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Understanding the Role of Caustic Addition in Oil Sands Processing

by

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Abstract

Sodium hydroxide (NaOH) is used as a chemical additive to enhance bitumen recovery from oil sands by surface-mining extraction process. The addition of NaOH adjusts the pH of the slurry water to pH ~8.5 (approximate pH of process water). The change in pH of oil sand slurry affects the process performance. In the current study, the effect of pH was investigated by varying the caustic usage up to about 0.7 wt. % (based on the mass of oil sand). Many parameters such as: Naphthenic acid, divalent cations and the surface charges of particles, bitumen and air bubbles have a significant impact on bitumen recovery and froth quality. A Study of the extraction process at a fundamental level improves our understanding of the key parameters that govern bitumen recovery.

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CHAPTER 1 INTRODUCTION

1.1 Oil sands deposit and processing

Oil sands also known as tar sands or bituminous sands, is a mixture of sand, clay, bitumen and some water. A large proportion of the oil sand is located in Alberta, Canada, with established reserves exceeding 3 trillion barrels of oil [1]. About 20% of the deposit is accessible by surface mining techniques. The recoverable oil is estimated to be 170.4 billion barrels, the third largest proven reserve in the world behind Saudi Arabia and Venezuela [2]. According to the Oil and Gas Journal in 2011, Canada ranked as the sixth largest crude oil producing country in the world, with the production of over 1.5 million barrels/day in 2011. Based on reserves and production rate, generation of oil in Canada can be sustained for more than 300 years. Alberta's prosperous oil sands industry not only satisfies Canada's energy consumption, but also brings huge profits and provides many job opportunities.

Oil sands processing includes mining, bitumen extraction, bitumen froth treatment and upgrading the extracted bitumen to synthetic crude oil. A generalized process diagram is shown in Figure 1.1 [3].
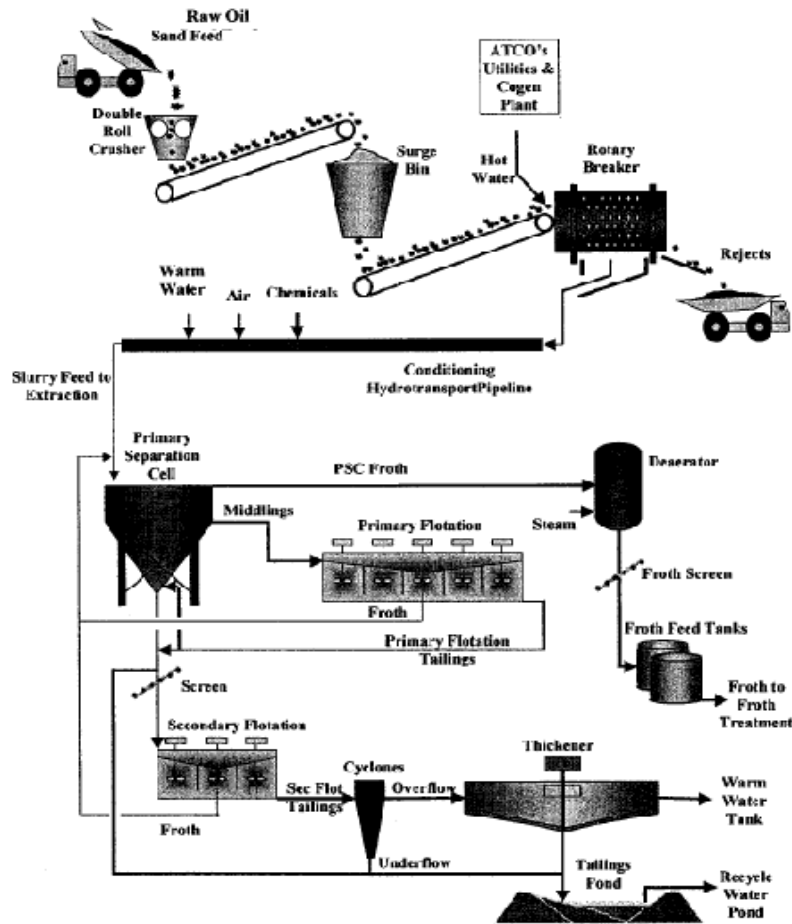
Figure 1.1 Schemes for oil sands processing using water-based extraction processes [3]

The oil sands are first mined in the open-pit mine and transferred into trucks and shovels. Then the raw oil sand lumps are crushed down to smaller size in mixing boxes, stirred tanks, surge bins or rotary breakers. The prepared oil sands are introduced to hydro-transport pipeline or to tumblers and mixed with warm recycled process water to generate the oil sands slurry. The operating temperatures of the slurry vary in different extraction companies ranging from 3 ℃ to 75 ℃ in the hydro-transport pipeline. The slurry is conditioned and bitumen is started to detach from the sand grains in the hydro-transport pipeline with chemical additives in this stage. The introduced air attaches to

the liberated bitumen surface and floats to the top of the slurry in large gravity separation vessels, which are normally referred to as Primary Separation Vessels (PSV) or Primary Separation Cell (PSC). There are three outlets of the PSV: primary froth (usually has 60% bitumen, 30% water and 10% solids), middlings, and tailings. The primary froth goes to the de-aerator where de-aeration has been taken place. Froth is screened and fed to the tanks for froth treatment. The froth is then diluted with solvent such as naphtha and paraffin. The diluted froth is centrifuged to remove the solids and water and then sent to upgrading. Middlings in PSV with small amount of bitumen are further recovered in Primary Flotation Cell (PFC) with introduced air flotation. The recovered froth goes back to PSV, and the reject stream of PFC joins in with the tailings of PSV to be screened and transferred to the Secondary Flotation Cell (SFC). Recovered bitumen from SFC also goes back to the PSV. The secondary flotation tailings go to tailings pond for settling. At Albian, the tailings from the extraction plant are sent to the cyclone. Overflow with many fine particles in the tailings is pumped to the thickeners to recycle the process water directly to the warm water tank and the recovered bitumen goes back to bitumen extraction plant. The underflow goes into the tailings pond for tailings management. Water in tailings pond usually contains high concentration of salt and organic contaminants, which is detrimental to the environment. Different technologies such as consolidated tailings, paste technology, and polymer flocculation were applied to reduce the time of tailings recycling. Reduction of the inventory of existed tailings ponds and the development of new technologies to avoid the generation of new tailings are always the goals of tailings treatment. Early studies on the reduction of oil sands tailings were

focused on the mechanical treatment such as filtration and centrifugation. In 1981, Liu et al. proposed to filter the extraction tailings by adding 300 ppm to 700 ppm lime [4]. Bakhshi et al. attempted to filter Suncor's tailings by adding fly ash at the ratio of 6g fly ash per 50 g tailings [5]. The addition of lime converted the extraction tailings into non-segregation mixtures leading the development of composite tailings (CT) technology.
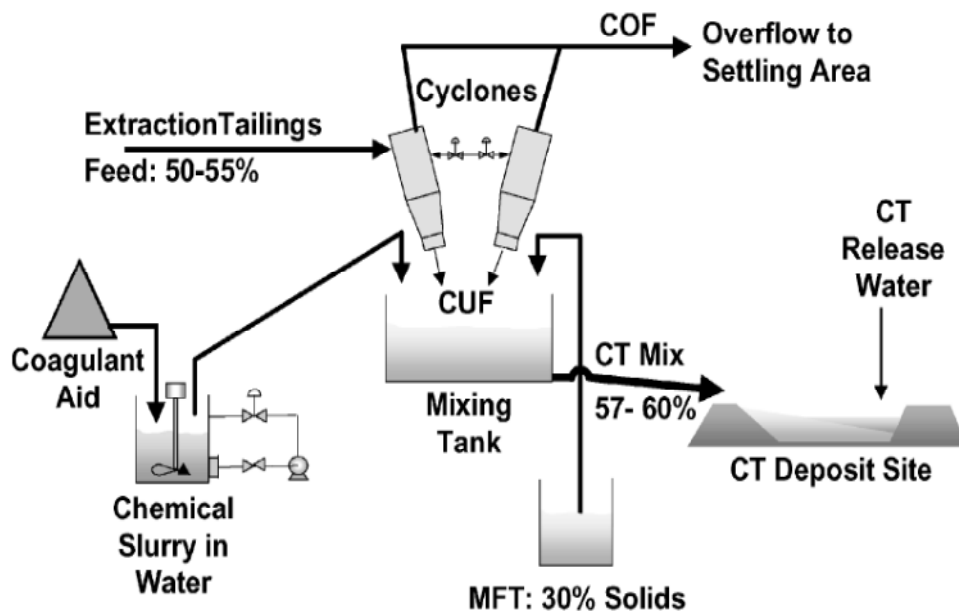
Figure 1.2 A schematic of CT process [6]

CT process: CT process is still being employed in Canada at present. Coarse tailings from the underflow of the cyclone is mixed with mature fine tailings (MFT) that are coagulated by adding coagulants as shown in Figure 1.2[6]. CT technology is designed to deposit the slurry to release water rapidly with no segregation. Lime, H_2SO_4, gypsum, alum ($Al_2(SO_4)_3 \cdot 12H_2O$) and organic polyelectrolyte are used as coagulants in the process. Although CT technology has been used for more than ten years, it is not applicable to transform CT ponds into trafficable deposit.

Flocculation technology: Flocculation destabilizes the dispersion through

bridging the colloidal particles together by polymeric flocculants, which have been studied for many years. Mechanisms involved in polymer flocculation include bridging, charge neutralization, polymer-particle surface complex formation, and depletion flocculation [7, 8].

Due to the "zero-discharge" policy, operators have to retain all process waste on site, which has resulted in the creation of tailings ponds [9, 10]. Fine solids (d < 44μm) settle extremely slowly and consolidate to approximately 30% solids to form mature fine tailings (MFT) that resist further consolidation, hence, minimizing water recycling. The Alberta Energy Resources Conservation Board's Directive 74, announced in February 2009 a requirement for oil sand operators to convert at least 20% of the fine particles in tailings ponds to solid waste by June 2011[11], commonly referred to as 'dry-stackable' tailings. Different approaches by different operators have been considered to address such requirement. Suncor has considered drying MFT, a key component of TRO (Tailings Reduction Operations), since 2003 [11]; while Canadian Natural Resources Ltd. (CNRL) mixes CO_2 rather than gypsum as a coagulant with fine clays and silts in the tailings [11].

1.2 Bitumen extraction

Oil sands are a major global energy source, with the energy retained in bitumen which accounts for approximately 10% of the oil sand; the rest constitutes solids (85%) and water (5%). Extraction of bitumen has become a well-developed technology since inception of the Clark hot water extraction (CHWE) process [12].

The whole CHWE flotation process involves two fundamental steps: liberation

and aeration. Oil sands are first agitated in hot water with caustic addition. Then bitumen liberates from oil sand and detached from the surface of sand grains, which is known as liberation. Liberation is mainly dependent on the interaction between bitumen and solids. The surfaces of bitumen droplet and solids are all negatively charged at pH greater than 7. The bitumen droplets are repelled away from oil sands by the electrical repulsive force. The high pH of the solution amplifies this repulsive effect and enhances bitumen liberation. After conditioning, air is introduced into the flotation system. Air will float the light bitumen droplets up to the top and left the heavy solids at the bottom, this process is called aeration. In the aeration, the bitumen surface is occupied by the cations existed in the process water. Fine particles usually have comparably small particle size and are easily to be attached to the cations associated with the bitumen to float as a part of froth, which is called slime coating. Lower pH can tolerant more cations in the process water, so slime coating is somewhat dependent on the pH.

Variability in ore characteristics: achieving 90% or greater total bitumen recovery via hot water extraction can be relatively simple in some cases especially if the bitumen content is high and the fines content is low. However for low grade oil sand ores (low bitumen content and high fines), recovery can be substantially lower sometimes as low as 30% [13].

Chemical aids are frequently used to maintain high bitumen recovery. A 1% reduction of bitumen recovery is estimated to be equivalent to a loss of 1.44 million US dollars daily, at current operational outputs (1.5 million barrels/day in 2011). Therefore, fully understanding the fundamentals of bitumen extraction is important not only from a financial perspective but also from an

environmental point of view making the process more efficient.

1.3 Objectives

The objective of the current study is to evaluate the impact of caustic addition on bitumen recovery from oil sands ores via a water based extraction process. In addition to extraction, air-bitumen attachment time and bitumen-fines interactions are characterized to have a better understanding of flotation performance and slime coating effects. Natural surfactant concentration (naphthenic acids) is quantified as a function of process water pH, with the study designed to evaluate the importance of both pH and surfactant concentration.

Two hypotheses are proposed:

1) Caustic prevents slime coating of bitumen droplets by fines.

2) Caustic causes the release of natural surfactants which enhances bitumen-air attachment.

1.4 Thesis Outline

The whole thesis is divided into six chapters:

Chapter 1: A typical water-based bitumen extraction process is introduced in this chapter to illustrate the importance of bitumen recovery to the oil sands processing.

Chapter 2: This chapter is to summarize the research done in bitumen extraction. The impacts of many factors such as caustic, naphthenic acid, water chemistry and air bubble size are discussed.

Chapter 3: The characteristic of the oil sand ores and process water used in this

study are listed to provide a background, followed by the procedures of bitumen flotation by Denver cell, dean stark, induction time measurement and zeta potential distribution.

Chapter 4: The impact of the caustic addition on bitumen recovery of four ores is compared for in this chapter. Froth quality represented as bitumen, water and solids mass are compared with different caustic addition for all the four ores.

Chapter 5: Naphthenic acid concentration released from the fresh tailings at different caustic addition for the four ores is plotted verse bitumen recovery to clarify the role of naphthenic acid in the bitumen flotation. Induction time and slime coating results are discussed to study the flotation mechanism – the balance among the interaction of bitumen emulsion, air bubble and fine solids.

Chapter 6: The impacts of caustic addition on bitumen extraction of two average fines ores and two high fine ores are concluded. And some future work is proposed for the continue research.

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CHAPTER 2 LITERATURE REVIEW

2.1 Characteristics of oil sands

The oil sands contain bitumen, sand grains, water and electrolytes in Athabasca, Alberta. In 1974, Cottrell proposed a model structure of the oil sands as in Figure 2.1. Sand particle is believed to be surrounded by a water envelope. This water envelope (a 10 nm thick layer) is further encased by bitumen, with the bitumen also partially filling the voids between the individual sand grains [1, 2]. Normally, some water-soluble ions (RCOOH, $ROSO_3$, RNH_2, Na^+, K^+, Ca^{2+} and Mg^{2+}) are also existed in the water envelope [3].
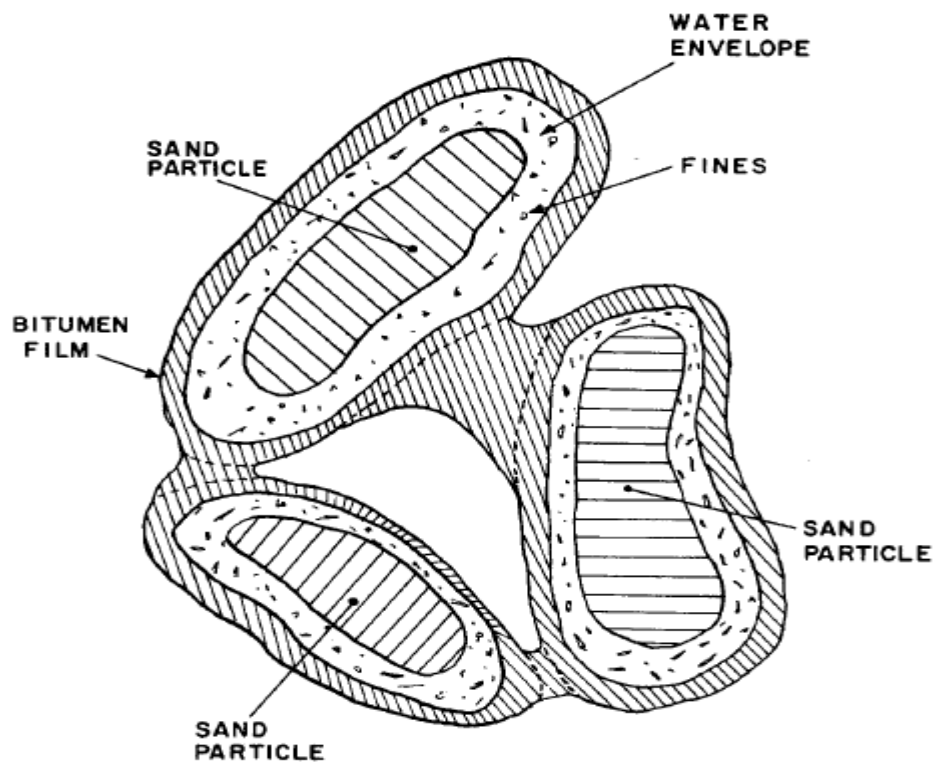
Figure 2.1 A model structure of oil sands [1]

The majority of the fines (defined as the solids less than 44 micron in size) are contained in the water film layer surrounding the sand grains which are generally water saturated. The mineral composition of the sands is over 90% quartz with minor amount of potash, feldspar, chert and muscovite [4]. For clay composition, they are mainly kaolinite, illite and a small amount of montmorillonite. Alteration of this physical configuration tends to result in some oil-wetting of solids, and it results in oil-rich sludge and solids-stabilized emulsions. So it is important to develop a process to float the bitumen from the sands before rupturing the connate water envelope [1].

According to the bitumen content, oil sand ore is classified as low-grade (poor) ore, which has 6-8% bitumen, average-grade (medium) ore which has 8-10% bitumen and high-grade (good) ore, which has more than 10% bitumen. Bitumen content varies in different oil sands; however, the mineral solids content is fairly constant in the range of 83% to 86%, balanced with connate water. Fine content is another parameter to classify the oil sand ore - processability. Low bitumen content and high fine content of associated sand grains are the primary reason of poor processing characteristic. In contrast, good processing ore has comparably low fine content and high bitumen recovery. Improving the bitumen recovery of poor-processing ore is always the challenge in bitumen extraction.

2.2 Water Based Extraction (WBE) process

2.2.1 Hot water extraction

In commercial surface mining oil sands plant, the bitumen is extracted by

various Clark Hot Water Extraction (CHWE) technologies because the solids in the oil sands are hydrophilic [5]. Dr. Clark developed the CHWE process for bitumen extraction in 1920's. Then he patented his HWE process and related apparatus in the United State in 1930's. Since then, considerable research efforts have led to the HWE process for recovering bitumen from oil sands in Athabasca area [6, 7]. The oil sands are mixed with water and caustic (such as NaOH) at slurry pH 8 to 8.5 and temperature 80 ºC (by injecting steam) in HWE process. A Low Temperature Extraction (LTE) process was proposed and patented in 1990 by Dr. Sury to reduce energy consumption and associated operating cost in the oil sands extraction [8]. Oil sands are mixed with water and digested in the hydro-transport pipeline at temperature 2 - 15 ºC in this low temperature extraction process. Bitumen extraction happens during the transportation process by the help of shear force. Then 100 - 800 ppm kerosene and 50 - 400 ppm Methyl Isobutyl Carbinol (MIBC) are introduced to facilitate bubble generation and bitumen aeration in the pipeline. After four years, two novel technologies: Warm Slurry Extraction (WSE) and Low Energy Extraction (LEE) have been developed in Syncrude [9, 10]. WSE is operating at 50 ºC, while LEE is operating at 25 ºC.

2.2.2 Additives and parameters

The effects of the process parameters on bitumen recovery, such as caustic addition, surfactant, cations, air flow rate, the size of air bubble, have been studied for dozens of years. The summary of previous researches about the process parameters on bitumen recovery is listed as below.

Caustic addition on bitumen recovery: The positive contribution of caustic

addition on improving bitumen recovery goes back to the work of Clark and Pasternack in 1932[5]. Sanford and Seyer developed a laboratory-scale Batch Extraction Unit (BEU) to standardize bitumen flotation tests in 1979 [11]. In BEU tests, caustic soda (NaOH) was identified as an additive which neutralized the organic acids in the bitumen. With addition of NaOH required to achieve a desired level of bitumen recovery was a function of fine solids content, the natural surfactant had been generated and it facilitated the bitumen flotation process. In 1983, Sanford reported that the maximum NaOH required to achieve a desired level of bitumen recovery was a function of fine content [12]. As shown in Figure 2.2, more NaOH are need for the high fine content ore to reach its maximum recovery. It seemed that pH was not the important parameter as such but rather NaOH addition level and that it should be regulated in response to fines level in feed [12].
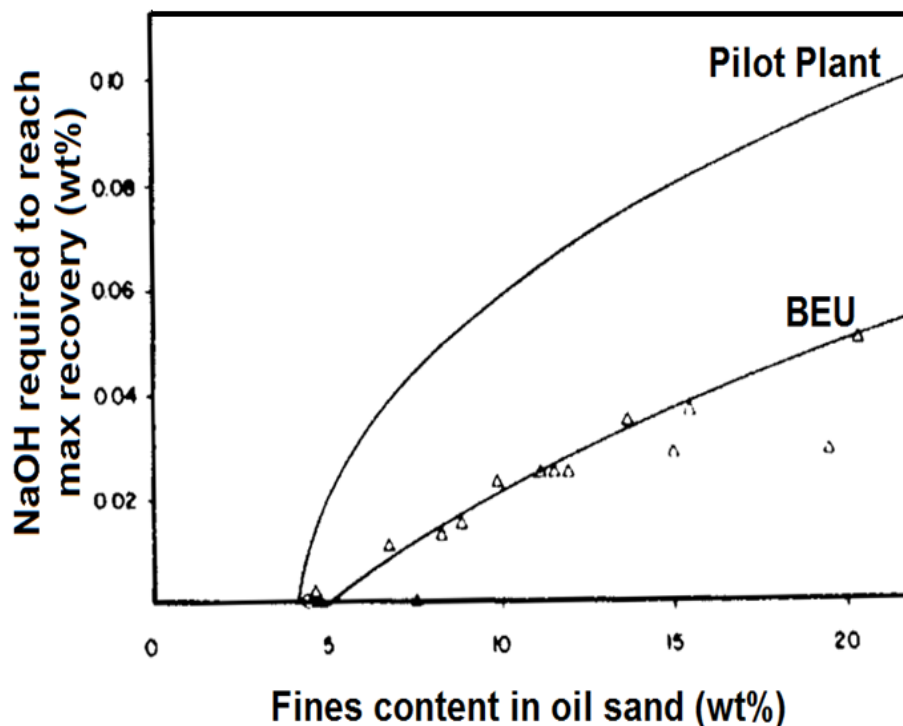
Figure 2.2 Fines content vs. NaOH required reaching maximum recovery [12]

Yamazaki showed in his research that steam- alkaline injection achieved a better bitumen recovery than the pure steam in 1989. And the alkaline steam also lowered the process operating temperatures [13]. In 1992, Smith and Schramm found that certain amount of caustic is required to produce needed natural surfactant, and the bulk of NaOH reacted with multivalent metal ions and minerals [14]. Dai and Chung studied the effect of NaOH addition on bitumen liberation in 1995[15], they concluded that increasing pH always favored bitumen liberation. In 1996, they identified that a critical NaOH dosage was needed to achieve an optimum bitumen recovery, and over-dose of NaOH caused bitumen to emulsify and form smaller sized bitumen droplets, which resulted in a lower bitumen recovery [16].

Surfactants also play a very important role in bitumen extraction process. In 1944, Clark noted the importance of surfactants in displacing the bitumen from sand grains in the hot water extraction process [17]. In 1969, Baptista and Bowman proved that excess surfactants might induce the floatability of the associated mineral solids [18]. Same conclusion was drawn by Sanford and Seyer in 1979 [11], Sanford in 1983[12], Schramm et al. in 1984 [19].

In 1985 and also in 1987, Schramm mentioned that there was a critical concentration of surfactant in the equilibrium, solution of the oil sands process slurry that corresponds to the maximum bitumen recovery as shown in Figure 2.3 [20, 21]. Recently, natural surfactants have been studied for their structures [22] and toxicity [23, 24] to the environment. In 2006, Del Rio degraded the naphthenic acids by sediment micro- organisms [25]. And he found two Pseudomonas species isolated from the active tailings sediment could degrade more than 95% commercial naphthenic acids in short periods.
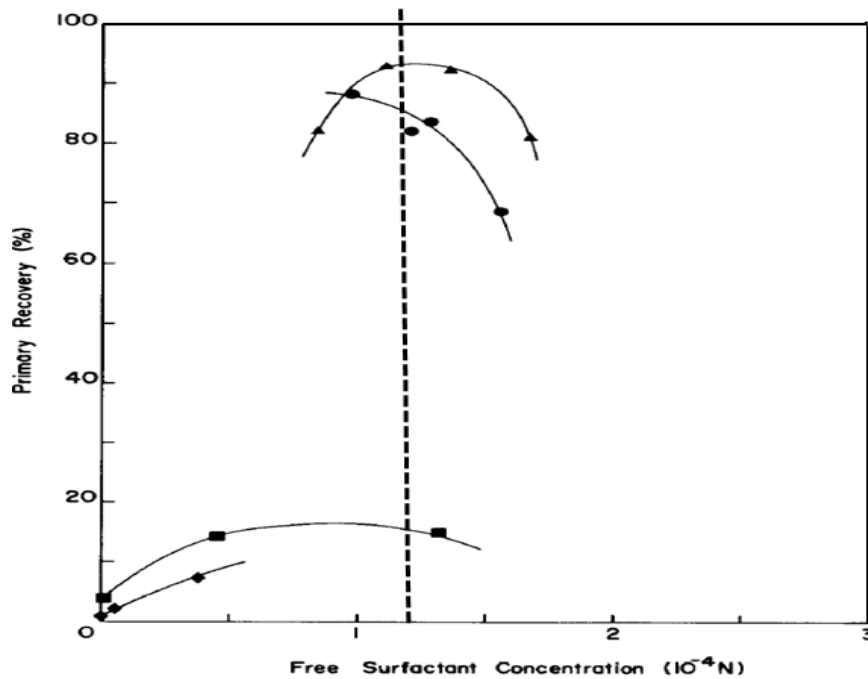
Figure 2.3 Free surfactant concentrations vs. primary recovery [21]

Cations such as Ca^{2+}, Mg^{2+} in the process water also impact the bitumen recovery in some extent. In 2000, Kasongo et al. conducted doping tests by adding a given amount of calcium into a rich estuarine oil sand ore by using a modified batch extraction unit [26]. Addition of 40 ppm calcium or 1 wt. % (based on oil sand ore) clay had a marginal effect on bitumen recovery. However, 1wt. % montmorillonite clays and 30 ppm calcium ions together in the solution led to a huge reduction of bitumen recovery. Such decrease in bitumen recovery was not observed with the combination of calcium ions with kaolinite or illite [26]. Divalent ions were believed by Fong et al. that could increase the interaction between solids and polar oils [27].

Other chemical additives: solvent and polymer addition. In 1980, Ramachandra et al. flocculated tailings by anionic Polyacrylamide (PAM) after Mg^{2+} and Ca^{2+} treatment [28], which reduced the moisture to less than 40 wt.%. In 1999, Xu et al. proved that anionic polymers with a narrow range of

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charge densities could flocculate the fine tailings at pH 8.5 [29]. And they were unable to obtain a clear supernatant even at polymer dosage above 20 mg/L. In 2007, 400 ppm temperature sensitive polymer N-Isopropylacrylamide (NIPAM) was added in extraction process to obtain a clear supernatant [30]. In 2008, Li et al. applied Hydrolyzed Polyacrylamide (HPAM) and Aluminum - polyacrylamide (Al-PAM) dual system to process low grade oil sands, which achieved a holistic improvement in bitumen recovery, froth quality and tailings settling [31].

The size of the air bubble is critical to bitumen aeration process. Therefore, the introduction of air bubbles is another important process parameter for bitumen recovery. As early as in 1976, Camp noted that too much air would entrain more mineral fines into the froth [32]. Drelich et al. proposed that the air bubble attaches to bitumen before bitumen was detached from sand grains in 1995[33]. In 2000, Moran et al. examined that a positive spreading coefficient of bitumen on air bubble did not always lead to the bitumen aeration [34]. In 2001, Flynn et al. found that insufficient air depressed the bitumen flotation rate [35]. In 2003, Gu et al. investigated the effect of bubble size on the bitumen - air bubble attachment, increasing the air bubble size was found to decrease the efficiency of air bubble and bitumen attachment [36].

Temperature is another process parameter in bitumen extraction. Adewusi and Adetona reported that bitumen recovery increased 5% at 50 ºC when compared with at 27 ºC in alkaline hot water process. However, the cumulative bitumen recovery showed a decline when the temperature is higher than 50 ºC in both experimental and numerical simulation models [37]. Pathak also observed that recovery decreased with increasing temperature and

pressure of the steam injection system. When experimental temperature is only slightly higher than the saturation temperature of the solvent used, bitumen recovery reaches the highest point [38].

Other parameters such as shear action, sand grain size, oil grade, and salinity of the process water also play the vital roles in bitumen extraction. Normally, high grade ore will has higher bitumen recovery. Low grade ore has too many fine solids to float, so the froth quality decreases to reduce the primary recovery.

2.3 Fundamental study on interaction among air bubble, bitumen and solids

2.3.1 Liberation and aeration

Bitumen extraction fundamentals have been studied by using different oil sand ores and model oil sand systems for dozens of years. It is recognized that liberation and aeration are the two critical steps in bitumen extraction. The conceptual steps of liberation and aeration are shown in Figure 2.4 [39]. Bitumen liberation has three steps [40]: i) bitumen film thinning and rupture; ii) bitumen droplet formed; iii) droplet detachment. Bitumen liberation and its subsequent stabilization against hetero-coagulation (also known as slime coating) with mineral fines are prerequisites steps for bitumen extraction. The bitumen recovery could greatly be improved by reducing slime coating while achieving a high quality of bitumen froth.
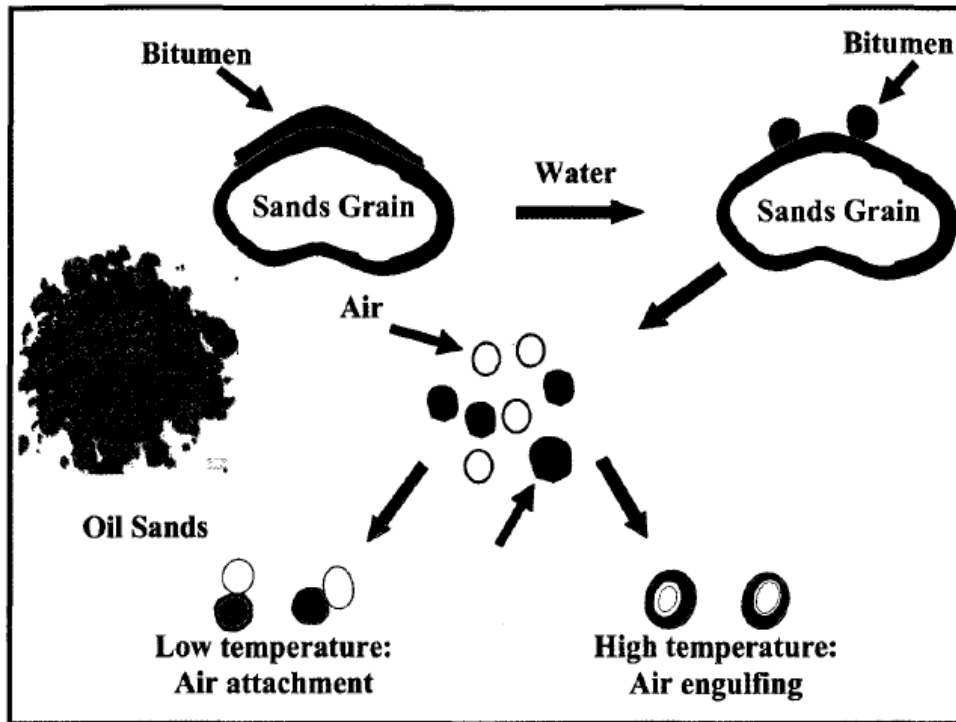
Figure 2.4 Conceptual steps of bitumen liberation and bitumen aeration [39]

Liberation is influenced by several different factors such as conditioning temperature, agitation speed, pH of the process water, and water chemistry of the process water including type and concentration of cations and surfactant. Aeration is another prerequisite step in the bitumen extraction. Like the liberation, aeration also has three steps [41]: i) air- bitumen collision; ii) water film thinning; iii) water film rupture and formation of a stable attachment. Since bitumen has a similar density with process water, it could not float without attaching to the air bubbles. The attachment of air bubble and bitumen droplet is weak at a low temperature. However, this attachment will become strong at certain high temperature, and air will be engulfed by bitumen in some cases, which helps bitumen float to the surface.

2.3.2 Interaction between bitumen, solids and air bubbles

Bitumen and solids interaction involved in liberation mainly depends on their surface activities. Bitumen and solids are negatively charged in process water, which indicates that there is electrical repulsive force between bitumen and solids. This repulsive force will become more intensive in the solution with higher pH value.

Conditions are more complex if air bubble exists in the system. Most of the surfaces of solids are hydrophilic, and bitumen surfaces are hydrophobic. Although the dissolved air bubble is negatively charge in the process water, the air bubble will still attach to the bitumen droplet rather than solids because of the hydrophilic nature of the solid surface.

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CHAPTER 3 MATERIALS AND METHODS

3.1 Oil sands composition

Four oil sand ores provided by Syncrude Canada Ltd. and Canadian Natural Resources Ltd. were used throughout the study. To ensure homogeneity of the mixture all oil sand ores were passed through a mill and mixed several times before separating into 600 g batches. To prevent aging of the ores, samples were stored in a freezer unit at -20 $^\circ$C. Two of the ores were classified as high fines (AS and CN912) and two as average fines (AZ and MA). The overall composition of the ores determined by Dean Stark Analysis is shown in Table3.1; refer to section 3.3.2 for a detailed discussion on the techniques.

From the four ores – MA, CN912, AS and AZ, a range of fines, bitumen and water contents are studied, providing an opportunity to systematically identify the ore properties that govern bitumen recovery assisted by caustic addition.

Table 3.1 Characteristics of MA, CN912, AS and AZ

Ore	MA	CN912	AS	AZ
Bitumen%	8.2	8.3	9.8	11.6
Water%	8.3	7.4	3.8	3.7
Solids%	83.5	84.3	86.4	84.7
Fines%	15.3	37.5	39.7	21.2
Fines Contents	Average Fine	High Fine	High Fine	Average Fine
Processability	Average	Poor	Poor	Good

As shown in Table 3.1, MA and CN912 ores have similar bitumen contents but a significantly different level of fines, MA ~ 15% fines and CN912 ~ 38% fines. CN912 and AS ores have similar fines contents, but AS ore has 1.5% more bitumen (9.8%). AZ has 1.8% higher bitumen content than AS, and AZ fines contents ~ 21% is only half of AS ~ 40%. Although MA has the lowest bitumen content, its average fines content makes the processability to the average. The bitumen content of CN912 is similar low as MA, and it has very high fines content, so CN912 has the worst processability of these four ores. While AS has ~9.8% bitumen but very high fines contents, the processability is poor. AZ has the highest bitumen contents ~ 11.6% and average fine contents, so it defined as a good processing ore in this study.

3.2 Water chemistry of process water

Due to volume limitations, four pails of process water (7, 10, 11 and 12) were used during the study. All pails were provided by Syncrude Canada Ltd., with water recovered from the same batch run during recycling process. MA ore was processed with pail 7, CN912 ore pail 10, AS ore pail 11 and AZ ore pail 12. A simulated experiment with a higher divalent ion concentration was completed using pail 12 water and CN912 ore. Calcium chloride and magnesium chloride were purchased from Fisher Scientific, Canada.

Atomic Absorption Spectroscopy (AAS) was used to measure the divalent ion concentration. As shown in Table 3.2, the calcium ion concentration is 17.5 ppm ± 1.2 ppm, and the magnesium ion concentration is 45.2 ppm ± 7.5 ppm. It should be noted that the magnesium concentration varies within 10% while the calcium ion concentration shows more variability. While only small

differences, such variation may potentially impact the recovery data and at first sight should not be discarded as irrelevant.

Table 3.2 Calcium and magnesium ions concentration in process water

	MA	CN912	AS	AZ	CN912 + Ca^{2+}, Mg^{2+}
Pail	7	10	11	12	12
Ca^{2+} (ppm)	40.6	37.7	50.2	52.4	52.4 + 130
Mg^{2+} (ppm)	16.4	18.7	17.5	17.6	17.6 + 60

3.3 Experimental methods

3.3.1 Flotation
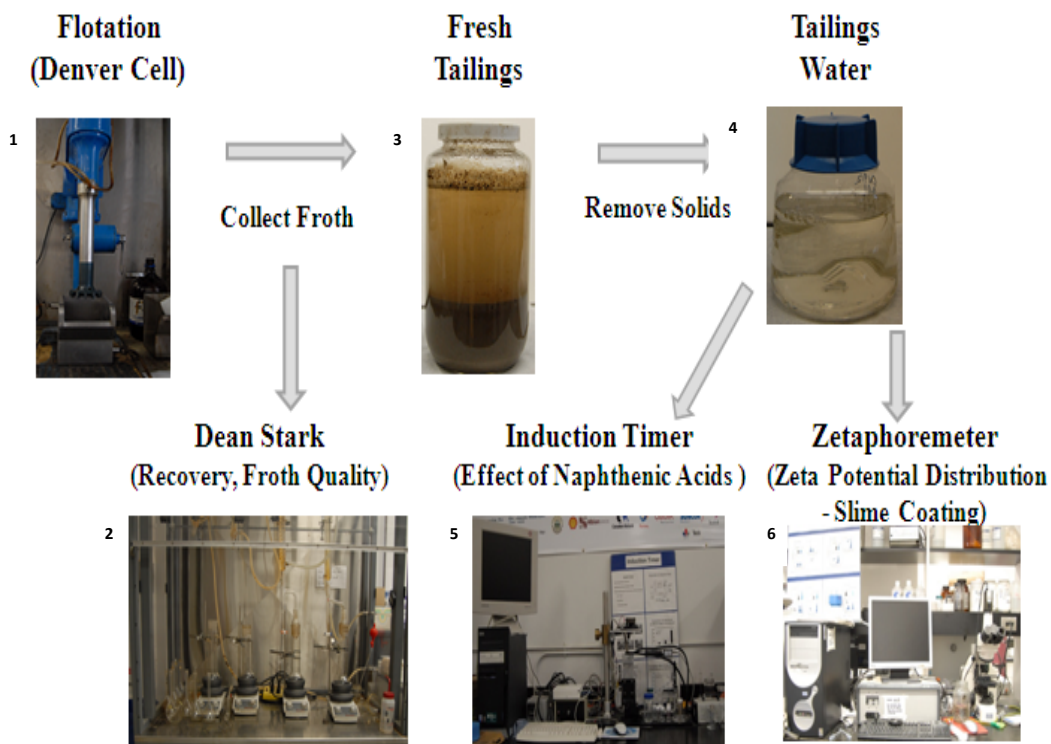
Figure 3.1 Summary of the methodology

Denver cell: A Denver cell flotation unit shown in Figure 3.1 was used to complete the extraction experiments. Agitator was turned on and adjusted the speed of 1500 rpm to check the Denver Cell before the tests. The airline (bench valve) and the air stopcock on agitator were examined to ensure the air

supply runs constantly. Flow meter was adjusted to the desired air flow rate (the reading for black ball at 80 and white ball at 40 is equivalent to 150 mL/min). Finally, air stopcock on the agitator was closed to complete the Denver Cell calibration and examination.

600 g of oil sand ore was thawed out for 3 hours at room temperature. Water bath of Denver Cell was controlled at 45 $^\circ$C. 900 mL of process water was heated to 45 $^\circ$C, and pH of process water was recorded. Caustic (NaOH, purchased from Fisher Scientific, Canada) ranging from 0 to 0.7 wt. % based on the weight of oil sands was added into this 900 mL process water to mix well and kept heating at 45 $^\circ$C. Then 500 g of oil sands was weighed out and added into the Denver Cell followed by the 900 mL process water. The agitator was carefully lowered into the sample until it came to rest. Agitation was controlled at 1500 rpm and continued for 5 minutes before air introduced. Froth was collected from the time air (150mL/min) turned on to 2 minutes for the first thimble. Second thimble was the froth collected from 2 to 5 minutes. Third one was from 5 to 10 minutes. Froth was weighed and sent for Dean Stark right after flotation finished.

3.3.2 Dean Stark Analysis

Dean Stark is a common used method to analyze the bitumen, solids and water content in oil sand ores or related products such as froth and tailings. Toluene is used as a solvent to dissolve all the bitumen. Since toluene could go through the thimble while solids could not, bitumen is separated from solids at this stage. Continuing heating evaporates toluene and water to the trap, and water settles down to the bottom because of higher density. Evaporated toluene is

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condensed by cooling water surround the condenser. After bitumen completely washed by toluene, solids and water are separated from bitumen.

Dean Stark: Approximately 200 mL of toluene was added to each of the four flasks as shown in the second picture of Figure 3.1. Three thimbles with froth sample and one thimble with 50g oil sands sample was placed into the flask by using basket and adapter. The top of the thimble was covered with a small screen before inserting them into the flask. Trap with closed stopcock and condenser were connected to each flask. Then condenser cooling water was opened to check the water leaking of the condenser. Periodically checked the bottom of the flask to ensure froth was not overflow and toluene was not dried out during the extraction process. Continuing heating the sample until the toluene dripping from the thimble was colorless and water was no longer dripped out. Then boiling was turned off. Water accumulated in the trap was collected and the weight was recorded. Waited until the samples getting back to room temperature and got the thimbles out drying in the vacuum oven for over-night at 70ºC. Bitumen extract liquid in the flask was rinsed with toluene and transferred into a volumetric flask, then toluene was added up to 250 mL.

5 mL out of 250 mL solvent was pipetted out and spread evenly on the filter paper. Weight difference of the filter paper was recorded after 20 minutes drying in the fume hood at room temperature (weight change is tested until negligible) to calculate the bitumen content. Solids weight was recorded after completely drying. All the calculation method is listed in the below:

Calculating weight% of composition (oil sand ore, laboratory extracted froth):

For oil sands characteristics analysis:

Bitumen content wt. % of oil sands =

$$\frac{\text{bitumen mass analyzed by filter (g)} * 50 * 100\%}{\text{mass of oil sands used in the thimble (g)}}$$

Δ only 5 mL bitumen mass out of 250 mL was analyzed, so the total bitumen mass need to amplify 50 times

$$\text{Solids content wt. \% of oil sands} = \frac{\text{mass of dried solids (g)} * 100\%}{\text{mass of oil sands used in thimble (g)}}$$

Water content wt. % of oil sands = 100% − bitumen% − solids%

$$= \frac{\text{mass of water (g)} * 100\%}{\text{mass of oil sands used in thimble (g)}}$$

For froth quality analysis:

Bitumen recovery% =

$$\frac{\text{sum of weight differences of three filters from froth (g)} * 50 * 100\%}{\text{weight of oil sands used for flotation (g)} * \text{bitumen\% of oil sands}}$$

$$\text{Solids recovery\%} = \frac{\text{sum of solids weight of three thimble from froth (g)} * 100\%}{\text{weight of oil sands used for flotation (g)} * \text{solids\% of oil sands}}$$

$$\text{Bitumen to solids ratio (B/S)} = \frac{\text{total bitumen mass of three froth (g)} * 50}{\text{total solids mass of the three thimbles (g)}}$$

$$\text{Bitumen to water ratio (B/W)} = \frac{\text{total bitumen mass of three froth (g)} * 50}{\text{total solids mass of the three thimbles (g)}}$$

The solids of oil sands thimble recovered from Dean Stark Analysis were wet sieved to determine the fines content (< 44 μm). A sieve of mesh 325 was cleaned and dried before sieving. The weight of empty sieve was recorded, and then the weighed solid sample was wet sieved until the water clear. All the water with clay solids was collected and dried in the oven at 70 ℃ for over-night to obtain clay solids which are used for zeta potential distribution measurement in section 3.3.5.

3.3.3 Fresh tailings

Fresh tailings as shown in the third picture of Figure 3.1 were collected into a 1L bottle and settled for over-night. Then the tailings water was centrifuged at 17500 rpm for 30 minutes to remove all the solids. Centrifuged supernatant was filtered three times by 0.1 micron meter vacuum filter to obtain tailings water, which was used as a base solution for induction time [1] and zeta potential distribution measurement [2].

3.3.4 Induction time measurement – air-bitumen attachment

Air bubble-bitumen attachment is an elemental process in the successful extraction of bitumen from oil sand ore. The attachment process involves thinning and rupture of the intervening liquid film between the two interacting phases. Induction time is defined as the contact time of an air bubble to a bitumen surface with 50% probability of coalescence [3].
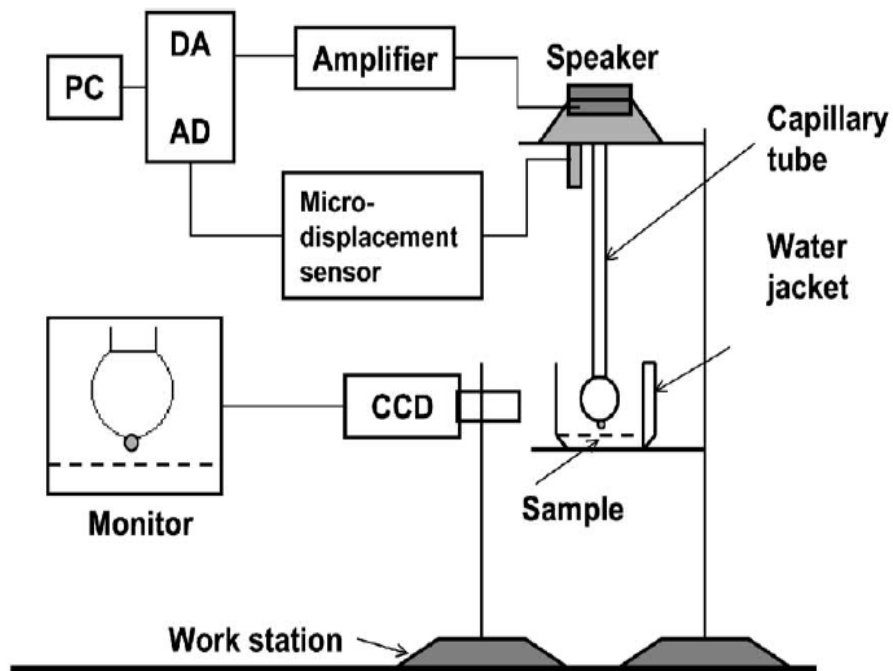
Figure 3.2 The schematic of the setup used for measuring induction time [4]

A schematic of an in-house induction timer is shown in Figure 3.2. Approach and retraction of air bubble was controlled by applying a voltage to a speaker drum, with displacement measured using a micro-displacement sensor mounted 4 mm above the substrate surface (University of Alberta, Canada). An air bubble at the end of a glass capillary tube (ID = 0.89 mm, and OD = 1.33 mm was generated using a Gilmont micro-syringe. The volume of the air bubble was controlled to $1\mu L \pm 0.1\mu L$. To measure the induction time 20 measurements were completed in which the contact time (air-bitumen contact) increased from 100 ms to 3000 ms. Within these time intervals a probability distribution of coalescence was formed from which induction time is equivalent to the 50% probability of coalescence. A camera positioned perpendicular to the capillary direction of motion was used to collect images. Using image analysis software (Induction Time) conditions of non-coalescence and coalescence were easily identified [4].

A snapshot of an air bubble approaching and retracting from bitumen coated surface is shown in Figure 3.3[4]. From left to right (Case a): Image 1 shows the initial position of the air bubble, image 2 represents the point of air bubble-bitumen contact and image 3 shows the retraction phase as the air bubble is withdrawn from the bitumen surface. Clearly, with deformation of the air bubble under retraction, the contact time is sufficient to result in coalescence. However, in case (b) the bubble and the surface separate without any noticeable deformation or interaction, hence, the condition is not suitable for coalescence.
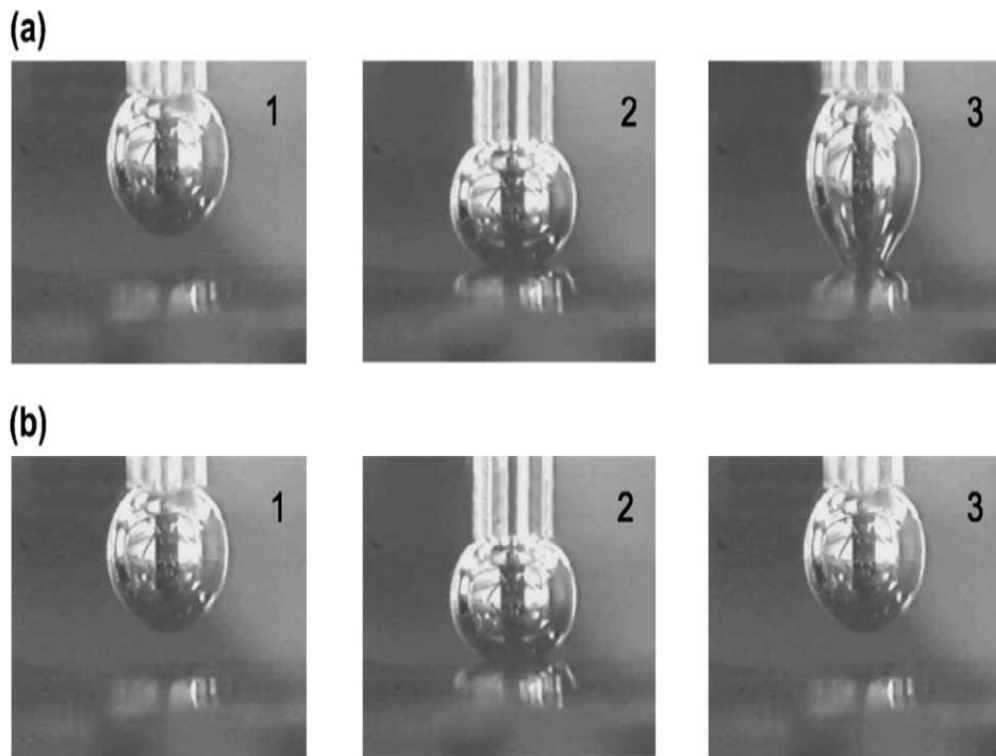
Figure 3.3 Pictures of air bubble–bitumen attachment and non- attachment [4]

Preparation of a bitumen coated surface: A Teflon holder (hemispherical grove, depth 7 mm, width 9 mm) provided a suitable surface to deposit a layer of bitumen. Prior to each measurement the holder was cleaned in toluene to remove all bitumen components and subsequently washed in sulfuric acid to remove adsorbed organic matter. Finally, the holder was washed in excess de-ionized water and dried using dry nitrogen. Vacuum distillation feed (VDU) (bitumen provided by Syncrude Canada Ltd. was used throughout the study. Using a micro-spatula to coat the holder with bitumen, the surface was smoothed by heating at 50 °C for 2 minutes in a vacuum oven. All samples were preconditioned in tailings water by soaking for 2 hours prior to each measurement.

Preparation of tailings water: Tailings water was prepared as in section 4.3.3. Three solutions by using tailings water with different caustic loadings were

prepared for induction time measurements: 1] tailing water at its original pH (pH set by caustic loading); 2] tailings water with the pH readjusted back to pH = 8.75); 3] third series were the fresh tailings without filtration and pH adjustment, in which there were some fine clay particles.

Three Teflon cells with bitumen were used for each solution, and 20 spots were picked to measure the induction time for each Teflon cell. Those data were sent to origin software to calculate the frequency of the contacting time, and Boltzmann Fit was used to fit the curve as shown in Figure 3.4.
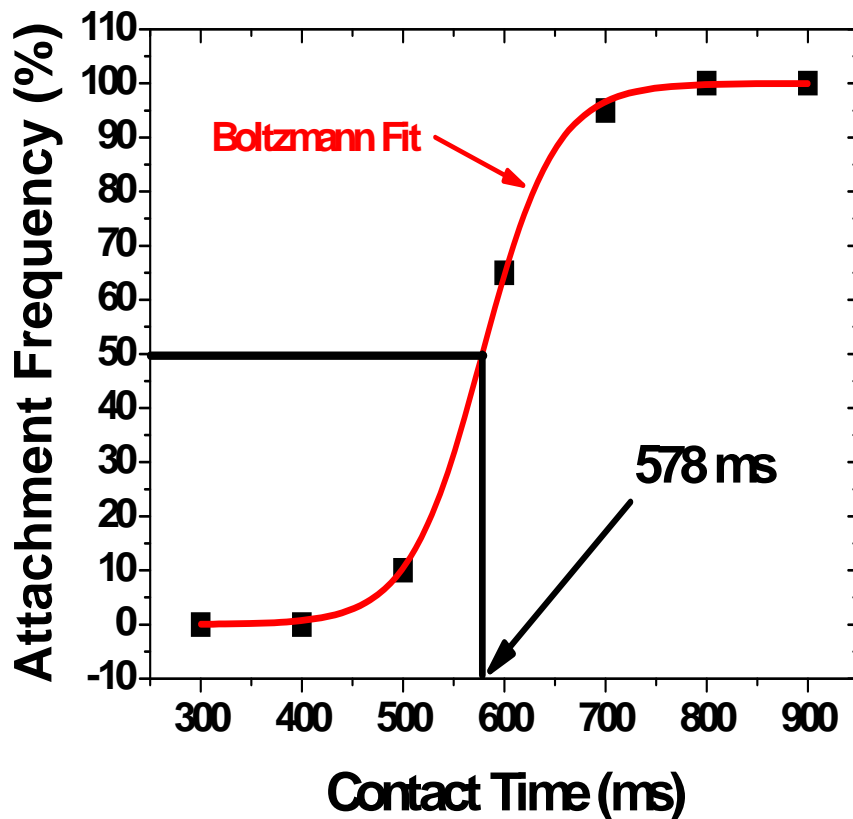
Figure 3.4 Definition of induction time

Induction time was defined as the contact time at which attachment frequency reached to 50%, which was 578 mini-second in this case. It meant that 50% of the air bubbles would attached to the bitumen surface if they contacted 578 mini-seconds in this solution. Induction time results indicated the attachment

efficiency of air bubbles and bitumen in some extent. Shorter induction time results represent higher attachment efficiency, which leads to a higher bitumen recovery in the extraction.

3.3.5 Slime coating - zeta potential distribution

As previously discussed in the introduction, slime coating can have a detrimental impact on bitumen recovery. There are limited methods to assess slime coating potential, however, a novel approach measuring the zeta potential distribution of individual and a combination of species has been proposed by Liu et al. in 2002.

The technique, Zetaphoremeter III (CAD, France) measures the electrophoretic mobility of particles (fines and bitumen) producing a relative frequency (%) distribution of zeta potentials. The distributions are then interpreted to provide a qualitative assessment of slime coating. Figure 3.5 illustrates how the data is used to infer the degree of slime coating.

If there is no slime coating, two distinct peaks of zeta potential distribution would be detected after mixing the two components together, as shown in Figures 3.5[2]. However, if there is strong hetero-coagulation or slime coating, only one zeta potential distribution peak would be detected after mixing of two components. The peak position in this case depends on the extent of slime coating, as shown in Figure 3.5(c) and (d) for complete coating and Figure 3.5(e) for partial slime coating.
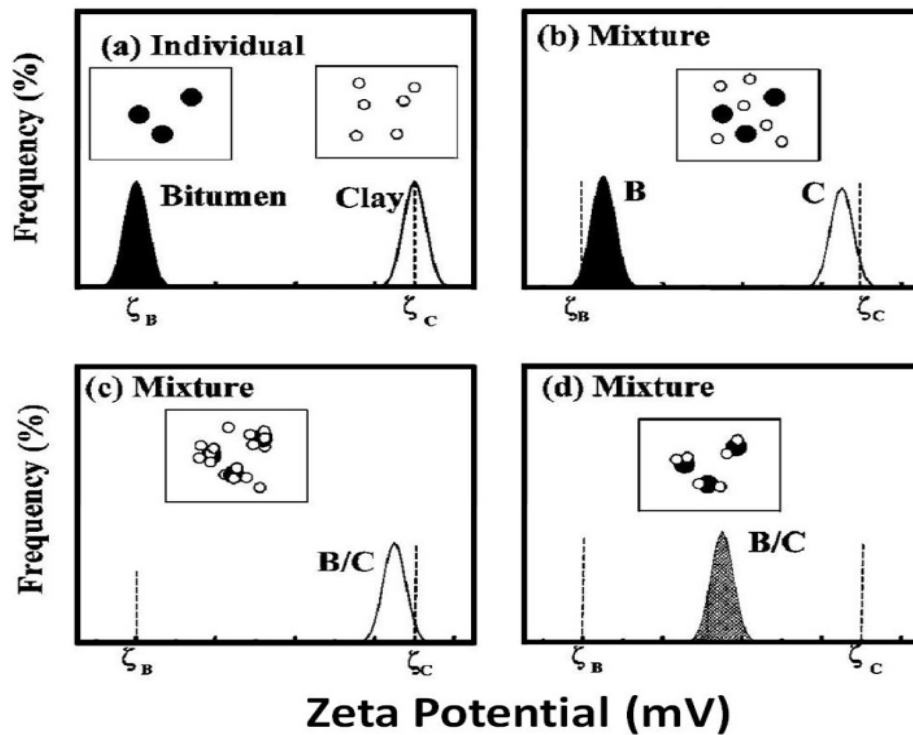
Figure 3.5 Interpretation of zeta potential distributions in a binary mixture as compared with single component systems: a) two components measured individually; b) mixture of two components without slime coating; c) mixture of two components with complete slime coating; and d) mixture of two components with partial slime coating [2]

The preparation of required samples for zeta potential distribution measurements was as follows.

Fine solid suspension: 0.05 wt.% solids were added into the prepared tailings water (by centrifuging fresh tailing at 11500 rpm for 30 minutes and filtered by using 0.1μm vacuum filter for three times).

Bitumen emulsion: 0.1 wt. % of bitumen sample (VDU feed) was emulsified in clear tailings water by using a 550 ultrasonic dismembrator (Fisher) for about 60 minutes.

Binary bitumen–fines mixture: the prepared samples of fines suspension and bitumen emulsion at the same pH were mixed at a 1:1 volume ratio. The mixture was conditioned in an ultrasonic bath (Fisher) for 5 minutes before zeta potential distribution measurements.

Bitumen froth emulsion: 0.1 wt. % of the bitumen froth was placed in clear tailings water. The mixture was emulsified / dispersed by 550 ultrasonic dismembrator for 15 minutes and then further diluted to 0.01 to 0.05 wt. % if needed.

Zeta potential distribution was measured by using Zetaphoremeter III. About 40 ml of the prepared suspension was used to fill the electrophoresis cell. Through the laser-illuminating and video-viewing system, the movement of particles in the stationary layer was traced. The captured images are then analyzed by a built-in imaging processing software. The mobility data were then converted to zeta potential distribution by using Smoluchowski equation as desired.

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CHAPTER 4 ROLE OF CAUSTIC ADDITION ON BITUMEN RECOVERY

The role of caustic addition on the bitumen recovery from MA, CN912, AS and AZ ores has been investigated by Denver Cell flotation at different caustic loadings (0%, 0.01 wt.%, 0.015 wt.%, 0.03 wt.%, 0.05 wt.%, 0.1 wt.%, 0.19 wt.%, 0.5 wt.% and 0.7 wt.% based on total weight of oil sands).
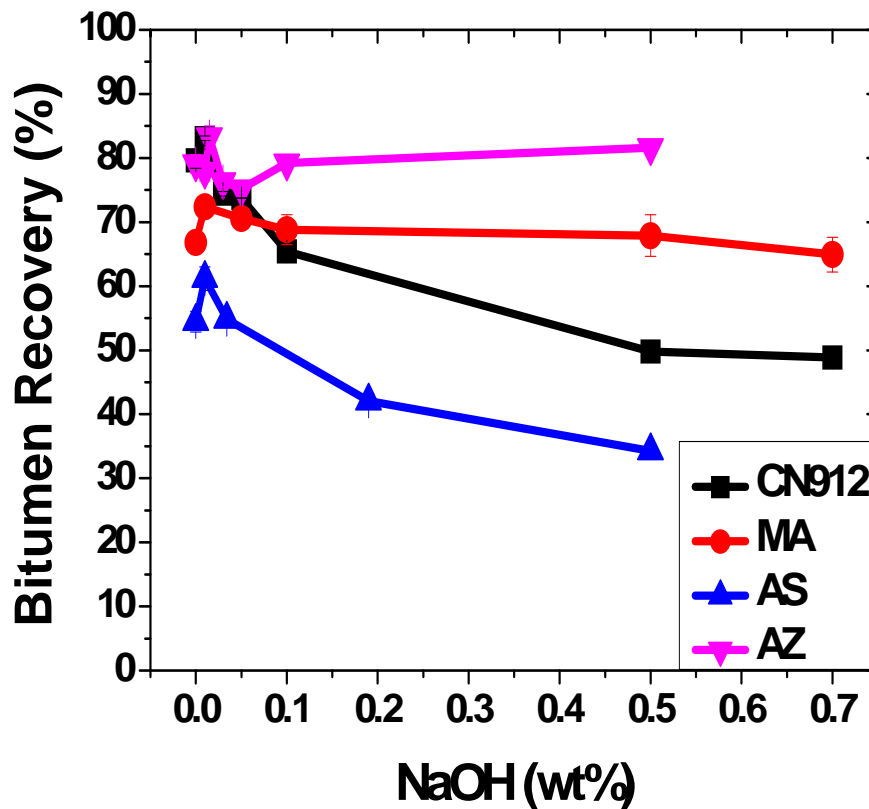
4.1 Bitumen recovery at different caustic loadings

Figure 4.1 Bitumen recoveries vs. NaOH wt. % for CN912, MA, AS and AZ

Bitumen recovery of AS ore at 0.5 wt.% NaOH and AZ at 0.05 wt.%, 0.1 wt.% and 0.5 wt.% NaOH levels are provided by Meghan Curran (graduate student in our group). As shown in Figure 4.1, bitumen recovery is not consistent for all ores. With no caustic addition recovery can be as low as ~55% (AS) and up to ~80% (CN912 and AZ). With the addition of caustic, two ores show a clear dependency on caustic loading, decreasing by ~30% (CN912), and ~15% (AS) from the 0 wt. % NaOH case. However, MA and AZ show little change with caustic loading and in some respect can be regarded as caustic independent. Even though the caustic curves are dissimilar, it appears that all ores show an optimum in bitumen recovery at 0.01 wt. % NaOH addition. The percentage increase in bitumen recovery is within 15% for all ores， which agrees with Clark's finding in 1932 [1] that a little caustic is required to achieve higher recovery (0.013 wt.% NaOH addition increased the bitumen recovery 10% – 30%). Figure 4.1 begins to show the difficulties associated in attempting to identify process markers that govern bitumen recovery. For example, CN912 recovery is significantly higher than AS at all equivalent caustic loadings. When considering the ores composition, the fines content is equivalent (~38 to ~40 wt.%), the bitumen content is 1.5 wt.% greater in AS than CN912, and the water content of AS is almost 50% lower than in CN912. Based on composition data, one might suggest that the low recovery of AS is due to the low water content. However, AZ has similar water content to AS and recovers substantially more bitumen (~150%) at equivalent caustic loadings. It is reasonable to think that not one but several physical and chemical properties combine to control bitumen recovery. The contribution from water chemistry and naphthenic acid concentration are also important and are discussed later in

the next chapter.
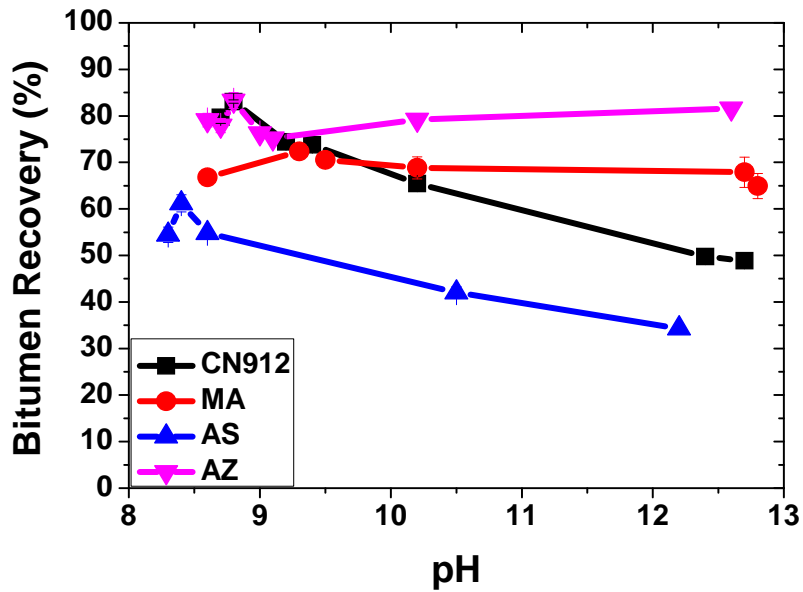
Figure 4.2 Bitumen recoveries vs. pH for CN912, MA, AS and AZ

Bitumen recovery has very similar change trend as shown in Figure 4.2. MA and AZ (average fine ores) still show little change with pH increasing, also are regarded as pH independent. AZ, CN912 and MA have almost same pH at the same caustic loading.
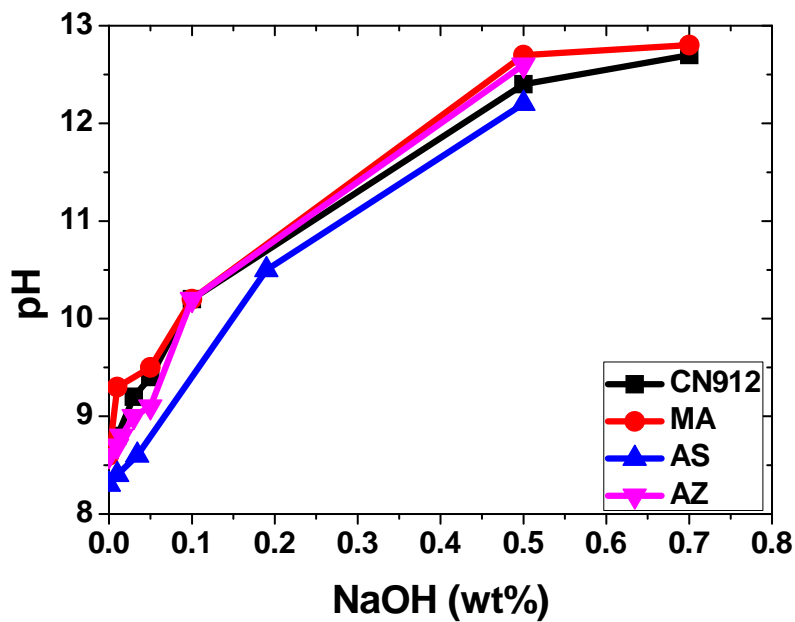
Figure 4.3 Tailings water pH vs. NaOH wt% for CN912, MA, AS and AZ

Figure 4.3 clearly shows that high fines (CN912 and AS) ores have lower pH than low fines ores at the equivalent NaOH wt.%, in some extent high fines ores consume more NaOH which agrees with the conclusion of Stanford in 1983[2] that higher caustic dosage was need to reach maximum bitumen recovery for high fines ores.

4.2 Froth quality improvement with caustic addition
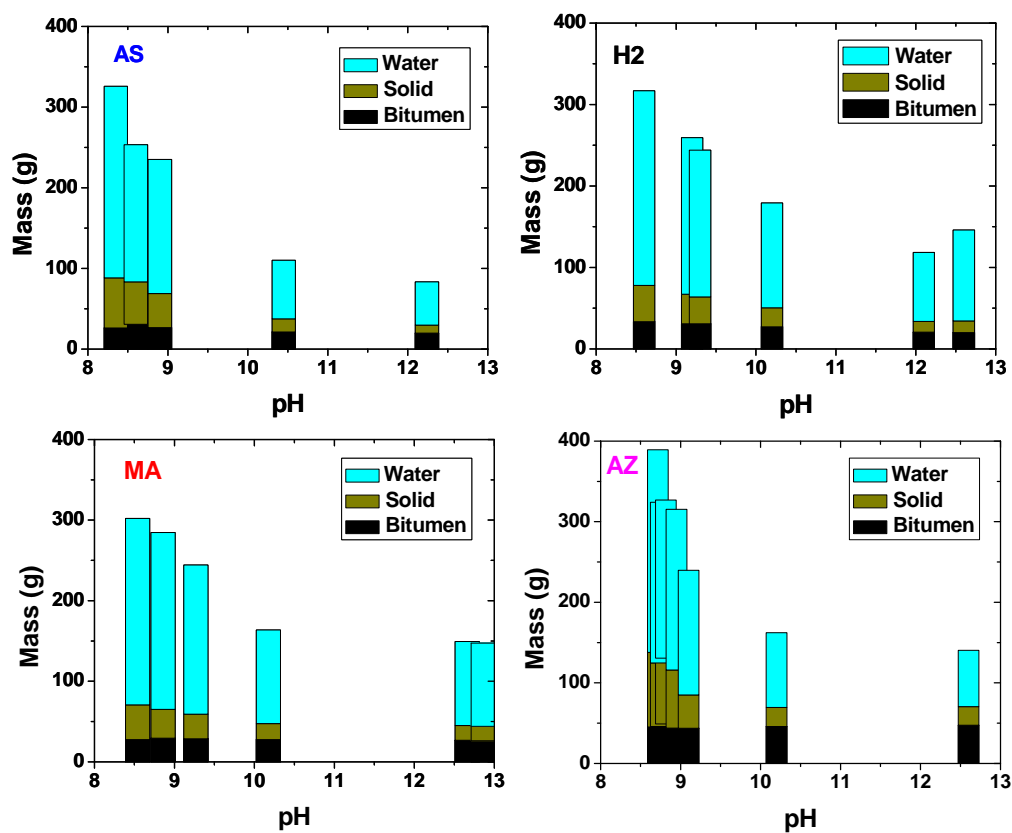
Figure 4.4 Bitumen, solid and water mass of froth for AS, CN912, MA and AZ

While percent bitumen recovered is an important operational marker, the quality of the bitumen froth should also be considered. Froth quality is commonly described by the bitumen to solids (B/S) and bitumen to water ratio (B/W). However, the bitumen, solid and water mass varied with caustic loadings, B/S and B/W could not clearly indicate the actual bitumen mass

changes. So froth qualities represented as bitumen, solid and water mass for each ore as a function of pH are shown in Figure 4.4. Total mass of the froth is decreased as caustic added into the flotation for all four ores. As pH increases, bitumen mass of AS and CN912 are slightly reduced, while bitumen mass of AZ increase a few grams and bitumen mass of MA has no changes. Solid mass of all four ores shows reductive trends, and the most severe one is AZ. As same as solid mass, water mass decreases as in the higher caustic loadings. Water and solids mass are all reduced at high pH levels for these four ores, so froth quality is largely improved (agrees with slime coating study which will be discussed in the next chapter). However, bitumen recovery is only related to the bitumen mass in froth. For high fines ores AS and CN912, bitumen recovery decreases even though the froth quality is improved by caustic loadings. Bitumen recovery of average fines ores MA and AZ almost have no changes, although the froth quality is improved by caustic loadings. Other factors (naphthenic acid and water chemistry) need to be evaluated to govern the principles.

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CHAPTER 5 FLOTATION MECHANISM WITH CAUSTIC ADDITION

Bitumen extraction is mostly controlled by two elemental processes; i) liberation and ii) aeration [1]. Liberation is influenced by a range of properties which include; adhesion force between bitumen and sand [2], bitumen viscosity [3] and hydrodynamic conditions [4]. In flotation, the attachment time is one parameter that influences overall flotation performance. To achieve flotation an air bubble has to be in intimate contact with a bitumen drop long enough to drain the thin liquid film and initiate coalescence. The coalescence time which is commonly referred to as attachment time is a function of; i) bitumen size, ii) density and contact angle of the bitumen, iii) air bubble diameter, iv) approach and retract velocities, v) initial gap between the bubble and bitumen bed, vi) viscosity, density and surface tension [5]. In the flotation column, if the bubble slide time is shorter than the attachment time no fruitful collisions will occur. Also, the buoyancy force should be of sufficient magnitude to carry the bitumen drop into the collector zone.

5.1 Induction time results for MA, CN912, AS and AZ

5.1.1 Induction time in tailings water

Air bubble-bitumen attachment in the tailings water at all different caustic loadings is plotted verse pH as shown in Figure 5.1. Induction time results of AZ, MA and CN912 are very similar from ~600 ms to ~800 ms at pH ranges from 8.6 to 9.3. After pH 9.3, induction time of CN912 increases faster than

MA, and reaches ~ 1400 ms at pH 12.7, while MA reaches ~1200 ms at the equivalent pH. Air bubble-bitumen attachment time of AS starts from ~ 500 ms at pH 8.3, and overlaps with AZ and CN912 of ~ 620 ms at pH 8.7. Then induction time of AS increases to ~750 ms at pH 10.5, which is much lower than MA and CN912 at the equivalent pH because of its very high calcium and magnesium ions concentration.
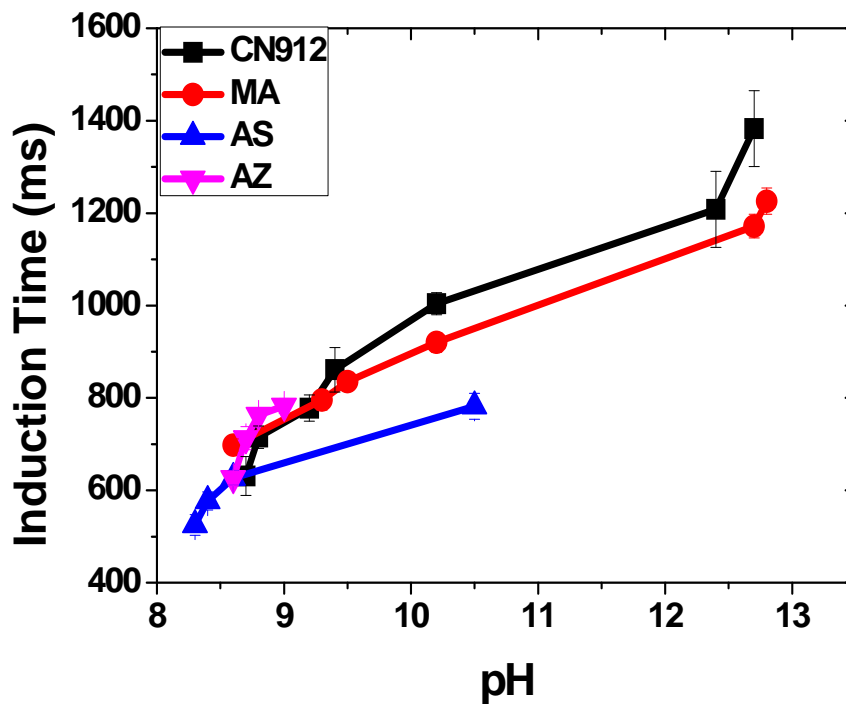
Figure 5.1 Induction time of tailings water for CN912, MA, AS and AZ

5.1.2 Fine solids and pH impacts on induction time

Since pH (caustic loading levels), water chemistry and naphthenic acids concentration are all the parameters to impact the induction time results in Figure 5.1, another series of induction time test (adjust pH to the same level) is designed to evaluate the pH and solids impact on air bubble and bitumen attachment.

Fine solid is another factor to impact the induction time results. Because of cations existed in the tailings water, bitumen surface might be occupied by the fines solids (bridging by calcium and magnesium ions), which makes the air bubble more difficult to attach to the bitumen surface. A series of induction time measurement by using the solids suspension (0.01 wt. %) is conducted to examine the influence of solids.

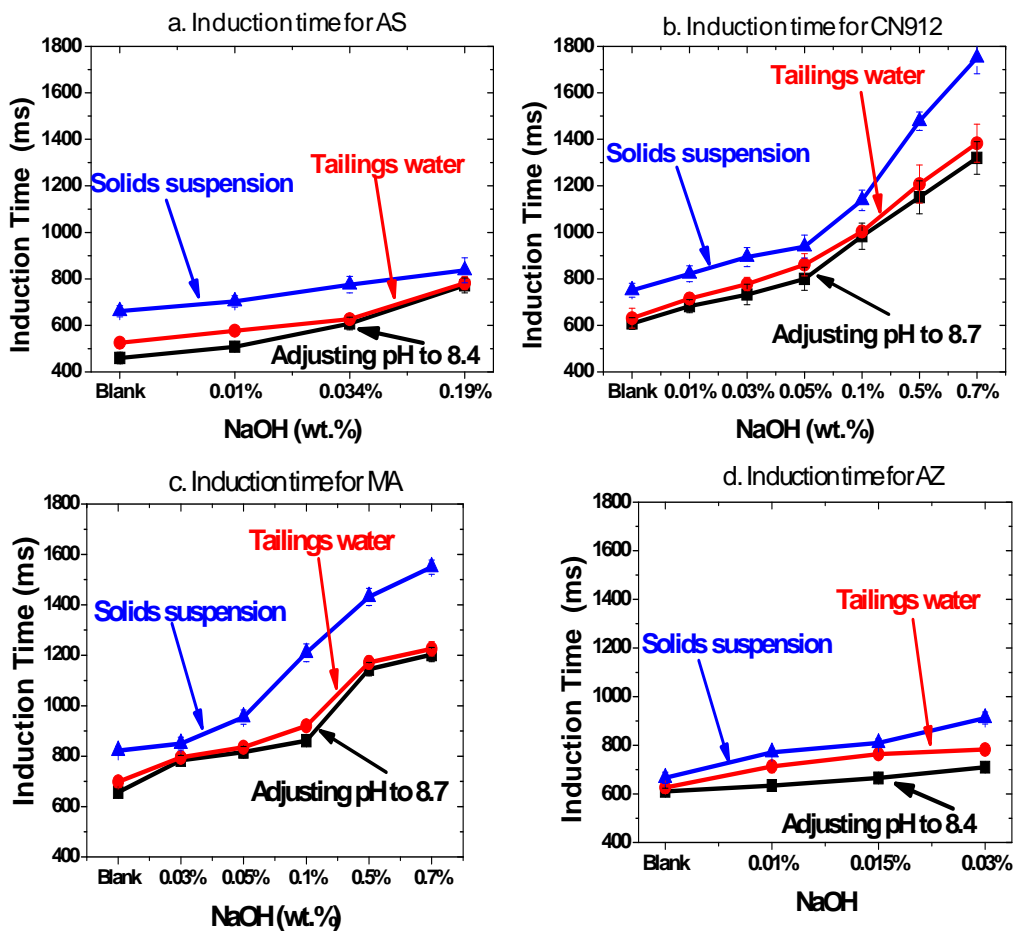Figure 5.2 Induction of solids suspension, tailings water and tailings water with adjusting pH for AS, CN912, MA and AZ.

With adjusting pH of tailings water to 8.7 (plotted in black lines), induction time is almost identical as the induction time of tailings water for MA (Figure 5.2c) and CN912 (Figure 5.2b). For AS and AZ, pH were adjusted to 8.4 (to make it the same as the pH of tailings water without caustic loading).

Induction time of tailings water in their original pH (red line in the figure) are slightly higher than the attach time with adjusting pH to 8.4, the differences are within 100 ms. For all the four ores, induction time could be regard as pH independent.

Induction time conducted by using fine solids (0.01 wt. % solids) suspension is ~ 200 ms longer than the tailings water at equivalent caustic loadings for AS (Figure 5.2a) and AZ (Figure 5.2d). Air bubble-bitumen attach time of AS and AZ only evaluated at low caustic loadings, fine solids seem have a negative impact on the induction time. Attach time of higher caustic loading levels need to be examined to draw a further conclusion for AS and AZ ore. For MA and CN912, induction time by using fine solids suspension is higher than its equivalent tailings water, and this interfere is more severe at high caustic loading with ~ 400 ms difference at 0.7 wt. %. Induction time results of all four ores by using solids suspension show a clearly negative impact of fine solids.

5.1.3 Naphthenic acids concentration impacts on induction time

The term "naphthenic acids" refers to a complex group of saturated cyclic and acyclic carboxylic acids that occur naturally in conventional petroleum from various parts of the world [6]. Natural surfactant was found to facilitate the bitumen liberation at low concentration in the 1970s [7, 8, 9, and 10].

Naphthenic acid concentration of tailings water at different caustic loadings was evaluated to build a relationship with bitumen recovery. Tailing water was first acidified to pH 2.3, then the carboxylic acids was extracted three times using dichloromethane. The organic phase was collected to determine the

carboxylic (naphthenic acid) concentration in tailings water by Fourier Transform Infrared Spectroscopy (FTIR) (data was collected by graduate student Marjan Tamiz).

The standard model compounds of carboxylic acids are shown in Figure 5.3. Carboxylic acid (also mentioned as naphthenic acid in this study) has the molecular weight of 142.2 g/mol.
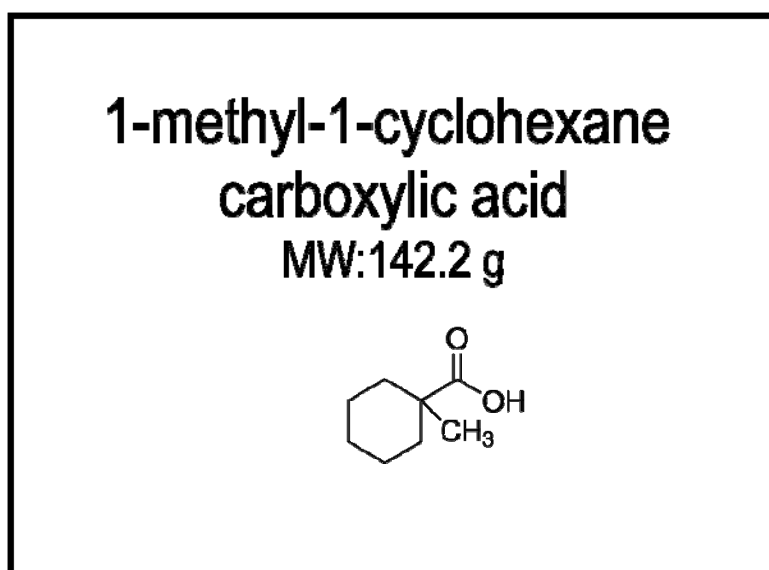
Figure 5.3 Structure of carboxylic acid model compound

Naphthenic acids concentration is shown in Figure 5.4. At 0 wt. % caustic loadings levels (pH 8.3 to 8.5), naphthenic acid concentrations of the tailings water are not consistent. CN912 has ~85 ppm, AZ has ~70 ppm, while AS and MA has ~55ppm. The naphthenic acid concentration increased as the pH goes higher. At pH 12.7, naphthenic acid concentration of CN912 reaches ~140 ppm and MA reaches 100 ppm. Caustic loading helps the naphthenic acid release from the oil sands and the releasing extent is dependent on the ore characteristics.
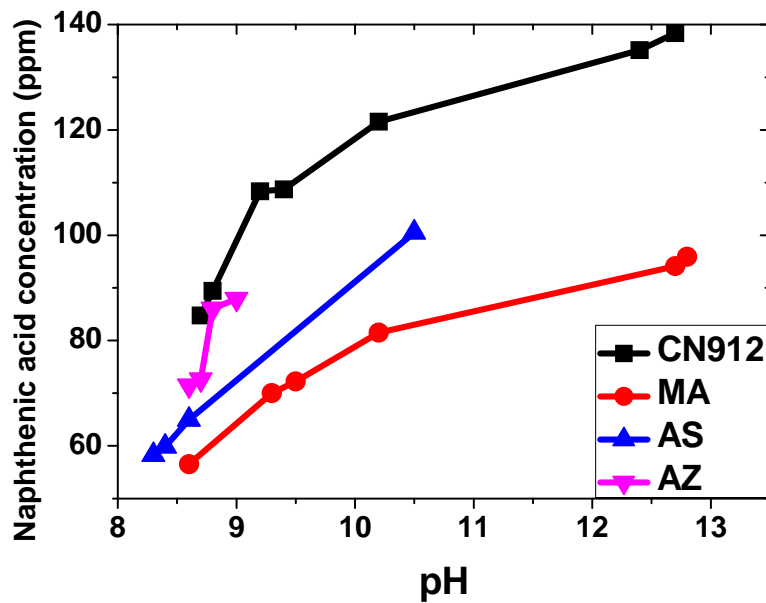
Figure 5.4 Naphthenic acids concentration vs. pH for CN912, MA, AS and AZ

When naphthenic acids concentration is plotted verse induction time as shown in Figure 5.5, it is obvious that all four ores show a same non-linear increasing trend. There was a hypothesis that air bubble-bitumen attach is dependent on the naphthenic acid concentration of the solution.
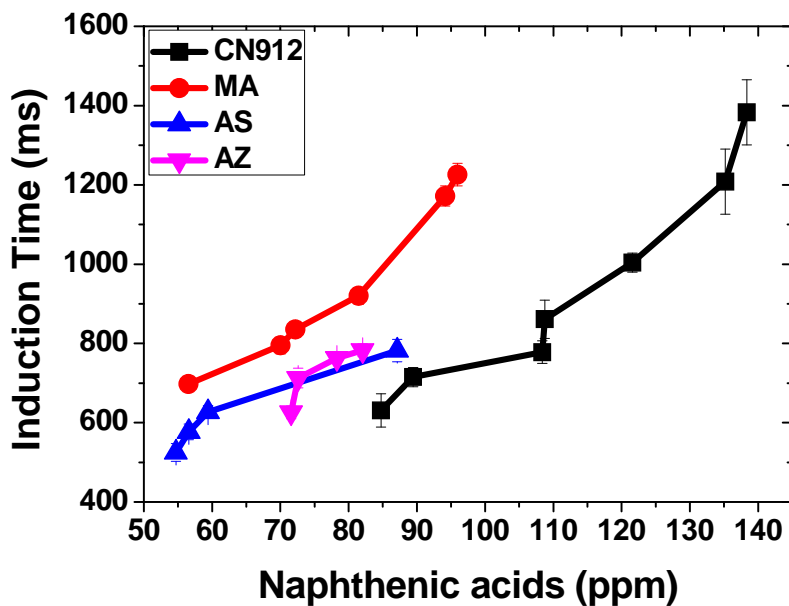
Figure 5.5 Induction time vs. naphthenic acids for CN912, MA, AS and AZ

An experimental test was designed to evaluate the naphthenic acid impact on air bubble-bitumen attachment. Naphthenic acid purchased from Fisher Scientific is used to make two series of 0 ppm, 50 ppm, 100 ppm and 200 ppm solution, one by using the process water having 50 ppm calcium and 18 ppm magnesium ions and the other by using DI water. Since naphthenic acid is not dissolved at low pH, the two series solutions are controlled at pH 12. Then air bubble-bitumen attachment is examined for these solution, the results are shown in Figure 5.6.
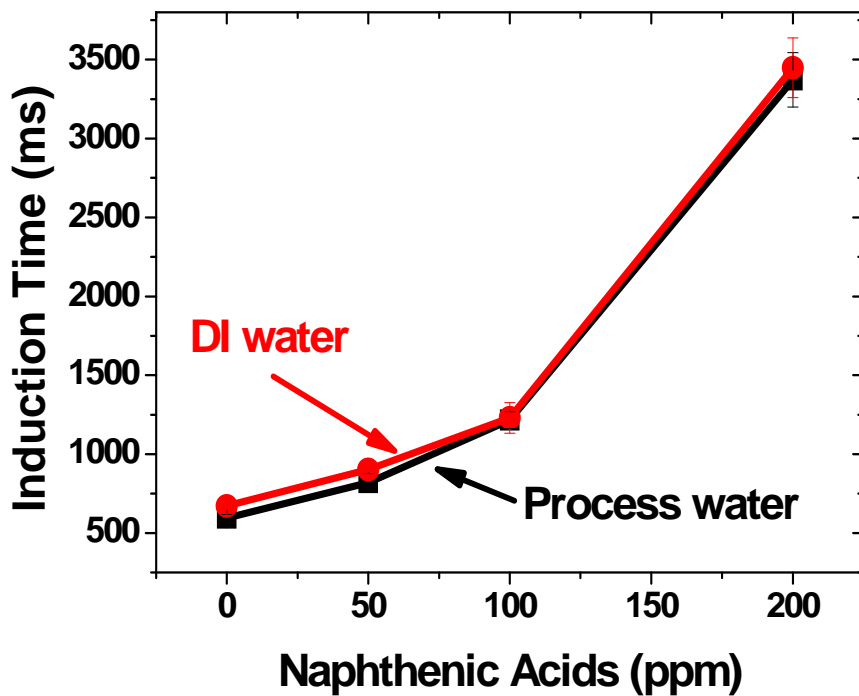
Figure 5.6 Impact of naphthenic acids on induction time in both DI and process water at pH =12

200 ppm standard naphthenic acids extend the induction time from 500 ms to 3500 ms, almost seven times. Induction time using DI water and process water show the same trends. Induction time of different naphthenic acid concentration by using DI water shows that air bubble-bitumen attachment is

dependent on the naphthenic acid concentration of the solution. One more thing could be concluded is that, at pH 12, water chemistry of process water has no impact on induction time.

To further clarify naphthenic acids impacts on induction time, 0.7 wt.% NaOH tailings water of CN912 examined having 138 ppm naphthenic acid, was used to acidify and extracted with dichloromethane to remove the organic phase. The remaining water phase is used to conduct the induction time measurement with adjust pH to 12.
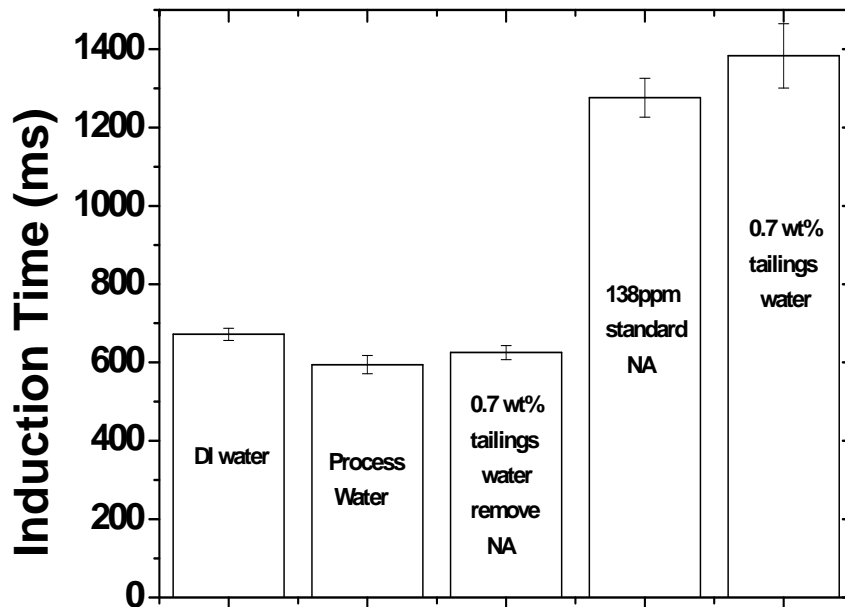
Figure 5.7 Impact of the extracted naphthenic acids on induction time at pH= 12

As clearly shown in Figure 5.7, after removing naphthenic acid, 0.7 wt. % tailings water has the same induction time as process water. And the air bubble-bitumen attach time of 138 ppm standard naphthenic acid solution is slightly lower or could be considered as the same as the 0.7 wt.% tailings

water. Induction time is highly dependent on naphthenic acid concentration of the solution.

5.2 Naphthenic acids impacts on bitumen recovery
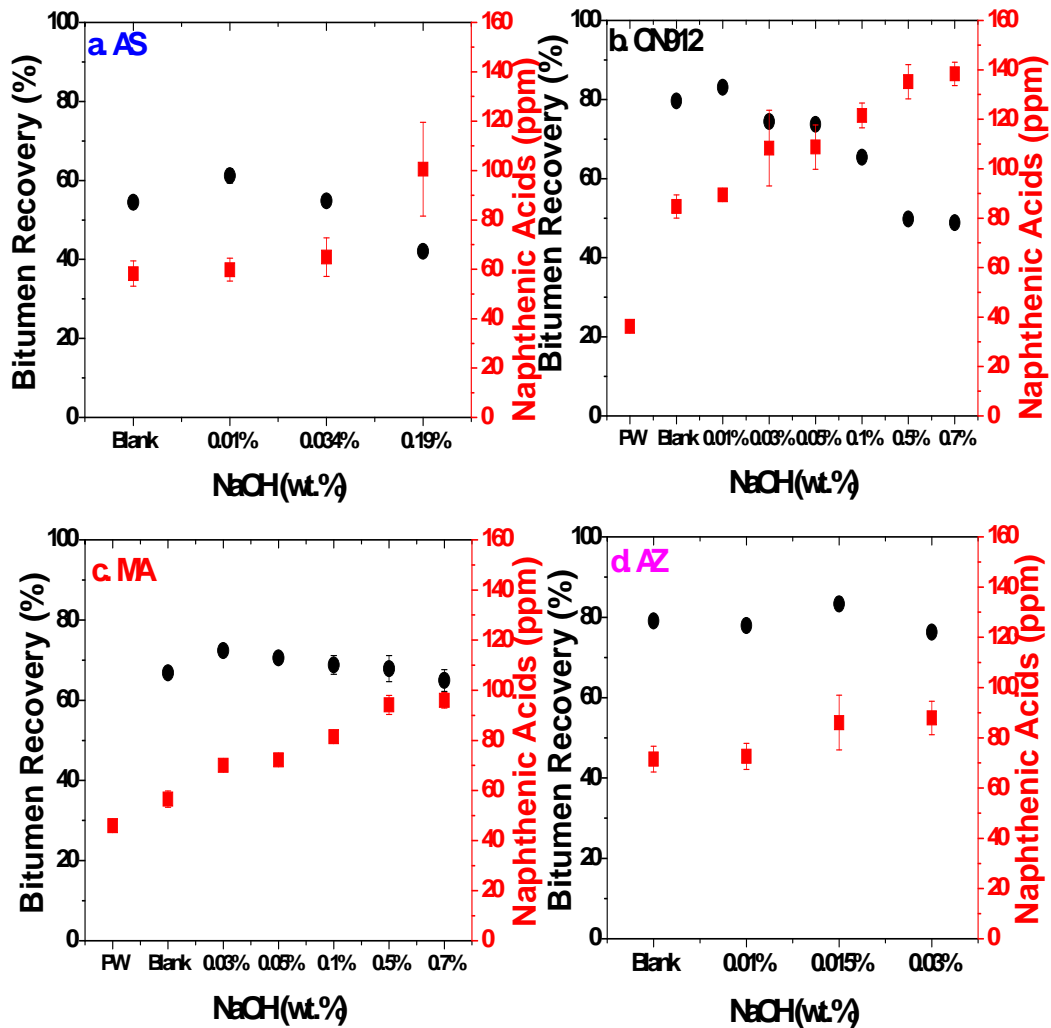
Figure 5.8 Naphthenic acids concentration and bitumen recovery for AS, CN912, MA and AZ

Bitumen recovery and naphthenic acid concentration of the tailings water of all caustic loadings for AS, CN912, MA and AZ are shown in Figure 5.8. For CN912 in Figure 5.8b, the naphthenic acid concentration of the process water is ~ 40 ppm. Although process water has a same naphthenic acid concentration between 40 – 45 ppm, the naphthenic acid concentration of AS increases to 60

ppm, CN912 to 85 ppm, MA to 55 ppm and AZ to 70 ppm after a flotation without any caustic addition. The increasing extent is not consistent for these four ores. For AS, there is 100 ppm naphthenic acid in tailings water at 0.19 wt.% NaOH level with bitumen recovery decreased from ~55% to 40%. The naphthenic acid concentration of CN912 increased to ~140 ppm at 0.7 wt. % NaOH level with the bitumen recovery decreased from ~80% to ~50%. For average fine ores, MA and AZ, naphthenic concentration increasing seems having no impact on the bitumen recovery.

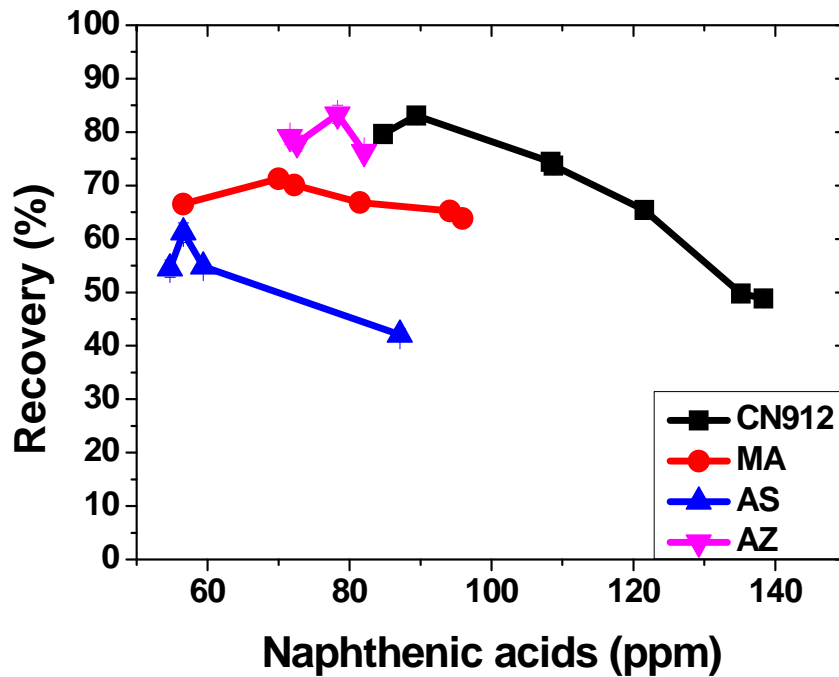Figure 5.9 Naphthenic acids concentration vs. bitumen recovery for AS, CN912, MA and AZ

As shown in Figure 5.9, bitumen recovery is not related to the naphthenic acid concentration. For high fine ores AS and CN912, bitumen recovery reduced as naphthenic acid concentration increased. However, this impact is not happened on average fine ores. This is not conflict with the conclusion of induction time

dependent on naphthenic acid concentration of the solution. Induction time is only one of the factors to represent the aeration efficiency, naphthenic acid impair the air bubble-bitumen attachment in the aeration does not mean it will lead to a poor bitumen recovery. The role of naphthenic acid on bitumen liberation is needed to be evaluated to draw a further conclusion.

5.3 Zeta potential distribution for MA, CN912, AS and AZ

5.3.1 Water chemistry of tailings water

Zeta potential distributions of fine solids (froth clays), bitumen droplets, a mixture thereof, and fresh froth were examined in tailings water of different caustic loadings.

Water chemistry has been shown to be a critical parameter in bitumen extraction [11, 12], more specifically the concentration of divalent ions that can have a dramatic effect on bitumen-solids interactions [11]. The concentrations of calcium and magnesium ions in the tailings water of the four ores are shown in Figure 5.10.
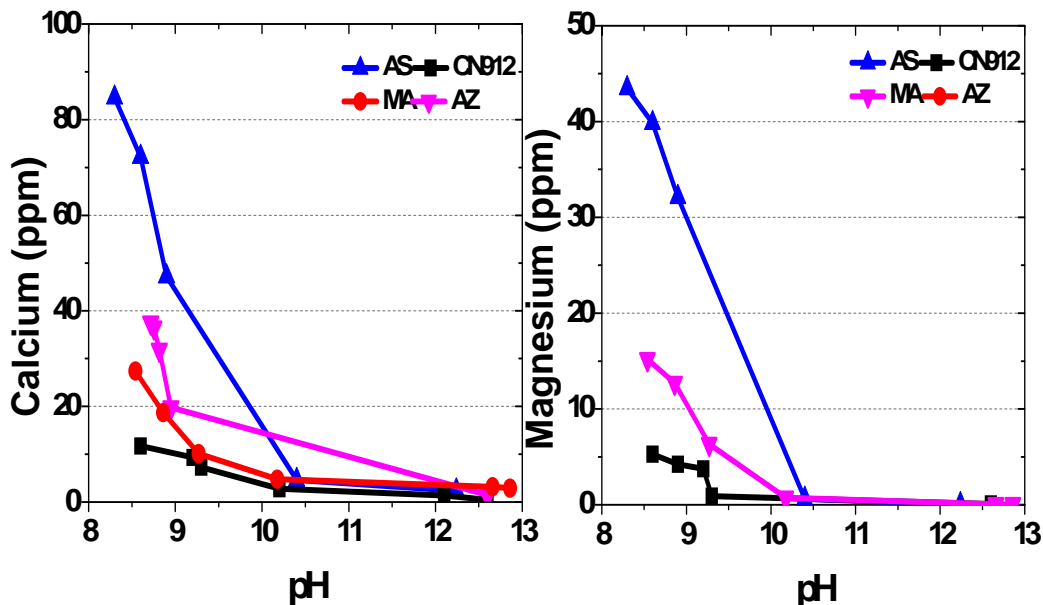

Figure 5.10 Calcium and magnesium vs. pH for CN912, MA, AS and AZ

Calcium and magnesium ions concentration are decreasing as pH increased for all the four ores. In the pH range of 8.2 to 8.5, there are ~85 ppm calcium and 45 ppm magnesium ions (even higher than in the process water used for flotation) in the tailings water with 0 wt. % NaOH loading for AS ore. The exceed calcium and magnesium ions released from AS ore might consume some of the free naphthenic acid and OH^- ions, so the pH is lower than the equivalent caustic loadings of CN912, MA and AZ. Until pH 9.0, the calcium and magnesium ions concentration of AS are still higher than the process water (process water have 50 ppm Ca^{2+} and 17 ppm Mg^{2+}). It indicates that NaOH in the bulk solution is not enough to consume those released Ca^{2+} and Mg^{2+} ions even at 0.034 % NaOH level (pH = 9.0). For AS, Ca^{2+} ions are decreased into 4.6 ppm at 0.19%NaOH level, and Mg^{2+} ions concentration is down to only 0.64 ppm. However, calcium and magnesium ions concentrations of four ores are consistently decreasing as the caustic loadings getting higher. Ca^{2+} ions concentration of AZ decreases from 40 ppm to 20 ppm and Mg^{2+} decreases from 20 ppm to 14 ppm in 0.03%NaOH tailings water (pH 9). For MA, 30 ppm Ca^{2+} reduces to 2 ppm and 16 ppm Mg^{2+} reduces to 0 ppm at 0.7 wt. % caustic loadings (pH 12.7). CN912 has the lowest calcium and magnesium ions in the tailings water at 0 wt. % caustic loading, with 10 ppm Ca^{2+} and 5 ppm Mg^{2+}, and there is no cations left when pH is larger than 10.

5.3.2 Zeta potential distribution for MA, CN912, AS and AZ

Zeta potential distributions of fines, bitumen droplets, mixture and froth are shown in Figure 5.11 for the MA ore at different caustic loadings.
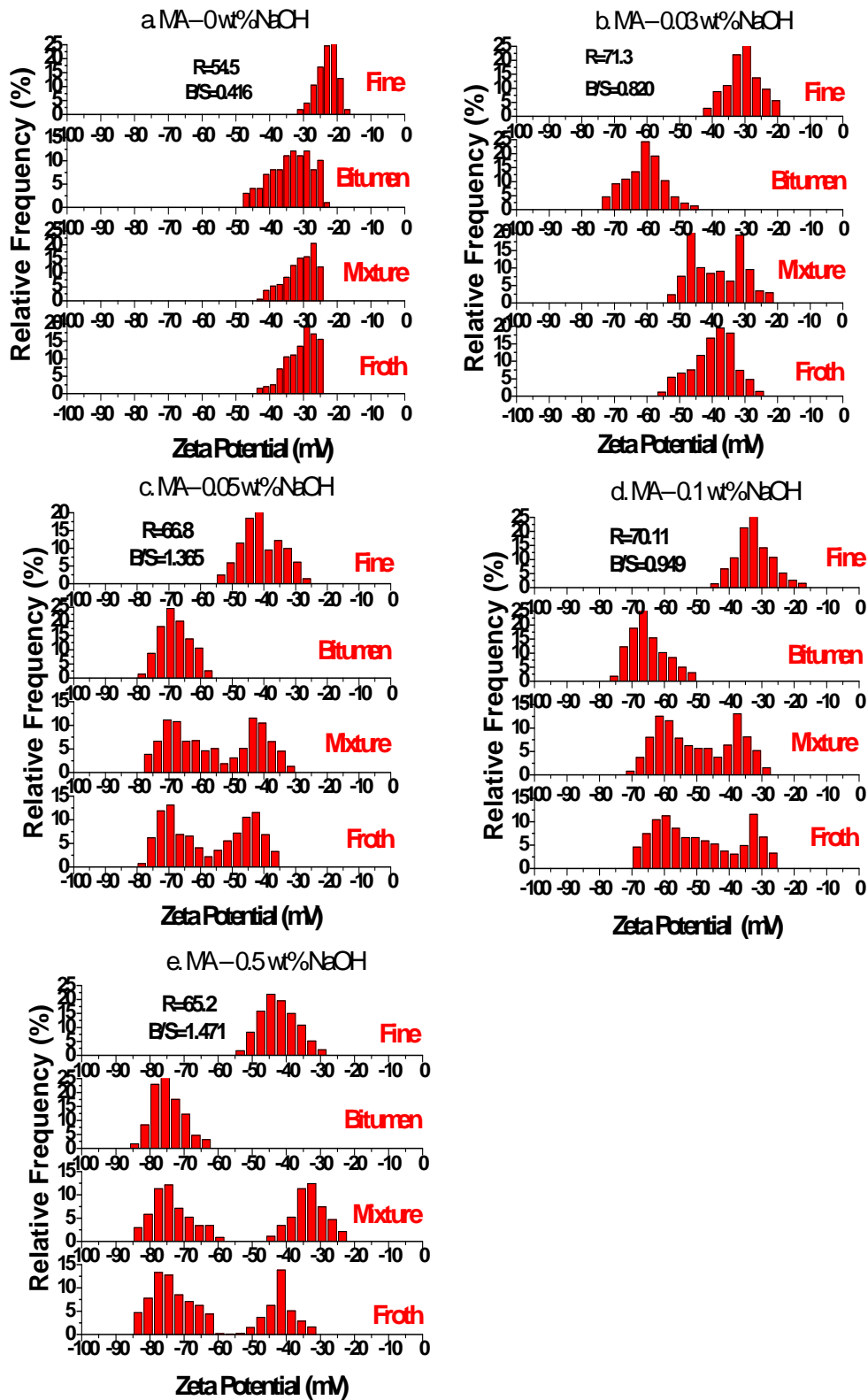
Figure 5.11 Zeta potential distribution of fine, bitumen, mixture of bitumen and fine solution with 1:1 volume ration, and fresh froth for MA at 0 wt. %, 0.03 wt. %, 0.05 wt. %, 0.1wt. % and 0.5 wt. % NaOH loadings.

Zeta potential distribution does not include 0.7 wt. % NaOH because the pH of 0.7 wt. % NaOH tailings water is beyond the pH limit of Zetaphoremeter [13].

As shown in Figure 5.11a, fine solids have a negative charge with the peak around -23 mV. Bitumen droplet surface is also negative, with the peaks between -30 to -40 mV, because the naphthenic acid is ionized in the alkaline solution and attached to the surface of bitumen. At low caustic loading levels, calcium and magnesium ions still existed in the tailings water as a bridge to connect bitumen droplet and fine solids. So the mixture of bitumen droplet and solids only has one peak; slime coating is severe at 0 wt. % NaOH loadings. Fresh froth shows a similar peak range with the mixture. As caustic loadings become higher, the surfaces of bitumen and fine solids are more negatively charged, bitumen is about -75 mV and fine solids is about -45 mV at 0.5 wt. % caustic loadings. Partially slime coating starts at 0.05 wt. % NaOH level, and there is no slime coating at 0.5 wt. % caustic loading for MA as shown in Figure 5.11, because there is no free calcium and magnesium ions in the tailings water. The slime coating situation agrees with the froth quality results that solids content of the fresh froth is decreasing when more caustic is added into flotation. Caustic addition improves the froth quality and prevents the slime coating.

Figure 5.12 Zeta potential distributions of fine, bitumen, mixture of bitumen and fine solution with 1:1 volume ration, and fresh froth for CN912 at 0 wt. %, 0.03 wt. %, 0.05 wt. %, 0.1wt. % and 0.5 wt. % NaOH loadings.

Only partially slime coating happens at 0 wt% NaOH loading for CN912 as shown in Figure 5.12a, because of the low calcium and magnesium ions concentration. Higher naphthenic acid concentration consumes the calcium and magnesium faster, and mixture/fresh froth starts to have two individual peaks at 0.1 wt. % NaOH loading level.
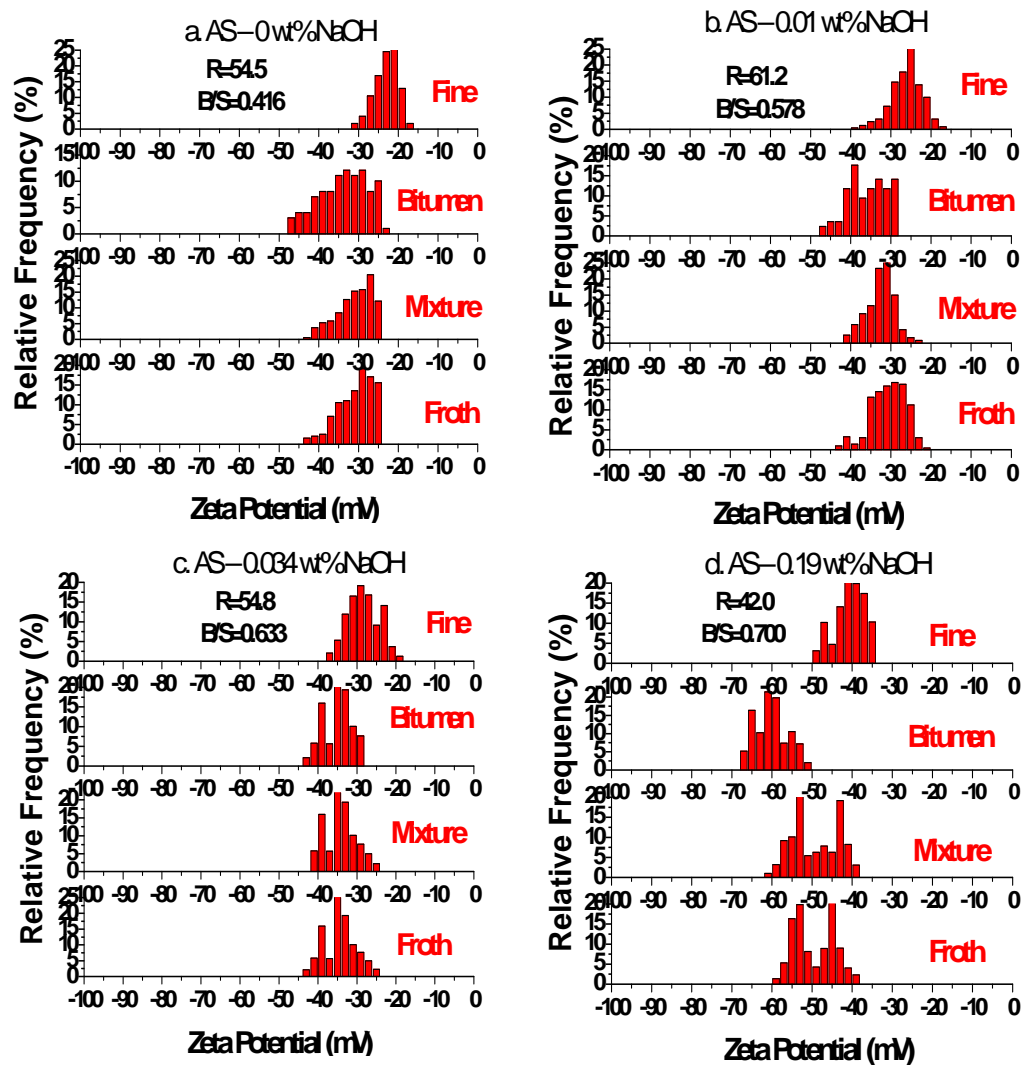
Figure 5.13 Zeta potential distribution of fine, bitumen, mixture of bitumen and fine solution with 1:1 volume ration, and fresh froth for AS at 0 wt. %, 0.01 wt. %, 0.034 wt. %, and 0.19 wt. % NaOH loadings.

Figure 5.13 are the zeta potential distribution of AS from 0 wt. % to 0.19 wt. %. As mentioned in Figure 5.10, AS tailings water has extraordinary high

calcium and magnesium ions, so the slime coating happens for 0 wt. %, 0.01 wt. % and 0.034 wt. % caustic loading levels. Even at 0.19 wt. % NaOH loading, partially slime coating situation is still existed in the froth and mixture.
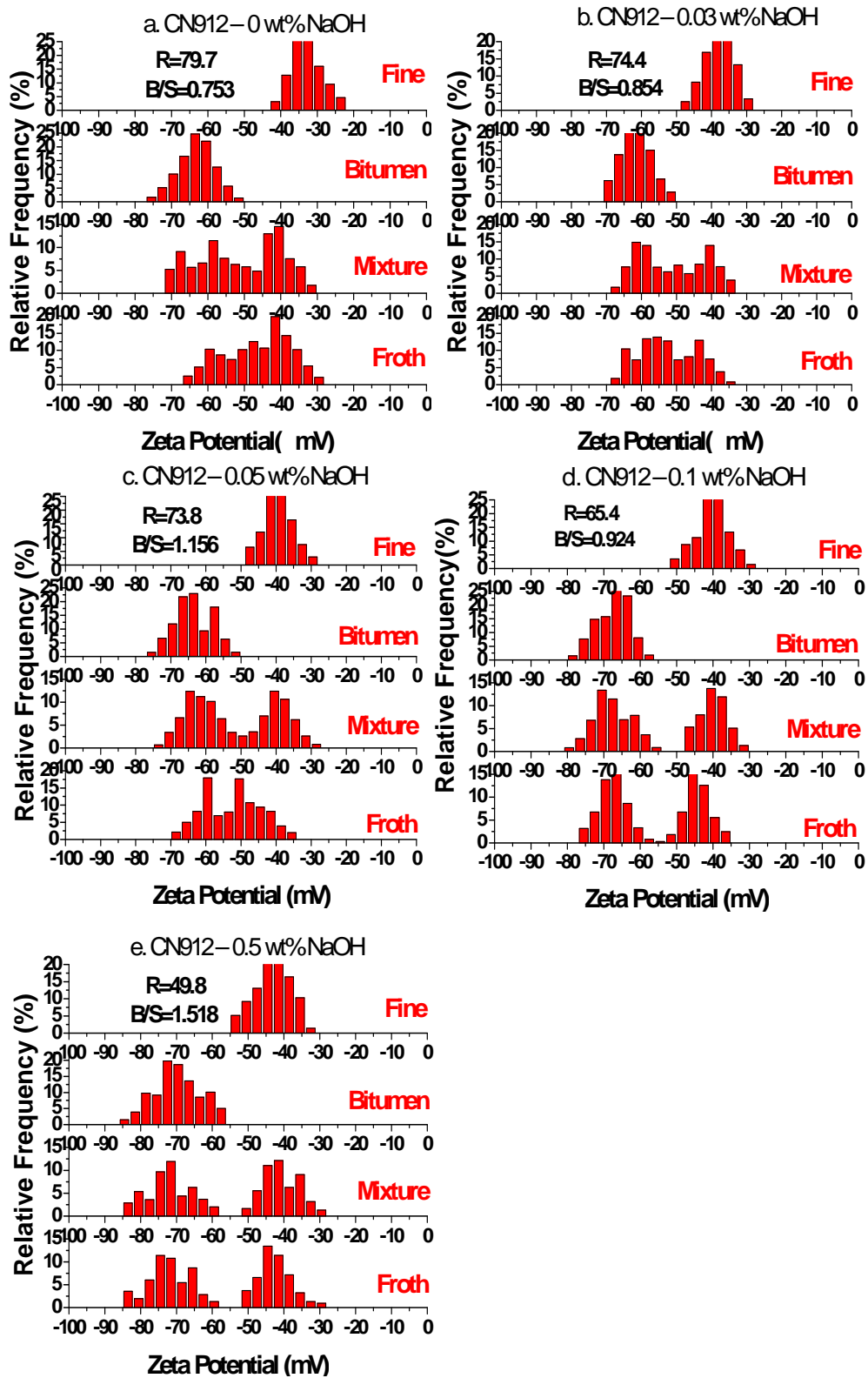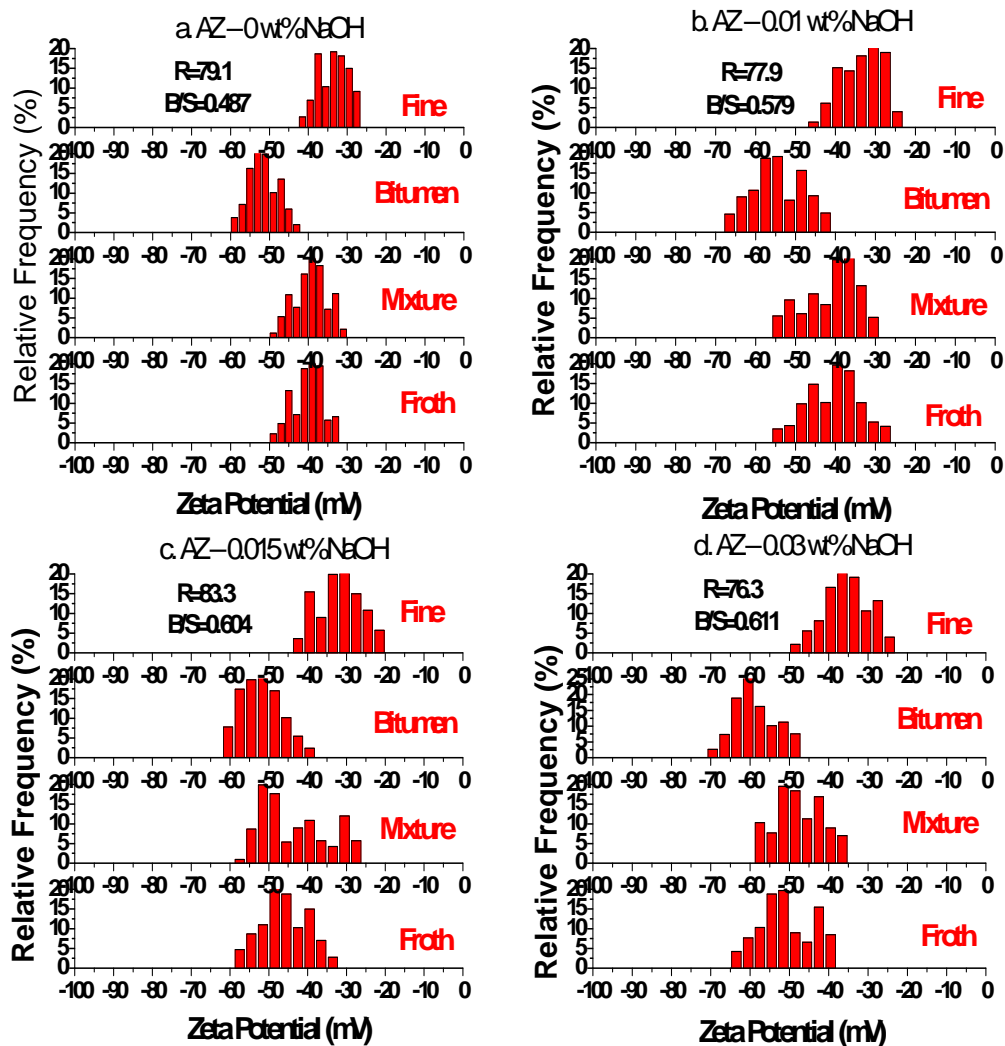

Figure 5.14 Zeta potential distribution of fine, bitumen, mixture of bitumen and fine solution with 1:1 volume ration, and fresh froth for AZ at 0 wt. %, 0.01 wt. %, 0.015 wt. %, and 0.03 wt. % NaOH loadings.

Caustic loading levels of AZ are not high enough to consume all the calcium and magnesium ions of the tailings water, so only one peak for the mixture and fresh froth for all these four caustic loadings as shown in Figure 5.14. It seems

that the slime coating situation is dependent on the calcium and magnesium ions concentration of the solution, which is related to the pH (caustic loading). A good quality of froth does not have slime coating situation and it is normally associated with high caustic loading of the flotation.

5.4 Comparison of AS and CN912 with Calcium and Magnesium addition

5.4.1 Determination of calcium and magnesium ions concentration added into process water for CN912

In order to study the influence of Ca^{2+} and Mg^{2+} on bitumen recovery from CN912 ore, process water was artificially doped with $CaCl_2$ and $MgCl_2$ to increase the divalent ion concentration. Several combinations were tried for CN912 ore at blank level to obtain the tailings water with same amount of Ca^{2+} and Mg^{2+} ions as the blank tailings water of AS. Finally, it is decided to add 130 ppm Ca^{2+} and 60 ppm Mg^{2+} into the process water to run the comparison flotation.

Calcium and magnesium ions concentration of tailings water for CN912 ore with $CaCl_2$ and $MgCl_2$ addition are listed in Figure 5.15. CN912 with 130 ppm Ca^{2+} and 60 ppm Mg^{2+} addition (light blue line in Figure 5.15) has 80 ppm Ca^{2+} and 50 ppm Mg^{2+} at pH 8.5, which is very close to 84 ppm Ca^{2+} and 44 ppm Mg^{2+} of the equivalent pH for AS. The decreasing trend of CN912 with calcium and magnesium addition is sharper than AS, one of the reasons is because the high naphthenic acid concentration of CN912 tailings.
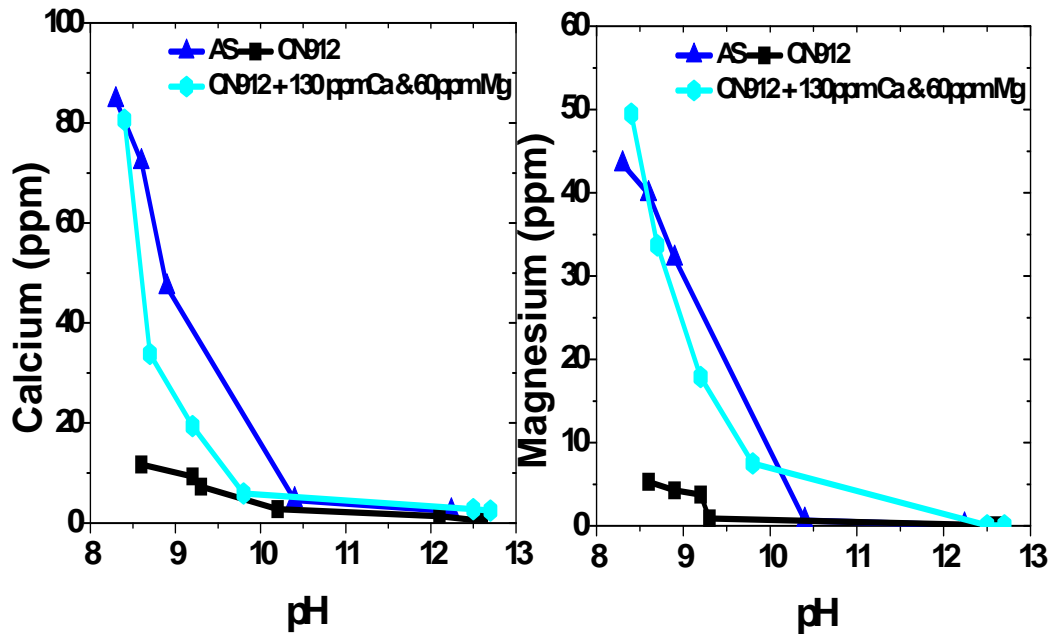
Figure 5.15 Comparison of calcium and magnesium ions for AS, CN912 and CN912 with 130 ppm Ca^{2+} and 60 ppm Mg^{2+}

5.4.2 Bitumen recovery and naphthenic acid for CN912 with Ca^{2+} and Mg^{2+} addition

As shown in Figure 5.16, naphthenic acids concentration of CN912 ore with Ca^{2+} and Mg^{2+} ions addition is reversely proportioned to bitumen recovery, the same trend as un-doped CN912. Doped CN912 has lower pH than un-doped CN912 at low caustic loading levels. Added calcium and magnesium ions not only consume the OH^- ions, but also react with naphthenic acid, so the free naphthenic acid concentration of doped CN912 is also lower than un-doped CN912. For 0.5 wt. % and 0.7 wt. % NaOH loadings, doped CN912 has about 20-30 ppm higher naphthenic acid concentration, one of the hypothesis is that there is some stable naphthenic acid existed with the solids, calcium and magnesium ions could help to release those stable surfactant.

Bitumen recoveries of doped CN912 are lower than un-doped CN912 at

equivalent low caustic loadings as shown in Figure 5.16. Excess calcium and magnesium ions in the process water impair the froth quality (solids and water content of the doped froth are higher than the un-doped one), and consume some of the naphthenic acid.
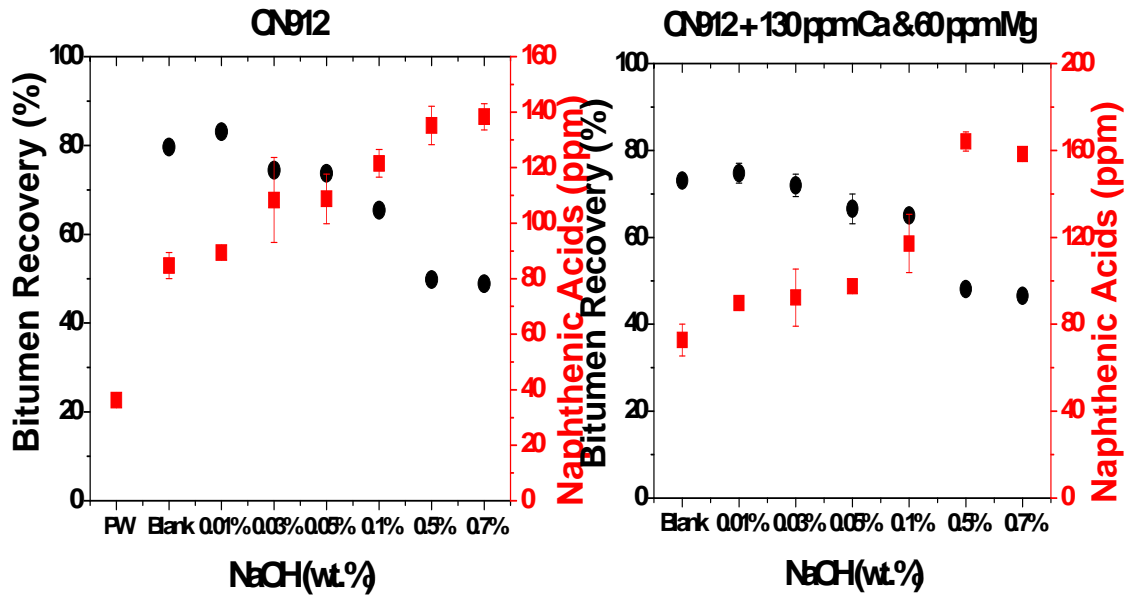

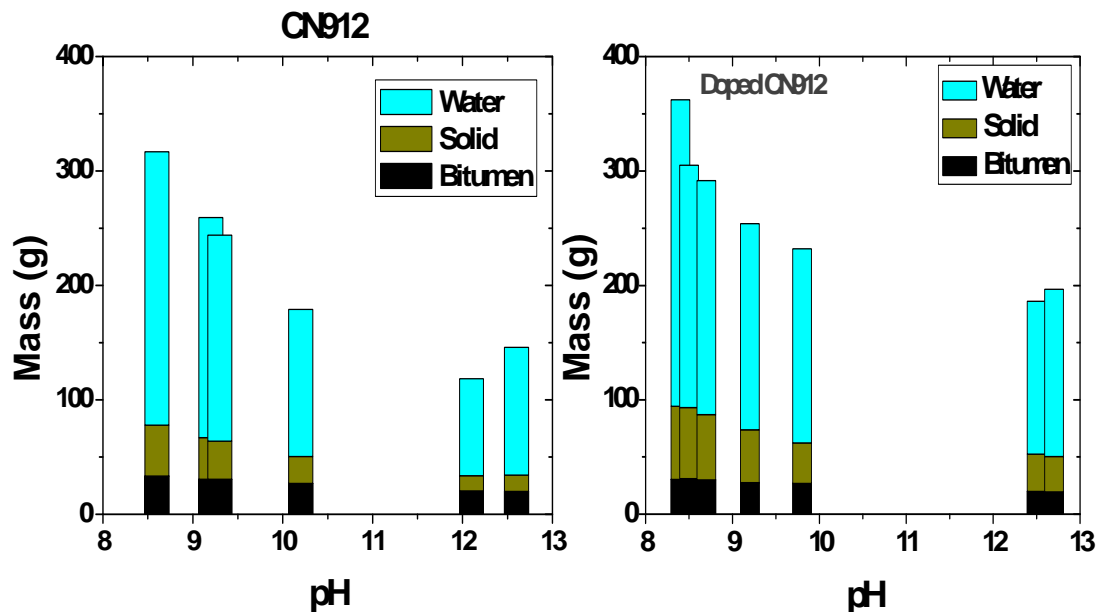Figure 5.16 Naphthenic acids concentration and bitumen recovery for doped CN912

Figure 5.17 Mass of bitumen, solids and water in froth for doped CN912.

Mass of bitumen, solids and water in froth for doped CN912 is shown in

Figure 5.17, 130 ppm calcium and 60 ppm magnesium addition increases the water and solids content of the froth, and it impairs the bitumen recovery.

5.5 Naphthenic acids impacts on flotation

5.5.1 Procedures of flotation for MA using CN912 tailings water

With noticed that it seems there is no upper limit of naphthenic acid release from CN912, CN912 0.7 wt. %NaOH tailings water having about 140 ppm naphthenic acid, was used to extract MA ore to evaluate the naphthenic acid impact on the bitumen flotation.

The procedure of designed set up is: i) CN912 was floated with 0.7 wt. % NaOH addition to obtain 0.7 wt. % NaOH of CN912 tailings water; ii) MA ore was floated by using tailings water of 0.7 wt. % NaOH of CN912 and new tailings water marked as MA (0.7CN912) was used as a basis for induction time measurement; iii) MA was floated with 0.5 wt. % NaOH by using tailings water from step 1) and marked as 0.5MA (0.7CN912).

5.5.2 Bitumen recovery and naphthenic acids concentration for MA using CN912 tailings water

Naphthenic acids concentration and bitumen recovery for MA using CN912 tailings water are shown in Figure 5.18. Using CN912 0.7 wt. % NaOH tailings water to float MA, makes the bitumen recovery of MA (0.7CN912) is slightly lower than original MA at 0.5% and 0.7% NaOH loadings and releases about 180 ppm naphthenic acids. Theoretically speaking, naphthenic acids concentration should be equal to 140 ppm existed in tailings water of CN912 ore plus 100 ppm released from MA ore at this caustic level. However,

the naphthenic acids concentration of tailings water for MA (0.7CN912) is 60 ppm lower than what we expected. Naphthenic acid concentration of 0.5MA (0.7CN912) is identical as MA (0.7CN912) with the bitumen recovery slightly higher. One of the hypotheses is that there is a solubility limit of naphthenic acids released to the tailings water. Naphthenic acids would not be released from oil sands if the naphthenic acids concentration in the solution is high enough (in this case would be 180 ppm). There is another possibility that naphthenic acid releasing is related to the calcium and magnesium ions concentration, high cations concentration facilitates naphthenic acid releasing, however, cations would consume free naphthenic acid of the tailings water.
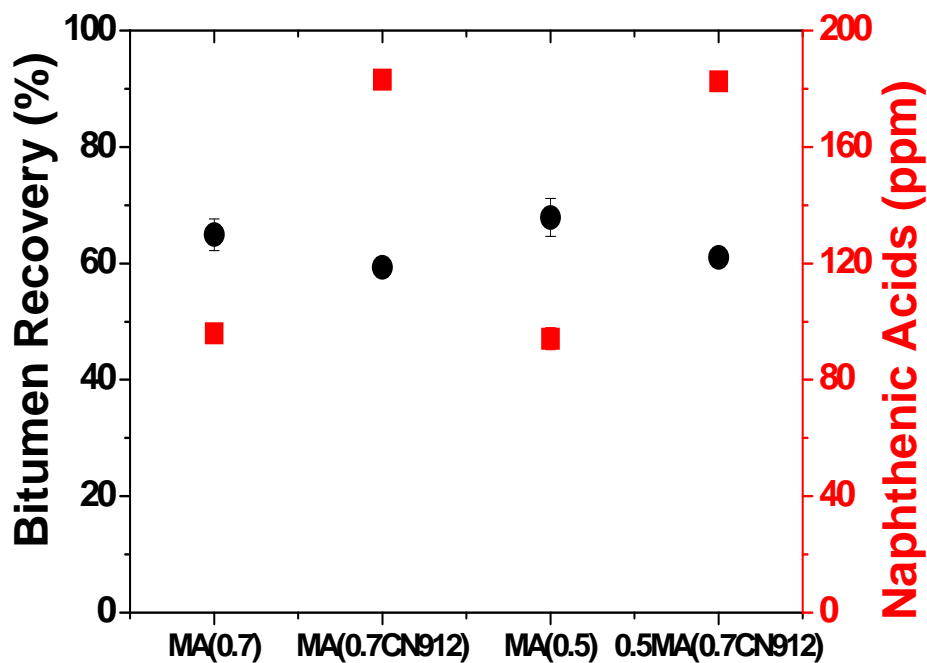

Figure 5.18 Naphthenic acids concentration and bitumen recovery for MA using CN912 tailings water

5.5.3 Induction time for MA (0.7CN912)

Induction time of tailing water of MA (0.7CN912) was measured to evaluate the naphthenic acid impact as shown in Figure 5.19. MA (0.7CN912) tailings water has the highest naphthenic acid concentration, and the induction time of its tailings water reaches to 1500 ms. It seems that the induction time is proportion to naphthenic acid concentration of the bulk solution. The extension of induction time by naphthenic acids is not obvious at naphthenic acids concentration more than 150 ppm.

27 ppm Ca^{2+} and 15 ppm Mg^{2+} ions was added into the tailings water of MA (0.7CN912) to determine the role of calcium and magnesium concentration on air bubble-bitumen attach time. Doped MA (0.7CN912) has slightly shorter attach time than original 1500 ms. Cations has very limit impact on induction time when there is high naphthenic acid in the solution. Even the fine solids suspension has identical result as un-doped MA (0.7CN912). And induction time seems independent on pH of the bulk solution.
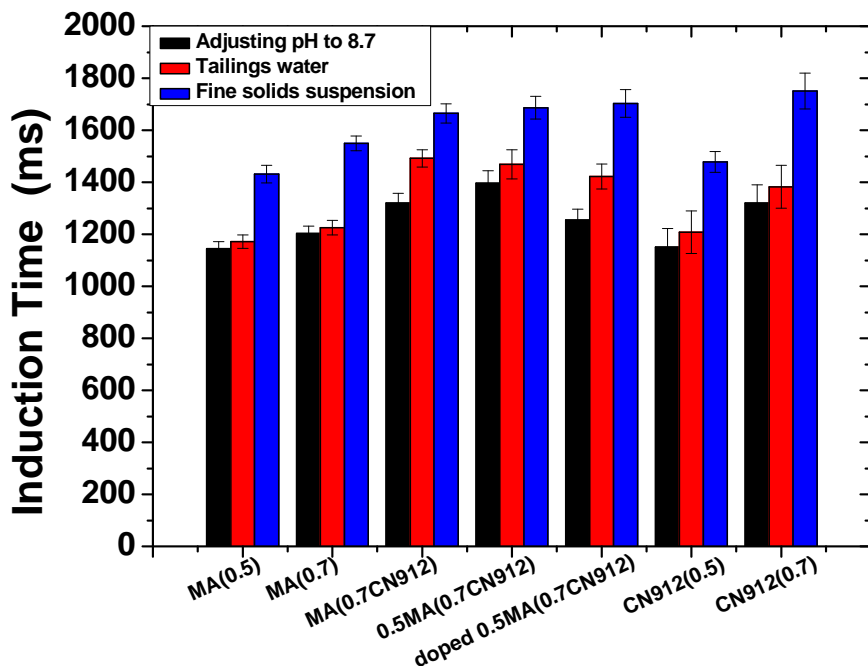
Figure 5.19 Induction time results for MA using CN912 tailings water

5.5.4 Naphthenic acids impacts on zeta potential distribution

To determine the pH influence on zeta potential distribution, the pH of 0.1 wt. %NaOH tailings water of CN912 was adjusted to 8.7, as same as the blank level, to measure the zeta potential distribution as shown in Figure 5.20. Adjusting pH of the solution definitely makes the bitumen and solids surfaces less negative than their original values. Partially slime coating happened at 0.1 wt. %NaOH tailings water of CN912 with adjusting pH to 8.7. One of the reasons for this phenomenon is that the repulsive force between bitumen and solids is weakened by decreasing pH of the bulk solution.
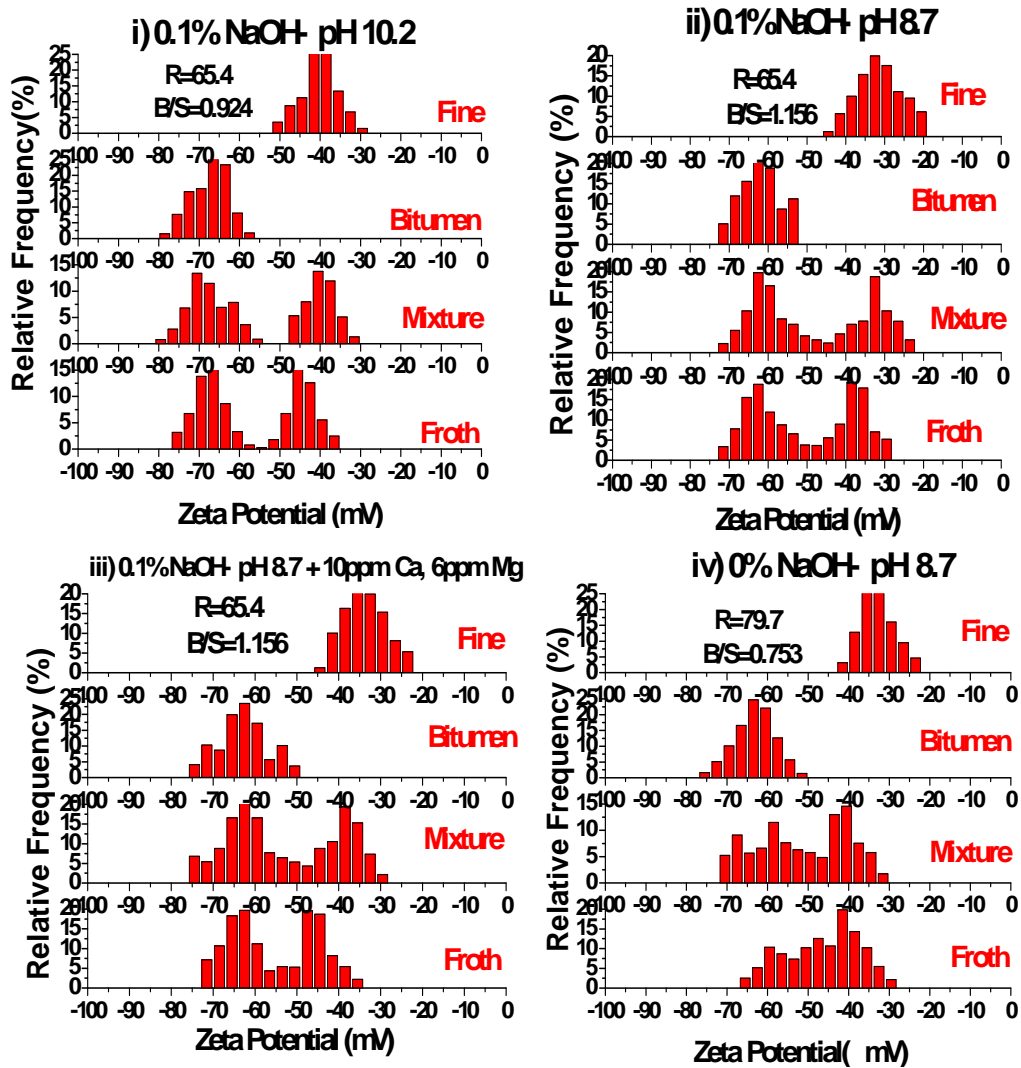
Figure 5.20 Zeta potential distributions for CN912: i) 0.1 wt. % NaOH tailings at pH 10.2, ii) 0.1 wt. % NaOH with adjusting pH to 8.7, iii) 0.1 wt. % NaOH tailings with adjusting pH to 8.7 and10 ppm Ca^{2+} , 6 ppm^{2+} Mg addition, iv) 0 wt. % NaOH tailings at pH 8.7.

Based on the water chemistry of tailings water for CN912 ore, 10 ppm Ca^{2+} and 6 ppm Mg^{2+} were added into the 0.1 wt. %NaOH tailings water 0f CN912 ore to evaluate naphthenic acid impact on slime coating, and the pH was adjusted to 8.7 exactly same as 0 wt. % NaOH tailings water for CN912. The only difference between 0.1 wt. %NaOH tailings water (pH= 8.7 and with 10 ppm Ca^{2+} and 6 ppm Mg^{2+} addition) used in Figure 5.18 and the blank caustic

loading tailings water of CN912 is the naphthenic acids concentration. Partially slime coating happens at 0.1 wt. % NaOH CN912 with pH adjusting and Ca^{2+}, Mg^{2+} addition. Doped CN912 has very similar zeta potential distribution as 0.1 wt. % CN912 with adjusting pH to 8.7. 10ppm Ca^{2+} and 6ppm Mg^{2+} addition seem has very little impact on zeta potential distribution because of the naphthenic acid existed in the solution. Compared the doped CN912 with 0 wt. % CN912 zeta potential distribution, it shows that less slime coating happens for doped CN912 with has more naphthenic acid in the solution. High concentrated naphthenic acid is found to help avoiding the slime coating in the froth, which agrees with the froth quality improvement by high concentration of naphthenic acids.

5.6 Summary

5.6.1 NaOH role of the bitumen flotation

As shown in Figure 5.21, adding sodium hydroxide into the flotation first increases the pH of the slurry, and makes the air bubbles, bitumen droplets and fine sands more negatively charged. It also decreases divalent cations concentration by associating with OH^- ions, which will improve the liberation and reduces the chance of slime coating. Meanwhile, high pH will help oil sands to release natural surfactant (mainly naphthenic acids in this study), which will also improve bitumen liberation but hinder the aeration by decreasing the air bubble and bitumen attachment efficiency.
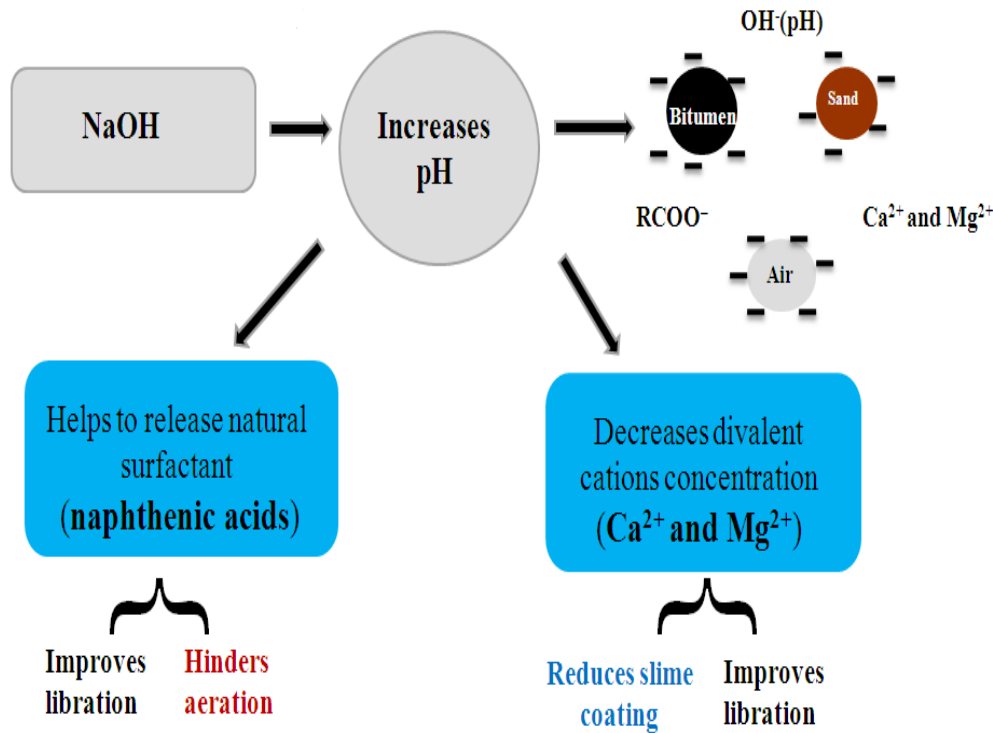
Figure 5.21 Impacts of caustic addition on flotation

5.6.2 Naphthenic acids impacts on bitumen liberation

Naphthenic acid impact on bitumen liberation is not in the discussion range of this paper. However, some related researches are undergoing. And one result of bitumen liberation with naphthenic acid addition is shown in Figure 5.22. Images are provided by Chris Flury (one of graduate students in our group). Naphthenic acid addition of the process water makes the bitumen surface more negatively charged and improves the bitumen liberating from the sands. As in the right image of Figure 5.22, bitumen droplet coagulated on the sand surface and float left with the clean white sands with naphthenic acid facilitation.
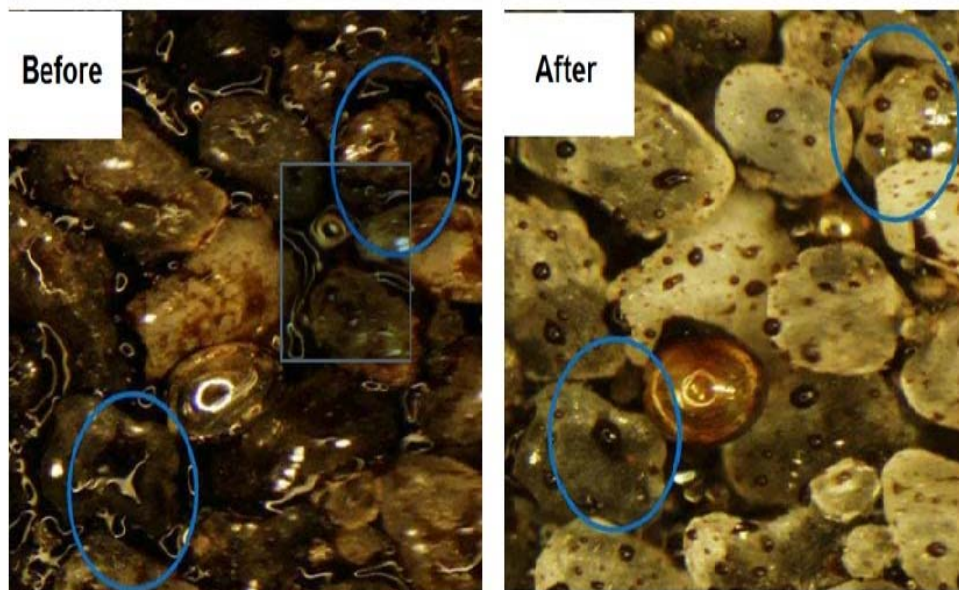
Figure 5.22 Naphthenic acid impacts on bitumen liberation

5.6.3 Conclusions

Role of caustic addition: low NaOH (0.01 wt. % based on ore weight) improves bitumen recovery. For high fine ores, bitumen recovery is dependent on NaOH dosage that high caustic loading impair bitumen recovery. For average fine ores, bitumen recovery is not related to caustic loading levels. Caustic addition facilitates the natural surfactant (naphthenic acid) releasing and decreases calcium and magnesium ions concentration of tailings.

Role of naphthenic acid: naphthenic acid extend the air bubble-bitumen attach time, however, it improves the froth quality by avoid the slime coating and has positive influences on bitumen liberation. It is believed that there is an optimum dosage of naphthenic acid to balance the increased induction time and enhanced bitumen froth quality for each ore.

Role of cations: calcium and magnesium ions are worked as a bridge to

connect bitumen and fine solids in alkaline water, and they are found to facilitate the slime coating. However, high cations limit the naphthenic acid releasing of the flotation. As shown in Figure 5.23, CN912 has the lowest calcium and magnesium ions concentration of the tailings water, and its bitumen recovery is quite high even though it has 38% fines content. Bitumen recovery of AS ore is quite low, because it releases calcium and magnesium ions during the flotation process. And those cations limit the naphthenic acid concentration; impair the froth quality for bringing solids and water to float.
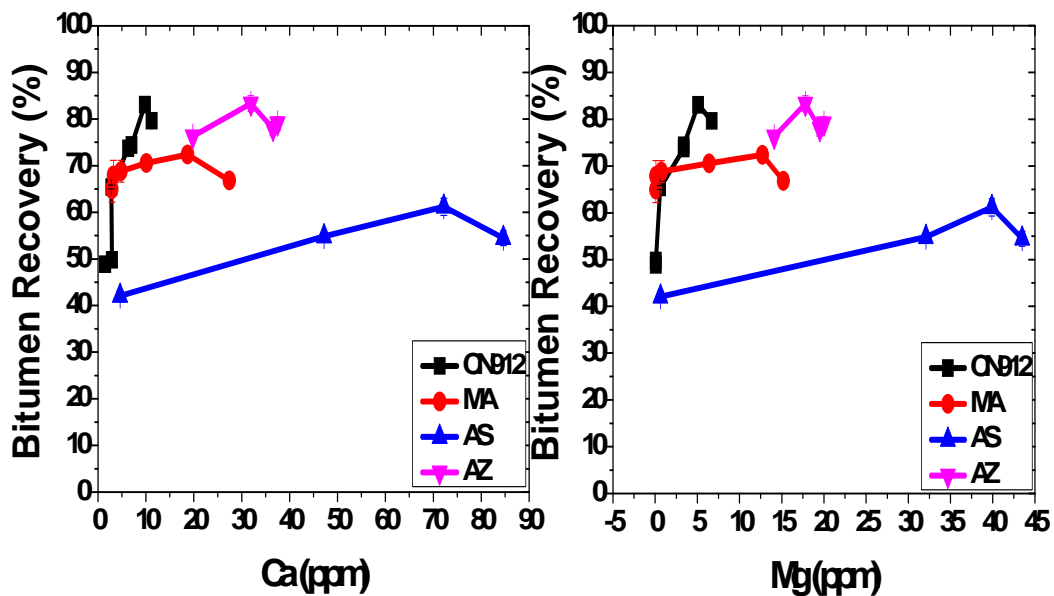

Figure 5.23 Bitumen recoveries vs. calcium and magnesium ions concentrations of tailings water for MA, CN912, AS and AZ

Solids recovery: one of the ultimate goals of the commercial process is to obtain froth with high bitumen recovery with low solids recovery. Bitumen recoveries vs. solids recoveries from the froth of MA, CN912, AS and AZ are plotted in Figure 5.24.
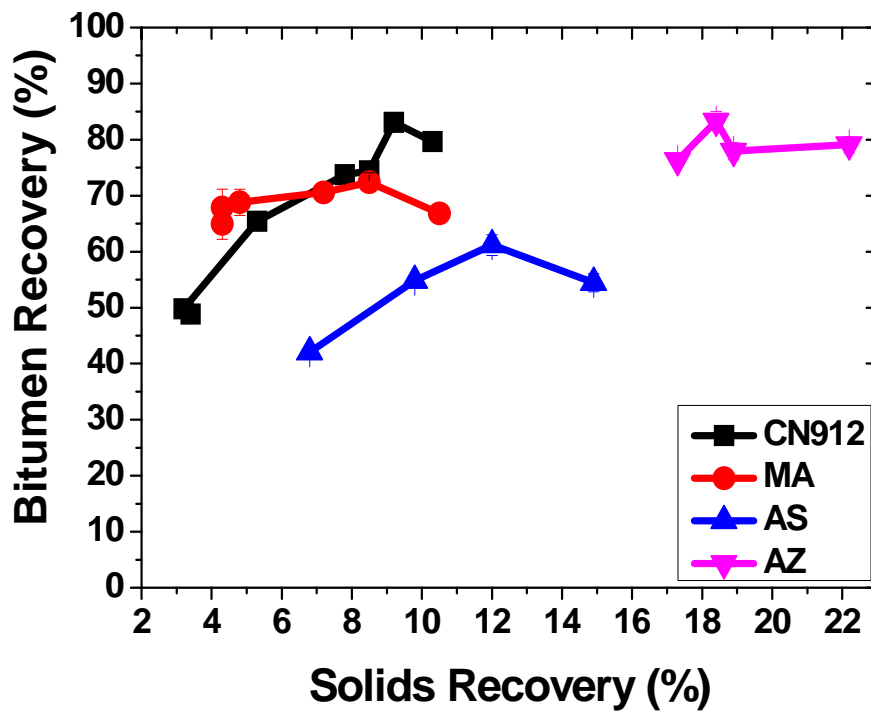
Figure 5.24 Bitumen recoveries vs. solids recovery for MA, CN912, AS and
AZ

Recall the sequence of bitumen recovery is: AZ= CN912> MA>AS. AZ could
have high bitumen recovery performance because of its high bitumen content
and average fine content, however, the solids recovery is extremely high. For
CN912, low concentrated cations limit solids recovery of froth, which makes
the bitumen recovery seems high at the low caustic loadings, as soon as
naphthenic acid reaches its upper limit, bitumen recovery dramatically
decreased. MA seems independent of NaOH addition. The solids recovery of
AS is in the middle range, however, the high cations releasing makes the
bitumen recovery to an unexpected low level.

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CHAPTER 6 CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH

6.1 Conclusions

Based on current study, the impacts of caustic addition on recovery of bitumen from four different ores can be summarized as follows.

Induction time of air bubble-bitumen attachment was found to increase with increasing sodium hydroxide addition for all the ores studied. The induction time measurement in the DI water with naphthenic acid addition clearly showed that increasing the concentration of naphthenic acid increases the induction time of air bubble-bitumen attachment. The measured induction time is appeared to be independent of pH. Fine solids (clays) were found to interfere with bitumen-air bubble attachment.

Zeta potential distribution measurement showed that bitumen and fine solids surfaces became more negative when increasingly amount of caustic was added during the flotation. Slime coating happened at low caustic addition level, and fine solids did not attach to the bitumen surfaces at extremely high caustic addition level, which agrees with the decreased mass of bitumen, solids and water in froth for these four kinds of oil sands.

The concentration of divalent cations such us calcium and magnesium in the tailings water decreased with increasing caustic added during the flotation. However, the concentration of these ions was found to be dependent on the ore characteristics. High concentration of calcium and magnesium ions led to significant interactions of these ions with naphthenic acid, which impacts the

surface activity of naphthenic acid.

High naphthenic acid concentration enhances bitumen; however it also hinders the air bubble – bitumen attachment. In order to obtain high quality bitumen froth without sacrificing bitumen recovery, a small amount of caustic (0.01 wt.% NaOH based on ore weight) could be added during the flotation to improve liberation and fines dispersion. Because each oil sand has its own characteristics such as bitumen content, fines content of the solids, types and amount of salt and surfactant, etc., the optimum dosage of caustic is different for each specific ore. High fines ores are found to be more sensitive to NaOH loading. Bitumen recovery of high fines ores decreases dramatically after the optimum dosage of caustics. While average fine ores seem to be less sensitive to the caustic addition.

One of the major conclusions from this study is that low caustic addition improves bitumen recovery; while highly alkaline water helps natural surfactant release. To explain this finding, the bitumen flotation subprocess liberation and aeration were studied. For bitumen liberation from sand grains, high pH and high naphthenic acid concentration are desirable as they make the surface of solids and bitumen to be more negative, and the resulting repulsive forces make the bitumen liberation easier and attachment of bitumen to sands/fine solids more difficult. For bitumen aeration, the electrical repulsive force between fine solids and bitumen reduces the solids and water content of bitumen froth dramatically with caustic addition. A cleaner froth is obtained, which has a positive impact on subsequent bitumen froth cleaning. Caustic addition also helps to release more naphthenic acids which reduce the efficiency of air bubble-bitumen attachment. Since bitumen extraction with

caustic addition is a competition process among the interactions between air bubble, bitumen and/or fine solids, naphthenic acid concentration plays a crucial role in determining air bubble-bitumen attachment.

There exists a proper naphthenic acid concentration below which froth quality increases with increasing naphthenic acid concentration without significantly impacting bitumen recovery and above which bitumen recovery decreases significantly without improving bitumen froth quality. The extent of decreasing bitumen recovery depends on the type of oil sands, most likely related to the fine content of the oil sands. The fine solids contents of CN912 and AS are comparably high. And their bitumen recovery decrease dramatically, especially for CN912, from 85% to 50%. MA ore has much lower fines content, and the decrease in its recovery is within 10%. Further experiment is needed to further verify this conclusion.

6.2 Recommendations for the Future Work

The recommendations for future research on the impact of caustic addition on oil sands processing are listed as follows:

1) Complete the oil sands flotation for AZ and AS ore at high caustic level to compare with CN912 ore, then a clear conclusion could be made with all the caustic addition levels for all the four ores.

2) Evaluate the impact of caustic addition and naphthenic acids concentration on liberation to verify the role of naphthenic acid concentration in bitumen extraction.

3) Investigate the effect of divalent cations (Ca^{2+}, Mg^{2+}) on naphthenic acids addition to the tailings water by induction timer. Understanding the

interaction of cations with naphthenic acid would provide us a panorama of how does the naphthenic acid function in the bitumen flotation.

4) Explore the induction time measurement by using centrifuged bitumen from oil sands instead of vacuum distillated feed bitumen to minimize the bitumen characteristic influence.

5) Test the clay type for each oil sand to understand the influence of fine solids.

6) Determine the slime coating on bitumen surface by using QCM-D. QCM-D not only provides a quantitative analysis of the fine solids – bitumen surface attachment, but also eliminates the solids deposit impact of the induction time.

7) Analyze the impact of naphthenic acid concentration on flotation. Adding naphthenic acid directly through flotation process would help us to find out an optimum range of naphthenic acid to achieve the highest recovery for each oil sand.

8) Extent the study to other types of oil sands to approve the existed findings and generalize a conclusion with consideration of all types of oil sands.