highly influenced by physical, chemical and hydrodynamic variables with interfacial phenomena playing a critical role in successful bitumen recovery from oil sands.

Sanford and Seyer (1979) went one-step farther in proposing an operating procedure for hot water extraction with their laboratory scale Batch Extraction Unit (BEU). The unit was designed specifically for studying the chemical and physical properties of the oil sands. They also successfully managed to demonstrate the importance of surfactants in the hot water extraction process. Their study highlighted that NaOH, when used as a process aid in hot water extraction improves bitumen recovery forming surfactants. They also indicated that NaOH addition leads to neutralization of organic acids in the bitumen, inducing the release of surfactants from the bitumen in the oil sand ores. The surfactants released played an important role during bitumen extraction and acted as primary agents responsible for improved bitumen recovery. Sanford (1983) further studied the possibility of ionic and inorganic processing aids in hot water extraction of bitumen from oil sands. Both inorganic bases and anionic surfactants were found to be identically effective in improving bitumen recovery, while non-ionic surfactants were found to be inefficacious towards improving bitumen recovery. Sanford also indicated that there exists an optimal amount of dosage for NaOH addition beyond which, was found detrimental for bitumen recovery. The amount of required NaOH addition in order to achieve maximum bitumen recovery was a function of the period of aging of the oil sands and the percentage of fines content in it. Importance of shear during bitumen extraction was highlighted and experimentally proven that sufficient amount of mechanical energy was needed to maximize bitumen recovery.

Ali (1975) studied aged or weathered oil sands for their poor processability and bitumen recovery. He ascribed the loss of connate water as the major reason behind the poor processabilty of the weathered ores. He associated the connate water loss from the oil sands matrix due to the destruction of structures of the oil sand ore.

Two types of natural surfactants (i.e., carboxylates and sulfates/sulphonates) were indentified to be released during extraction process into the oil sand slurry (Ali, 1978; Schramm and Smith, 1987). Further research by Drelich and Miller (1992) suspected the release of a cationic surfactant into the oil sands slurry during the course of their interfacial experiments at the bitumen/water interface. They suggested that in addition to viscosity considerations, interfacial tensions play an important role in hot water processing of oil sands

To reduce operating costs and to cope with the increasing costs of energy supply, Sury (1990), Hepler and Smith (1994) researched the idea of low temperature extraction processes. It comprised of slurrying the oil sands in water preferably in the range of 2^o to 15 ^oC, with a conditioning agent for sufficient time to release the bitumen in the oil sands. The resulting slurry was later subjected to froth floatation for the recovery of the bitumen. The conditioning agent was preferably a floatation agent having characteristics of kerosene, diesel or both together.

Lam et al. (1992) compared two samples of oil sands at temperatures of 50 ^oC and 15 ^oC. Interestingly, he observed different bitumen recovery pattern for both ores under different temperatures. In the first ore with low fines content, he observed increased bitumen recovery with higher temperature but in the second ore having high fines percentage there was no difference found. He concluded that bitumen viscosity to be an important parameter affecting bitumen recovery while he attributed the presence of high fines in fostering a negated effect of increased temperature. Dai and Chung (1995) proposed a mechanism for the hot water extraction process based on their results from extraction tests using model oil sand. They suggested that high recoveries were obtained by adding NaOH to either connate water or slurry water. They attributed the incomplete bitumen/

sand separation and bitumen/water emulsification because of deficiency or overdose of NaOH, respectively. They also claimed that size of aerated bitumen droplets increased as the oil content and/or the size of particles increased. Increasing the amount of slurry water was found to have detrimental impact on aeration.

Basu et al. (1996, 1997a and 1998a) studied and modeled the three-phase contact angle displacement of bitumen/water interface on a glass surface. The time variation of the dynamic and static contact angles of bitumen was measured at different conditions of temperature and pH. At a higher pH, lower equilibrium contact angle of bitumen was observed leading to better recovery while faster rate of recession was observed when temperature was increased. They also investigated the effect of salts, hydrophilic and hydrophobic clays on bitumen displacement using the same setup. They observed that the addition of montmorillonite clay lowered the bitumen static contact angle when compared to the case of no addition. Kasongo et al. (2000) studied the effect of calcium ions and clays on bitumen extraction by doping calcium ions and/or clays into good grade oil sands ores. Pronounce reduction in bitumen recovery was observed when 30 ppm of calcium ions and 1% of montmorillonite clays were present together. The wettability of bitumen was identified as the important parameter governing bitumen recovery. It was also noted that calcium ions had stronger adsorption tendencies on montmorillonite than on kaolinite or illite leading to increased bitumen wettability and hence reduced bitumen recovery.

Liu et al. (2003) investigated the effect of solution pH, salinity, divalent ion addition and temperature on interaction forces/adhesion forces between bitumen-silica surfaces. High solution pH and temperature and lower salinity and calcium concentration resulted in stronger repulsive forces and weaker adhesive forces, which is favorable for bitumen detachment from silica surface. He also observed that increasing the salinity of solution decreased the repulsive forces between bitumen and silica significantly.

Dang-Vu et al. (2008) studied the wettability of solids isolated from oil sands from Athabasca. They also investigated the effect of the protocol for isolating the solids from oil sands and its effects on surface properties of the solids. A correlation between solids wettability and silica/aluminum content as well as carbon/sulphur content was observed. Wettability of the solids and its close linkage with bitumen recovery was ascertained

Understanding the mechanism of oil film rupture and its displacement by water on sand grains is of importance in both mined oil and *in situ* recovery. A typical Clark hot water extraction process, which is commonly used to extract bitumen from mined oil sands deposits, employs an aqueous phase with controlled pH and temperature to be contacted with oil sands in an extraction vessel to facilitate the disengagement of bitumen from the sand grains.

Basu et al. (1996) described the study of mechanisms involved in oil-water displacement on a solid surface to be beneficial in improving not just bitumen recovery but also help in other applications such as *in situ* recovery of petroleum using water flooding or enhanced-oil- recovery processes that need oil to be displaced from the pores of a reservoir. In each of the above situation, it is necessary to know (i) whether water can displace and disengage oil from the sand particles; (ii) how quickly the displacement process takes place and finally; and (iii) the equilibrium contact angle formed by the oil droplet on the sand grain. Preferential wetting by water occurs if the free energy per unit area of water/sand interface is less than the free energy per unit area of the oil/sand interface. If this condition is satisfied, oil can be liberated from the sand surface. They proposed that the rate of disengagement of the bitumen from oil sands ore is dependent on the following sequential steps: (i) thinning and rupture of the bitumen film present as a coating on the hydrophilic sand particle in presence of an aqueous phase; (ii) displacement of the bitumen/water interface leading to the formation of oil droplets on the sand surface; (iii) disengagement of the adhered bitumen droplets from the sand surface. Figure 1 shows a pictorial diagram of the bitumen recession and liberation from an oil sands ore.

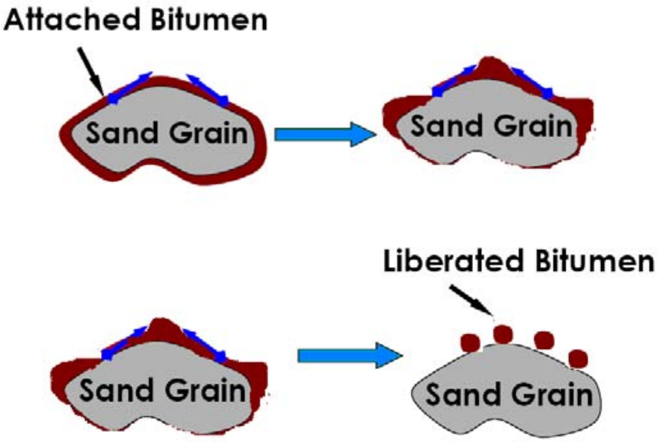

Figure 1. Bitumen liberation from an oil sands grain

The complex bitumen recession and its extraction are highly influenced by physical, chemical and hydrodynamic variables with interfacial phenomena and surface characteristics playing a critical role in successful bitumen recovery from oil sands. The intrinsic difficulties related to oil sands processing have led to numerous attempts in the literature, trying to determine the mechanism of bitumen recession on sand grains in oil sands leading to development of various experimental setups and theories.

In one of the studies, Basu et al. (1996) carried out experiments to study the spontaneous displacement (dewetting) of bitumen by aqueous solution under different conditions both on hydrophilic and hydrophobic solid surfaces. He studied bitumen film rupture on a glass plate (hydrophilic) and on a polytetrafluoroethylene (hydrophobic) surface. His quantitative analysis included measurements of the three-phase contact line displacement. The time variation of the apparent dynamic contact angle of the bitumen on the model surfaces was measured at different pH and temperature. Finally, a model was proposed which was found to be in good quantitative agreement with their measured data. According to their observations, bitumen film thins down and ruptures on a glass surface while no rupture was observed on the polytetrafluoroethylene surface. The bitumen displacement rate on the glass surface was found to be higher at lower pH while the corresponding equilibrium angle was smaller. Temperature was observed to have no effect on the equilibrium contact angle while was found to have significant influence on bitumen displacement rate. Finally, they also compared their experimental data and its congruence with various displacement models.

In continuation of the previous work, Basu et al. (1997b) developed a model for the detachment of a partially wetted liquid drop from a solid surface by a shear flow. The model was developed with the help of experimental data available in the literature. Basu et al. (1997a) also analyzed the effect of NaCl and MIBC-kerosene on bitumen displacement on glass surface using the previous experimental setup. It was found that above a certain concentration of NaCl at a specific pH, the dynamic and static contact angles reduced in comparison with a no salt case. The decreased bitumen dynamic/static contact angles could be restored to a higher value with the addition of MIBC-kerosene. Finally, NaCl was found to have no impact on bitumen displacement rate.

Furthermore, Basu et al. (1998a) studied the effect of hydrophobic and hydrophilic clays in water, on the rate of bitumen displacement and contact angle. The dynamic contact angle decreased in presence of hydrophobic clays at high pH while static/dynamic contact angle was independent of the clay concentrations. However, the effect of hydrophobic clays was less pronounced at higher temperature, e.g., 80 ^{o}C and had no significant effect on dynamic/static contact angle at different pHs. Basu et al. (1998b) studied the bitumen liberation in water based extraction process visually by observing the bitumen displacement on oil sand grains in water through a microscope. This study provided a photogenic evidence of bitumen displacement by water on the sand grain. Bitumen droplets were seen to form on the sand grains. The static contact angle of bitumen droplet on a sand grain was congruent with the observations of bitumen displacement on a glass slide.

Basu et al. (2000) studied the recession of rectangular shaped bitumen film coated on a glass slide. The rectangular film moved in spanwise and lengthwise direction after exposure to water and formed daughter droplets. The bitumen/water/glass contact line velocity was not constant throughout the strip length. The bitumen present on the oil sands grain was also in an arbitrary fashion; therefore, instabilities existed and grew at the free interface leading to the formation of a large number of daughter droplets on the sand grains. This could be detrimental to the bitumen liberation in oil sands extraction process. Basu et al. (2003) also studied the effect of an aqueous environment containing calcium ions and clays on bitumen displacement on a glass slide. Presence of calcium ions in the solution decreased the rate of displacement and the static contact angle of bitumen droplet formed. They suggested that the calcium ions modified the bitumen and silica surfaces leading to the decrease in static contact angle and rate of displacement. Addition on montmorillonite clay led to further decrease of the static contact angle. The data presented in their study was linked to the industrial practice of using process water with high level of carbonate and bicarbonate ions. Even though at high pH, e.g., pH=9, majority of calcium ions would precipitate but the presence of even 50 ppm of calcium ions could prove harmful for bitumen displacement from a sand grain in water based extraction processes.

Long et al. (2006) presented a study in which bitumen films were prepared at the toluene/water interface using Langmuir –Blodgett (LB) upstroke deposition technique. The surface of the bitumen film was found to be hydrophobic having a worm like aggregates containing a relatively high content of oxygen, sulfur and nitrogen. He measured the colloidal interactions between the LB bitumen films and fine solids using atomic force microscope. The solids were model silica particles and clay particles directly chosen from an oil sand tailing stream. The interactions between LB bitumen films, fine solids was measured in industrial process water and compared with data from simple electrolyte solutions at controlled pH and divalent cation concentrations. Moderate long-range repulsive with a slightly weaker adhesion forces were noted in plant process water despite of its high electrolyte content. The presence of anionic species present in plant process water ascribed to the weaker adhesion force observed between fine solids and bitumen, which was beneficial to the liberation process of bitumen from the fine solids. Whereas, in the case of simple electrolyte solutions, stronger long-range repulsive force and a weaker adhesion force was noted, suggesting that these solution conditions could be favorable for separations of bitumen from solids.

The hot water extraction process comprises of numerous intertwined complex mechanisms many of which are rich in surfactant chemistry. General principles of mineral floatation apply to oil sand extraction process, but oil sands composition and structure have a dominant influence on the floatation conditions. Early studies led to the idea that addition of NaOH was an important process variable for better recovery and since then much work was aimed at determining the amount of base needed. pH was believed to be the most important parameter, and the belief that better recoveries are achieved if the process could be controlled at a constant pH became stronger. Leja and Bowman (1968) recommended the middlings layer pH kept in the region 7-8.5 while Floyd (1968) et al. recommended the pH range to be 8- 8.5. It was eventually shown by Sanford and Seyer (1979) that pH was not the important factor governing bitumen separation rather NaOH addition level was the critical parameter. NaOH addition neutralized the organic acids in bitumen leading to surfactant production, which play an important role in bitumen liberation from oil sands. The main role of a base (e.g., NaOH) is to produce and release natural surfactants from the bitumen into the slurry. Leja and Bowman (1968) established that the natural surfactants produced in the extraction process were primarily carboxylic salts of naphthenic acids with the possibility of sulfonic salts as well. They used a foam fractionation and spectroscopic characterization to obtain an isolated waxy material during bitumen extraction in their experiments.

It was later found that rich grade oil sands ore did not need the addition of a base and simple slurrying with hot water resulted in release of sufficient quantities of natural surfactants into the aqueous phase leading to good recovery. While for lower grades of oil sands, NaOH addition was needed to boost bitumen recovery. Schramm and Smith (1987) successfully isolated the natural surfactants from the tumbler slurry sample at Syncrude's continuous pilot plant. After series of centrifuging, filtration and foam fractionation, the final fractionate was characterized using proton and carbon-13 NMR. They found the natural surfactants to be predominantly aliphatic carboxylates and aliphatic sulfonates having hydrocarbon chains of at least five carbons (typically C15 to

C17). They also found traces of species comprising methoxyl and aromatic character. Misra et al. (1981) found similar results of paraffinic carboxylate surfactant presence in their studies involving the processing of Utah tar sands. Shuhua and Jialin (1998) also attempted to isolate and characterize natural surfactants from Chinese oil sands. They suggested that the natural surfactants found in the aqueous phase were predominantly carboxylic acid compounds, while natural surfactants in the oil phase were phenolic compounds.

Schramm and Smith (1985) studied the action of natural surfactants in detail. They predicted there impact was a result of their adsorption at surfaces and interfaces, by which they could alter the interfacial tensions and the surface electric charges. The adsorption of surfactants molecules is known to affect the electrophoretic mobilities of dispersed bitumen droplets, gas bubbles and fine solid particles. The electrophoretic movements can be directly linked to zeta potentials at the surfaces and therefore to the surface electric charges on the bitumen drops and bubbles. Hupka and Miller (1991) showed that the ionization of the surfactant groups and the adsorption of charged surfactants lead to increase in electrostatic repulsion which increases the disjoining pressure in the aqueous film separating the bitumen and the solids, leading to optimized bitumen liberation.

After bitumen-solid separation, bitumen air attachment is also an important step. The process conditions of high degree electrostatic repulsion favoring bitumen-solid separation ironically oppose the air bubble-bitumen attachment. Houlihan (1976) in his studies showed that for low alkali addition levels and/or reduced temperature conditions bitumen droplets could attach to air bubbles as discreet particles. Under optimum conditions, if the interfacial tension between bitumen and aqueous phase is low, this favors the balance of interfacial tensions in the system and facilitates the filming of the bitumen around the gas bubbles.

Zhou et al. (1999) tried to develop a model system to explore the effect of surfactant present in bitumen on bitumen/silica coagulation. The model system was actualized by dissolving surfactant (dodecylamine or/and palmitic acid) in a hydrocarbon oil. They observed that at acidic pHs, silica was rendered hydrophobic while inducing coagulation due to its attraction to the positively charged amine head groups of surfactants. It was also observed that presence of calcium ions decreased coagulation efficiency and set barriers for cationic amine interaction with silica. Calcium ions triggered bitumen/silica coagulation at pH>10 thus bridging the oil droplets and silica leading to reduced recovery. While in the absence of calcium ions, palmitic acid could not induce coagulation over alkaline conditions. Interestingly, with their experimentation with model oil systems, they found that electrostatic interaction alone could not alone account for the observed coagulation and thermodynamic conditions were an equally important parameter. They could observe a good agreement in coagulation behavior between bitumen/silica system only when both cationic and anionic surfactants were present in oil. This directly suggested synergetic effect of the various surfactant constituents. There model system proved to be a good example of simulating the coagulation behavior of complex bitumen systems.

Zhou et al. (2000) further investigated the effect of natural surfactants released from estuarine and marine oil sands on air hold up using a water column. In their studies, they observed that the air holdup in the supernatant of conditioned oil sand slurry to be much higher when compared with that in de-ionized water. When the oil sands slurry was conditioned with caustic, a further increase in the hold up was observed. The presence of even small amounts of fines in the supernatant was seen to have an increase in the air holdup. Further, aging of the ore before extraction caused an increase in the air holdup. For all observations, they found that the marine ore supernatant resulted in a higher air holdup than estuarine ore supernatant. Finally, their studies showed that the higher holdup observed in marine ores can be related to the poorer processability of the ores when compared to estuarine ores. Furthermore, all of the findings were directly linked to the release of larger amount of surface-active species while also pointing out the presence of fine clays in the ores.

Chapter 2: EXPERIMENTAL SYSTEM AND PROCEDURES

2.1. Objective of thesis

One of the goals in oil sands research is to develop a robust process to recover bitumen from poor quality oil sands while reducing energy consumption. There have been numerous studies on bitumen liberation but all of them always have involved studying simulated oil sands. The similarity of the characteristics and properties of these simulated oil sands to the actual oil sand is always in question. This study focuses on developing a unique apparatus to obtain set of observations and quantification, which will be beneficial for better understanding of bitumen liberation kinetics by observing bitumen liberation directly from an oil sands ore in its natural state.

A flow cell is designed and developed to study the bitumen liberation directly from an oil sands ore using a flow visualization technique. The effect of temperature and pH, effect of salt addition, effect of weathering on ores, effect of kerosene addition on bitumen liberation will be examined. Experiments will be also performed on ores varying in percentage of fines thereby helping us to understand better the impact of fines on bitumen liberation. The study also involves developing a quantification procedure to extract meaningful information from the unique and novel set of results obtained from the flow visualization technique.

2.2. Experimental setup

Bitumen liberation from oil sands was studied using a flow visualization technique. Figure 2 shows the schematic diagram of the experimental setup. A 1L glass jar was used as a feed solution container and was placed in a water bath **(**Contraves, rheotherm 115**)** at least 2 hours prior to experimentation. The feed solution was circulated through the flow cell using a peristaltic pump from Cole Parmer (Masterfex C/L). The flow rate of the solution was kept constant at 1.5 mL/s. Bitumen liberation was observed using a stereo-optical scope from Olympus **(**SZX 10**)** equipped with a high-resolution camera, which captured and transferred high quality images to the computer screen at 10 frames per second (fps).

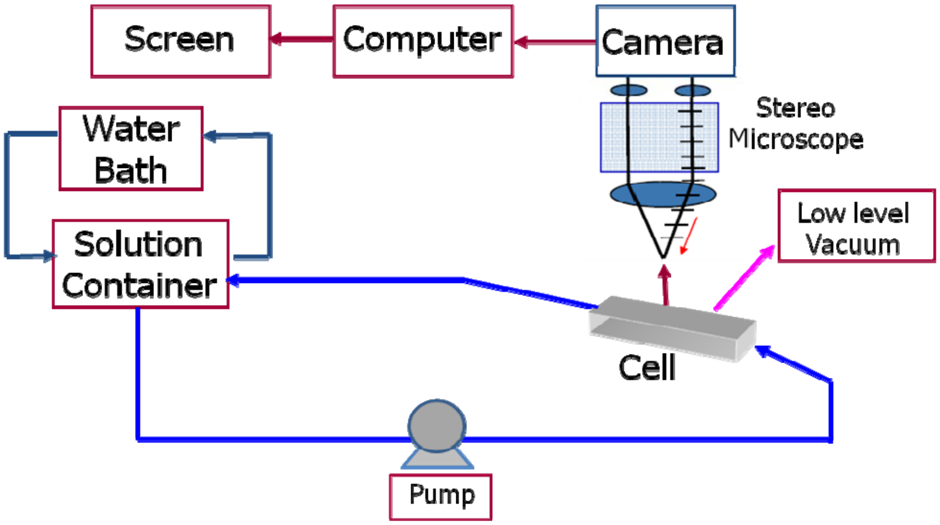

Figure 2. Experimental setup for the bitumen liberation technique observation

In this study, a unique flow cell is used to observe bitumen liberation directly from an oil sands ore. The flow cell used in this study is designed based on existing flow cell model proposed by Walker (2006). The existing flow cell is modified to include a low-level vacuum line. The modified flow cell consists of a pocket in which a sample holder with oil sands was fitted. The sample holder comprises of a glass frit of 5-10 μm pore size, which is fused into a solid glass. The oil sand ore is placed on a filter paper on the top of the frit and held in place by a low level vacuum. Without applying the vacuum, the oil sands ore would have crumbled and erode away with the water flowing on top of it. Figure 3 shows the schematic diagram and detailed dimensions of the flow cell.

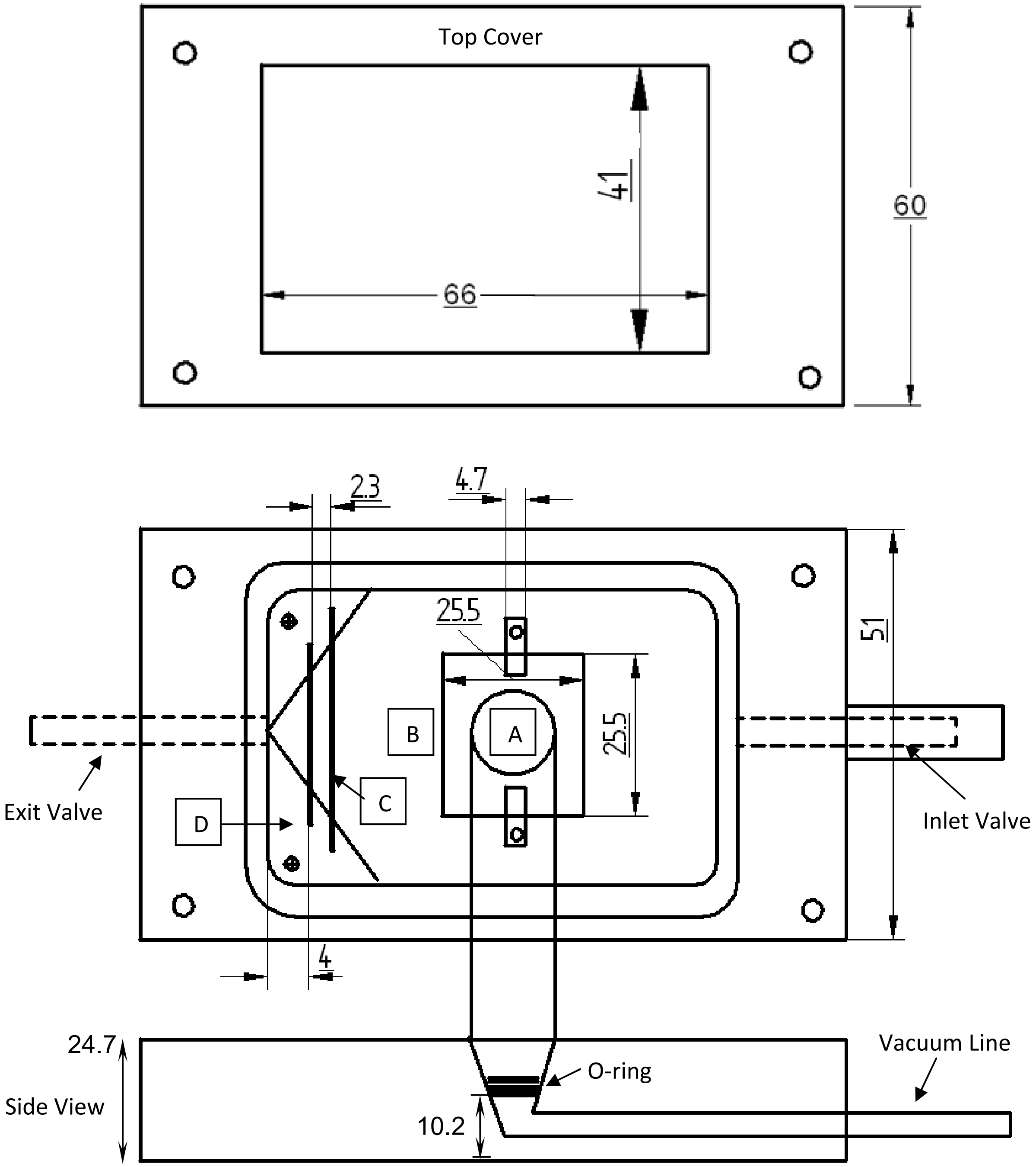

Figure 3. Schematic of the novel vacuum flow cell: A: Sample holder, B: Sealing plate, C: Baffles, D: Triangulated section to prevent eddy formation. (All the dimensions are in mm)

2.3. Experimental Procedure

Prior to each experiment, the oil sands sample from the freezer is kept out overnight in a sealed container. The feed container was filled with approximately 500 mL of the desired solution before placing into the water bath. All solutions were prepared using de-ionized water with a resistivity of 18.2 MΩ cm and solutions of 1N NaOH and 1N HCl were used for pH adjustments. The water from the exit valve of the flow cell was fed back to the feed container in all cases and the flow rate was maintained constant for all experiments. At the start of each run, a layer of bitumen (vacuum distillation unit feed) was spread on a filter paper, which was cut to the same dimensions as the glass frit. A small lump of oil sand ore approximately 3 g was then allowed to stick onto the bitumen-smeared filter paper and pressed into the sample holder. Once placed into the sample holder, the oil sands sample was sheared from the top and sides using a knife in order to obtain a flat surface and expose the untouched oil sands as the top layer as shown in Figure 4. The sample holder with the oil sands was then carefully placed into the vacuum hole of the cell and an oval ring and plate was used to seal it from the top. The plate was further pressed and sealed completely by a set of screws and once again the cell was sealed from the top with the help of a glass slide and a cell cover designed to incorporate the glass slide. Finally, with the help of four screws the cell was sealed from the top. Each set of observation of bitumen liberation was recorded as a function of time and bitumen liberation was quantified from the obtained observations.

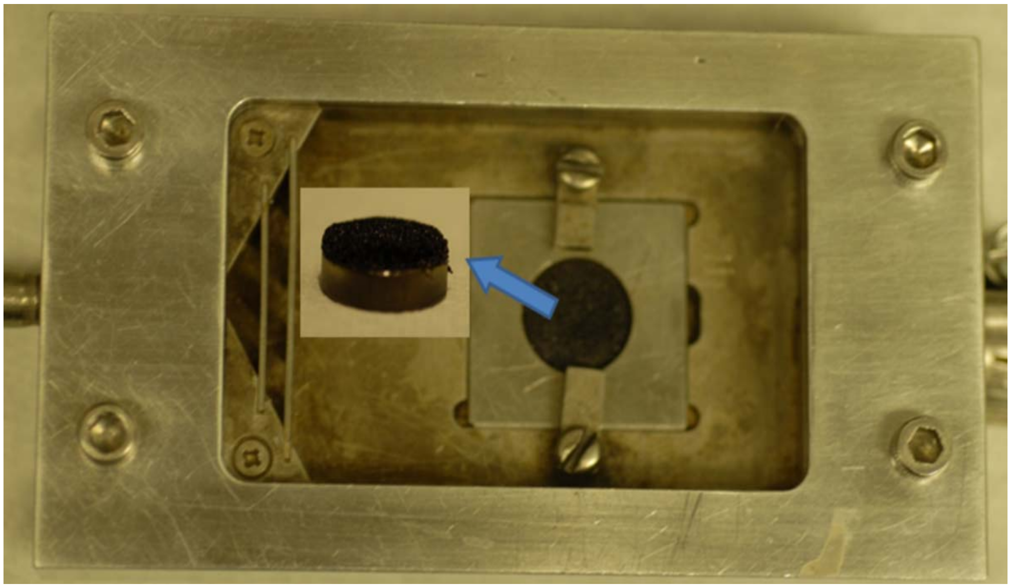

Figure 4. Image of the flow cell with sample holder

Chapter 3: RESULTS AND DISCUSSIONS

Bitumen liberation from an oil sands ore was clearly viewed and analyzed with the help of the designed flow cell. Our observations show that in the presence of water the bitumen covering the oil sand grain recedes inward due to three-phase contact angle formation. Preferential wetting by water leads to the bitumen displacement and recession on the sand grain due to the free energy per unit area of water/sand surface, which was less than the free energy per unit area of the oil/sand surface. The wetting behavior of a system is expressed as:

$$S = \gamma_{S/V} - \gamma_{S/L} - \gamma_{L/V}$$

Where, S is the spreading coefficient and $\gamma_{I/J}$ is the interfacial tension between two phases represented by S for solid, L for liquid and V for vapor. Complete spreading will occur if S ≥0, while for S <0 partial wetting is expected. The hydrophilic nature of the sand grains found in oil sands ores of Alberta, lead to partial spreading of oil drops on the sand grains leading to profitable separation of the bitumen and sand using hot water extraction methods. Unless otherwise mentioned, a high-grade ore with 14.8 wt% bitumen, 0.8 wt% water, 82.9 wt% solids of 2.5 wt% fines is used in all the experiments. The d_{10}, d_{50} and d_{90} values of the ore are 140.1, 272.7 and 514.2 micron, respectively. All solutions used in experiments are prepared using de-ionized water. In all the experiments, the solution was directly pumped into the vacuum flow cell using a peristaltic pump and the flow velocity was kept constant at 0.65 mm/s for all runs.

3.1. Effect of temperature and pH on degree of liberation

The effect of temperature on bitumen recovery has been widely studied for various types of ores (Dai and Chung, 1995; Schramm et al., 2003; Long et al., 2005). The studies have attributed the sharp decrease in bitumen viscosity at lower temperatures to be the dominant parameter for low recovery of oil sands ores. All of these observations did not provide a concrete fundamental explanation of the controlling parameters and mechanisms on bitumen liberation. Their conclusions are based on experiments on either silica-bitumen interactions or model oil sands whose resemblance in properties to real oil sands is always in question. It is therefore important to understand the effect of solution temperature on bitumen liberation kinetics directly from an oil sand grains. To observe the effect of temperature on bitumen liberation the first set of observations was carried out at three different solution temperatures of 46, 30 and 23 ^{o}C, keeping the solution pH constant of 11.3. For the test, the solution pH was modified by adding NaOH and placed in a water bath for an hour to attain the desired temperature, prior to each test. The high-grade oil sand ore was employed for the liberation analysis at the different solution temperatures. The liberation analysis show sharp images of bitumen droplets formation. Figure 5 displays the image of the degree of liberation at 46 ^{o}C, where clear formation of spherical bitumen droplets can be seen along with clear (clean, devoid of bitumen) sand grains within 300 seconds of solution flow inside the cell. While Figure 6 also exhibits majority of sand grains with clear bitumen droplets formed on them at 30 ^{o}C, but there exist many bitumen films that have not yet receded at the end of 300 seconds. In Figure 7 very few bitumen films have receded to form bitumen droplets at 23 ^{o}C at the end of 300 seconds.

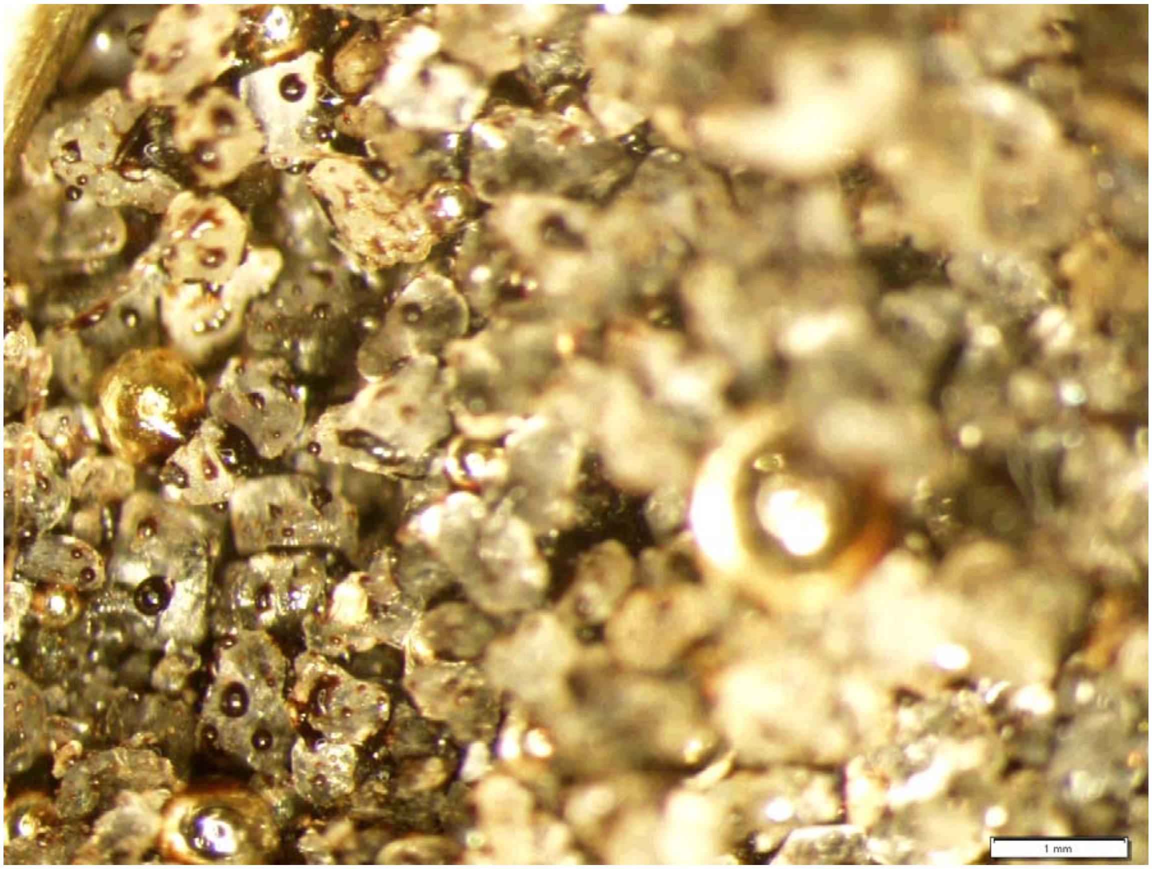

Figure 5. Bitumen droplets being formed at pH 11.3 at 46 ^{o}C for a high-grade ore after 300 seconds of solution flow

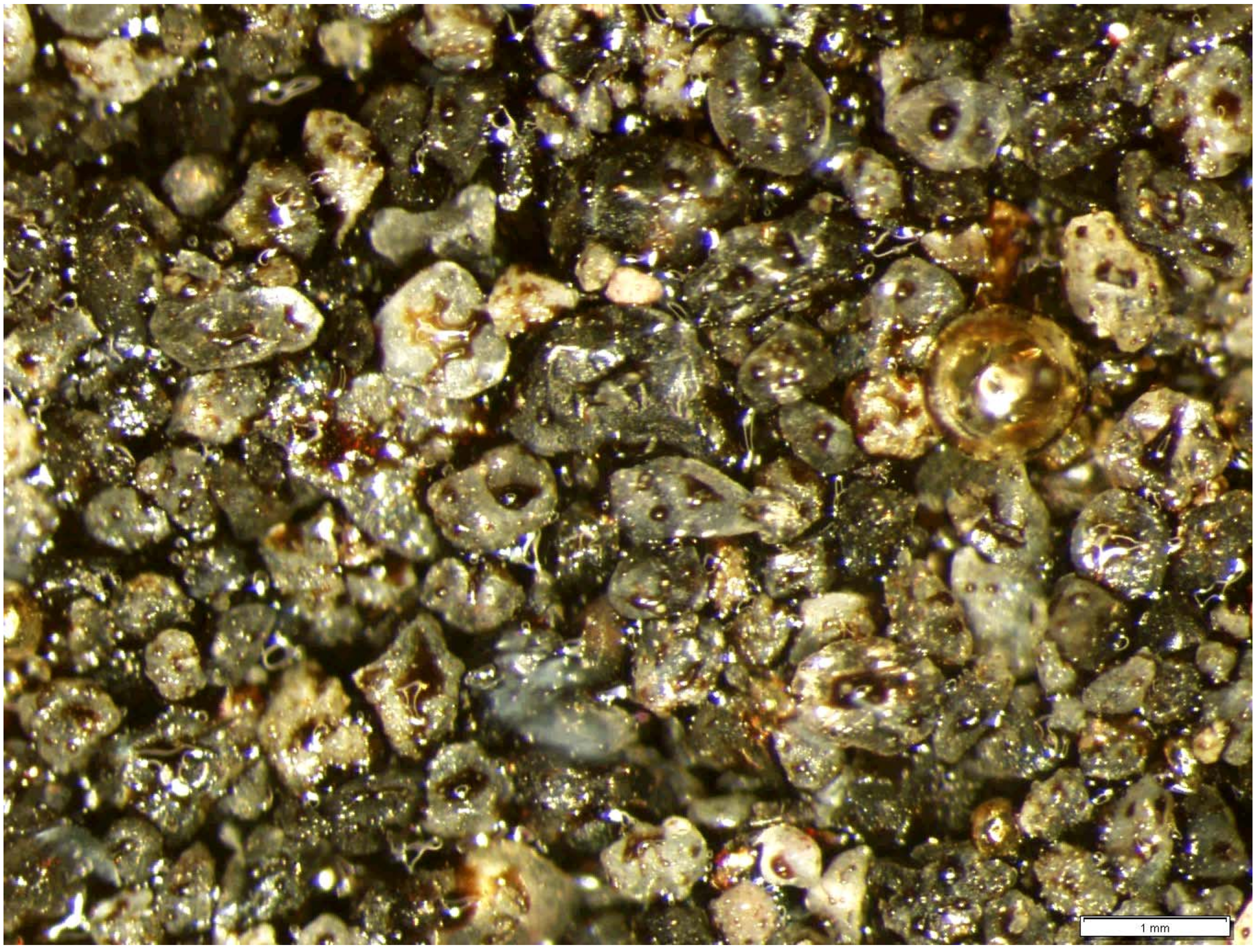

Figure 6. Bitumen droplets being formed at pH 11.3 at 30 °C for a high-grade ore after 300 seconds of solution flow

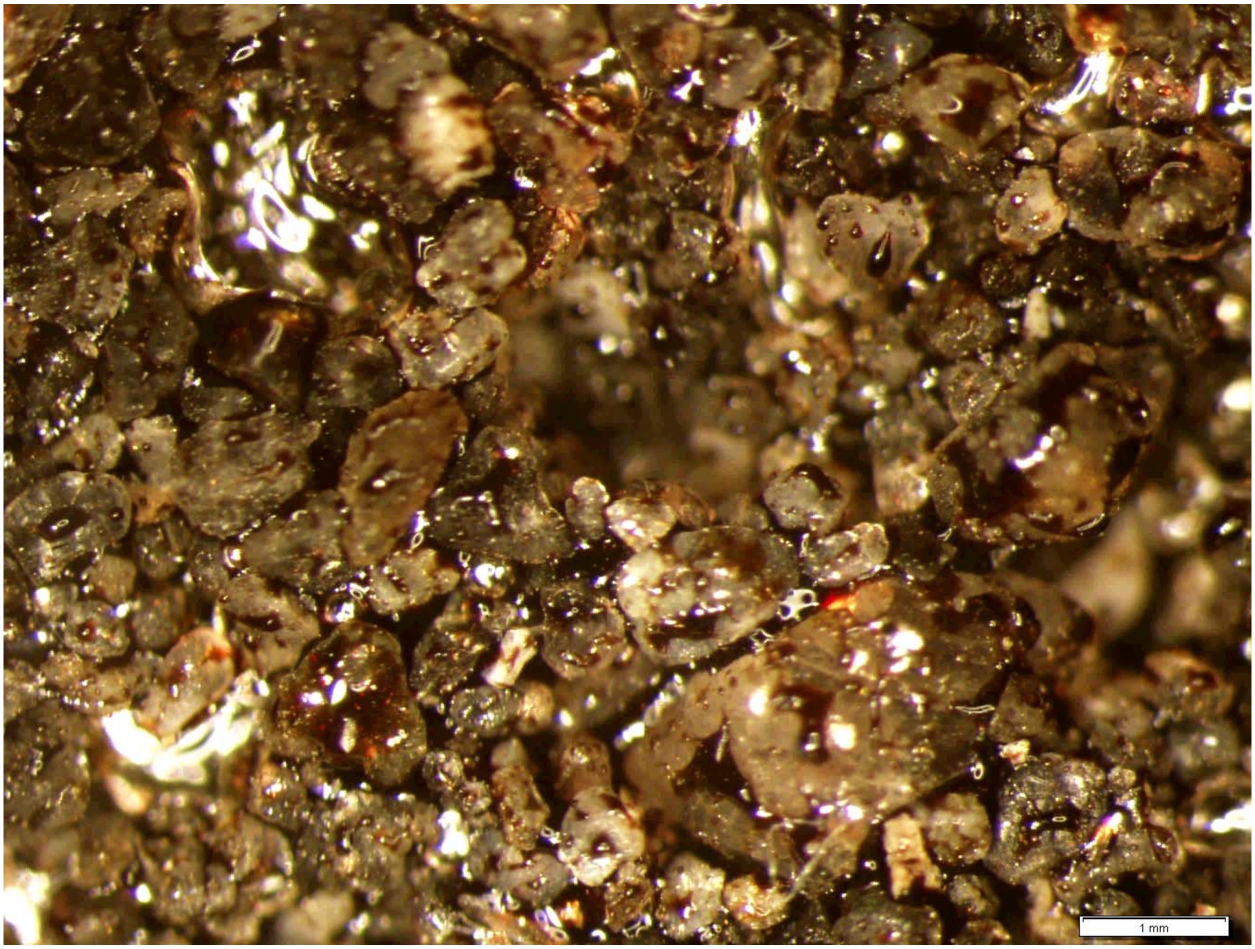

Figure 7. Bitumen droplets being formed at pH 11.3 at 23 ^{o}C for a high-grade ore after 300 seconds of solution flow

Bitumen film on the sand grain starts to recede and form a droplet with a lower contact angle and least contact area in the presence of water. This bitumen droplet can be detached either from the sand grain surface by coming in contact with an air bubble or by self-disengagement due to shear force.

Basu et al. (1996) through numerous experiments showed that low contact angle bitumen droplets form on a glass substrate at high pHs favouring high bitumen liberation, however, the experiment's closeness to reality was always in question. For our tests a high-grade oil sands ore is subjected to bitumen liberation analysis at solution pH values of 11.3, 9.7 and 7.8 but at a constant temperature of 46 ^{o}C. Figures 8 to 10 show the images extracted after 300 seconds after the oil sands ore came in contact with water of pHs 11.3, 9.7 and 7.8, respectively, but at constant solution temperature of 46 ^{o}C. In Figure 8, for pH 11.3, at the end of 300 seconds, bitumen films have receded to form bitumen droplets as clearly seen on all the sand grains. While for pH of 9.7, as shown in Figure 9, the majority of sand grains have bitumen films receded on them but there still exist many sand grains on which bitumen films have not yet receded. Figure 10, for pH 7.8, shows that majority of the sand grains appear to be clear but a closer look confirms that the majority of the bitumen films have not formed bitumen droplets at the end of 300 seconds. Bitumen droplets with lower contact angle were observed in high pH solutions as found by Basu et al. (1996).

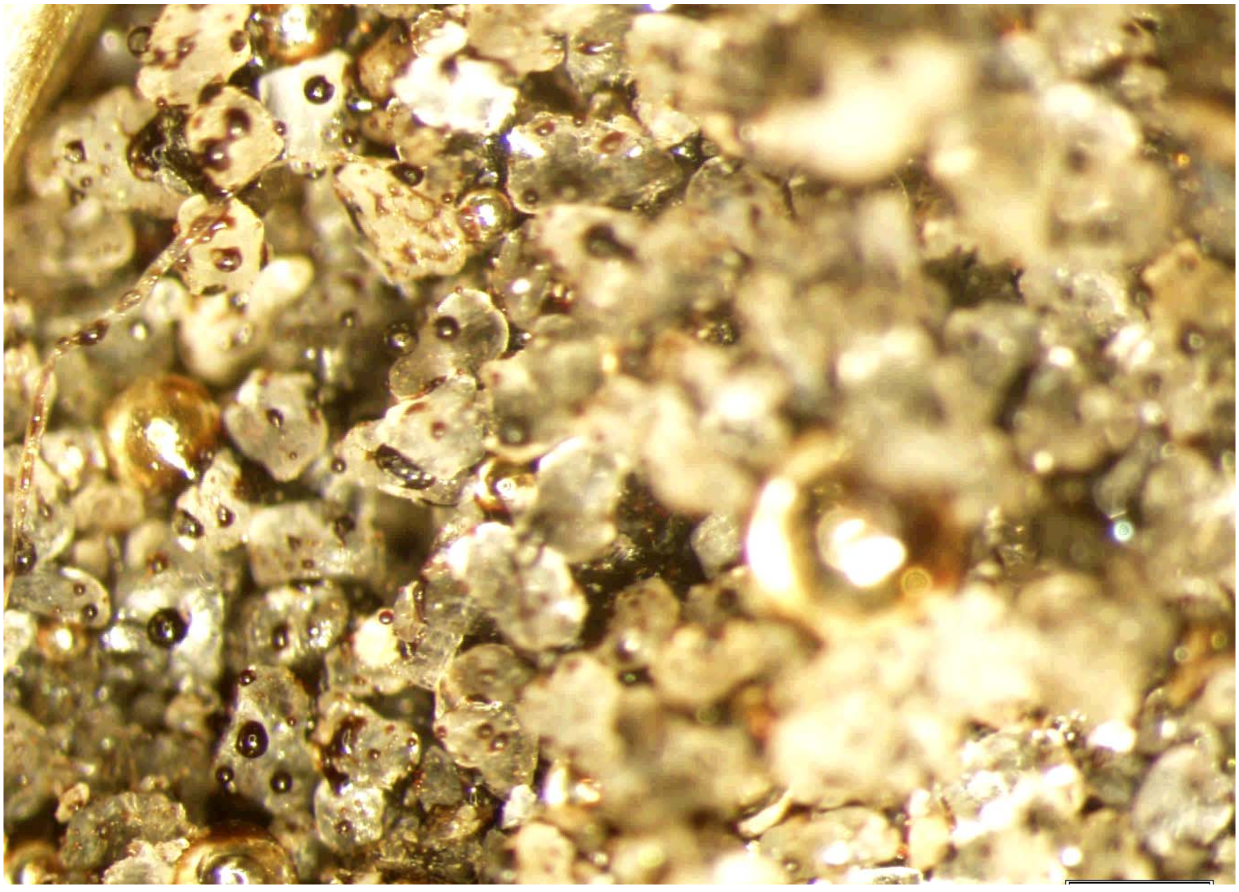

Figure 8. Bitumen droplets being formed at 46 °C and pH 11.3 for a high-grade ore after 300 seconds of solution flow

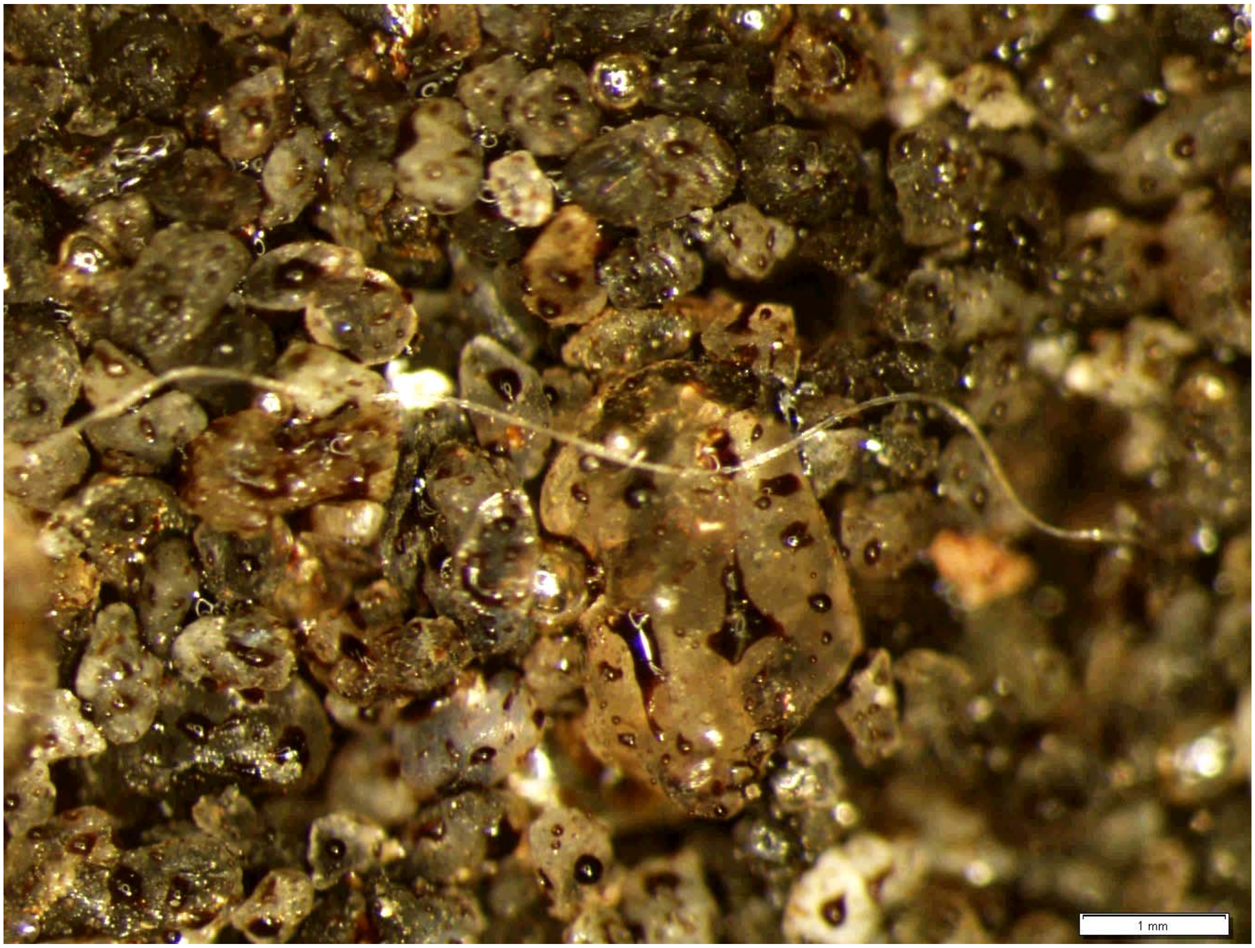

Figure 9. Bitumen droplets being formed at 46 ^{o}C and pH 9.7 for a high-grade ore after 300 seconds of solution flow

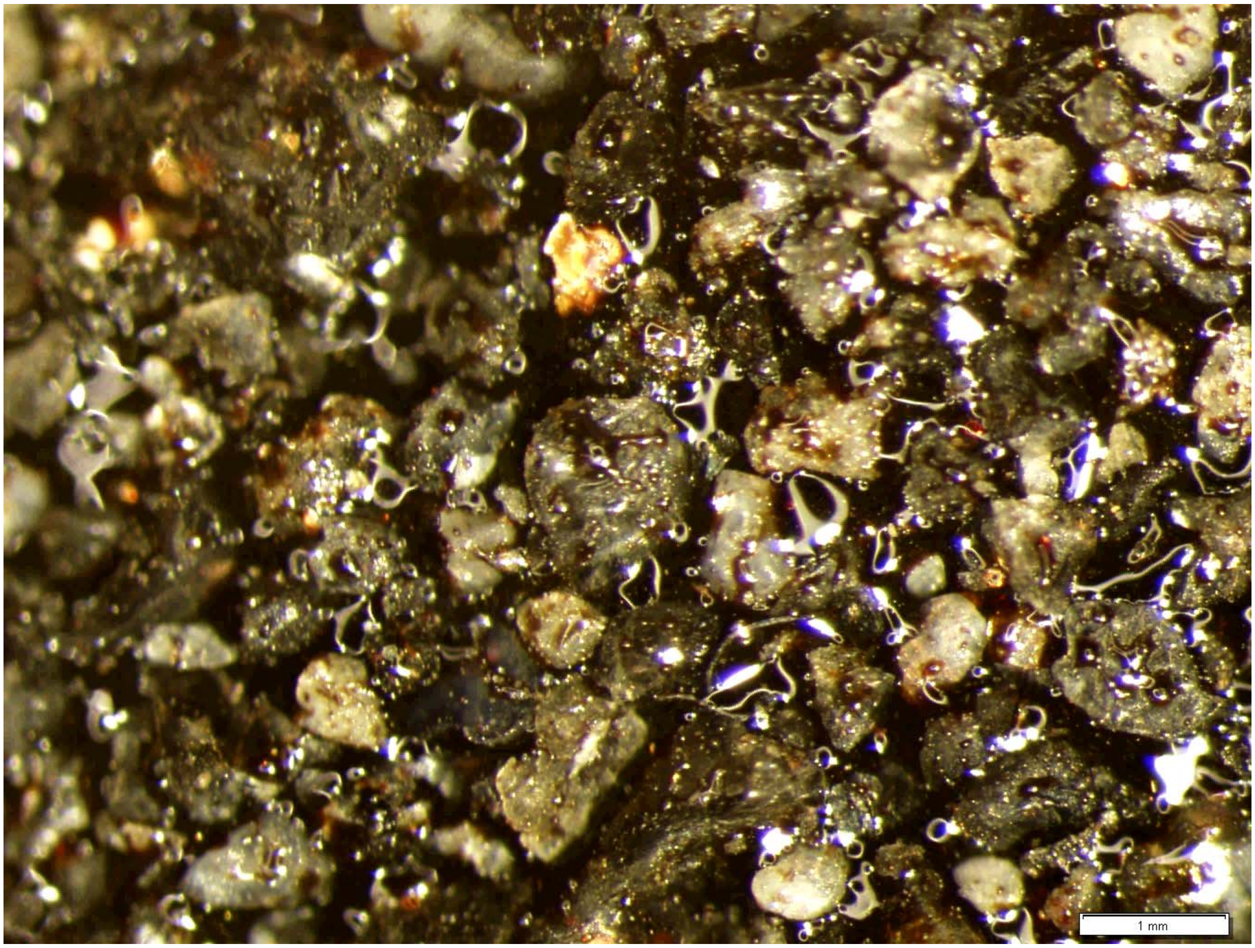

Figure 10. Bitumen droplets being formed at 46 ^{o}C and pH 7.8 for a high-grade ore after 300 seconds of solution flow

The degree of liberation analysis carried out in this research is a method by which we try to calculate the total percentage of clear sand grains out the total sand grains visible on each frame that was recorded. Clear grains in our analysis are the sand grains, which are either being clean having no bitumen film on them or having bitumen droplets that are capable of detaching from the surface of the sand grain. In the analysis, it was assumed that the bitumen droplets, which are completely or approximately close to being spherical in shape, were capable for detachment due to lower contact angle and less area of contact with the sand grain. Figure 11 shows a high grade oil sands ore in its natural state before coming in contact with water. In Figure 12, the black circles represent the bitumen droplets on sand grains, which according to our criteria are capable to disengage, while the red circles indicate the bitumen films, which have not yet formed spherical droplets that can disengage itself from the sand grain. The video of the bitumen liberation is recorded for each condition and images are extracted at different intervals of time, these images are scrutinized and analyzed grain by grain, which is very laborious and time-consuming process. For each condition the number of clear sand grains as observed on the frame were counted as a function of time and the degree of liberation curves were obtained.

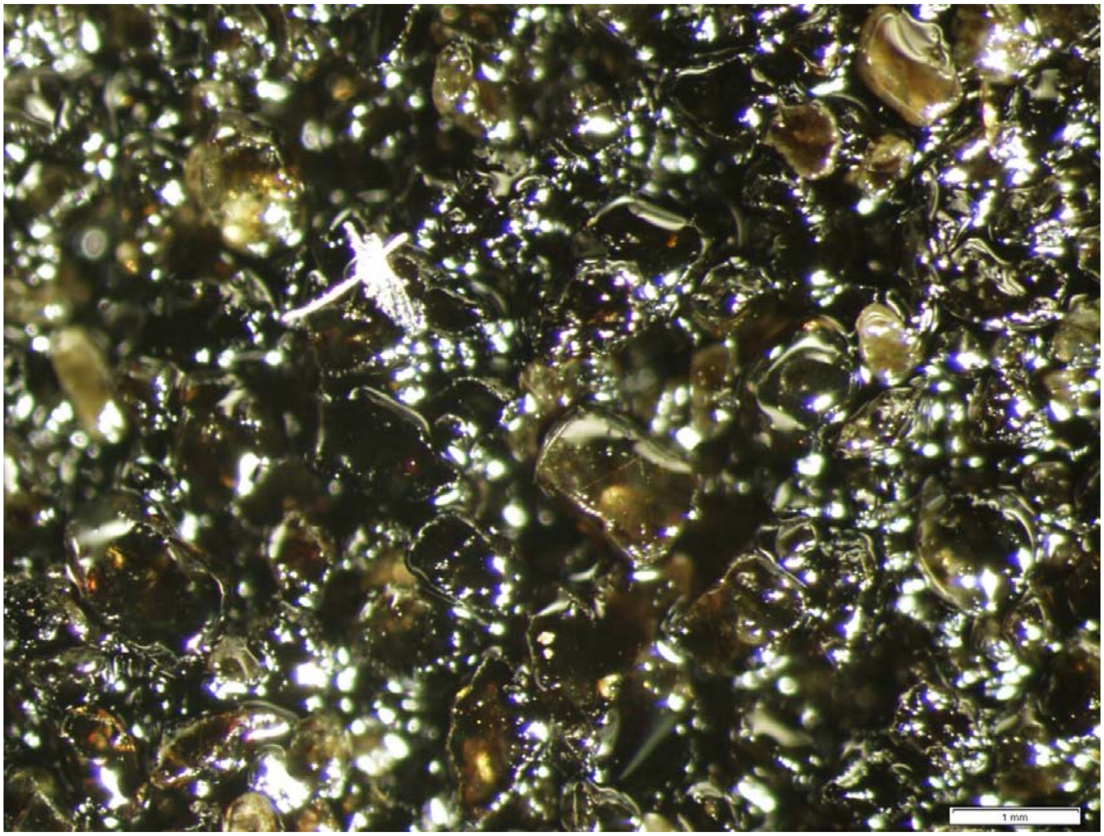

Figure 11. Oil sands ore in its natural state with bitumen present as a coating on sand grains

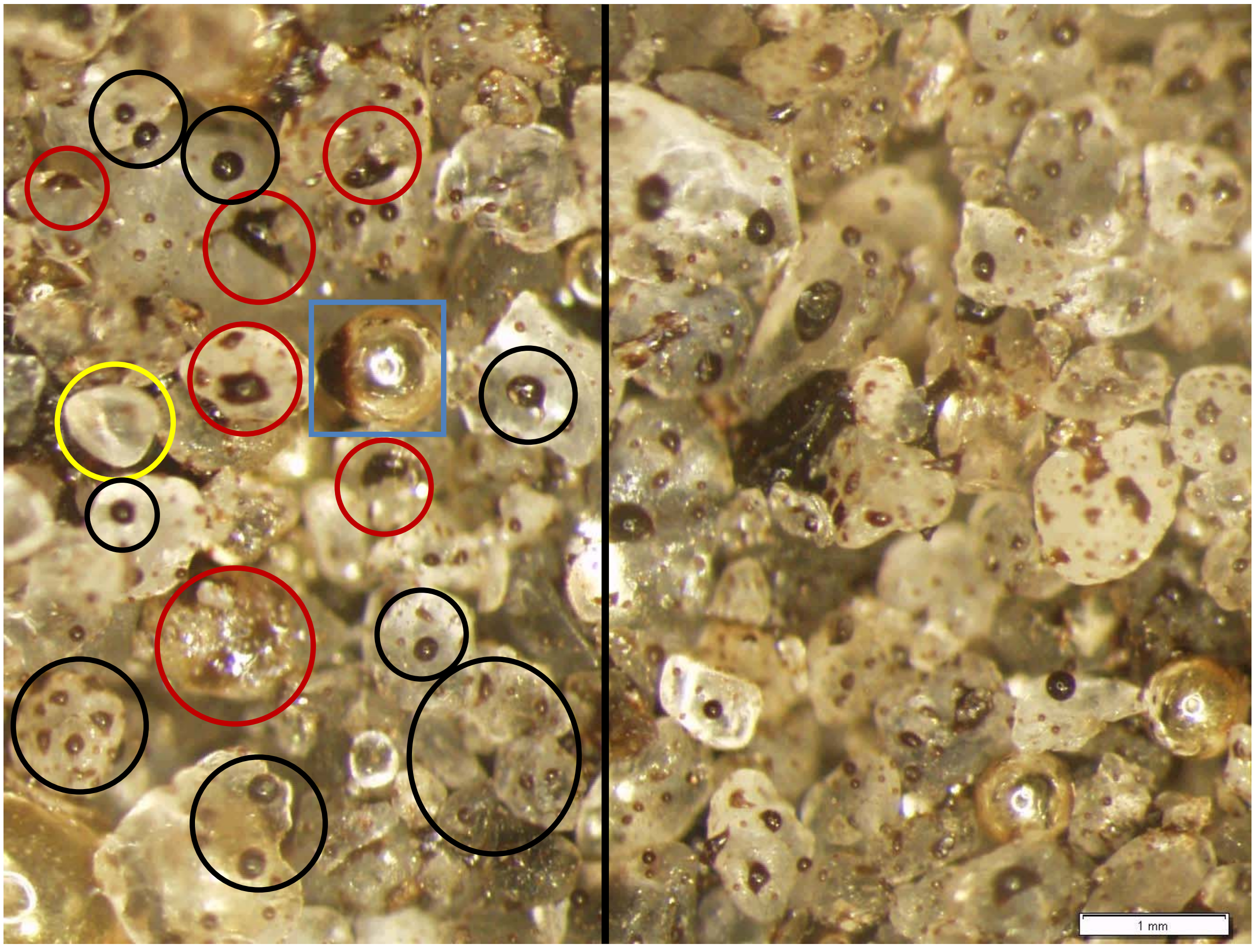

Figure 12. Bitumen droplets being formed at pH 9.7 and 46 ^{o}C for a high-grade ore after 375 seconds of solution flow

Based on the above analysis, Figures 13 to 15 show the bitumen liberation curves for a high-grade ore plotted against time for three different pH values and at three different solution temperatures. The degree of liberation is seen to increase with time towards the final bitumen liberation percentage, which is found to be distinct for each set of condition. Regardless of the pH, as shown in Figures 13 to 15, increasing the solution temperature increases the degree of liberation and the rate of liberation. Dai and Chung (1995) with their bitumen-sand interaction studies suggested that on increasing temperature not only reduces viscosity to facilitate bitumen liberation but also increases the repulsion force between bitumen and silica leading to faster recession. At pH of 11.3 as shown in Figure 13, at the end of 300 seconds the degree of liberation was 98% at 46 ^{o}C, which was marginally higher than 77% obtained at 30 ^{o}C. In contrast, at the end of 300 seconds, the degree of liberation at 23 ^{o}C was found to be much lower at 32% as compared to > 75% observed for temperatures 46 ^{o}C and 30 ^{o}C. Similarly, at pH 9.7 as shown in Figure 14, at the end of 400 seconds, the degree of liberation at 30 ^{o}C was 20 percent lower when compared to the case at 46 ^{o}C. However, at 23 ^{o}C the degree of liberation at pH 9.7 was only 35% when compared > 65% observed for temperatures 46 ^{o}C and 30 ^{o}C at the end of 400 seconds.

Figure 16 shows a comparison of the degree of liberation curves at 46 ^{o}C and pHs of 11.3, 9.7 and 7.8. Interestingly, as shown in Figure 16, when the solution temperature was kept constant, lowering the pH leads to a lower degree of liberation and slower rate of recession. At high pH of 11.3 the degree of liberation is highest with almost 100% liberation observed within 300 seconds while 60% and 45% are observed at pH 9.7 and 7.8 at the end of 400 seconds. It took 250 seconds to achieve 70% degree of liberation at 11.3 pH while it took 350 seconds and 400 seconds to achieve the same in the case of pH of 9.7 and 7.8. The solution with high pH of 11.3 took the least time to reach it's highest degree of liberation, highlighting the importance of pH on bitumen liberation and recession. The attraction/repulsion model of the charged bitumen-sand surfaces can explain such a phenomena. Takamura and Chow (1983) suggested that at high pH both silica and bitumen surfaces are negatively charged and a strong repulsive force separates them, when the pH is lowered the surface charge of bitumen-silica surfaces decreases leading to weak force of repulsion and lower bitumen liberation. Dubey and Doe (1993) used a base/acid ratio to describe the wetting properties of oil. They suggested that at neutral and alkaline pH the presence of acid-type surfactants in bitumen gives bitumen a highly negative charge and a hydrated surface, which was beneficial to bitumen liberation.

Comparing Figures 13 to 15, interesting deviation at pH 7.8 is observed at 30 ^{o}C, the degree of liberation was found to be much lower at 20% as compared to 74% at 46 ^{o}C at the end of 400 seconds. Both 46 and 30 ^{o}C had similar degree of liberation at pH 11.3 and pH 9.7, but notable deviation was observed at pH 7.8. The interesting sudden drop of degree of liberation at 30 ^{o}C and 7.8 pH implies that it would be difficult to liberate bitumen at both low pH and temperature. The low degree of liberation observed at low pH and low temperaure, highlights the importance of both temperature and pH in bitumen liberation. Another interesting point to be observed here is that degree of liberation was similar for temperature 46 and 30 ^{o}C at pH higher than 9.7, which relates the possibilty of carrying bitumen extracion at lower tempertures with higher pH. The results closely match the findings of Ding et. al. (2006) who observed similar reductions in bitumen recovery from oil sands ore when the processing temperature and pH was reduced. Through colloidal force measurements using atomic force microscope, Long et al. (2005) showed that the interactions and adhesion forces between bitumen and sand grains in water decrease with increase in temperature until a critical value of about 32-35 ^{o}C, above which there is no adhesion. These findings correlate well with the results from this study.

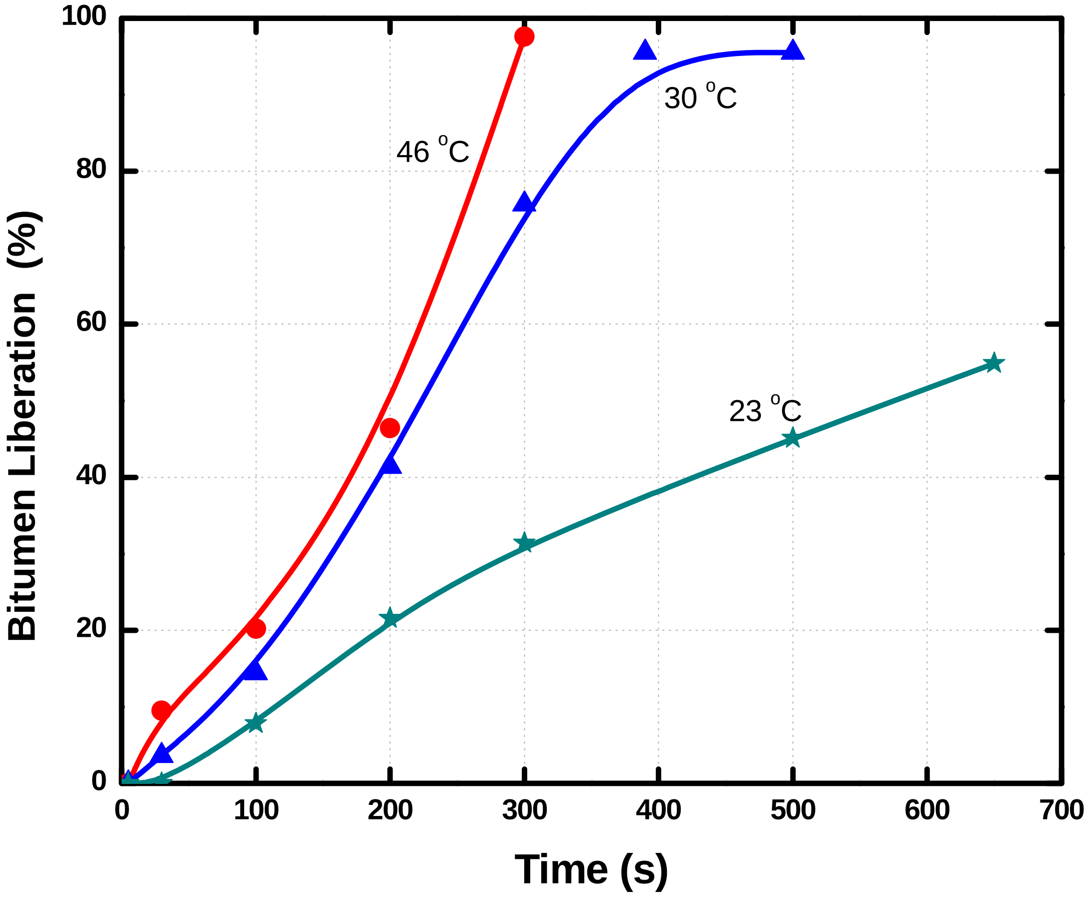

Figure 13. Effect of temperature on degree of liberation as function of time at pH of 11.3

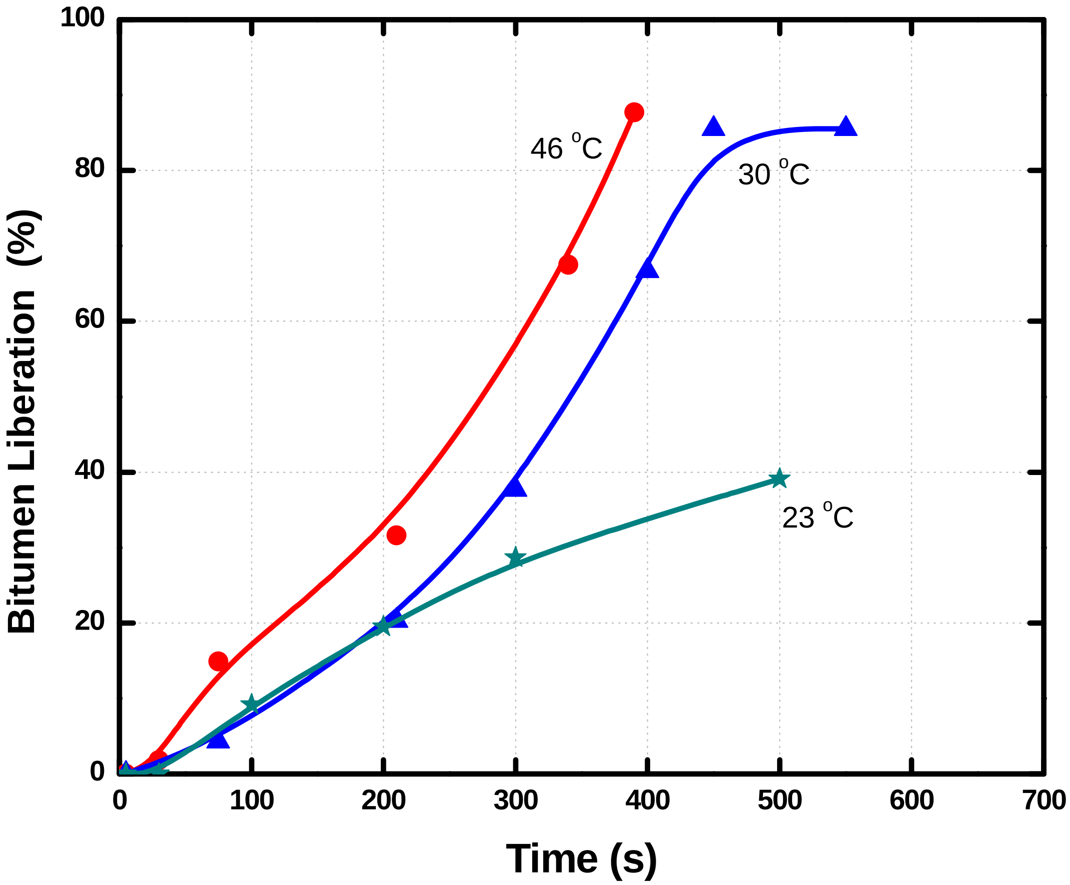

Figure 14. Effect of temperature on degree of liberation as function of time at pH of 9.7

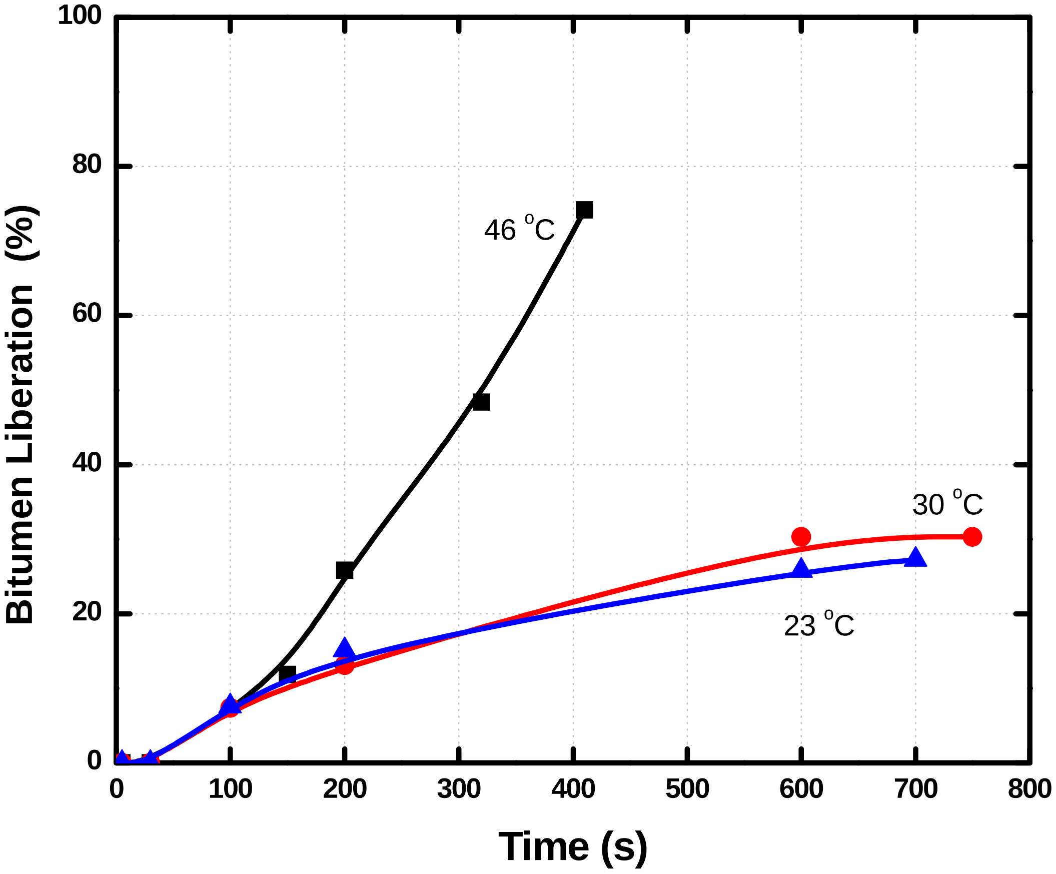

Figure 15. Effect of temperature on degree of liberation as function of time at pH of 7.8

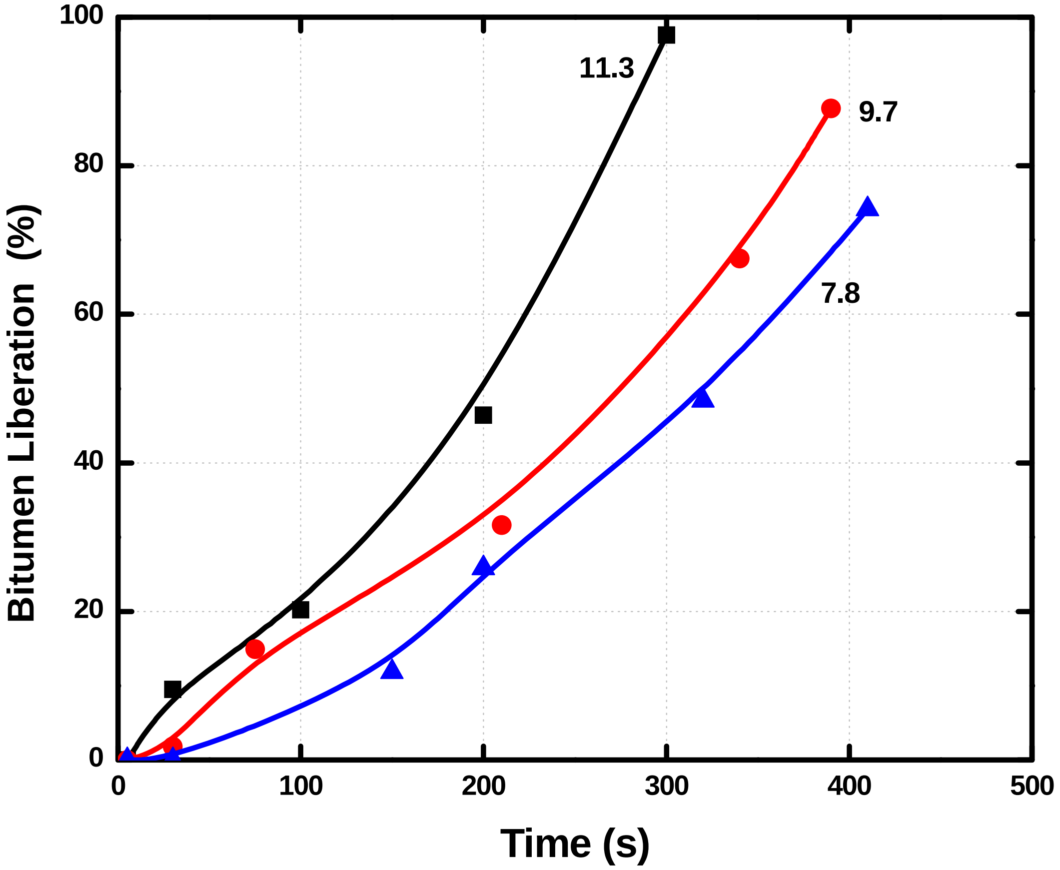

Figure 16. Effect of pH on degree of liberation as a function of time at temperature 46 °C

3.2. *Effect of salts on degree of liberation*

The salt concentration in process water increases each time it is recyclyed back for bitumen extraction from the tailings pond. Forseeing the future, understanding the effects of salts on bitumen extraction particularly at the conditioning stage is very important.

It forms the basis of analysis of observing bitumen liberation in saline solutions. Prior to experimentation, the saline solutions were prepared and used for bitumen liberation analysis within 1 hour of its preparation. Figures 17 to 20 show images bitumen liberation at the end of 600 seconds for a high grade ore at pH of 10 and solution temperature of 46 ^{o}C for different salt concentrations. It can be seen clearly that the bitumen liberation is drastically affected as NaCl concentration is increased from 0 to 16000 ppm as shown in Figures 17 to 20. When compared to Figure 17 without salt addition case, adding 8000 ppm of NaCl lead to lowering of bitumen liberation as very few bitumen films receded on the sand grains to form droplets as shown in Figure 19. Further increasing the concentration of the solution to 16000 ppm of NaCl severely hampered bitumen liberation as shown in Figure 20, where no bitumen liberation is observed.

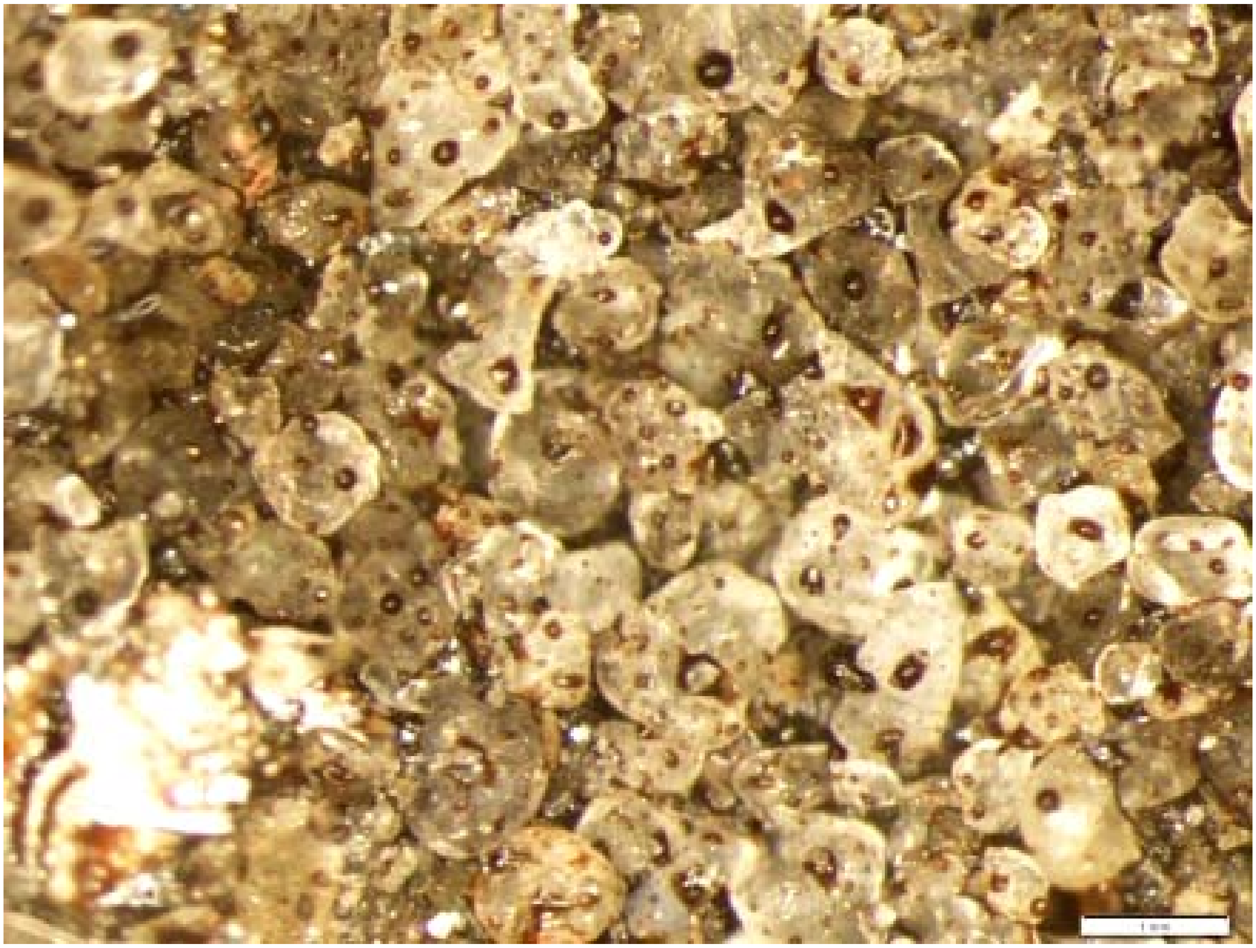

Figure 17. Bitumen droplets formed at pH 10 and 0 ppm of NaCl for a high-grade ore after 600 seconds of solution flow

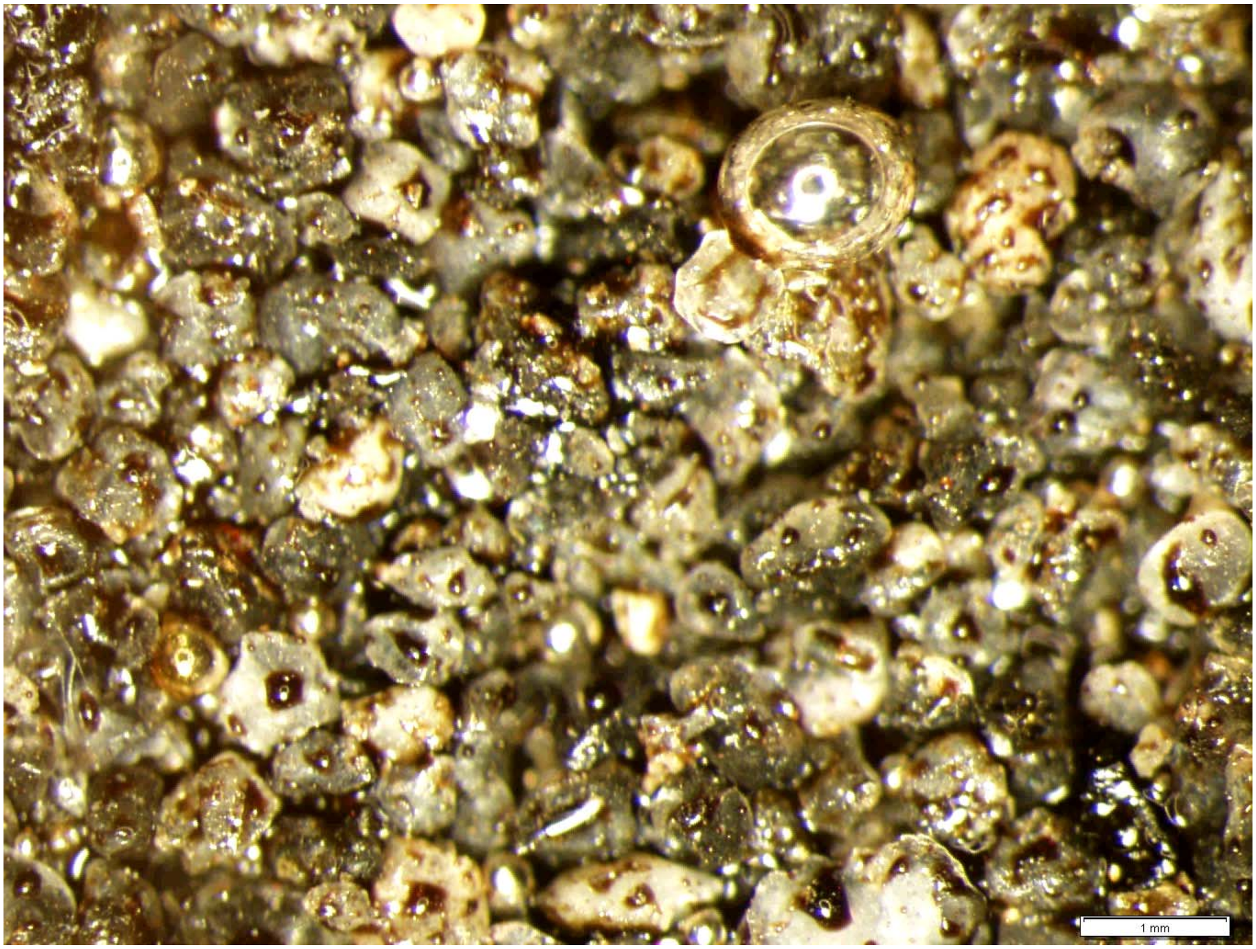

Figure 18. Bitumen droplets formed at pH 10 and 4000 ppm of NaCl for a high-grade ore after 600 seconds of solution flow

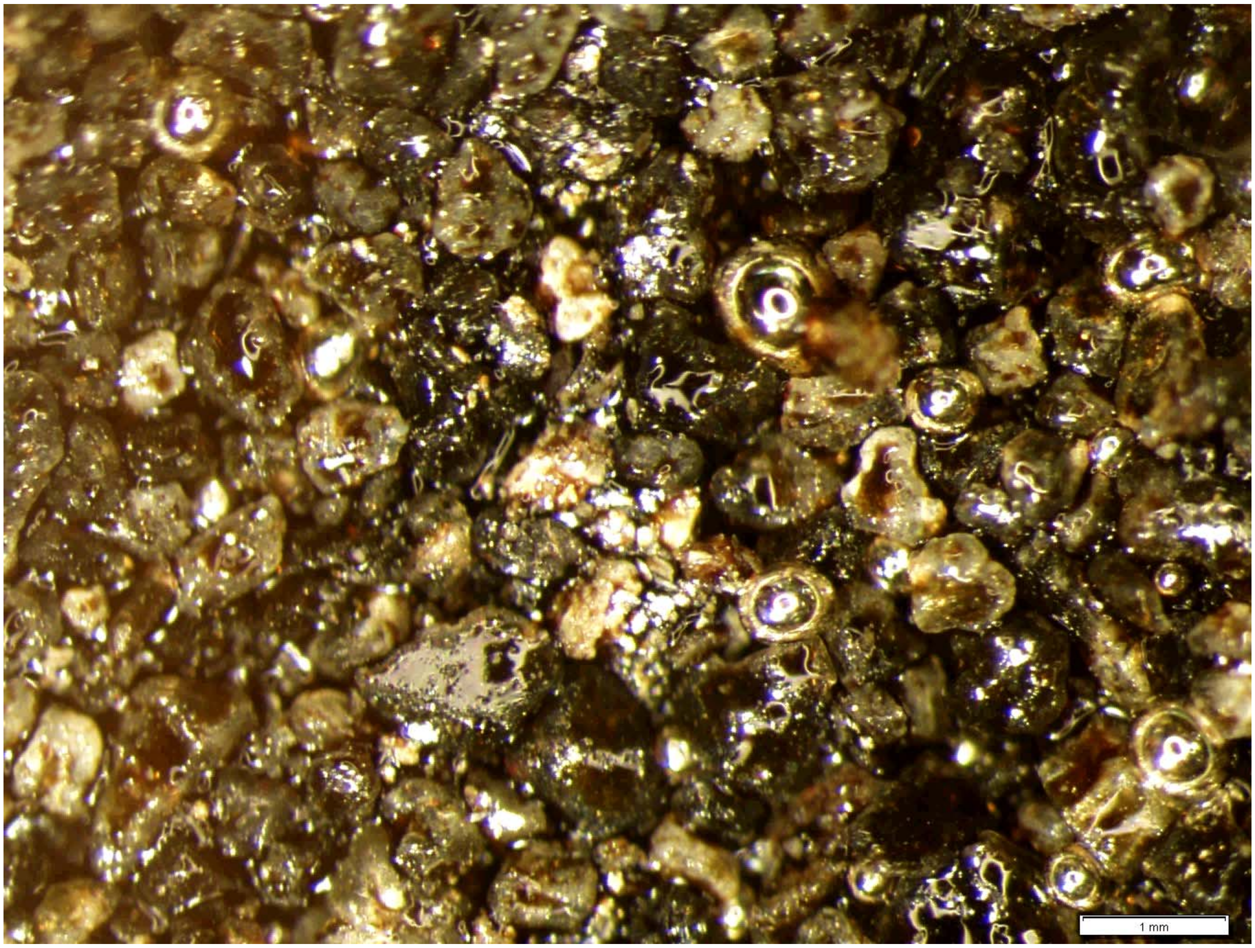

Figure 19. Bitumen droplets formed at pH 10 and 8000 ppm of NaCl for a high-grade ore after 600 seconds of solution flow

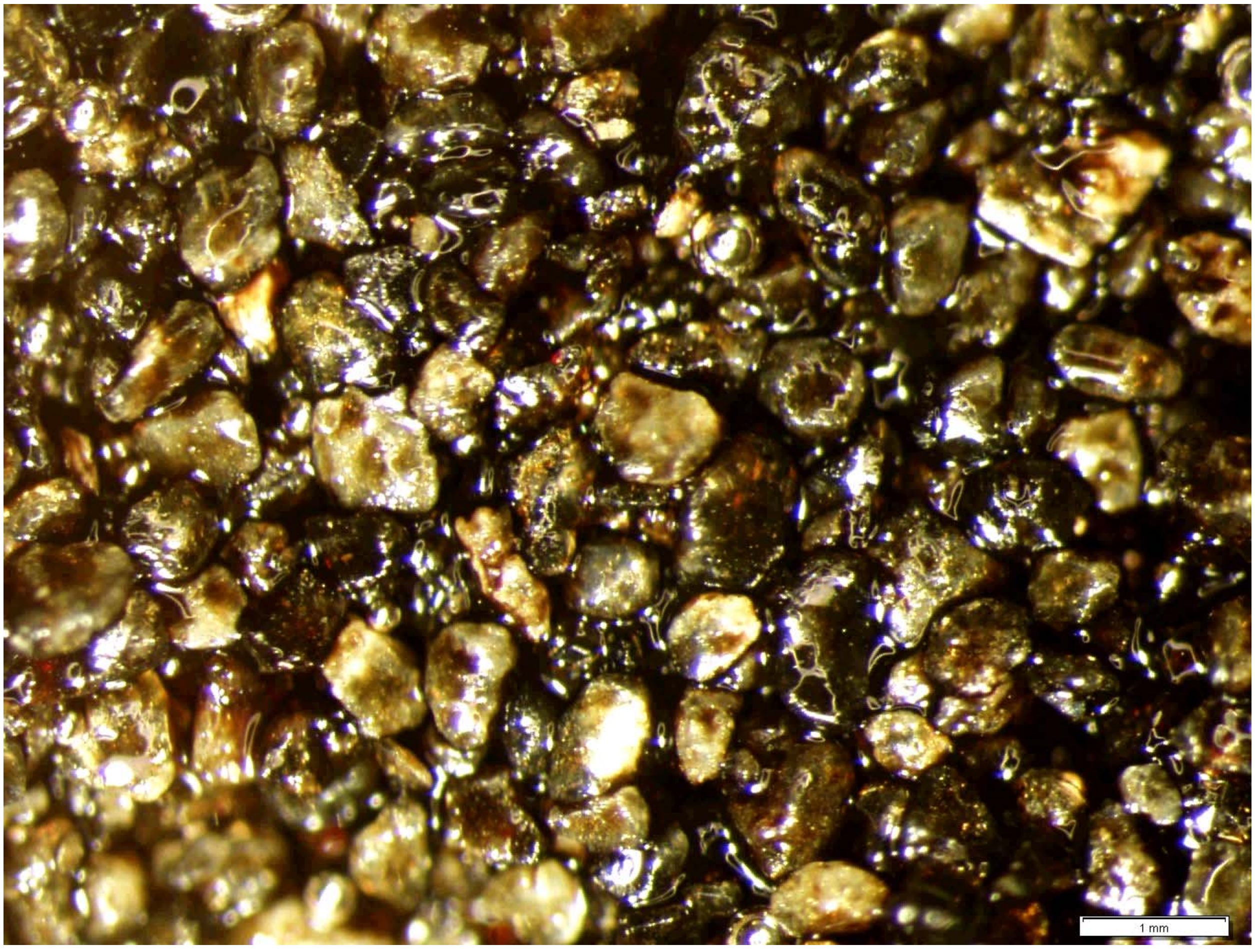

Figure 20. Bitumen droplets formed at pH 10 and 16000 ppm of NaCl for a high-grade ore after 600 seconds of solution flow

Figure 21 shows the quantitative analyis and the degree of liberation curves at various salt concentrations at pH 10 and at 46 ^{o}C. It can be seen that, the effects of NaCl on the degree of liberation is drastic at high pH of 10, which on the contrary favours the bitumen liberation in no salt condition. The degree of liberation at no salt case was 90% while adding only 4000 ppm lowered it to 40%. Further increase in NaCl concentration to 16000 ppm lead to no bitumen recession with no degree of liberation observed. The effect of NaCl was also investigated at a lower pH of 7.8 and at solution temperature of

46 ^{o}C. Similar trends of lower degree of liberation and lower rate of recession with increase in NaCl concentration were observed at pH of 7.8 as shown in Figure 22 when compared to the case with pH of 10 as shown in Figure 21. Interestingly, as shown in Figure 22, the degree of liberation at 4000 ppm of NaCl and 7.8 pH reduces only by 10% when compared with no salt addition case at the same pH. Increasing the salt concentration to 16000 ppm further reduced the degree of liberation to 50%, which is very high compared to the case of 16000 ppm at pH 10 as shown in Figure 21, where no liberation was seen. The effect of NaCl on bitumen liberation is less pronounced at lower pHs and becomes more pronounced leading to no bitumen liberation at high pHs. It is quite difficult to rationalize this dramatic decrease in degree of liberation in saline solutions at high pH. One of the possible reason could be slow production of natural surfactants in the presence of NaCl. Another reason could be due to the decrease in the repulsive force observed between bitumen and sand surface with increase in the salinity of the solution as suggested by Liu et al. (2003). Further studies are needed to understand the exact reason for reduced bitumen liberation in saline solutions.

Despite the increase in concentration of ions and salts in the industrial recycle process water with time, only few studies on bitumen recovery in the presence of ions and salts were conducted. To determine the effect of observed decrease in bitumen liberation by increasing salt concentration on bitumen recovery, bitumen extraction tests were conducted using the Denver flotation cell. The tests were carried out at 46 °C using industrial recycle process water following procedures used by Harjai (2007), but with slight modification. In this study, the bitumen froth was collected during the conditioning stage (i.e., agitation without aeration) for 5 min. The bitumen flotation continued at an aeration rate of 150 mL/min and a rotor speed of 1500 rpm, bitumen froth collected during 2-5, 5-10, and 10-15 min intervals. The composition of bitumen froth (bitumen, solids, and water) was determined using Dean-Stark extraction using toluene as the solvent. Figure 23 shows the flotation results for a high-grade oil sands ore at pH 10 and various saline concentrations. Each curve represents the floatation kinetics for a specific saline concentration. As can be noted, during the conditioning stage (agitation without aeration), 18% bitumen is recovered for the case without salt addition, while increasing the salt concentration to 16000 ppm reduced the bitumen recovery to 8% over the same conditioning period. Furthermore, the initial slope of the flotation kinetics curve is the highest for the case without salt addition and the lowest with the addition of 16000 ppm NaCl. The observed depression of bitumen recovery by salt addition correlates well with the observed decrease in the degree of bitumen liberation with salt addition.

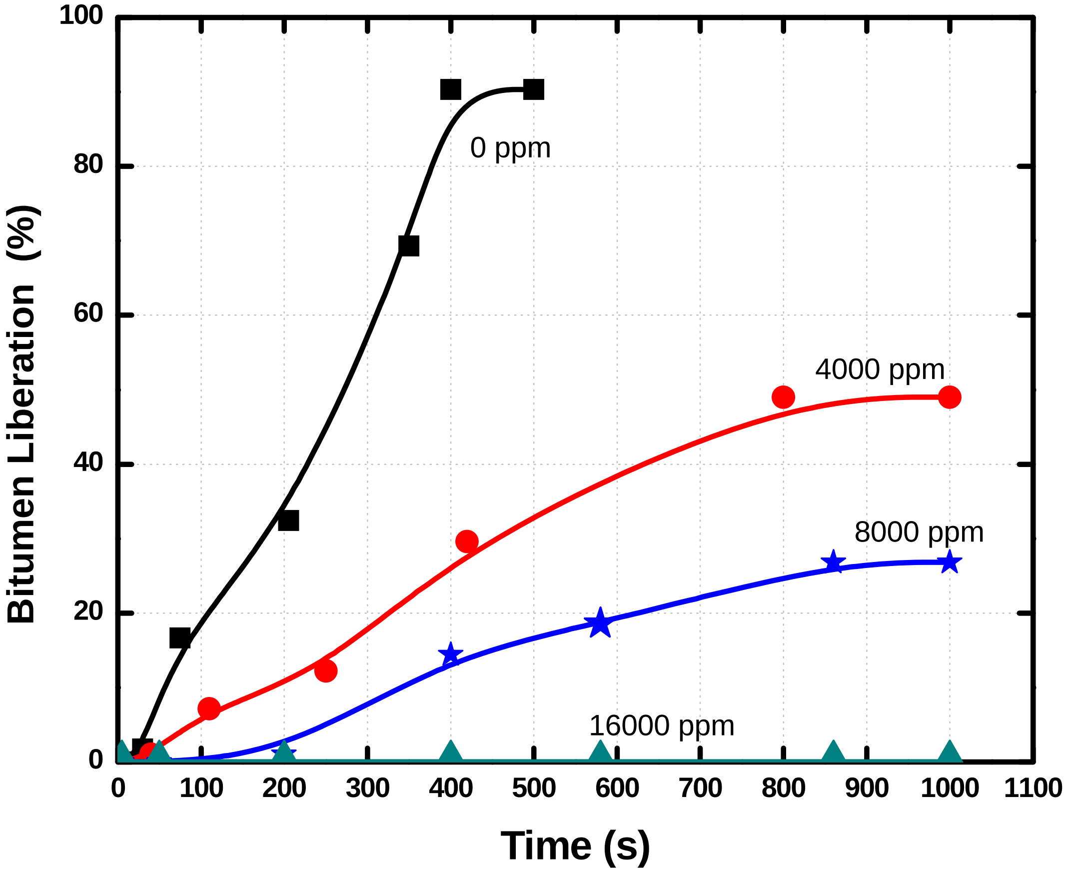

Figure 21. Effect of NaCl addition on degree of liberation as a function of time at pH of 10 and 46 °C

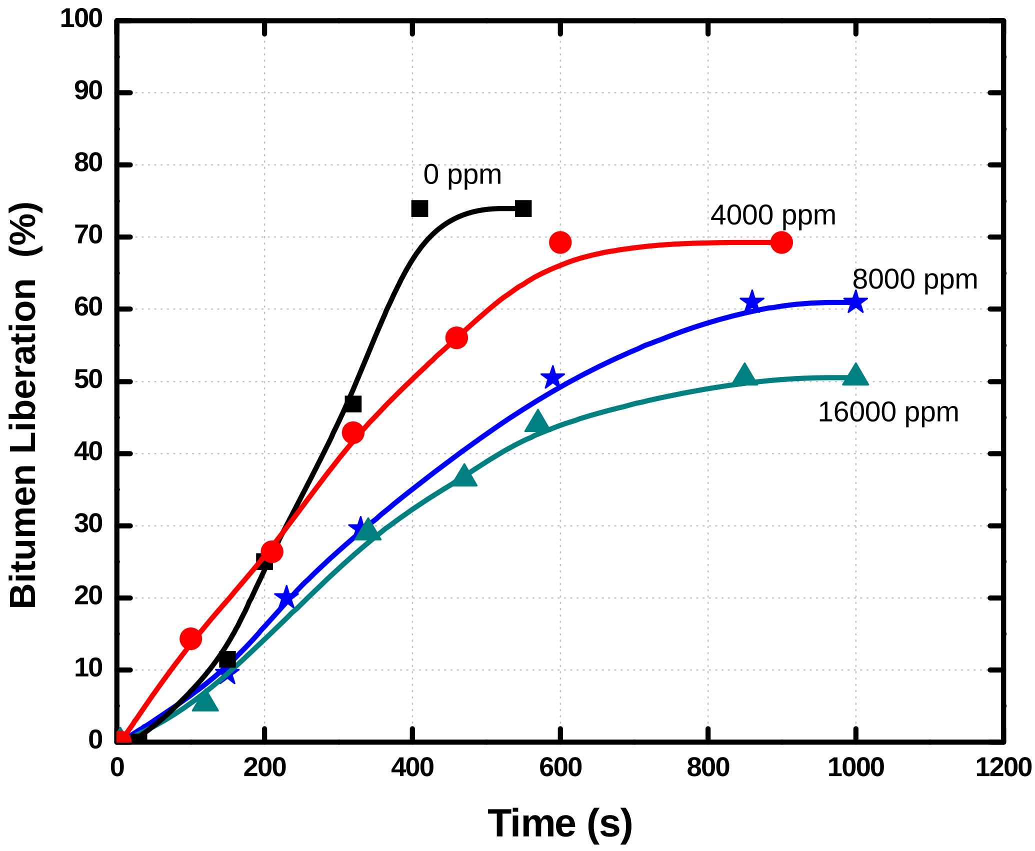

Figure 22. Effect of NaCl addition on degree of liberation as a function of time at pH of 7.8 and 46 °C

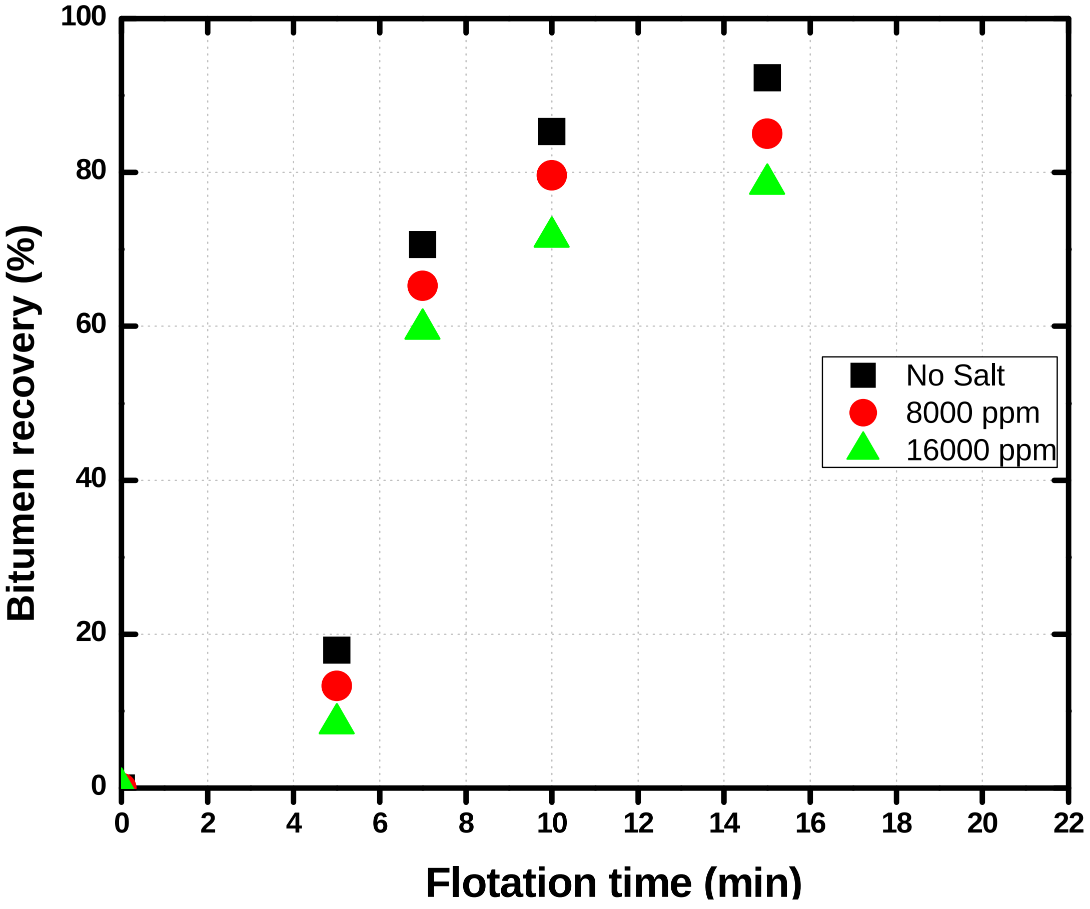

Figure 23. Flotation kinetics using Denver cell flotation for a high-grade oil sands ore at 46 ^{o}C, pH 10 and at various saline concentrations

3.3. Effect of weathering on degree of liberation

Weathering is known to drastically reduce the bitumen recovery from oil sands (Ali, 1975; Schramm and Smith, 1987). It is therefore important to investigate whether weathering of oil sands has any impact on bitumen liberation and recession. For the test, 250 g of the high-grade oil sand ore was weathered at 60 ^{o}C in an oven with air ventilation. A sample for analysis was withdrawn from the oven for three consecutive days with the final sample withdrawn after 7 days. These oil sand samples weathered for different periods of time were subjected to bitumen liberation analysis one at a time at pH of 10 and solution temperature of 46 ^{o}C. Figures 24 to 26 show distinct images of bitumen liberation at the end of 500 seconds from ores weathered for different time periods. Figure 24 shows images of bitumen liberation from an un-weathered ore while Figure 25 shows bitumen liberation from an ore weathered for three days. It can be clearly seen in Figure 25 that at the end of 500 seconds, majority of bitumen films have not yet receded to form droplets when compared to the un-weathered ore as shown in Figure 24. While an ore weathered for one week, as shown in Figure 26 is seen not to recede at all even at the end of 500 seconds. The drastic effects of weathering is seen in Figures 24 to 26, which displays clear images of lower bitumen recession after weathering when compared with the no-weathering case.

Quantitative analysis of the effect of weathering on bitumen liberation is shown in Figure 27. It can be seen that the degree of liberation was drastically affected with increase in weathering time. Weathering for one day dramatically affects the bitumen recession rate and lowers the degree of liberation by 35% when compared to the case un-weathered ore at the end of 400 seconds. For each additional day of weathering bitumen recession rate decreases with less than 25% degree of liberation observed for the 3-day weathered ore at the end of 400 seconds.

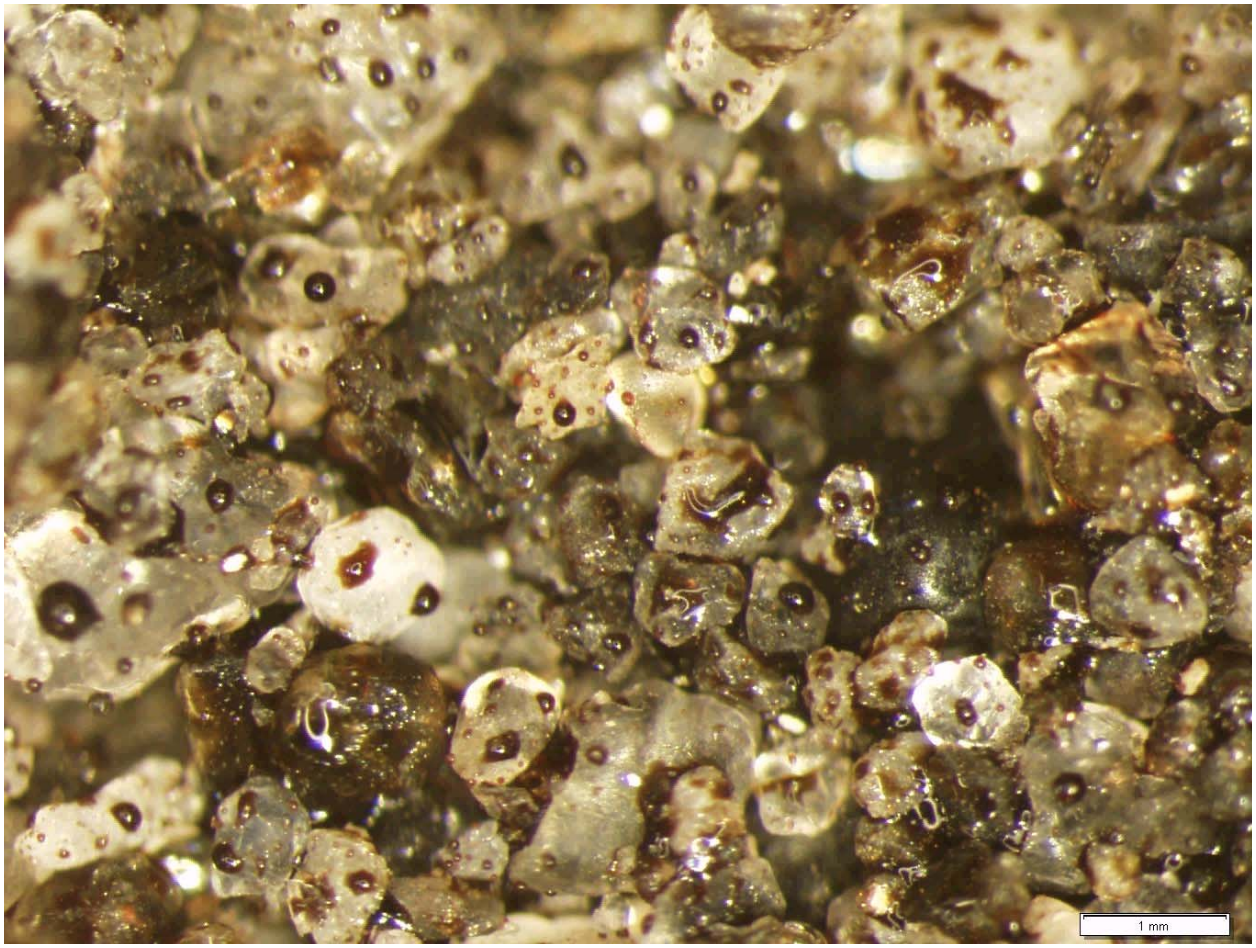

Figure 24. Bitumen liberation observed at pH 10 and 46 °C for an un-weathered ore after 500 seconds of solution flow

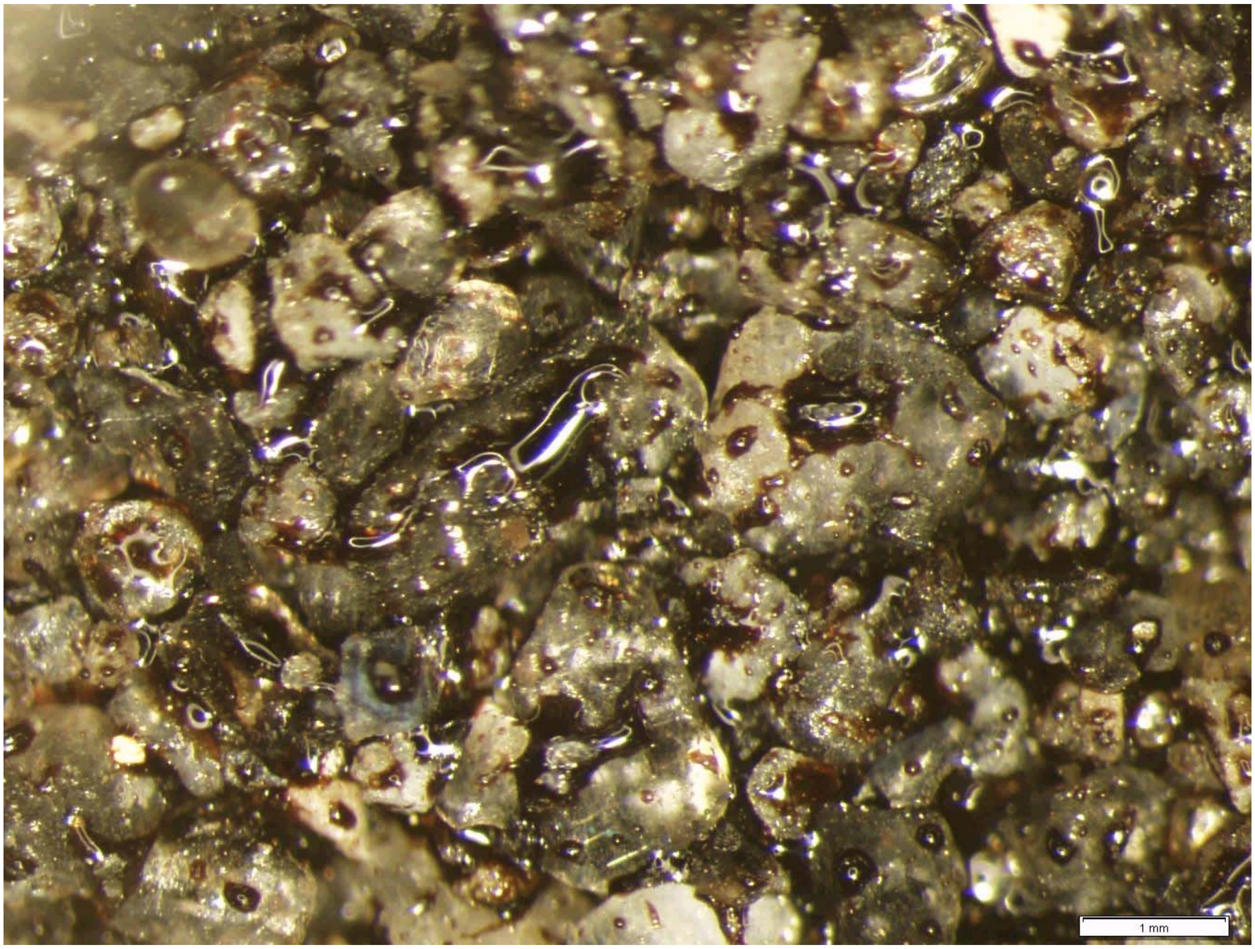

Figure 25. Bitumen liberation observed at pH 10 and 46 °C for a 3-day weathered ore after 500 seconds of solution flow

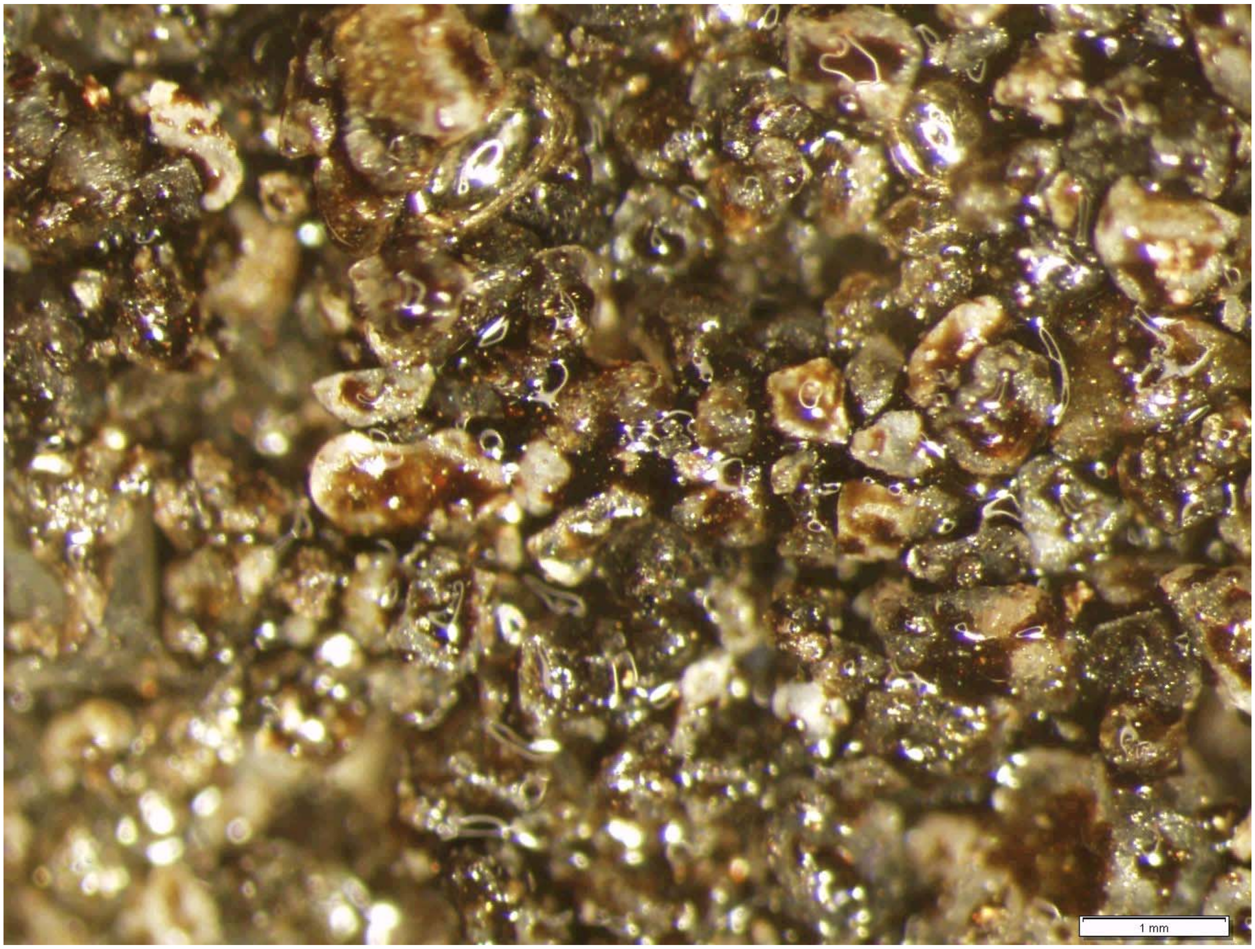

Figure 26. Bitumen liberation observed at pH 10 and 46 °C for one week weathered ore after 500 seconds of solution flow

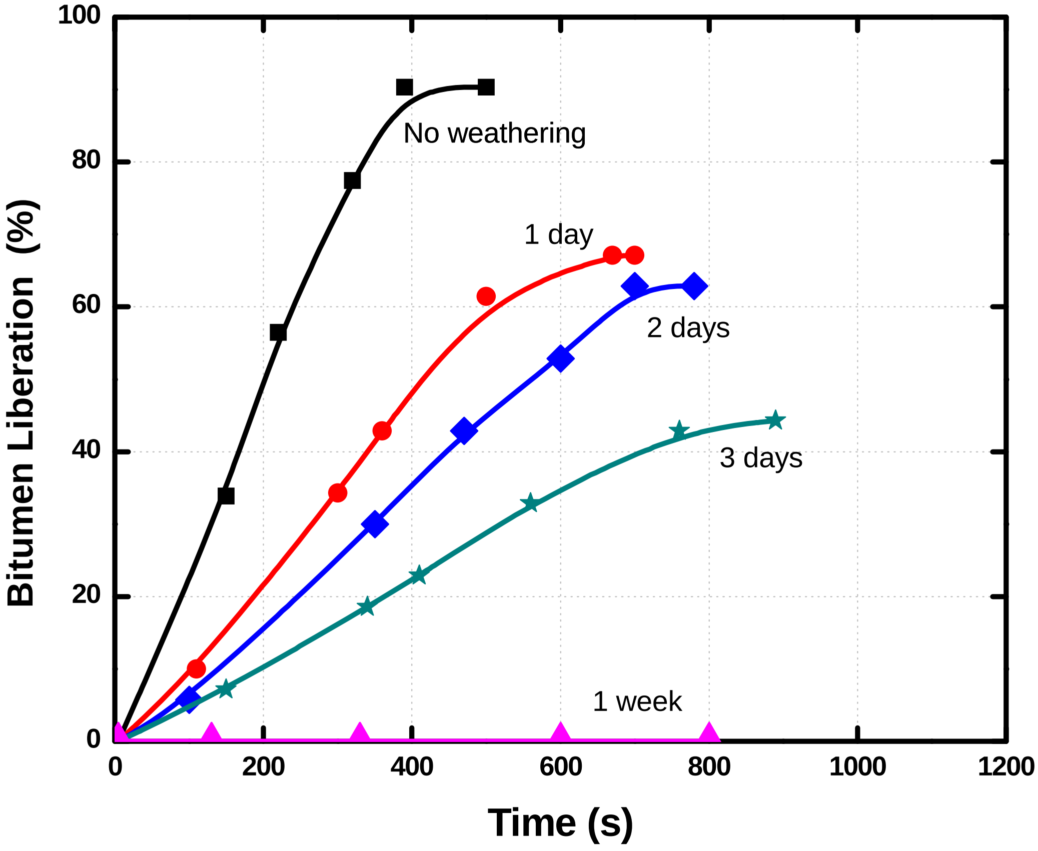

Figure 27. Effect of weathering on degree of liberation as a function of time at pH of 10 and temperature 46 ^{o}C

An un-weathered ore achieved 90% degree of liberation within 400 seconds at pH 10 and solution temperature of 46 ^{o}C while an ore weathered for three days achieved 45% in about 800 seconds, which is double the time taken by the un-weathered ore with half the achieved degree of liberation. Finally, an ore weathered for one week did not recede leading to no bitumen liberation even after 900 seconds, highlighting the severe effects of weathering on bitumen liberation. The reason for slower bitumen recession and lower degree of liberation could be attributed to the water-loss due to weathering or the change in hydrophobicity of the solids triggered due to the water loss, forcing stronger attachment of bitumen films on the sand grain leading to low bitumen liberation. Mikula et al. (2003) in their effort to characterize bitumen properties using microscopy observed that when ores were weathered or oxidized, there was a loss of aliphatic carbons and a relative increase in hydroxyl groups of the bitumen. They attributed the changes in bitumen chemistry to be the dominant parameter responsible for lower bitumen liberation of weathered ores. By characterizing wettability using a variety of techniques, Ren et al. (2008) and Dang-Vu et al. (2009) reported a significant increase in hydrophobicity of solids from weathered oil sands ores. Solids extracted from weathered ores were most hydrophobic of all tested ores, suggesting difficult bitumen liberation from the sand grains. They found that laboratory weathering caused a significant decrease in bitumen recovery, which confirms the findings of this study.

3.4. Effect of diluent (kerosene) on degree of liberation

Schramm et al. (1998) with their experiments and studies have shown the importance of solvent addition in increasing bitumen recovery and froth quality. However, there is no direct evidence whether solvent addition helps in bitumen liberation or aeration or both as the studies were based on results from the batch extraction unit (BEU). Consequently, in this study, independent tests were carried out to observe the effect of kerosene addition on bitumen liberation. Since we showed that oil sand ore weathered for one week does not to recede at all. This weathered ore would be an ideal candidate for studying the effect of kerosene addition on bitumen liberation.

In this study, to a sample of weathered ore weighing 3 g loaded into the sample holder two drops of kerosene were added and was allowed to soak for 15 mins, prior to liberation test. In contrast to the case without kerosene addition where no bitumen liberation is observed, the bitumen films on the weathered ore after kerosene addition receded instantly or all the bitumen films washed away with the water flow, leaving behind clear sand grains. In Figure 28, image of clear sand grains observed after kerosene addition to the weathered ore can be seen. Figure 29 shows the degree of liberation curve obtained for an weathered ore with and without kerosene addition. The degree of liberation for a weathered ore with kerosene reached 100% within 350 seconds, while the weathered ore without kerosene was not seen to recede at all. Kerosene improves bitumen liberation by reducing the viscosity of bitumen and facilitating the removal of bitumen from the sand grain leading to improved bitumen recovery. Bitumen recovery tests using Denver flotation cell by Harjai (2007) showed that kerosene soaking in oil sands ore before extraction improved bitumen recovery substiantially. His findings correlate well with the observations from this study. In Harjai's work, an optimal solvent dosage was identified, beyond which the bitumen recovery starts to decrease. For this reason, further independent analysis to study the effect of kerosene dosage on bitumen liberation would be beneficial.

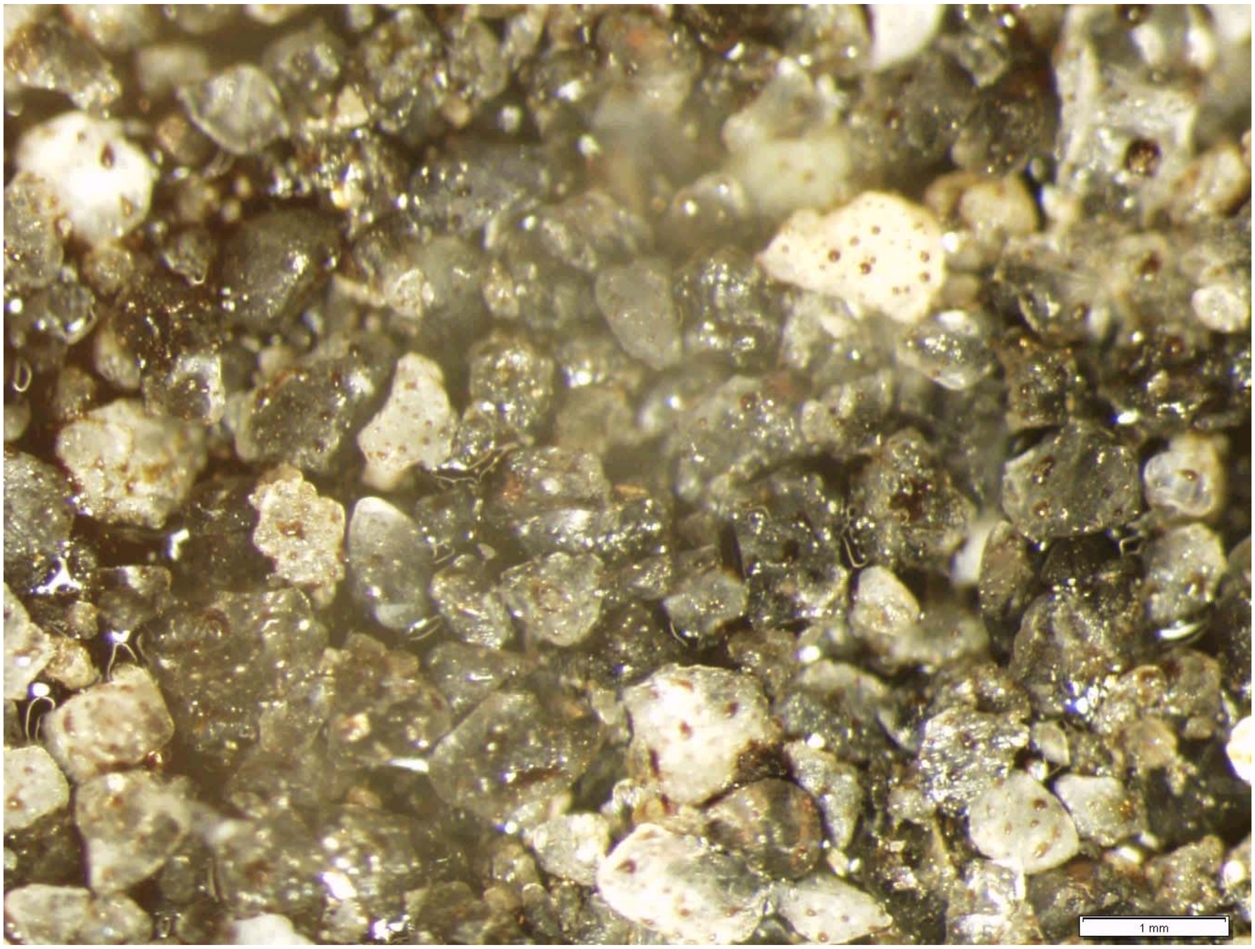

Figure 28. Bitumen film washes away after kerosene addition at pH 7.8 and 46 °C, after 300 seconds of solution flow

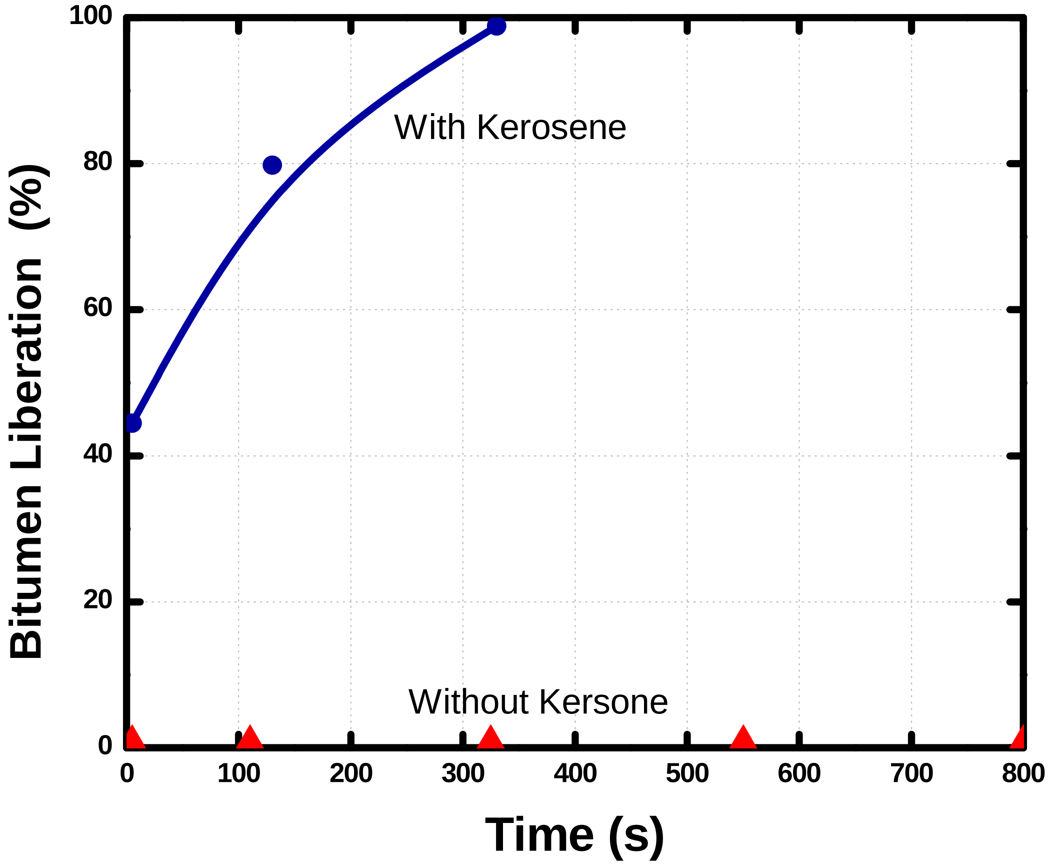

Figure 29. Effect of addition of kerosene on degree of liberation as a function of time at pH of 7.8 and 46 °C

3.5. Effect of fines on degree of liberation

Fines found in oil sands ore are mainly clays and are defined as particles, which are less than 44 μm in size. Effect of fines on bitumen liberation has always been a widely researched topic, Sparks et al. (2003) and Ding et al. (2006) with their experiments using Denver flotation cell found that the presence of fines reduces bitumen recovery significantly. However, no concrete evidence is present to indicate whether, fines hamper bitumen liberation, bitumen aeration or both. Consequently, an attempt to observe the effect of fines, if any, on bitumen liberation and recession from the sand grain is well justified.

Oil sands ores have different bitumen recoveries based on their difference in processabilty, bitumen and fines content. Two similar ores A1 and A2 are chosen for the degree of liberation analysis. These two ores form an ideal comparison as they have very similar bitumen, water and solids content but primarily differ from each other by their fines content as shown in Table 1. It would be interesting to visually observe any characteristic difference in the degree of liberation based on their difference in fines percentage and help us better understand the effect of fines on bitumen liberation.

Table 1 Ore description for ores differing in fines content

Code Name	Bitumen (wt %)	Water (wt %)	Solids (wt %)	Fines (wt %)
A1	11.8	2.2	84.4	0.1
A2	11.1	3.3	83.6	12.6

Figures 30 and 31 show distinct images of bitumen liberation at the end of 800 seconds from ores A1 and A2 at pH of 11.3 and at solution temperature of 46 ^{o}C. Clear bitumen droplets can be seen to form on the sand grains as shown in Figure 30 for ore A1 with nearly no fines. The severe impact of fines can be clearly observed in Figure 31 where no bitumen film recession and no bitumen droplet can be seen to form on the sand grains in ore A2, which has equal percentage of bitumen as ore A1. Fines can be seen to severely reduce bitumen recession and bitumen liberation by inhibiting the bitumen film to recede and form bitumen droplets. Similar trends and observations were also observed for solutions at lower pH values of 9.7 and 7.8. Comparing ores A1 and A2 in Figures 30 and 31 it is observed that ores with higher percentage of fines have a lower average particle size than the ores with lower percentage or no fines in them. Consequently, due to the very small diameter of the sand grains and even smaller bitumen droplet that form on them, it is very difficult to quantify the degree of liberation from ore A2. Figure 32 shows bitumen liberation percentages for ores A1 and A2 at different pH values and at solution temperature of 46 ^{o}C. The absolute value of the bitumen liberation percentages for ore A2 is not reliable but the trend of bitumen liberation curves can be seen in Figure 32.

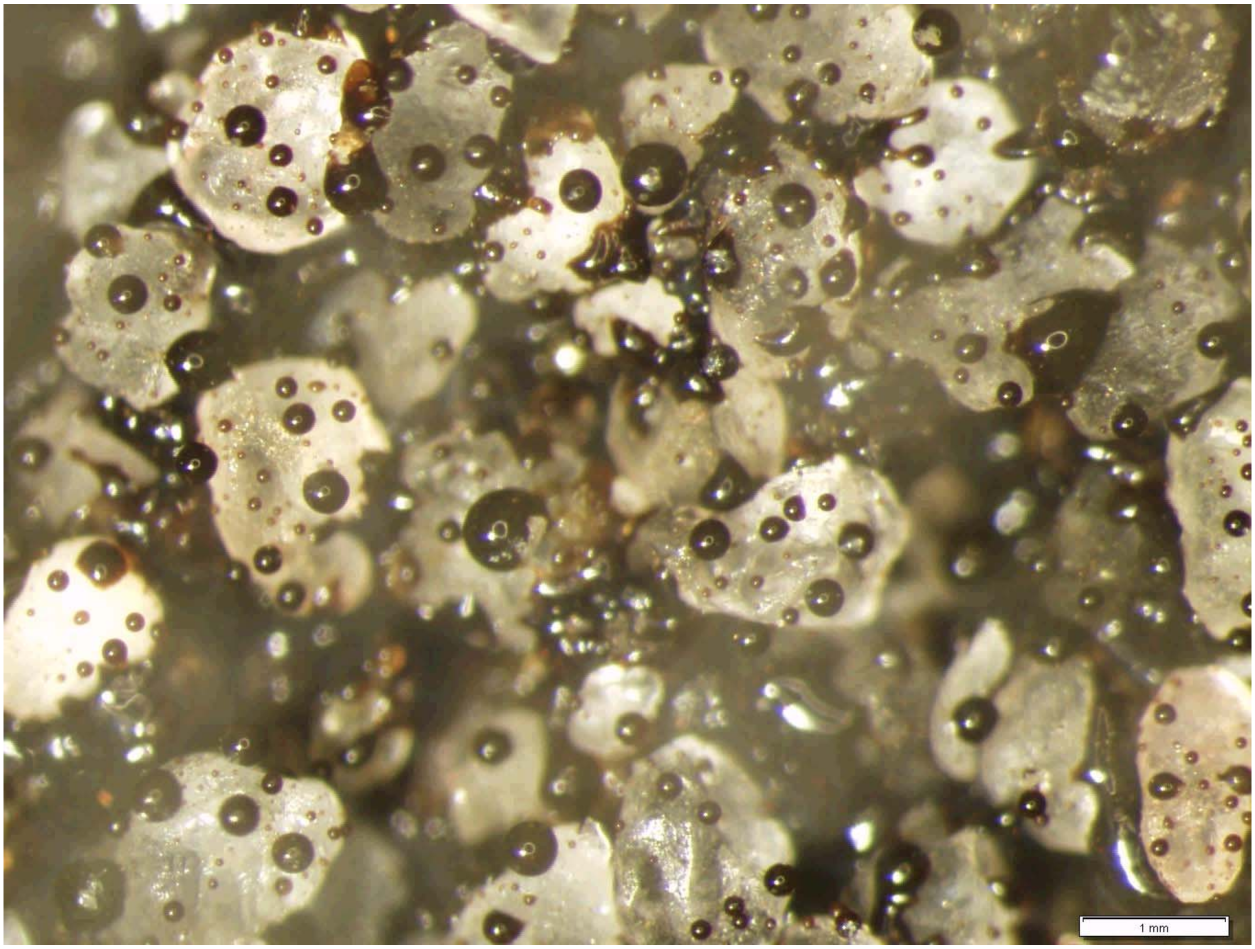

Figure 30. Bitumen droplets formed at pH 11.3 and at 46 °C for ore A1 after 800 seconds of solution flow

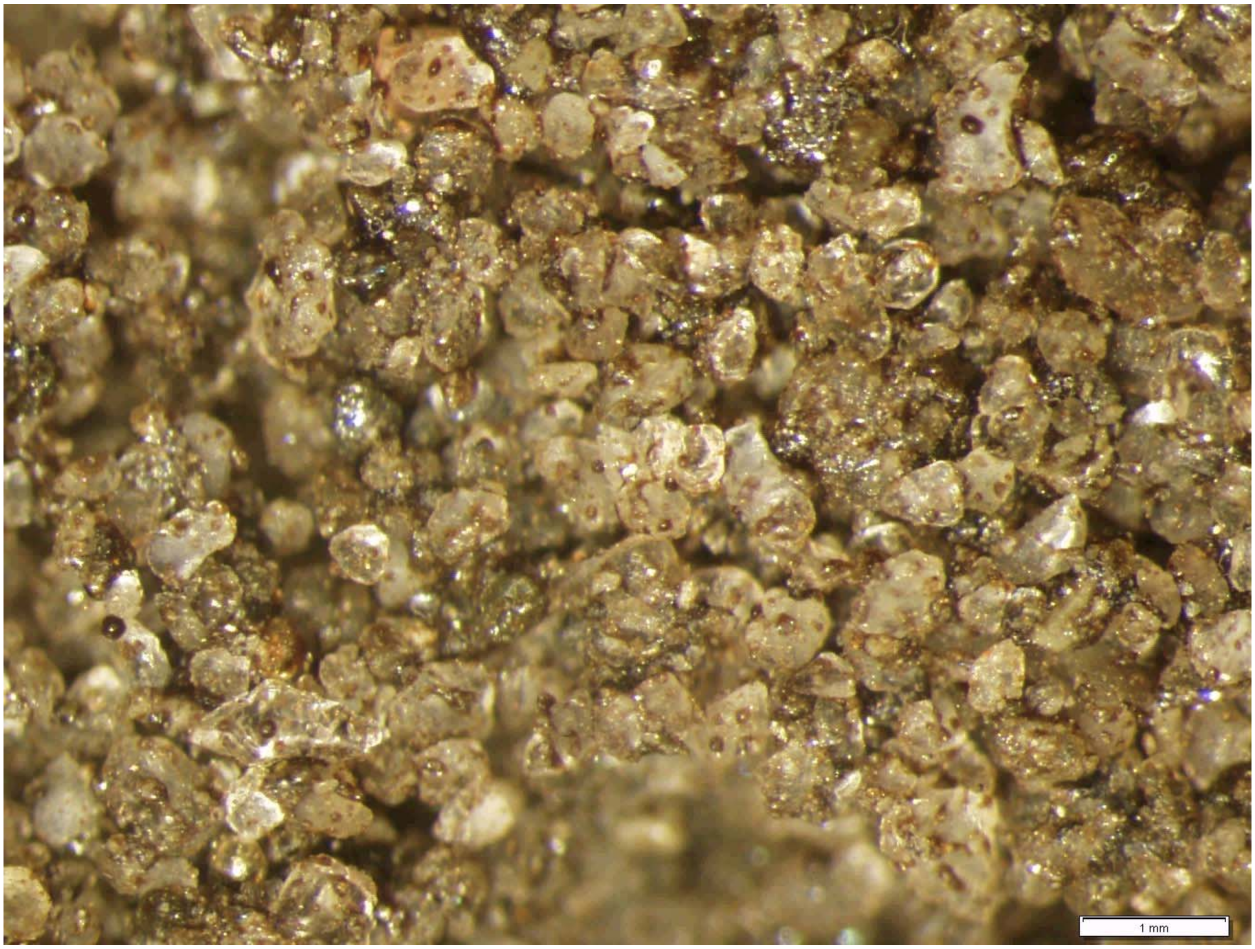

Figure 31. Bitumen droplets formed at pH 11.3 and at 46 °C for ore A2 after 800 seconds of solution flow

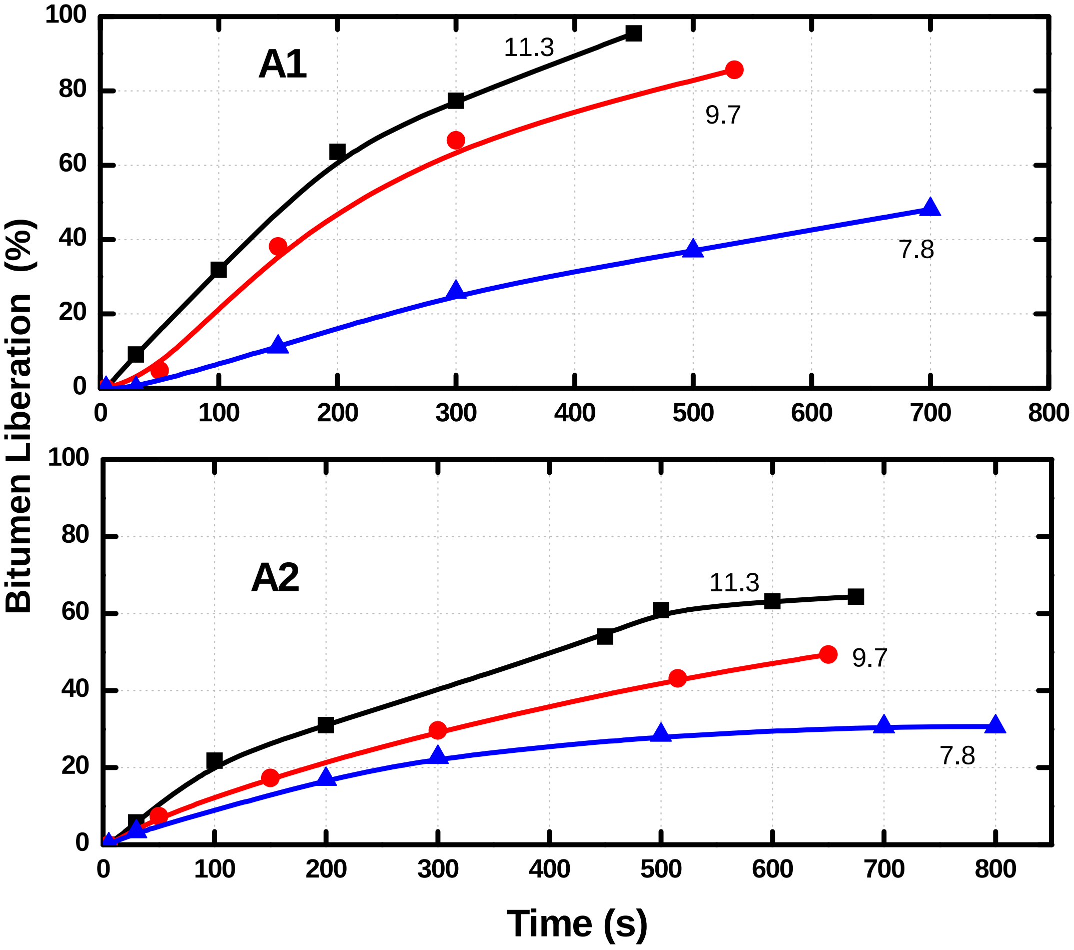

Figure 32. Effect of fines on degree of liberation as a function of time at various pHs and at temperature 46 °C

An attempt to go one-step further and observe degree of liberation of oil sand ores with relatively higher percentage of fines forms the basis of the present set of results. The analysis is carried out for pHs of 11.3 and 9.7 and at solution temperature of 46 °C for two ores SYN 704 and D, both ores have higher than 20 wt% of fines as described in Table 2. The quantification of the degree of liberation was very hard for both the ores, as the sand grains were very small and plagued with fines, which severely hampered bitumen liberation as can be seen in Figures 33 and 34.

Table 2 Ore characteristics for high fine ores SYN 704 and Ore D

Code Name	Bitumen (wt%)	Water (wt%)	Solids (wt%)	Fines (wt%)
SYN704	9.7	6.2	85	25.5
D	9.6	2.28	87.02	39.1

Due to the very small size of the sand grains and even smaller bitumen droplet that form on them, it is very difficult to quantify the degree of liberation from both ores SYN 704 and D. The absolute value of the degree of liberation cannot be provided but an approximate value of the degree of liberation is estimated. SYN 704, an average grade ore, with lower percentage of fines was estimated to have 75% degree of liberation at the end of 800 seconds at high pH of 11.3, while ore D was estimated at 65%. At lower pH of 9.7, which is close to the operating pH followed by most industries, SYN 704 and ore D were found to have approximately 50% degree of liberation at the end of 800 seconds. A high operating pH is advisable for optimum bitumen recovery for ores with high percentage of fines when bitumen liberation is concerned. In Figures 33 to 34, fines can be seen to severely reduce bitumen recession and bitumen liberation by inhibiting the bitumen film to recede and form bitumen droplets. The analysis clearly indicates that bitumen liberation is a limiting step in presence of fines, due to which low bitumen recoveries are observed in high fines ores.

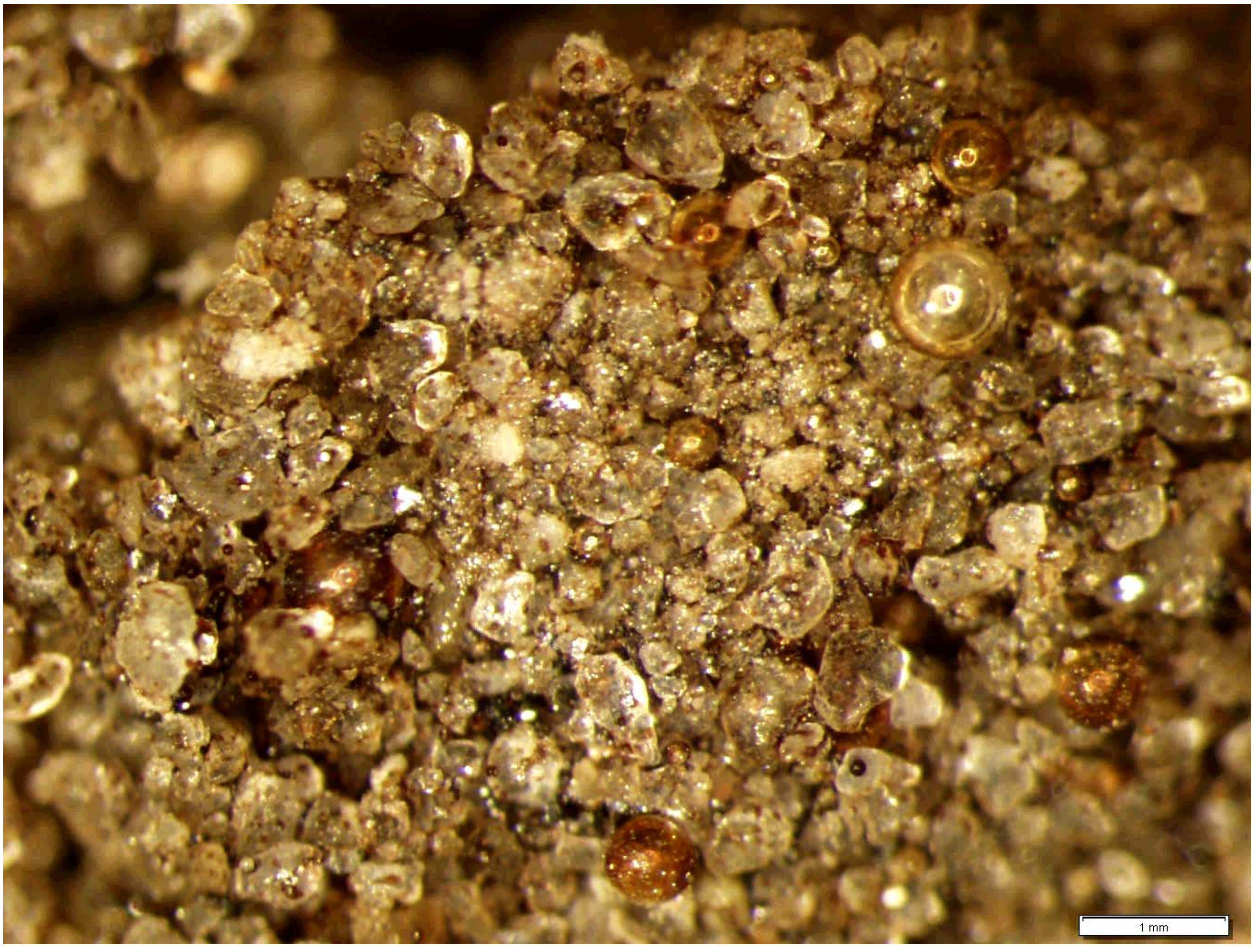

Figure 33. Bitumen droplets formed at pH 11.3 and at 46 °C for ore D after 850 seconds of solution flow

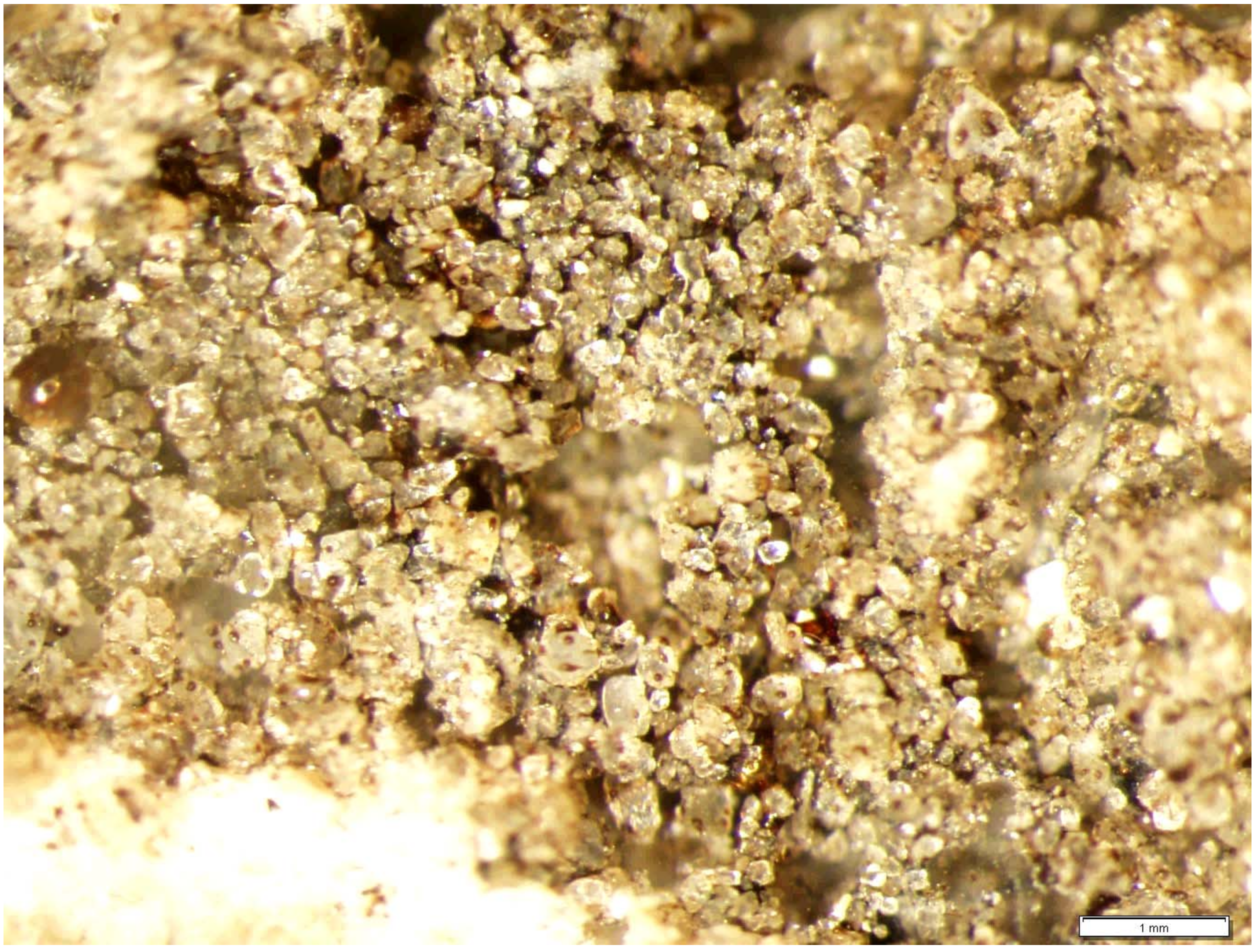

Figure 34. Bitumen droplets formed at pH 11.3 and at 46 °C for ore SYN704 after 850 seconds of solution flow

The last set of results involves performing the degree of liberation analysis on another set of ores, differing in their processabilty. For the analysis, a high-grade ore, a good ore, an oxidized ore and a poor ore were chosen as shown in Table 3. Figures 35 to 38 show clear images of bitumen liberation at pH 7.8 and 46 ^{o}C for the four different ores selected. SUN 805 a high-grade ore receded and formed bitumen droplets within 200 seconds of solution flow as shown in Figure 35. In contrast, the majority of the bitumen films did not recede for Ore C, Ore OXSUN and Ore D at the end of 200 seconds as shown in Figures 36 to 38.

Table 3 Ore characteristics for ores differing in processability

Code Name	Processabiltity description	Bitumen (wt%)	Water (wt%)	Solids (wt%)	Fines (wt%)
SUN 805	High grade ore	15.9	1.5	82.6	2.6
C	Good ore	12.0	1.0	87.0	4.1
OXSUN	Oxidized ore	9.7	6.2	85	25.5
D	Poor processing ore	9.6	3.4	87.0	39.1

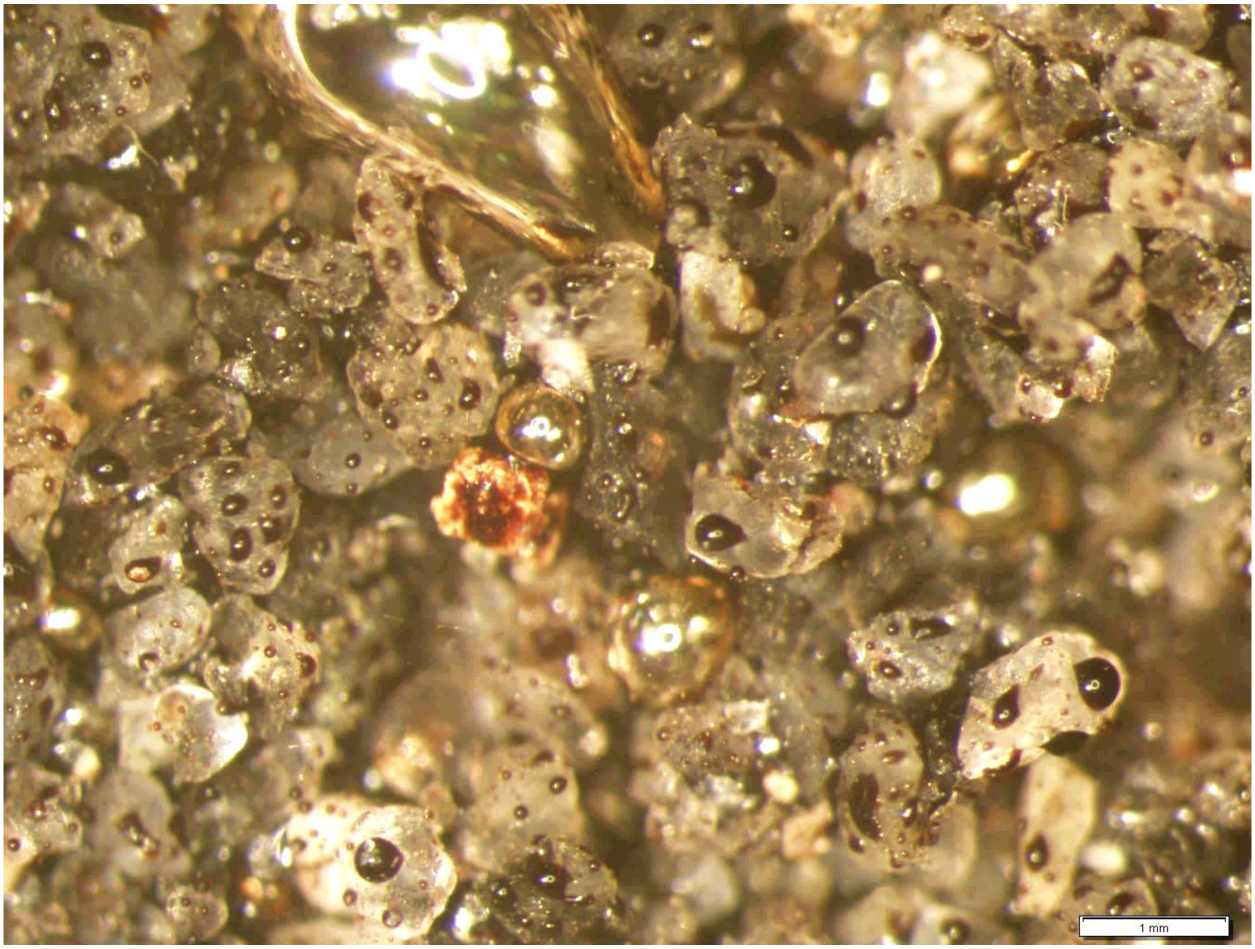

Figure 35. Bitumen droplets formed at 46 °C and pH of 7.8 for ore SUN 805 after 200 seconds of solution flow

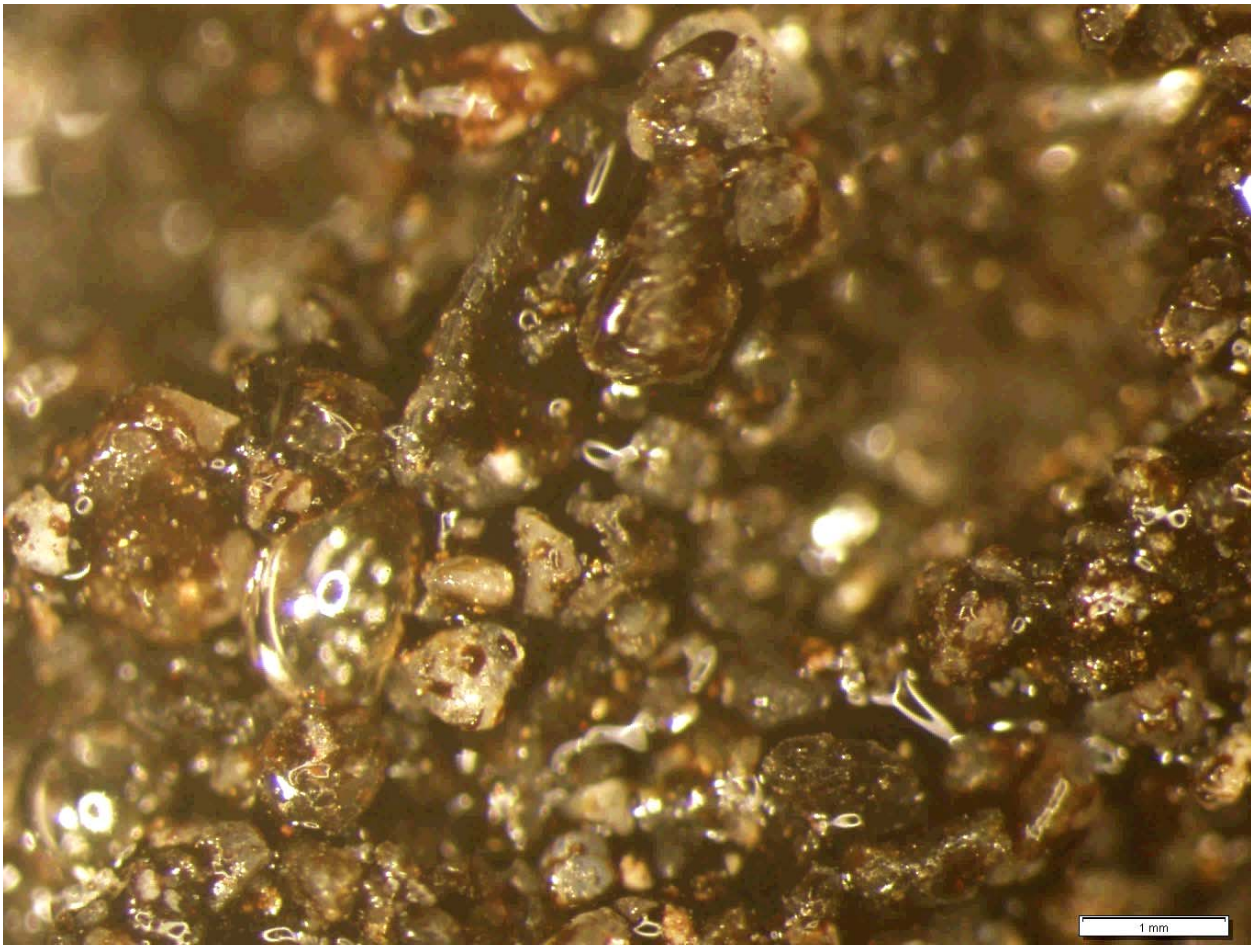

Figure 36. Bitumen droplets formed at 46 ^{o}C and pH of 7.8 for ore C after 200 seconds of solution flow

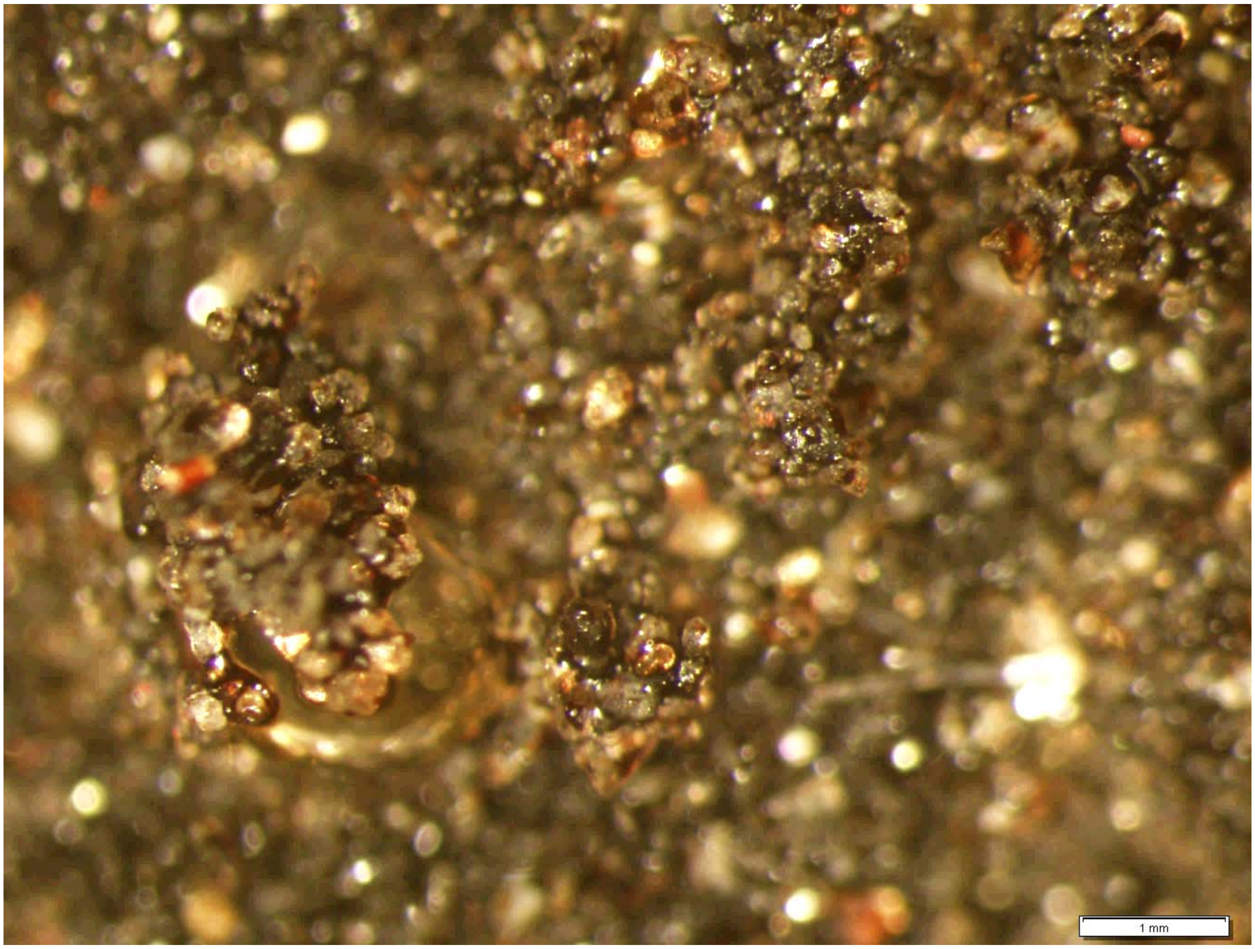

Figure 37. Bitumen droplets formed at 46 ^{o}C and pH of 7.8 for ore OXSUN after 200 seconds of solution flow

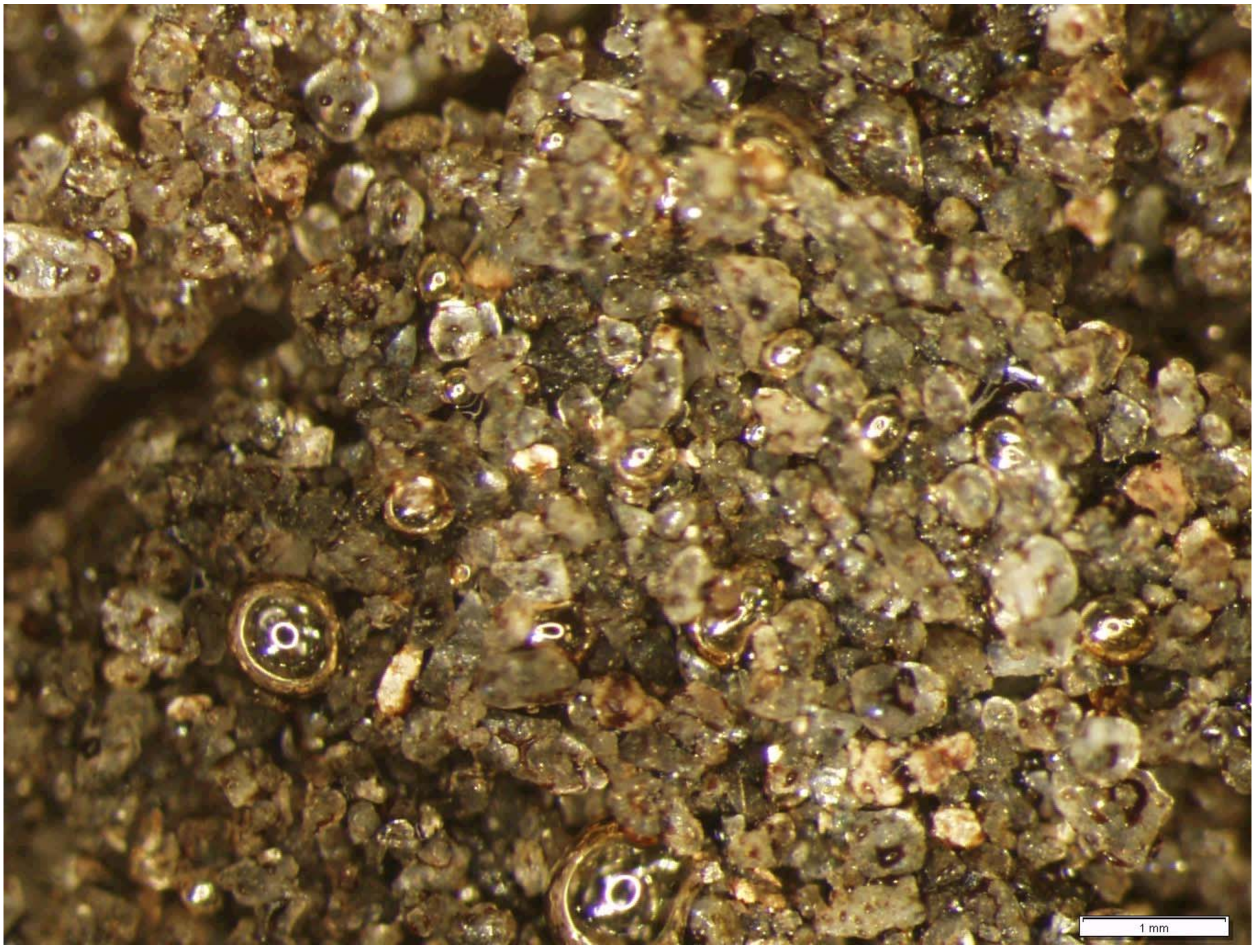

Figure 38. Bitumen droplets formed at 46 °C and pH of 7.8 for ore D after 200 seconds of solution flow

Figure 39 shows the degree of liberation at pH 7.8 and 46 °C for ores SUN 805, ore C, ore OXSUN and ore D. SUN 805, a high-grade ore had 96% degree of liberation within 300 seconds while Ore C (a good ore) reached 45% in 300 seconds. The average particle size of ore C was bigger than Ore SUN 805 but surprisingly the recession of bitumen films in ore C was slower. The reason for low bitumen recession can be attributed to the low hydrophilicity of the sand grains in ore C as all other parameters governing bitumen liberation were quite similar to ore SUN 805. It was very difficult to quantify oxidized ore OXSUN and poor ore D due to their comparatively smaller particle size but a rough analysis is presented. During analysis the presence of fines in ore OXSUN and ore D impeded the bitumen film recession into droplet reducing the degree of liberation significantly. Both ores OXSUN and ore D broke into collection of smaller particles during analysis and these small aggregations attached to the air bubbles that formed in the gaps due to the breaking of the ores. The adherence of these aggregations to the air bubbles as seen in all the results could be the possible reason for poor quality of froth obtained from the above-mentioned two ores. Both ores OXSUN and D have less than 50% degree of liberation at the end of 600 seconds.

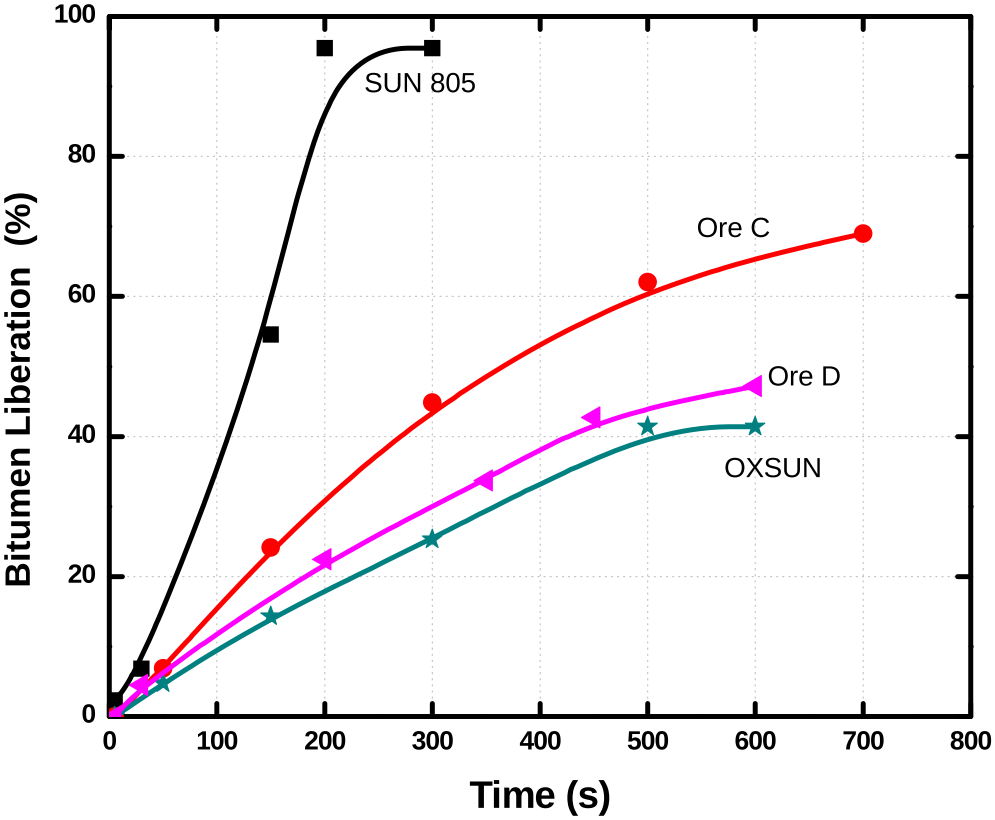

Figure 39. Effect of fines on degree of liberation as a function of time at pH of 7.8 and at 46 °C

Fines severely reduce bitumen liberation by inhibiting the bitumen film to recede and form bitumen droplets. Using Denver flotation cell, Ding et al. (2006) observed reduction in bitumen recovery from oil sands ore in the presence of clays. He suggested that the negative effect of clays could be reconciled by increasing the pH, his findings correlate well with the observations from this study.

Chapter 4: CONCLUSIONS

In this study, a novel flow cell was designed for viewing bitumen liberation directly from an oil sand ore sample. Analysis was conducted at various temperatures, pHs and varied conditions e.g. weathering, high salt concentrations which are known to effect bitumen recovery from oil sand ores. Analysis was also conducted to test the feasibility of the method on poor processing ores. From the experimental findings, the following conclusions are drawn:

- Bitumen liberation from an oil sand ore is high at alkaline conditions. Temperature also plays an important role in bitumen recovery from oil sands. Bitumen recovery percentage quantification could effectively identify the role of pH and temperature and illustrates its importance on bitumen liberation from an oil sand ore.
- Bitumen liberation was found to be very similar for temperatures 46 and 30 ^{o}C. Effectively extraction could be carried out at lower temperatures of around 30 ^{o}C with similar bitumen liberation patterns. Bitumen liberation was seen to take a drastic change for temperatures below 30 ^{o}C.
- High salt (NaCl) content in process water was found detrimental to bitumen liberation from oil sands. Bitumen liberation was seen to decrease with increase in NaCl concentration. High salt concentration proved to be more adverse leading to no bitumen liberation at conditions of high pH.
- Bitumen recovery from weathered ores was seen to decrease with increase in weathering time. Ore weathered for one week had zero bitumen liberation.

Weathering of oil sand ore was found to affect the conditioning stage of bitumen recovery process from oil sands.

- Kerosene addition to oil sands ore prior to water flow proved to be helpful in disengaging the bitumen from the weathered oil sands ore which otherwise never receded with no solvent addition.
- Presence of fines has a detrimental impact on bitumen recovery. Fines were seen to impede the recession of bitumen films to form bitumen droplet in an oil sands ore.

CHAPTER 5: RECOMMENDATIONS AND FUTURE WORK

It is recommended that a new cell should be designed based on the present experience, to be able to quantify high fines ores with a more magnified detailed viewing abilities. Software should be developed to digitally quantify the images, which would have faster, and accurate quantifications of the degree of liberation from the oil sands ores. A better software could be developed, which has an advanced contact-angle measuring tool, which can efficiently measure the contact angle of the bitumen droplets formed on the sand grains. More work on the role of surfactants in bitumen liberation can be carried out. Such a study will help to pin point whether a given surfactant has an effect on bitumen liberation or otherwise on aeration. A cell can also be designed with an artificial air bubble generator, which might help, to study the role of air bubbles in extraction. Further study with analysis in process tailings recycle water is needed to determine the role of natural surfactants and other process conditions in bitumen liberation.

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Chapter 7: APPENDIX A

This appendix contains the tabulated and inferred data for all experimental work carried out for this study. The tabulated data represents the data used for various figures shown in the thesis.

Table A.1: Tabulated data for Figure 10: Effect of temperature on degree of liberation as a function of time at pH 11.3

Temperature 46 ^oC			**Temperature 30 ^oC**			**Temperature 23 ^oC**		
Time (s)	**# of clear grains**	**Degree of liberation %**	**Time (s)**	**# of clear grains**	**Degree of liberation %**	**Time (s)**	**# of clear grains**	**Degree of liberation %**
5	0	0	5	0	0	5	0	0
30	8	9.54	30	4	3.60	30	0	0
100	17	20.21	100	16	14.41	100	4	7.84
200	39	46.41	200	46	41.44	200	11	21.56
300	82	97.64	300	84	75.67	300	16	31.37
			390	106	95.49	500	23	45.09
			500	106	95.49	650	28	54.90
Total grains	84		Total grains	111		Total grains	51	

Table A.2: Tabulated data for Figure 11: Effect of temperature on degree of liberation as a function of time at pH 9.7

Temperature 46 ^{o}C			**Temperature 30 ^{o}C**			**Temperature 23 ^{o}C**		
Time (s)	**# of clear grains**	**Degree of liberation %**	**Time (s)**	**# of clear grains**	**Degree of liberation %**	**Time (s)**	**# of clear grains**	**Degree of liberation %**
5	0	0	5	0	0	5	0	0
30	2	1.83	75	3	4.3	30	0	0
75	17	14.96	210	14	20.28	100	8	9.2
210	36	31.62	300	26	37.7	200	17	19.5
340	77	67.53	400	46	66.7	300	25	28.7
390	100	87.77	450	59	85.5	500	34	39.1
			550	59	85.5			
Total grains	114		Total grains	69		Total grains	87	

Table A.3: Tabulated data for Figure 12: Effect of temperature on degree of liberation as a function of time at pH 7.8

Temperature 46 °C			**Temperature 30 °C**			**Temperature 23 °C**		
Time (s)	**# of clear grains**	**Degree of liberation %**	**Time (s)**	**# of clear grains**	**Degree of liberation %**	**Time (s)**	**# of clear grains**	**Degree of liberation %**
5	0	0	5	0	0	5	0	0
30	0	0	30	0	0	30	0	0
150	11	11.82	100	9	7.37	100	5	7.57
200	24	25.80	200	16	13.11	200	10	15.15
320	45	48.38	600	37	30.32	600	17	25.75
410	69	74.19	750	37	30.32	700	18	27.27
Total grains	93		Total grains	122		Total grains	66	

Table A.4: Tabulated data for Figure 16: Effect of pH on degree of liberation as a function of time at temperature 46 ^{0}C

pH 11.3			**pH 9.7**			**pH 7.8**		
Time (s)	**# of clear grains**	**Degree of liberation %**	**Time (s)**	**# of clear grains**	**Degree of liberation %**	**Time (s)**	**# of clear grains**	**Degree of liberation %**
5	0	0	5	0	0	5	0	0
30	8	9.54	30	2	1.86	30	0	0
100	17	20.21	75	17	14.92	150	11	11.82
200	39	46.41	210	36	31.61	200	24	25.80
300	82	97.64	340	77	67.56	320	45	48.38
			390	100	87.77	410	69	74.19
Total grains	84		Total grains	114		Total grains	93	

Table A.5: Tabulated data for Figure 21: Effect of NaCl addition on degree of liberation as a function of time at pH 10 and 46 ^{0}C

0 ppm NaCl			4000 ppm NaCl		
Time (s)	**# of clear grains**	**Degree of liberation %**	**Time (s)**	**# of clear grains**	**Degree of liberation %**
5	0	0	5	0	0
30	0	0	100	13	14.28
150	11	11.45	210	24	26.37
200	24	25	320	39	42.85
320	45	46.87	460	51	56.04
410	71	73.95	600	63	69.23
550	71	73.95	900	63	69.23
Total grains	96		Total grains	91	

8000 ppm NaCl			16000 ppm NaCl		
Time (s)	**# of clear grains**	**Degree of liberation %**	**Time (s)**	**# of clear grains**	**Degree of liberation %**
5	0	0	5	0	0
150	10	9.52	120	5	5.37
230	21	20	340	27	29.03
330	31	29.52	470	34	36.55
590	53	50.47	570	41	44.08
860	64	60.95	850	47	50.53
1000	64	60.95	1000	47	50.53
Total grains	105		Total grains	93	

Table A.6: Tabulated data for Figure 22: Effect of NaCl addition on degree of liberation as a function of time at pH 7.8 and 46 ^{0}C

0 ppm NaCl			**4000 ppm NaCl**		
Time (s)	**# of clear grains**	**Degree of liberation %**	**Time (s)**	**# of clear grains**	**Degree of liberation %**
5	0	0	5	0	0
30	2	1.75	40	1	1.02
75	19	16.66	110	7	7.14
205	37	32.45	250	12	12.24
350	79	69.29	420	29	29.59
400	103	90.35	800	48	48.97
500	103	90.35	1000	48	48.97
Total grains	114		Total grains	98	
8000 ppm NaCl			**16000 ppm NaCl**		
Time (s)	**# of clear grains**	**Degree of liberation %**	**Time (s)**	**# of clear grains**	**Degree of liberation %**
5	0	0	5	0	0
50	0	0	50	0	0
200	1	1.03	200	0	0
400	14	14.43	400	0	0
580	18	18.55	580	0	0
860	26	26.80	860	0	0
1000	26	26.80	1000	0	0
Total grains	97		Total grains	92	

Table A.7: Tabulated data for Figure 23: Flotation kinetics using Denver cell flotation for a high-grade oil sands ore at 46 °C, pH 10 and at various saline concentrations

0 ppm of NaCl		**8000 ppm of NaCl**		**16000 ppm of NaCl**	
Time (mins)	**Bitumen Recovery %**	**Time (mins)**	**Bitumen Recovery %**	**Time (mins)**	**Bitumen Recovery %**
0	0	0	0	0	0
5	17.9	5	13.26	5	8.34
7	70.61	7	65.28	7	59.66
10	85.29	10	79.63	10	71.59
15	92.3	15	85.02	15	78.47

Table A.8: Tabulated data for Figure 27: Effect of weathering on degree of liberation as a function of time at pH 10.0 and temperature 46 ^{0}C

No Weathering			**Weathering 1-day**		
Time (s)	**# of clear grains**	**Degree of liberation %**	**Time (s)**	**# of clear grains**	**Degree of liberation %**
5	0	0	5	0	0
150	21	33.87	110	7	10
220	35	56.45	300	24	34.28
320	48	77.41	360	30	42.85
390	56	90.32	500	43	61.42
500	56	90.32	670	47	67.14
			700	47	67.14
Total Grains	62		Total grains	70	
Weathering 2-day			**Weathering 3-day**		
Time (s)	**# of clear grains**	**Degree of liberation %**	**Time (s)**	**# of clear grains**	**Degree of liberation %**
5	0	0	5	0	0
100	4	5.71	150	5	7.14
350	21	30.0	340	13	18.57
470	30	42.85	410	16	22.85
600	37	52.85	560	23	32.85
700	44	62.85	760	30	42.85

780	44	62.85	890	31	44.28
Total grains	85		Total grains	83	

Weathering 1 week		
Time (s)	# of clear grains	Degree of liberation %
5	0	0
130	0	0
330	0	0
600	0	0
800	0	0
Total grains	87	

Table A.9: Tabulated data for Figure 29: Effect of addition of kerosene on degree of liberation as a function of time at pH 7.8 and 46 ^{0}C

Weathering 1 week			Weathering 1 week + Kerosene		
Time (s)	# of clear grains	Degree of liberation %	Time (s)	# of clear grains	Degree of liberation %
5	0	0	5	40	44.44
110	0	0	130	71	79.77
305	0	0	330	86	98.87
550	0	0			
850	0	0			
Total Grains	81		Total Grains	89	

Table A.10: Tabulated data for Figure 32: Effect of fines on degree of liberation as a function of time at various pHs and at temperature 46^{0}C

Ore A1								
pH 11.3			**pH 9.7**			**pH 7.8**		
Time (s)	**# of clear grains**	**Degree of liberation %**	**Time (s)**	**# of clear grains**	**Degree of liberation %**	**Time (s)**	**# of clear grains**	**Degree of liberation %**
5	0	0	5	0	0	5	0	0
30	2	9.09	50	1	4.76	30	0	0
100	7	31.81	150	8	38.09	150	3	11.11
200	14	63.63	300	14	66.66	300	7	25.92
300	17	77.27	535	18	85.71	500	10	37.03
450	21	95.45				700	13	48.14
Total grains	22		Total Grains	21		Total Grains	27	

Ore A2								
pH 11.3			**pH 9.7**			**pH 7.8**		
Time (s)	**# of clear grains**	**Degree of liberation %**	**Time (s)**	**# of clear grains**	**Degree of liberation %**	**Time (s)**	**# of clear grains**	**Degree of liberation %**
5	0	0	5	0	0	5	0	0
30	5	5.75	50	6	7.41	30	3	3.41
100	19	21.84	150	14	17.28	200	15	17.04
200	27	31.03	300	24	29.63	300	20	22.72
450	47	54.02	515	35	43.21	500	25	28.41
500	53	60.92	650	40	49.38	700	27	30.68
600	55	63.22	--			800	27	30.68
675	56	64.37	Total Grains	81		Total Grains	88	

Table A.11: Tabulated data for Figure 39: Effect of fines on degree of liberation as a function of time at 7.8 pH and 46^{0}C

SUN 805			**Ore C**		
Time (s)	**# of clear grains**	**Degree of liberation %**	**Time (s)**	**# of clear grains**	**Degree of liberation %**
5	1	2.27	5	0	0
30	3	6.81	50	2	6.89
150	24	54.54	150	7	24.13
200	42	95.45	300	13	44.82
300	42	95.45	500	18	62.07
			700	20	68.96
Total grains	44		Total grains	29	
Ore D			**OXSUN**		
Time (s)	**# of clear grains**	**Degree of liberation %**	**Time (s)**	**# of clear grains**	**Degree of liberation %**
5	0	0	5	0	0
30	4	4.49	50	2	4.77
200	20	22.48	150	6	14.29
350	30	33.70	300	22	25.29
450	38	42.69	500	36	41.38
600	42	47.19	600	36	41.38
Total Grains	89		Total Grains	87	