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The Influence of Interfacial Tension in the Hot-Water Process for Recovering Bitumen From the Athabasca Oil Sands

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ABSTRACT

Studies of the processibility of several types of Athabasca oil sands have been carried out to further elucidate the physical action of the natural surfactants in the water-based separation/flotation process. In particular, the interfacial tensions between bitumen and aqueous phases and the electrophoretic mobilities of the dispersed oil and fine mineral phases were all measured at process temperatures (50 and 80°C). By varying the level of alkaline process aid addition, sub-optimal, optimal and overdosed conditions were represented and it was found that the interfacial tension is reduced and passes through a minimum with increasing process aid addition. The condition under which this minimum is achieved is associated with a maximum in interfacial

electric charge, and with optimal primary recovery efficiency of the warm/hot-water flotation process.

INTRODUCTION

Athabasca oil sands are unconsolidated sandstone deposits composed of bitumen, water, quartz sand and clays. Bitumen is chemically similar to conventional crude oil but has a greater density (a lower API gravity) and a much greater viscosity. The quartz sand takes up the bulk of the mixture with either the oil or the water forming the continuous phase depending on the grade (oil content). In either case, a water film separates the bitumen from the sand and clay surfaces¹. The presence of a water film separating the bitumen from the solids forms the basis of the water-based conditioning and

flotation process. This process is currently being used on a commercial scale, in Canada, to recover bitumen from the Athabasca oil sands at production levels of over 300,000 Bbl/d.

In the classical water-based process, mined oil sand is slurried with water and a base (normally sodium hydroxide, NaOH) at about 80°C in a horizontal rotating drum into which steam is injected (in some newer operations lower temperatures, near 50°C, are being used and the conditioning is accomplished during pipeline hydrotransport instead). Here heat and shear are employed to overcome the forces holding oil sand lumps together. In this ablation process, successive layers of each lump are warmed and sheared off until everything is fairly well dispersed. Disengagement of bitumen from solids will be favoured if their respective surfaces can be made more hydrophilic since a lowering of surface free energy will accompany the separation. The phase separation is enhanced by the effects of mechanical shear and disjoining pressure. Air is not directly sparged in, but becomes worked in to aerate the bitumen by inclusion of about 30% v/v gas². The sodium hydroxide is added to raise the solution pH. An appreciable time is required to achieve a good distribution of the bitumen, minerals and reagents and to allow chemical and surface reactions to occur. Within 5 minutes or so a quasi-steady state is reached, although probably not full thermodynamic equilibrium. After conditioning the slurry is screened, diluted with additional water and transported to a flotation vessel. In this vessel aerated bitumen droplets float to form a primary froth which is subsequently collected. The greater part of the recoverable bitumen is obtained in this primary process step although a secondary froth and other streams from this vessel are further treated. Additional details can be found elsewhere^{2,3,4,5,6,7,8,9,10,11,12,13,14}.

From a chemical point of view, many aspects of the process are now understood. It is recognized that the role of sodium hydroxide in the process is not to adjust the slurry pH, but mainly to produce natural surfactants from precursors occurring in bitumen^{7,12}. Early work by Bowman and others^{21,15,16} established that the surfactants produced in the process are primarily carboxylic salts of naphthenic acids with the possibility of sulfonic salts as well. Schramm, Smith and Axelson¹⁷ isolated and characterised the natural surfactants from the process and found them to predominantly consist of aliphatic carboxylates having hydrocarbon chains of at least 5

carbons (typically C₁₅ to C₁₇) and aliphatic sulfonates having hydrocarbon chains of at least 5 carbons (reviewed elsewhere⁸). Misra, Aguilar and Miller⁹ have made a similar identification of paraffinic carboxylate surfactants as the principal surfactant type released in the processing of Utah tar sands.

The natural surfactants are now understood to be the active agents in the process. For rich grade oil sands, the addition of a base such as NaOH is usually not necessary and simply slurrying with hot water is all that is needed to release sufficient quantities of natural surfactants into the aqueous phase. For lower grades of oil sand, NaOH process aid addition is needed to optimise bitumen recovery. In this case, only a small fraction of the NaOH added in processing reacts to produce the natural surfactants; while the major portion (ca. 90%) reacts with minerals to produce mostly bicarbonate^{23,24,27,20}. Appropriate surfactants may even be added directly into the process instead of adding sodium hydroxide^{21,22,23}. Whether the surfactants employed are natural or synthetic, it has been shown^{23,24} that there exists a critical solution concentration of the surfactant which corresponds to optimum oil recovery. The mechanism(s) of the surfactant action have been studied in some detail^{25,26,23,24,27}. In essence, their impact arises due to their adsorption at surfaces and interfaces, by which they alter surface electric charges and interfacial tensions.

A spontaneous change in state will take place if there is a corresponding decrease in the free energy of a system. In terms of the Helmholtz free energy, for constant temperature and volume, we have,

$$dF = \sum \mu dn + \sum \phi dq + \sum \gamma dA \quad (1)$$

where F is the Helmholtz free energy and the three terms refer to the chemical, electrical and surface work, respectively, which may be involved. We need to consider conditions under which,

$$dF < 0 \quad (2)$$

Leja and Bowman¹⁶ have discussed the common practice of neglecting most of the terms in Eqn (1) and considering only changes in the interfacial tensions involved. One contribution made by these authors was to show how in fact large changes

in the interfacial areas will take place during the bitumen displacement process. They concluded that the large changes in the interfacial areas should drive the displacement and air-bitumen attachment processes. Schramm and Smith²⁵ showed that significant changes in the interfacial charges also take place during the process and concluded that the large changes in the interfacial charges should drive the displacement process. That chemical changes occurring in the process are also important has been demonstrated by the work of Schramm *et al.*^{18, 23,24,25, 26,27} and Miller *et al.*^{19,42,43} on the importance of the natural surfactants. Therefore, all of the terms in Eqn (1) are likely to be significant and closely interrelated. We will briefly discuss the phenomena underlying the electrical and surface work terms.

Electrical ($\Sigma \phi dq$) Work. Several research groups^{28,16,29,30} have either measured or shown that all of the major interfaces involved (solid/solution, bitumen/solution and air-gas/solution) can be negatively charged. Further, the charging can easily be sufficient to make the thermodynamic electrical-work term of similar magnitude as the surface-work term. This shows the need to consider the electrical nature of the interfaces.

In the conditioning process, under suitably alkaline conditions, both ionisation of functional groups at the bitumen surface^{1,31} and adsorption of the natural anionic surfactant molecules at the bitumen/aqueous interface^{25,26,27} occur. The adsorption of anionic surfactant molecules directly affects the surface electric potentials of dispersed bitumen droplets, gas bubbles and fine solid particles (usually represented through electrophoretic mobilities or zeta potentials)^{23,27,32,25}. Although the shapes of oil sand processibility curves can vary considerably, the various surface charges are always quite negative under realistic processing conditions. Whereas the surface charge on the solid particles reaches a plateau with increasing surfactant concentration, the surface charges on bitumen drops and gas bubbles reaches a maximum and thereafter decrease^{25,26,27}. Essentially the same trends have been independently confirmed by Hupka and Miller³³ and Drelich *et al.*³⁴. The correlation between maximum negative surface charge on bitumen droplets and optimum processing conditions for maximising primary bitumen recovery²⁵ has been shown to scale-up^{35,18}. The optimum emulsified bitumen zeta potentials achieved (about -35 mV) is consistent with "good stability" from the perspective of DLVO theory^{36,13}.

Under optimised conditions natural surfactants are thought to have adsorbed just enough on the bitumen and solids to impart a maximum charge. Since initially the bitumen and solids are barely separated (*ca.* 10 nm), this charging causes a large disjoining pressure which in turn, together with the applied mechanical and thermal energy, causes the separation of bitumen from solids.

Surface ($\Sigma \gamma dA$) Work. After bitumen-solid separation, bitumen-air attachment is desired. The process conditions that most favour bitumen-solids separation, that is a high degree of electrostatic repulsion due to charged surfactant molecules at the interfaces, also tend to oppose gas-bitumen attachment since the gas bubbles also acquire a surface charge of the same sign^{37,18}. In comparison, mineral flotation involves gas-solid attachment without filming and such electrostatic repulsion is not as important a factor as are inertia effects when the particles and bubbles are larger than, say, 10 to 40 μm diameter. It is in fact possible for bitumen droplets to attach to gas bubbles and form bubble droplet pairs or aggregates, as in mineral flotation. Houlihan³⁸ found that for low alkali addition levels or reduced temperature conditions bitumen droplets will attach to air bubbles as discrete particles. Under optimum process conditions however, something even better happens. If the interfacial tension between bitumen and the aqueous phase is low enough, then the balance of interfacial tensions in the system will favour filming of the bitumen around the gas bubbles¹⁸.

If a bitumen droplet and a gas bubble collide their mutual attachment is thermodynamically favourable if the attachment coefficient, A ,¹⁸ is positive (also termed entering coefficient; originally defined by Robinson and Woods³⁹ for defoamers).

$$A = \gamma_{\text{Aq}}^{\circ} + \gamma_{\text{Bit/Aq}} - \gamma_{\text{Bit}}^{\circ} \quad (3)$$

When bitumen attaches to a gas bubble a certain amount of gas/bitumen interface is created while some gas/aqueous and aqueous/bitumen interfacial areas are eliminated. The attachment is predicted to be favoured and spontaneous when $A > 0$. If $A < 0$, the bitumen should not attach.

If bitumen attaches to a gas bubble then bitumen would be predicted to spread spontaneously over a gas bubble if its spreading coefficient, S , is positive (Harkins⁴⁰):

$$S = \gamma_{\text{Aq}}^{\circ} - \gamma_{\text{Bit/Aq}} - \gamma_{\text{Bit}}^{\circ} \quad (4)$$

If bitumen spreads out over the gas/aqueous interface a certain amount of both gas/bitumen and aqueous/bitumen interface is created while some gas/aqueous interface is eliminated. The spreading is predicted to be favoured, and spontaneous, when $S > 0$. S and A are interrelated as shown below:

$$A = S + 2\gamma_{\text{Bit/Aq}} \quad (5)$$

If A is negative then S must be negative, in which case bitumen would neither attach nor spread at the aqueous solution-gas interface. Flotation is not expected in this case. If A is positive but S is negative then bitumen would attach but would not be expected to spread at the interfaces. This condition could cause flotation of the bitumen, depending on whether the flotation medium is sufficiently quiescent that the bitumen is not sheared away from the bubble. Finally, if both A and S are positive then bitumen would attach and then spread over the gas bubble. Once the bitumen encapsulates a gas bubble only very high mechanical shear would cause it to be stripped away. This is the best configuration for bitumen flotation in a primary separation (flotation) vessel. Table 1 shows some ranges of values that have been measured for samples from the process, at 80°C. It is clear that, under reasonable processing conditions, bitumen can spontaneously attach to and then spread over the gas bubbles, encapsulating them. The surfactant properties that most promote this behaviour are a major lowering of bitumen/aqueous interfacial tension with minor lowering of the aqueous phase surface tension. This behaviour is consistent with the structures attributed above to the natural surfactants.

Both laboratory studies¹⁸ and pilot plant studies³⁸ indicate that under normal (good) processing conditions the bitumen does indeed preferentially encapsulate air bubbles. Similar observations have been made independently by Miller *et al.*^{41,34,19,42,43,44} who also concluded that polar fatty-acid salts (carboxylate surfactants) stabilise a dispersion of air bubbles in bitumen during the hot-water processing of Asphalt Ridge bitumen. These aerated bitumen globules are the species that float upwards in the flotation vessels to form froth.

Given the importance of reducing interfacial tensions in the process, it is of interest to discover whether there may be some correlation between optimal recovery conditions and minimum interfacial bitumen/aqueous interfacial tension, in which case the latter would also correlate with maximum interfacial

electric charge at the same interface. We present here the results of an experimental investigation into the interrelationship between interfacial tension, interfacial charge and bitumen recovery in the water-based process for Athabasca oil sands.

EXPERIMENTAL

Three oil sand samples were used in this work. All were obtained from the Syncrude Mildred Lake oil sands operation. The compositions of these oil sands are given in Table 2. In all cases the oil sand samples were stored in the dark, in a freezer, to minimise ageing effects, as recommended by Schramm and Smith^{45,46}.

A laboratory-scale batch extraction unit (BEU) and operating procedure developed by Sanford and Seyer⁴⁷ for studying the oil sands hot-water process was used. This test simulates the conditioning (tumbler) step and the primary and secondary recovery steps of the continuous commercial process. The process was operated at either 80 or 50°C. A detailed description is given elsewhere^{1,26,27}. This test is reproducible and sensitive enough to be useful for evaluating process variables and the processibility of different oil sand samples^{1,26,27}.

Sub-samples of the primary and secondary froths from the batch extractions were collected and assayed using the "Syncrude method," reported elsewhere⁴⁸. From the assays primary and secondary recoveries and mass balances were obtained. Replicate samples were isolated for interfacial tension and electrophoretic-mobility determinations, stored in glass bottles and refrigerated whenever necessary; they were studied at the equilibrium pH values reached during the batch extractions. Secondary tailings were clarified by centrifugation at 10,000 rpm for two hours then by serial filtration with a final filter pore size of 0.10 µm. Bitumen froth was deaerated and solids settled by centrifuging samples for two hours at 10,000 rpm at 40°C.

Interfacial tensions at process temperature were determined by one of two methods. A high temperature capillary displacement differential maximum droplet pressure method (MDPM) for liquid/liquid interfaces was used as described in more detail in reference⁴⁹ (see also Figure 1). This absolute interfacial tension method is a modification of the capillary displacement differential maximum bubble pressure method (MBPM) instrument developed by Schramm and Green for

gas/liquid interfaces⁵⁰. Additional operating details are described in reference⁴⁹. Calibration was performed using ethyl acetate, methylisobutyl ketone, toluene and *n*-decane, verifying precision and accuracy of at least 0.6 mN/m. The high temperature drop volume method used was an adaptation of the classical drop weight method proscribed by Padday⁵¹. A positive displacement microsyringe was used to very slowly create oleic phase drops and measure their volumes delivered through a stainless steel needle, having a squared-off end, submerged into the aqueous phase. The needle tip was placed in a thermostated beaker so as to avoid any wall or surface effects. For this method, we reduced the impact of density measurement errors by a 30% *n*-decane in bitumen dilution⁴⁹. Separate work has shown that this level of added *n*-decane does not significantly alter bitumen/water interfacial tension⁴⁹.

Electrokinetic determinations were performed by microelectrophoresis, according to the procedure given in reference²⁵. Suspensions of fine solids for microelectrophoresis measurements were prepared by diluting a small portion of original secondary tailings with supernatant solution from a previously centrifuged aliquot and filtered aliquot. In this manner, dispersions of about 0.1% or less solids were obtained in the original equilibrium solution, and the original ionic strength and electrolyte composition were preserved²⁵. Emulsions of bitumen in the corresponding solids-free secondary tailings were also prepared. A small amount of primary bitumen froth was dispersed in clarified secondary-tailings solution by shearing in a Waring blender for six minutes to produce bitumen droplet radii of approximately 5 to 10 μm . The droplet and particle mobilities had a reproducibility of $\pm 2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$.

RESULTS

Processibility is the response in primary bitumen recovery to sodium hydroxide addition in the process. The processibility results, in terms of primary froth oil recoveries for the rich, average, and lean oil sands are given in Figure 2. In general, as the bitumen content of an oil sand decreases, the NaOH addition required to reach maximum primary oil recovery increases^{23,27,26}. For the rich oil sand the best NaOH addition level was zero (Figure 1), as is typically the case for such a high grade ore. The optimal sodium hydroxide addition levels for maximizing primary oil recovery for the average oil

sand was found to be 0.03% (mass %, oil sand basis), while for the lean oil sand it was found to be 0.08%.

The interfacial tension between the bitumen froth and the corresponding clarified secondary tailings solution were determined at 80°C by the maximum droplet pressure method for samples from the rich and lean oil sand studies, to match the processing conditions. The drop volume method was used, at 50°C, for samples from the average grade oil sand studies, again to match the processing conditions. The results are shown in Figure 3, as functions of sodium hydroxide added. By comparing Figures 2 and 3, it can be seen that the maxima in primary oil recovery correlates with the minima in interfacial tension. For the rich oil sand the interfacial tension is lowest for a zero NaOH addition level, where primary recovery is at a maximum. For the average grade oil sand the minimum in interfacial tension and maximum in primary recovery also match exactly. For the lean oil sand both the processibility curve and the interfacial tension behaviour with NaOH addition level are fairly broad curves. In this case primary recovery reaches a maximum and plateaus at approximately the same NaOH addition level as the interfacial tension reaches its broad minimum. Overall the correlation is quite good.

The electrophoretic mobilities of dispersed fine solid particles and bitumen droplets in clarified secondary tailings solution (mobilities measured at 25°C) are shown in Figures 4 and 5. In the range of process conditions investigated in the present work, the electrokinetic charge is expected to reflect sufficiently the true surface charge for the interpretations which will be offered in this paper. Taking an average bitumen-droplet radius to be 5 μm and an average clay-particle radius to be 1 μm , we obtain the following values for κa , the electric double layer thickness, for solution ionic strengths of 1 to 5 $\times 10^{-3} \text{ M}$,

$$\kappa a (\text{bitumen}) = 500 - 1100$$

$$\kappa a (\text{clay}) = 100 - 230$$

Both the fine solid particles and the bitumen droplets can then be considered to be large, with thin double layers, and their zeta potentials, ζ , can be calculated from electrophoretic mobilities, μ_E , to within ten percent using the Helmholtz-Smoluchowski formula,

$$\mu_E = \varepsilon \zeta / \eta \quad (6)$$

where ϵ and η are the dielectric constant and viscosity of the dispersing medium. We will refer to electrophoretic mobilities.

It can be seen that the electrophoretic mobilities of the dispersed fine (clay) solids and bitumen drops are always negative in the process conditions investigated. In the case of the solids, the negative electrophoretic mobility becomes more negative with increasing additions of sodium hydroxide to the process. The electrophoretic mobility of bitumen droplets pass through a maximum as a function of sodium hydroxide addition to the process. The maximum occurs at different sodium hydroxide additions depending upon the oil sand type.

By comparing Figure 2 with Figures 4 and 5, it can be seen that the maxima in primary oil recovery correspond to significantly negative electrophoretic mobilities on the part of the fine solids, and to maximum negative mobilities on the part of the bitumen droplets. For the rich oil sand the bitumen droplet electrophoretic mobility is greatest for very nearly the same (zero) NaOH addition level, where primary recovery is at a maximum. For the average grade oil sand the maximum in bitumen droplet mobility and maximum in primary recovery match almost exactly. For the lean oil sand both the processibility curve and the bitumen electrophoretic mobility behaviour with NaOH addition level are fairly broad curves. Here again primary recovery reaches a maximum and plateaus at almost exactly the same NaOH addition level as the bitumen mobility reaches its maximum. Overall the correlation is quite good.

DISCUSSION AND CONCLUSIONS

The warm/hot water flotation process normally relies on the adsorption and association behaviour of natural surfactants which, as a class, form one of several products of reaction of oil sand with sodium hydroxide^{47,44}. Earlier work has shown that at the critical free surfactant concentration, there is an optimum concentration of surfactant that, when present in the aqueous process equilibrium solution in the flotation cell, is associated with maximum oil recovery^{23,24,25,27,26,18}. Attaining this condition has long been thought to produce favourable interfacial conditions for bitumen separation and also for bitumen flotation.

For the grades of oil sand tested, the present processibility and electrophoretic mobility results are very consistent with

earlier work^{18,25,26} and demonstrate once again that maximum primary bitumen recovery is associated with maximizing the interfacial electric charge on the bitumen droplets (see also reference³⁵). Although the maxima occur at different sodium hydroxide levels for each oil sand type, previous work has shown^{23,24,18,25,26} that they all occur at the same, critical, free natural surfactant concentration.

The implication is that the natural carboxylate surfactants control the bitumen/solution interfacial charge by ionization and adsorption at the interface, and that the maximum in surface electrokinetic charge maximizes the disjoining pressure that pushes the bitumen away from the solids.

That there is also a correlation between the maximum in primary oil recovery and a minimum in the interfacial tension had been previously speculated by Schramm and Smith⁵² and by Schramm *et al.*¹⁸ who estimated that the optimum interfacial tensions probably lie in the range between about 2 and 14 mN/m. In the optimized systems here, the observed minimum interfacial tensions, between bituminous froth and clarified aqueous secondary tailings systems, were 9 mN/m for the rich oil sand, 14 mN/m for the average oil sand, and 6 mN/m for the lean oil sand. These values agree quite well with the previous process values summarized in Table 1, although the latter may not all represent optimized processing conditions. It may be that each oil sand sample will have maximum primary recovery associated with a minimum achievable interfacial tension rather than with a unique, independent value of interfacial tension.

It is concluded that maximum primary recovery in the process is associated not only with maximizing the bitumen/aqueous interfacial electric charge (mostly driving bitumen-solids separation), but also with minimizing the bitumen/aqueous interfacial tension (mostly driving bitumen attachment and spreading over gas bubbles, leading to flotation and recovery), in both cases via adsorption of natural surfactants at the bitumen/aqueous interface. Our present and prior^{18,53} work suggests that this applies to the warm and hot water-based processing of Athabasca bitumen, employing temperatures in the range 50 to 80 °C .

We are currently working to see to what extent the correlations and/or trends discussed above may apply to cold (25 °C) water processing of Athabasca oil sands, a direction that is currently of great interest to the oil sands industry.

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TABLE 1. Approximate thermodynamic properties for froth bitumens and clarified aqueous secondary tailings, for 80°C, all units in mN/m; from Schramm¹⁸.

Aqueous Surface Tension	Bitumen/Aqueous Interfacial Tension	Bitumen Surface Tension	A	S
50 to 60	2 to 12	22 to 28	24 to 50	10 to 36

TABLE 2. Compositions of oil sands studied ^a

Oil Sand	Bitumen (%mass)	Water (%mass)	Solids (%mass)	Fines ^b (%mass)
Rich	14	1	85	8
Average	10	6	84	35
Lean	9.3	4	87	25

^a All assay results are the mean of at least two replicate assays.

^b The fines level is defined as the mass fraction of solids smaller than 44 µm and is expressed as a percentage of total solids.

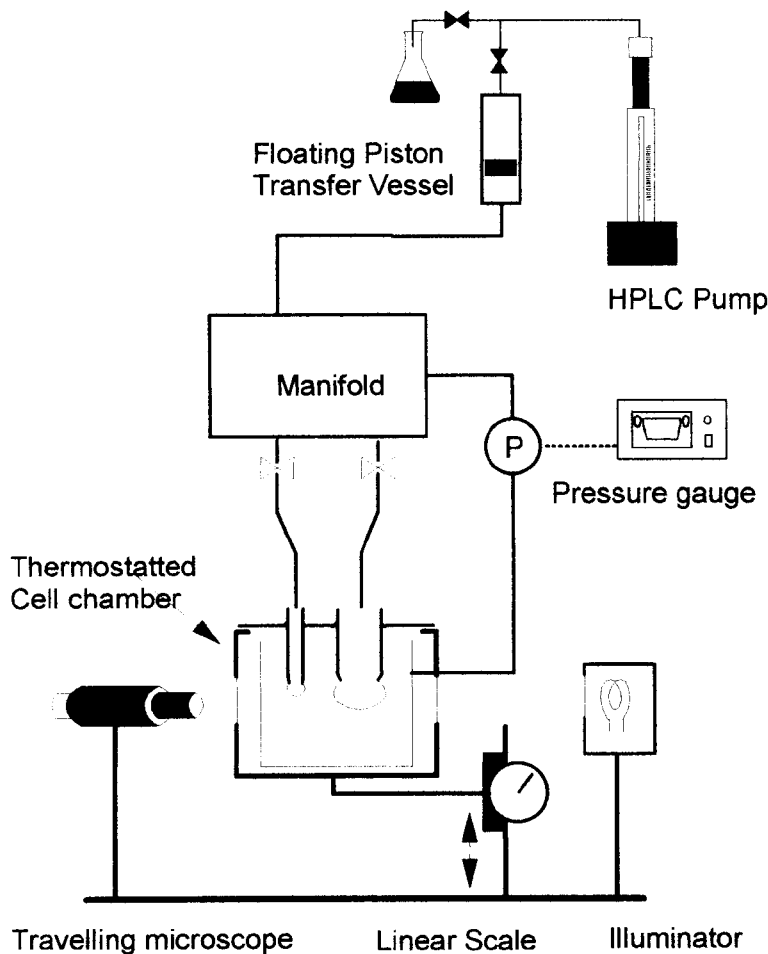


Fig. 1. Schematic of the capillary displacement maximum droplet pressure method (MDPM); adapted from Stasiuk and Schramm⁴⁹.

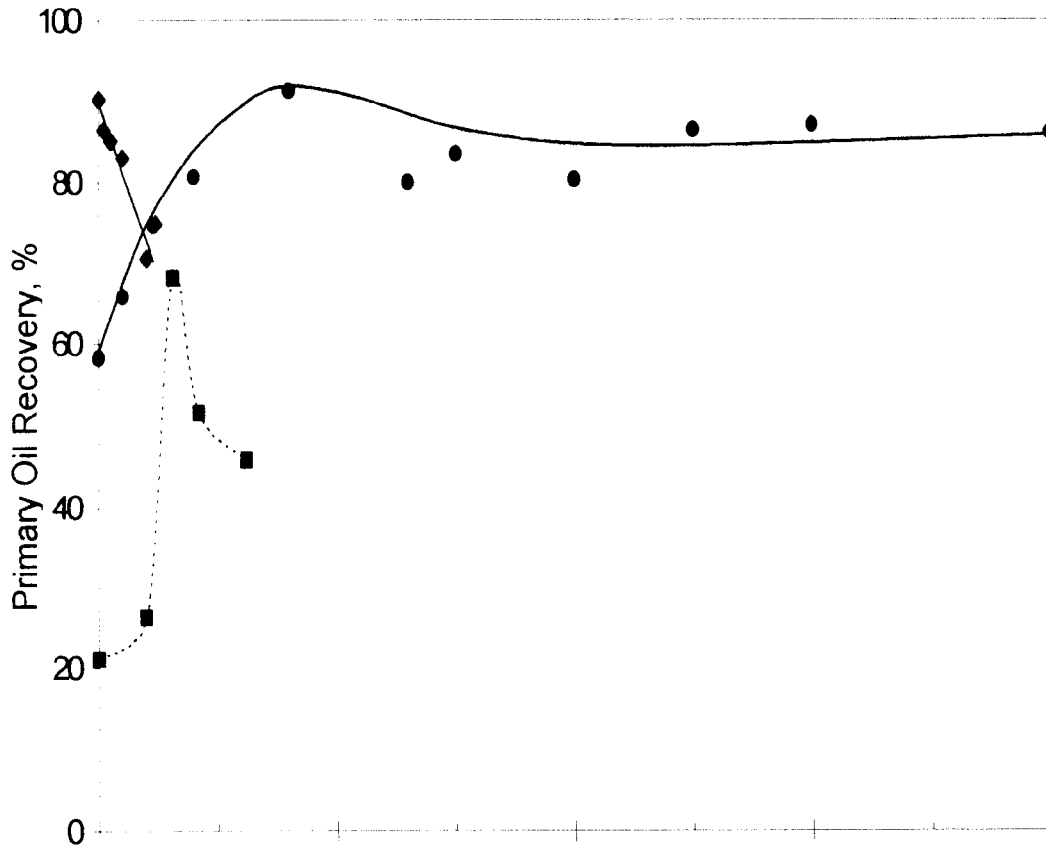


Fig. 2. Processibility curves of primary oil recovery versus NaOH added during the processing of three oil sands. The curves represent the processing of the rich (◆), average (■), and lean (●) oil sands.

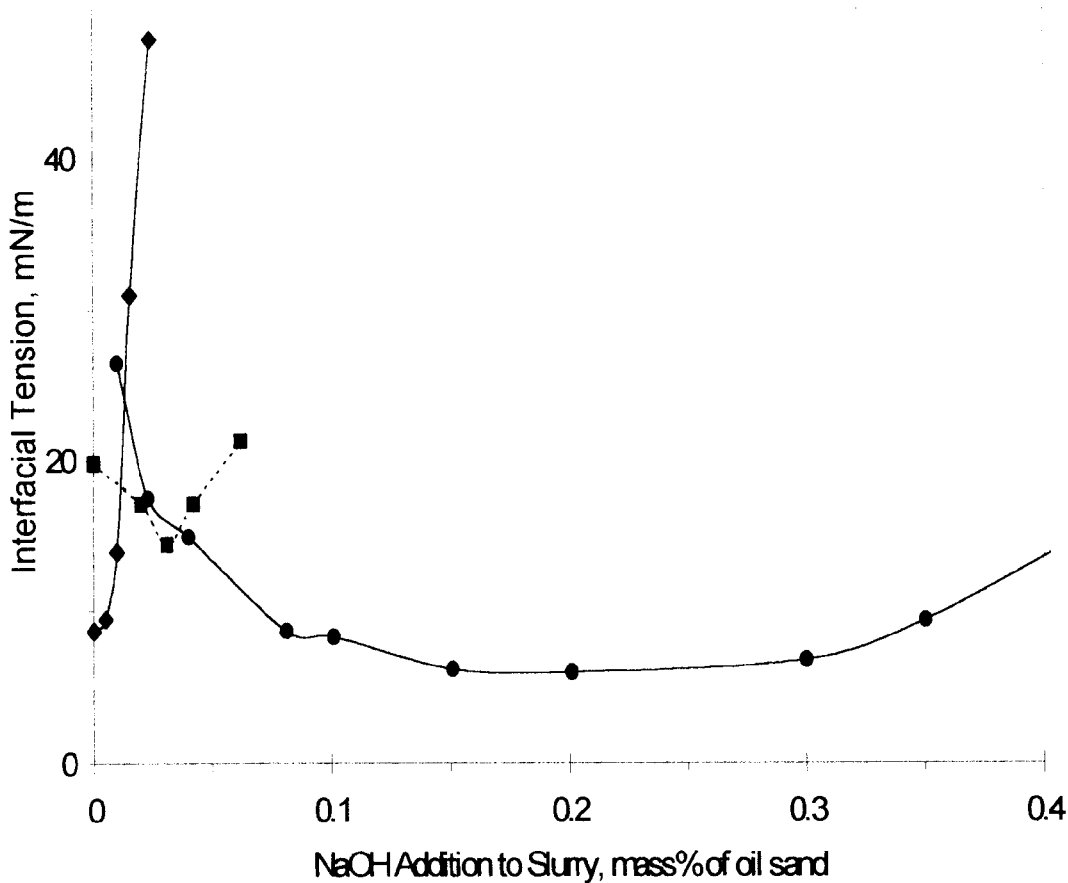


Fig. 3. Interfacial tensions of primary froths versus clarified secondary tailings solutions, as a function of NaOH added during processing. The curves represent the processing of the rich (◆), average (■), and lean (●) oil sands.

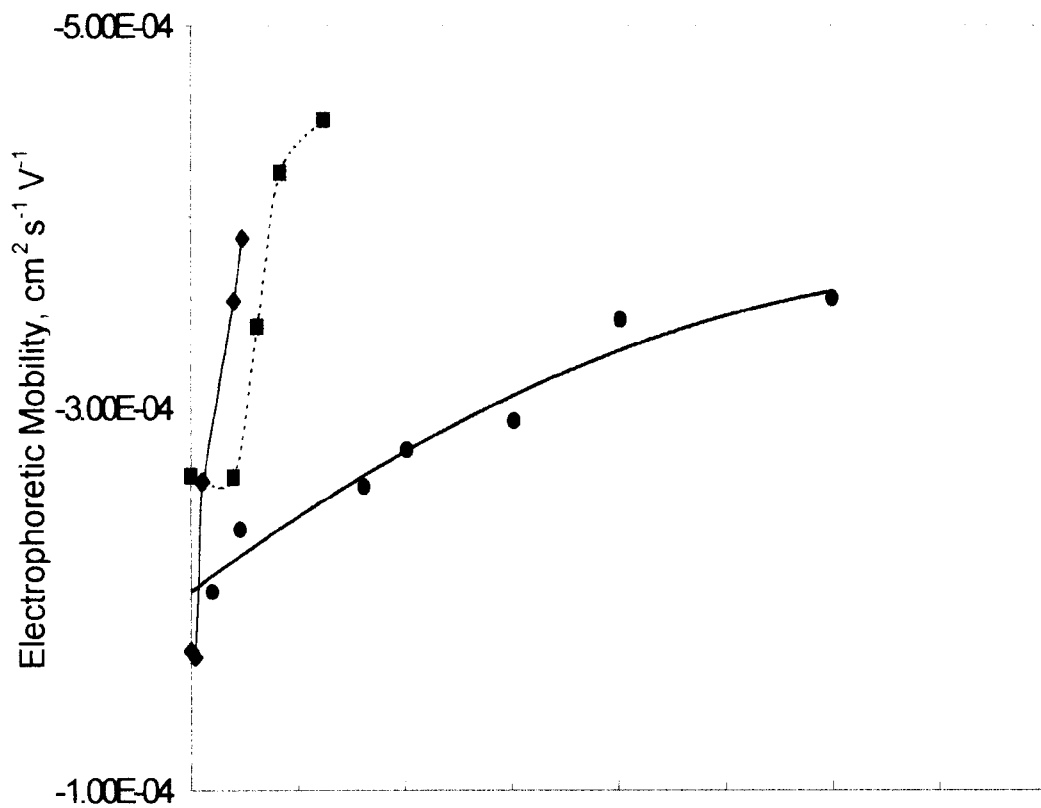


Fig. 4. Electrophoretic mobilities of fine solids, measured in clarified secondary tailings solutions, as a function of NaOH added during processing. The data represent the processing of the rich (◆), average (■) and lean (●) oil sands.

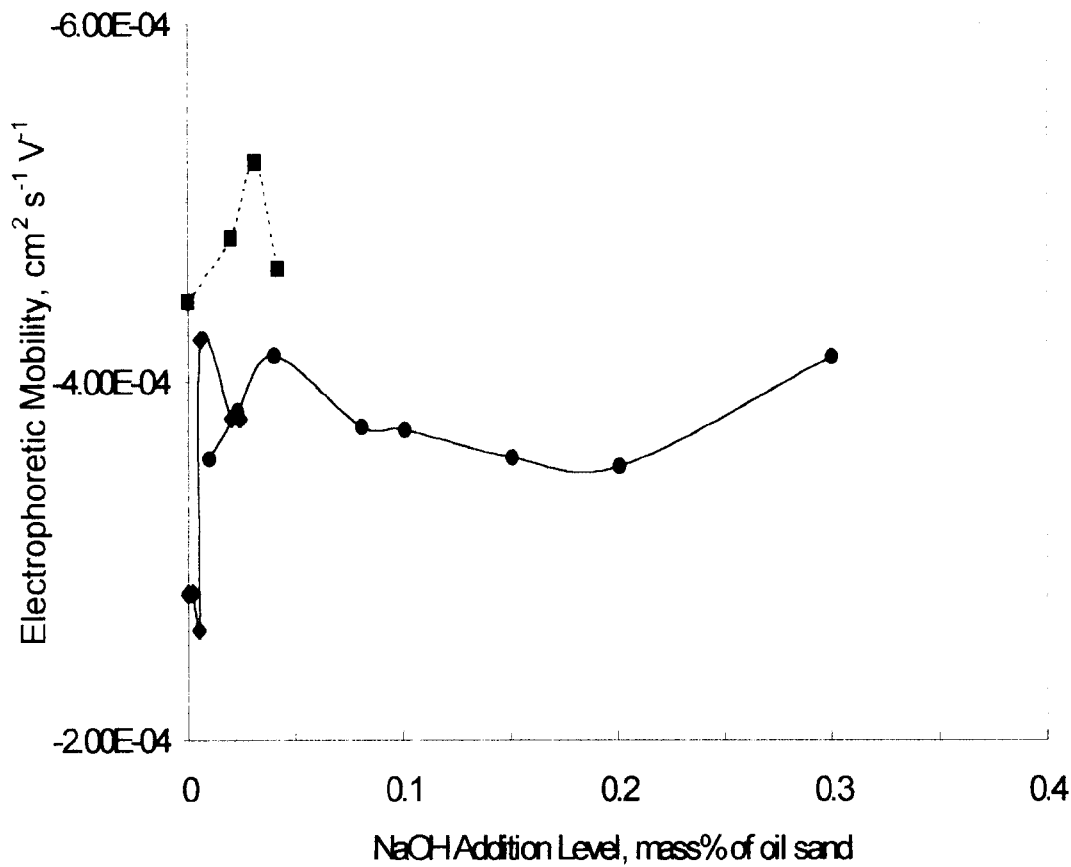


Fig. 5. Electrophoretic mobilities of bitumen drops, measured in clarified secondary tailings, as a function of NaOH added during processing. The data represent the processing of the rich (◆), average (■) and lean (●) oil sands.