IMPACT OF SALINITY ON WARM WATER-BASED MINEABLE OIL SANDS PROCESSING

Tong Chen,¹ Feng Lin,² Bauyrzhan Primkulov,¹ Lin He³ and Zhenghe Xu¹*

1. Department of Chemical and Materials Engineering, University of Alberta, Edmonton, AB, T6G 1H9, Canada

2. CanmetENERGY - Devon, Natural Resources Canada, One Oil Patch Drive, Devon, AB, T9G 1A8, Canada

3. Collaborative Innovation Centre of Chemical Science and Engineering, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, P. R. China

Continuous use of caustics and increased level of water recycling inevitably increase the salinity of process water, which is a growing challenge in the current warm water-based bitumen extraction process. The current study aims at understanding how salinity of process water affects bitumen recovery from mineable oil sands ores. Laboratory flotation results showed an ore-dependent effect of salinity on bitumen recovery and froth quality. Processing of low-grade ores suffered a dramatic loss in bitumen recovery with increasing NaCl up to 4000 ppm (i.e. 1574 ppm Na⁺) at pH 8.5, while only a marginal effect of salinity was found on the processability of a high-grade ore. The use of caustics as a conventional approach to increase bitumen recovery and froth quality of poor processing ores showed a more severe negative impact of salinity on the processability of low-grade ores. Salt addition was found to be detrimental to bitumen liberation and bitumen-bubble attachment in the presence of fines, more so at higher pH of processing water. Increasing salt concentration in solution led to a significant decrease in the magnitude of negative zeta potentials for both bitumen and fine solids. These findings provide scientific guidance to searching for remediation strategies other than using caustics. Such an approach studied was the blending of low-grade ores with high-grade ores to minimize the negative impact of increased salinity in recycle water on bitumen extraction.

Keywords: oil sands extraction, water salinity, bitumen liberation, bitumen aeration

INTRODUCTION

O il sands, a mixture of bitumen (an extremely viscous form of petroleum, 6 to 16 wt%), mineral solids (sands and clays, 80 to 87 wt%), and water (2 to 7 wt%), are known to be an important unconventional petroleum resource.^[1] The largest oil sands deposit, with a proven reserve of around 20 270 GL (170 000 000 000 barrels) of crude bitumen, is located in Northern Alberta of Canada, ranking the third largest petroleum reserve in the world, just behind Saudi Arabia and Venezuela.^[2] The current production of oil at 236 ML/day (1 980 000 barrels per day; 1.98 mbd) from Alberta oil sands accounts for 56 % of total Canadian oil output. The oil production from oil sands is forecasted to grow up to 620 ML/day (5.2 mbd) by 2030.^[3]

In practice, the method of producing oil or more precisely bitumen from oil sands depends on the location and depth of the oil sands deposits. For the deposits less than 75 m below the surface, hot or warm water-based extraction (WBE) following the open pit mining is commonly used to extract the bitumen. In general, the WBE process involves several steps, including mining of oil sands ores, crushing and slurry preparation of mined oil sands ores, recovery of bitumen by stationary gravity separation-flotation, cleaning/partial upgrading of bitumen froth by solvent-assisted froth treatment, and tailings treatment for water management (recycle) and solid waste disposal.^[2] Maximizing bitumen recovery and minimizing the use of fresh water by recycling of the process-affected water from the tailings are the two integrated tasks that the oil sands industries want to accomplish. Water chemistry (e.g. type and concentration of ionic species) of process water is a well-recognized key parameter that affects the processability of oil sands ores.^[3] Many interlinked physical and chemical processing parameters need to be considered to accomplish these two conflicting objectives. In common practices, caustics (e.g. sodium hydroxide) are used in the WBE process as a process aid to increase the bitumen recovery and froth quality. The purpose of adding caustics is to increase the pH of the oil sands slurry, which is shown to enhance bitumen liberation from sand grains as a result of increasing the surface charges on both bitumen and sand grains.^[4] The elevated pH also helps to release more natural surfactants from the bitumen, reducing the interfacial tension between water and bitumen, which thermodynamically favours bitumen liberation.^[5–11] The increase in electrostatic repulsion due to the increase in the surface charge of bitumen and fine solids prevents detrimental slime coating of fine particles on bitumen, which in turn increases the efficiency of bitumen-air bubble attachment. Furthermore, increasing pH by adding caustics can lead to an increased concentration of carbonates (CO_3^{2-}) and bicarbonates (HCO_3^{-}) as a result of increased dissolution of CO_2 in the process water. Carbonate ions are known to precipitate the divalent cations such as calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions in the process water. These divalent cations are known to be harmful to the bitumen extraction process. On the other hand, the majority of

E-mail address: zhenghe.xu@ualberta.ca

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^{*} Author to whom correspondence should be addressed.

sodium ions originated from the added caustics remain in the tailings water. By considering the repeated recycle of process-affected water from the tailings pond, sodium ions in the process water will inevitably increase due to the addition of caustics, which is compounded with the release of these ions from the oil sands ores as a result of ion-exchange activities. Unlike divalent cations, sodium ions cannot be precipitated out from the process water. The ultimate consequence is a gradual increase in sodium ion concentration with increasing the number of recycling of the process-affected water. In one of the oil sands operations, the salinity of the tailings pond water (TPW) was shown to increase at a rate of 75 mg/L per year from 1980 to 2001.^[12]

The oil sands industry is concerned that increasing the salinity of recycle process water will potentially affect the recovery of bitumen from the mined oil sands ores. From an economic point of view, a 1 % reduction in bitumen recovery at the current production rate is estimated to be equivalent to a loss of about 365 000 000 US dollars annually.^[3] In terms of the environmental impact, the unrecoverable bitumen in the tailings creates a big threat to wildlife such as birds in the area. Despite its practical importance, only a few scattered studies on the issues of water salinity on bitumen recovery from mineable oil sands ores were reported in the available literature. Takamura et al. reported that the addition of Na⁺ up to 1725 ppm could reduce bitumen recovery by as much as 45 %.^[13] Basu et al. suggested a threshold level of sodium ions in process water, above which bitumen displacement by water on a flat glass surface was greatly hindered.^[14-15] The depressing of bitumen displacement was found to be more pronounced at higher pH when salt was added, suggesting a more pronounced negative impact of NaCl on bitumen recovery at higher pH. Sundeep et al. reported a significant decrease in the degree of bitumen liberation from real oil sands with increasing sodium concentration in process water.^[16] Liu et al. measured the intermolecular forces between bitumen and silica probes in aqueous solutions of different KCl concentrations. Increasing salt concentration was found to reduce the repulsive forces between bitumen and silica as a result of compressing electrical double layers by added salts.^[17] Although these earlier studies provided convincing evidence of detrimental impact of increasing salt concentration on bitumen recovery, the underlying mechanisms of such negative impact remain to be studied in order to develop viable remediating strategies.

The main objective of the current study is to investigate the impact of salinity on bitumen liberation and aeration subprocesses of bitumen recovery from different types of oil sands ores. Together with the zeta potential measurement of both bitumen and fine solids and contact angle measurement using a modified micro-pipette technique, the findings from these essential measurements linked with bitumen extraction performance provide a scientific guidance to searching for remediation strategies other than use of caustics. As an example, blending of low-grade ores with high-grade ores was shown to minimize the negative impact of increased salinity in recycle water on bitumen extraction.

EXPERIMENTAL

Materials

Three types of oil sands ores (denoted as Sun08, MA, and AE13) were used in this study. The characteristics of these three ores in terms of bitumen, water, solids, and fines content are shown in Table 1. As conventionally used in the industry, the fines are

Table 1. Composition (g/100 g, wt%) of oil sands ores							
Ore	Solids	Bitumen	Water	Fines in solids			
Sun08	82.8	16	1.2	6			
MA	83.5	8.2	8.3	20			
AE13	86.8	8.3	4.9	38			

defined as mineral solids of particle sizes less than 44 μ m and expressed as a percentage of total solids in the ore. The industrial recycle process water provided from the Aurora plant of Syncrude Canada was used in flotation tests. The concentrations of major cations and natural carboxylic surfactant (CS) of the process water are given in Table 2. The salt content of the process water was adjusted by adding chemical-grade NaCl, while the pH of the process water was adjusted to 8.5 and 11.2 by analytical-grade sodium hydroxide and hydrogen chloride purchased from Fisher Scientific. Clay fines isolated from an oil sands deposit, supplied by Teck Resources Limited, were used in the induction time measurement of bitumen-air bubble attachment. The mineral composition of the clay (fines) is given in Table 3. The clay sample had D₁₀, D₅₀, and D₉₀ (10 %, 50 %, and 90 % passing size) values of 2.1, 15.4, and 61.2 μ m, respectively.

Experimental Procedures

Bitumen flotation

Bitumen extraction tests were performed using a Denver flotation cell. This cell consisted of a 1-L stainless steel cell, an impeller, and a 1/2 HP Baldor industrial motor. For each test, 500 g of thawed ore was added into the flotation cell containing 250 mL process water of desired pH at 80 °C, resulting in a slurry temperature of 50 ± 1 °C. The process water contained a different amount of additional sodium chloride, ranging from 0 to 4000 ppm. The oil sands slurry was agitated at 1500 rpm for 5 min during which an external air stream at 80 mL/min was added. This process is known as the oil sands conditioning. After the conditioning, 800 mL of process water with the same water chemistry at 50 °C was added into the cell. The agitation continued for another 10 min without air input, during which the primary bitumen froth was collected. Further bitumen froth was collected as the secondary bitumen froth during another 5 min of agitation at 1500 rpm with 150 mL/min air supply. After froth collection, the slurry remaining in the Denver cell was discharged as tailings. The primary and secondary froth collected in the thimbles were analyzed using the Dean Stark apparatus to determine the mass of bitumen, water, and solids in the froth. The entire flotation experiments were conducted at a constant temperature of 50 °C, maintained using a water bath attached to the Denver cell.

Bitumen liberation

Bitumen liberation process from real oil sands ores was analyzed online using a bitumen liberation flow visualization cell (BLFVC)

Table 2. Major cations and surfactant (CS) concentration of Syncrude process water						
Na⁺ (ppm)	Ca ²⁺ (ppm)	Mg ²⁺ (ppm)	K ⁺ (ppm)	CS (10 ⁻⁵ mol/L)		
660	40	17	23	25		

 Table 3. Mineralogy for fines (clays) used in the induction time measurement

Composition	Coarse fraction (g/100 g, wt%)	Fine fraction (g/100 g, wt%)	Overall (g/100 g, wt%)
All solids	59.86 ± 6.63	40.14 ± 6.63	100 ± 0.00
Total clay	19.40 ± 5.47	$\textbf{88.97} \pm \textbf{5.41}$	$\textbf{47.33} \pm \textbf{1.08}$
Quartz	77.00 ± 5.67	11.03 ± 5.41	50.51 ± 1.26
K-feldspar	1.14 ± 0.81	-	$\textbf{0.67} \pm \textbf{0.43}$
Plagioclase	0.41 ± 0.08	-	0.25 ± 0.08
Calcite	$\textbf{0.54} \pm \textbf{0.20}$	-	0.33 ± 0.16
Dolomite	0.31 ± 0.12	-	0.19 ± 0.10
Siderite	0.73 ± 0.13	-	0.44 ± 0.09
Pyrite	$\textbf{0.46} \pm \textbf{0.29}$	-	$\textbf{0.29} \pm \textbf{0.22}$
Chlorite	$\textbf{0.75} \pm \textbf{0.05}$	$\textbf{2.45} \pm \textbf{0.28}$	1.42 ± 0.04
Kaolinite	$\textbf{6.02} \pm \textbf{1.81}$	46.30 ± 2.81	$\textbf{22.22} \pm \textbf{1.51}$
Illite	12.63 ± 3.76	$\textbf{38.64} \pm \textbf{4.65}$	23.05 ± 2.07
Illite/smectite mixed layer	$\textbf{0.00} \pm \textbf{0.00}$	1.58 ± 0.27	$\textbf{0.64} \pm \textbf{0.19}$

developed by Srinivasa et al.^[16] For each test, a small amount (approximately 1 g) of thawed oil sands ore was placed in the sample holder with the surface being flattened with a small hammer and smoothed by a sharp razor blade. The process water of desired water chemistry was kept in a small beaker. A peristaltic pump (Masterflex, C/L) was used to circulate the process water through the liberation flow visualization cell. The liberation process was monitored and recorded using a stereo-optical microscope from Olympus (SZX 10), connected to a highresolution charge-coupled device (CCD) camera. The flow rate of water was controlled at 5 mL/min and the temperature of water bath was 23 °C for all the tests, unless otherwise stated. The degree of bitumen liberation was calculated based on the captured images using our in-house developed image processing method.^[18] A typical image processing transformation is shown in Figure 1.

Contact angle measurement

The contact angle was measured using a modified micro-pipette technique by analyzing the bitumen droplet relaxation on a

spherical glass substrate in process water.^[19,20] The details on the procedures of droplet relaxation experiment were already given elsewhere.^[19,20] Only a brief description is given here. A micronscale, ball-shaped glass tip was coated in air with vacuum distillation feed bitumen (VDFU) provided by Syncrude Canada Ltd. The sample was then placed in the Syncrude process water with the salt concentration and pH being adjusted as desired. Upon immersing the bitumen-coated glass tip in the process water, the bitumen droplet receded spontaneously from the glass substrate.^[21] The entire bitumen receding process was recorded with a high-speed camera on an optical microscope (Zeiss Axiovert 200). The dynamic contact angles (i.e. the angle between the two tangent lines at the three phase contact (TPC) point) were obtained by applying the automated angle acquisition method to analyzing still images, from which the dynamic and equilibrium contact angles were obtained. An example of this analysis on a real image is shown in Figure 2.^[19,20]

Induction time measurement

To investigate the effect of water salinity on bitumen aeration, a custom-built induction timer was used.^[21,22] The VDFU bitumen was placed on a circular Teflon disk. The bitumen surface was flattened by a sharp razor blade. The bitumen sample was then immersed in a desired amount of water in a small rectangular glass cell. Before each test, the bitumen sample was soaked in the water for around 30 min to allow the relaxation of the bitumen surface to a mirror-like smoothness and for the surface to reach pseudoequilibrium state. To better represent the real system of the measurement, the bitumen surfaces were allowed to interact with clay fines from the real oil sands deposit supplied by Teck Resources Limited prior to the induction time measurement. The clay fines were used without any further treatment. To overcome the difficulties of high suspension turbidity in viewing the bitumen-air bubble attachment process in a suspension containing as little as 0.5 wt% fines solids, a protocol of bitumen interaction with clay fines in the desired process water as shown in Figure 3 was used. Briefly, the bitumen surface on the desk was held by a pair of tweezers and immersed with the bitumen surface facing downwards in the suspension which was under stirring for 15 min. This configuration was used to avoid unwanted deposition of clays under gravity that would provide false results. The



Figure 1. Examples showing image transformation for degree of bitumen liberation analysis.



Figure 2. A typical image analysis of contact angle determination using an in-house developed shape fitting method.^[19,20]

treated bitumen was then transferred to clear tailings water of the same water chemistry for the induction time measurement. The details on the induction time measurement and data processing were given elsewhere.^[22]

Zeta potential measurement

The zeta potential of fine clay suspensions and bitumen emulsions was measured using a ZetaPALS (Brookhaven) which is based on the phase-analysis of scattered light by particles. In this study, the measurement was repeated for each sample at least ten times at room temperature. The clay fines suspension was prepared using fines separated from the froth in the above-mentioned flotation tests of three different oil sands ores. The isolated fines were mixed at a mass ratio of 1:1000 with tailings water of bitumen extraction tests at different sodium chloride concentrations. The suspension was then diluted with the same tailings water to about 0.01 wt%, dispersed by an ultrasonic dismembrator for 5 min. A similar procedure was used to prepare bitumen emulsions using VDFB in the same tailings water.

RESULTS AND DISCUSSION

Effect of Salinity on Bitumen Extraction

Figures 4 and 5 show the results of overall bitumen recovery and froth quality in terms of bitumen-to-solids mass ratio for three ores at various levels of sodium addition. At a given dosage of salt, the overall bitumen recovery decreases with increasing fines content

and/or decreasing the grade of the ores. It is evident that the response of bitumen recovery to increasing the salinity of the process water is highly dependent on the type of ores. For high-grade and low-fines ore Sun08, for example, the overall bitumen recovery appeared to be insensitive to increasing the salt addition. Even at a NaCl addition up to 4000 ppm (1574 ppm Na⁺), bitumen recovery at pH 8.5 remained satisfactory. However, for medium-and low-grade MA and AE13 ores, the overall bitumen recovery decreased with increasing sodium chloride addition. For example, the overall bitumen recovery from AE13 dropped from 66 % to 50 % when the salt addition into the process water increased from 0 to 4000 ppm.

As reported previously, increasing pH of process water by caustic (mainly sodium hydroxide) addition was beneficial for processing low-grade ores (He et al.^[7]). In this study, the application of caustic was used to evaluate whether the caustic addition could alleviate the negative effect of high salinity on flotation of poor-processing MA and AE13 ores. Results obtained at pH 11.2 show that the effect of increasing salt dosage on bitumen recovery is also ore-dependent. At a given level of NaCl addition, it is interesting to note a larger loss of bitumen recovery from medium (MA) and high (AE13) fines ores at pH 11.2 than at pH 8.5. With an increase in sodium chloride addition level from 0 to 4000 ppm (1574 ppm Na⁺) at pH 11.2, for example, bitumen recovery for medium- and high-fines ores dropped from 76 % to 53 % and 65 % to 40 %, respectively. In contrast, the bitumen recovery at pH 8.5 decreased by 4000 ppm sodium chloride addition from 77 % to 65 % and 66 % to 50 % for the mediumand high-fines ores, respectively. A similar trend was observed in bitumen froth quality as shown in Figure 5. Our finding is consistent with the findings of Takamura and Wallace.^[13]

To understand how the salinity of process water affects bitumen extraction at different pH levels, the effect of salt addition on bitumen liberation from the three ores, bitumen recession (dynamic and equilibrium contact angles) from model glass microsphere, induction time of bitumen-air bubble attachment, and zeta potentials of the froth fines and VDU bitumen suspension were studied at pH 8.5 and pH 11.2.

Bitumen Liberation

The degree of bitumen liberation (DBL) as a function of time is shown in Figures 6 and 7. Considering the ultimate DBL (i.e. the DBL at the equilibrium state) of the three ores at the same salt dosage, low-fines Sun08 ore showed a relatively higher degree of bitumen liberation, followed by the medium-fines MA



Figure 3. Procedures of preparing bitumen surfaces interacted with clay fines in recycle process water for induction time measurement of bitumen-air bubble attachment.



Figure 4. Effect of salinity on bitumen recovery from three ores at pH 8.5 (a) and pH 11.2 (b).

and high-fines AE13 ores. The results illustrate a detrimental effect of fines on bitumen liberation. Interestingly, NaCl addition up to 4000 ppm (1574 ppm Na⁺) showed only a marginal depression on both bitumen liberation kinetics and ultimate DBL for all three ores at pH 8.5, regardless of bitumen grade and fines content, as shown in Figure 6. Without NaCl addition, for example, about 40 % of bitumen was liberated from the MA ore within 10 s and the ultimate DBL was 54 %. When 4000 ppm (1574 ppm Na⁺) salt was dosed, 37.5 % bitumen was liberated from MA within 10 s, with ultimate DBL at 49.8 %. This finding suggests that bitumen liberation is unlikely to be the cause of the observed oredependency of the salinity effect on bitumen recovery and froth quality of medium- and low-grade ores at typical bitumen extraction pH of 8.5.

At pH 11.2, more drastic decrease in bitumen liberation kinetics and ultimate DBL with increasing NaCl addition was observed for all three oil sands ores as shown in Figure 7. With 4000 ppm NaCl addition for example, the ultimate DBL decreased from 72 %, 60 %, and 56 % to 41 %, 52 %, and 49 % for Sun08 (low-fine), MA (medium-fine), and AE13 (high-fine) ores, respectively, illustrating an increased negative effect of salinity on bitumen liberation with increasing pH.

Contact Angle Measurement

As a complementary experiment to online bitumen liberation tests from real oil sands ores, bitumen recession from a model glass micro-sphere (similar to silica sand) was investigated in the simulated process water at pH 8.5 and pH 11.2 at room temperature with a variable amount of NaCl addition. In the current setup, the three phase contact (TPC) line of bitumen with solids in water was observed to retract with time from the glass surface as water advanced until reaching an equilibrium configuration. The rate of TPC line movement decreased with time as bitumen retraction approached the equilibrium state. Quantitatively, the resulting water-advancing contact angle as a function of contact time was measured and the results are shown in Figure 8. The rate of decreasing the dynamic contact angle is expressed as the initial slope of the dynamic recession curve of bitumen droplets from solid sphere surfaces. A steeper curve indicates a quicker recession of bitumen, while a smaller equilibrium contact angle implies an easier detachment of bitumen from the solid surface. The results in Figure 8a show an insignificant effect of salinity at pH 8.5 on both dynamic and ultimate states of bitumen recession, as indicated by the two almost-overlapping contact angle profiles at two different salt concentrations.

In contrast, at pH 11.2 the equilibrium contact angle measured from the aqueous phase increased from 45° to 57° (i.e. less waterwet solid surface) when the sodium chloride concentration increased from 500 to 2000 ppm, which is larger than the corresponding value at pH 8.5 at a given salt addition level, as shown in Figure 8b. The trend obtained here is consistent with



Figure 5. Effect of salinity on bitumen-to-solids mass ratio of bitumen froth obtained from three ores at pH 8.5 (a) and pH 11.2 (b).



Figure 6. Effect of salinity on degree of bitumen liberation (DBL) at pH 8.5 from three ores: Sun08 (a), MA (b), and AE13 (c).

those reported by Basu et al.,^[14,15] who showed using flat glass substrates a more pronounced effect of NaCl on the contact angle in higher pH aqueous solutions.

Induction Time of Bitumen Aeration

To evaluate the effect of increasing sodium ion concentration on bitumen aeration, the probability of bitumen-air bubble attachment in the presence of fines as a function of their contact time was measured at 50 °C in the process water of pH 8.5 and pH 11.2. By soaking the VDFU bitumen in the tailing water containing 5 mg/g (0.5 wt%) clay fines, the fines are anticipated to deposit on the bitumen surface, increasing the wettability of bitumen surface from an oil-wet (favouring its attachment to the hydrophobic air bubbles) to a less oil-wet (or more water-wet) character. The more the fines are coated on the bitumen surface, the more water-wet it would be. Increasing the salinity of water decreases electrical double layer (EDL) repulsion between the fines and bitumen. As a result, more fines are anticipated to be deposited onto the bitumen surface, resulting in an increased resistance to the formation of three phase contact of bitumen, water, and air bubble.^[21] In other words, increasing salt dosage (from 0 to 4000 ppm) created detrimental conditions for the bitumen and air bubble attachment in the presence of fines, as indicated by the higher induction time of an air bubble attaching to bitumen surface after contact with fines in suspension, as shown in Figure 9. Considering an increased fines-coating of bitumen with increasing the amount of fines in the system, it is anticipated that the lower the grade of the oil sand ore, the higher the probability of fines coating on the bitumen surface, making bitumen aeration more difficult. In this aspect, the negative effect of salinity on the bitumen and air bubble attachment in the presence of fines would be the most likely reason for the ore-dependent nature of salinity on processability of mineable oil sands, explaining the observed reduction of bitumen recovery and froth quality for the medium-fines MA and high-fines AE13 ores.

For the measurement at pH 11.2, the same trend as observed at pH 8.5 was seen. Sodium ions induced more severe slime coating at pH 11.2 than at pH 8.5 on bitumen to prevent bitumenair bubble attachment, leading to an increase in induction time by 293 ms at pH 8.5 in comparison to 494 ms at pH 11.2. This difference in the effect of increasing salinity on induction time of bitumen-air bubble attachment indicates an easier slime coating of bitumen surface by increasing salinity, leading to a larger amount of fines attached to the bitumen surface and hence poorer attachment of the resultant bitumen surface to air bubbles at pH 11.2 than at pH 8.5. This larger increase in induction time of bitumen-air bubble attachment appears to be responsible for the observed larger decrease in bitumen recovery with increasing salinity at higher pH, more so for high-fines ores as shown in Figure 4.

Zeta Potentials of Suspended Fines and Bitumen Emulsions

Doping a significant amount of sodium ions is known to affect the ionic strength and hence the Debye length of (the particulates in) the solution. As a result, the electrokinetic properties of the suspended particles or droplets are anticipated to change, modifying the interactions between fines and bitumen surfaces. In order to study how the sodium ions affect the surface charges on solids and bitumen, zeta potentials of suspended fines from the froth of bitumen extraction and bitumen emulsions in the tailings water of bitumen extraction tests at pH 8.5 and pH 11.2 were measured. The results are shown in Figure 10.

It is not surprising to see negatively charged bitumen and fines in the tailings water of bitumen extraction without NaCl addition at pH 8.5, more so at pH 11.2. It is also interesting to see the fines from high-fines ores (MA and AE13 ores) were less negatively charged than fines from low-fines ore (Sun08) at pH 8.5. Less negative charge of fines from high-fines ores (MA and AE13) would indicate a weaker electrostatic repulsion between negatively charged bitumen droplets and fine solids as compared with interactions



Figure 7. Effect of salinity on degree of bitumen liberation (DBL) at pH 11.2 from three ores: Sun08 (a), MA (b), and AE13 (c).



Figure 8. Effect of salinity on dynamic and static contact angles of bitumen recession from a glass microsphere in simulated process water at pH 8.5 (a) and pH 11.2 (b).

between the bitumen droplets and more negatively charged fine solids from low-fines ore (Sun08). Compounded with more fines in high-fines ores, the more problematic slime coating for high-fines ores appears to account for the observed lower bitumen recovery and poorer froth quality as observed in Figures 4 and 5.

Although it is anticipated to decrease the magnitude of zeta potential with increasing NaCl concentrate as observed for both bitumen and fine solids isolated from bitumen froth, a more significant reduction was observed at higher pH (Figure 10b) than at lower pH (Figure 10a). Due to higher negative charges on the interfaces, sodium ions are easier to access and adsorb on the bitumen-water or solid-water interface. The greater change of zeta potential with sodium ion addition at higher pH for both bitumen and froth fines explains well the results of bitumen liberation, bitumen recession on glass tip, and bitumen-air bubble attachment. The more significant effect of sodium ion addition at higher pH on these interfacial properties resulted in a more significant decrease in bitumen recovery and froth quality for medium and high-fines ores, indicating that increasing pH cannot alleviate the negative effect of sodium ion accumulation in process water on bitumen extraction.

DISCUSSION



The results above demonstrated a severe negative impact of increasing salinity of process water on processability of medium

Figure 9. Effect of salinity on bitumen aeration in the presence of fines at pH 8.5 (a) and pH 11.2 (b), showing a greater increase at pH 11.2 than at pH 8.5.

and high-fines ores at typical bitumen extraction pH of 8.5, leading to a poorer bitumen recovery and froth quality. The liberation study showed that higher electrolyte concentration hinders the separation of bitumen from sand grains. Unlike the calcium ions which consume a certain amount of surfactant in the aqueous solution and therefore increase bitumen-water interfacial tension, a higher concentration of sodium ions was reported to decrease the bitumen-water interfacial tension.^[1,4] Heimenz and Cai confirmed a decrease in interfacial tension of a pure hydrocarbon-water interface with increasing the salinity of aqueous solutions, when a small amount of surfactant is present.^[23,24] Hanly et al.^[25] proposed that the solid-liquid interfacial free energy can be considered to consist of two contributions:

$$\gamma_{\rm SW} = \gamma_{\rm SW(pzc)} + \Delta F_{\rm dl} \tag{1}$$

where $\gamma_{SW(pzc)}$ represents the solid-water interfacial tension at point of zero charge (pzc), while ΔF_{dl} is defined as the formation free energy of the ionizable surface relative to the point of zero charge.^[25] At a low and constant surface potential, ΔF_{dl} is related to the surface potential as follows:

$$\Delta F_{\rm dl} = -1/2 \in \in_0 \kappa \psi_0^2 \tag{2}$$

where ϵ is the dielectric constant, ϵ_0 is the permittivity of free space, κ represents the Debye length, and ψ_0 is the surface potential.

Although adding sodium chloride into the system is anticipated to reduce the Debye length, compressing more on the electric double layer and hence increasing solid-water interfacial tension, the decrease in the magnitude of zeta potential with increasing salt concentration as measured at pH 8.5 was marginal due to the less negative surface charge at this pH. Overall the increase in the solidwater interfacial tension is rather small. As a result, both the liberation test and contact angle measurement showed a small depressing effect of sodium ion addition on bitumen recession. With increasing pH to 11.2, a more dramatic effect of sodium ion addition on zeta potential of bitumen and fines was observed. The bitumen-water interfacial tension was anticipated to decrease, but only to a smaller extent at pH 11.2. This smaller change in the interfacial tension at pH 11.2 is attributed to its lower original interfacial tension such that increasing sodium ion concentration could only lead to a limited further decrease in bitumen-water interfacial tension. For the solids, on the other hand, the decrease in Debye length with increasing sodium ion concentration



Figure 10. Zeta potential of suspended fines (taken from the froth) and VDFU bitumen emulsions in clear tailings water as a function of NaCl addition at pH 8.5 (a) and pH 11.2 (b).

decreased the magnitude of the zeta potential of solids more significantly (from -43 mV to -34 mV as an average change for the three types of fines) as anticipated. As a result, the solid-water interfacial tension exhibited a large increase, leading to a more pronounced spreading of bitumen on solid surfaces. The results collectively explain why the effect of increasing sodium ion concentration is more pronounced at a higher pH of 11.2 than at a relatively lower pH of 8.5.

With our experimental findings from each individual bitumen extraction sub-process, it is interesting to link these findings with the effectiveness of caustic addition as a remediation strategy. Figure 8 shows that caustic addition to oil sands slurry with high salt content causes a significant reduction in bitumen-water-sand equilibrium contact angle. Lower equilibrium contact angle in turn induces accelerated bitumen displacement from the solid surfaces as shown in Figure 8, leading to a more rapid liberation of bitumen from sand grains as seen in Figures 6 and 7. Furthermore, bitumen and fine solid surfaces become more negatively charged at pH 11 as shown in Figure 10, which reduces the likelihood of slime coating.^[1] Relatively cleaner bitumen surfaces allow much easier attachment to air bubbles (Figure 9).^[1] Overall, these findings would predict a higher bitumen recovery and better froth quality.

The froth quality was indeed higher at pH 11 as anticipated (Figure 5). However, caustic addition did not improve bitumen recovery at high slurry salinity (Figure 4). In fact, at 4000 ppm NaCl, bitumen recovery deteriorated when solution pH increased from 8.5 to 11 (Figure 4). This finding is opposite to the prediction from the results of analysis on each individual sub-processes. Such discrepancy can be explained by potential emulsification of bitumen into smaller droplets at high pH (pH = 11). It is well known that the excessively high pH environment (pH = 11) significantly reduces bitumen-water interfacial tension, leading to severe emulsification of bitumen to form small bitumen droplets. Small bitumen droplets of nearly matching density to the process medium of water are known to have ineffective contact with air bubbles, which leads to a lower bitumen recovery by flotation. The more quantitative link between bitumen recovery rate and bitumen droplet size is another interesting subject for future experimental investigations.

Remediation Strategy: Blending of Different-Grade Ores

Overall, the above results clearly illustrate the inability of adding caustics (increasing pH) to mitigate high-salinity effects on

bitumen recovery from medium- and high-fines ores. Considering a negligible effect of sodium ion concentration on processability of high-grade ore at a typical operating pH (pH = 8.5), we propose ore blending to control the fines content of ores as an alternative to reduce the impact of increasing salinity on processability of highfines oil sands ores. With this in mind, the experiments were carried out using Sun08 (high-grade and low-fines ore) and AE13 (low-grade and high-fines ore) at pH 8.5 with 4000 ppm NaCl (1574 ppm Na⁺) added. As shown in Figure 11, blending of ores at any mass ratio of two ores investigated showed a significant gain, where the calculated recovery is based on the assumption of recovery additive from flotation recovery obtained using individual ores (Sun08 and AE13). Similar advantages of blending oil sands have been reported by Takamura and Wallace^[13] and Schramm et al.^[26] Recently, Zhou et al. proposed "piggyback" as the main mechanism for improving processability by ore blending.^[27] Possibly, the increased bitumen-to-fines ratio helps alleviate the negative effect of sodium ion addition by piggyback mechanism, as sodium ion addition showed a negligible influence on processing high-grade and low-fines ores. There is an urgent need to conduct a detailed study on the mechanism of enhancing



Figure 11. Overall recovery from blends of high-grade Sun08 and low-grade AE13 ores processed at pH 8.5 in the presence of 4000 ppm NaCl (1574 ppm Na⁺).

processability by ore blending to alleviate negative impact of high salinity, as it will maximize utilization of oil sands reserves at minimal environmental impact of fresh water intake and treatment of process-affected water for safe discharge.

CONCLUSIONS

In this study, three different grades of oil sands ores were used to investigate the effect of salinity on processability of oil sands ores. Important findings derived from this study are summarized as follows:

- The effect of salinity on the bitumen recovery and froth quality was shown to be ore-dependent. Sodium chloride addition did not change bitumen recovery from the high-grade ore at different pH values studied. In contrast, increasing sodium ion concentration was shown to reduce bitumen recovery and froth quality for the medium- and high-fines ores, mainly due to less efficient bitumen-air bubble attachment. However, increasing pH to 11.2 cannot alleviate, but enhances the negative effect of sodium ion addition on bitumen recovery and froth quality for the medium- and high-fines ores.
- The results of examining the bitumen liberation and aeration processes support well the flotation data obtained at pH 8.5. A striking contrast of sodium ion effect on bitumen liberation and aeration at higher pH was observed. Compared with the data at pH 8.5, a more severe negative influence of 4000 ppm NaCl (1574 ppm Na⁺) addition on bitumen liberation was observed at pH 11.2 for three types of ores. The influence of sodium ions on aeration at higher pH was also more noticeable, although the induction time was shorter at lower pH than at higher pH. A more distinct effect of sodium ions on bitumen recession on glass microspheres in the simulated process water at higher pH was also confirmed. The zeta potential measurement revealed that sodium ions depressed the electric double layer of bitumen emulsions and fines, making the zeta potentials of bitumen emulsions and fines less negative. At higher pH, the bitumen and fines surfaces were more negatively charged, making sodium ions easier to adsorb and alter their surfaces properties.
- Ore blending seems to be a promising choice of alleviating the effect of sodium ion accumulation in process water.

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