The Effect of Oil Sands Bitumen Extraction Conditions on Froth Treatment Performance

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Abstract

Further development of oil sand deposits requires processing poorer quality oil sands while maximizing bitumen recovery, minimizing the water and solids content of the product bitumen, and minimizing overall energy consumption. Bitumen recovery requires two stages: extraction and froth treatment. This work focuses on the effect of process conditions in the Clark Hot Water Bitumen Extraction Process on froth treatment effectiveness. Laboratory approximations are used to represent the two commercialized froth treatment processes in Alberta: 1) the "Syncrude Process," which is dilution with an aromatic solvent followed by centrifugation; and, 2) the "Albian Process," which is dilution with a paraffinic solvent followed by gravity settling. Parameters considered are oil sand quality, extraction shear, extraction temperature, NaOH addition during extraction, froth treatment temperature, and froth treatment residence time. It was found that reduced extraction temperature results in lower bitumen recovery at least for low quality oil sands. Higher shear extraction may improve bitumen recovery, but decreases froth treatment effectiveness. For paraffinic solvent-based froth treatments, the addition of NaOH during extraction may be required to obtain optimum froth treatment of low quality oil sands.

Introduction

The Canadian oil industry is producing about 1 million barrels of bitumen and synthetic crude oil per day from oil sands and the production is expected to rise to 2 million barrels per day by 2012[1]. Currently, both in situ and surface mining operations contribute almost equally to the total production. However, the production of synthetic crude from surface-mined oil sands is expected to take the lead in the next decade[2]. Expansions of existing oil sand facilities are already underway and the addition of new facilities are planned within the next decade.

There are two main stages to oil sand processing: extraction and froth treatment. The most common extraction process is hot water bitumen extraction. The oil sand is conditioned with hot water, either in a process vessel (conditioning drum) usually with NaOH added, or more recently in a pipeline (hydrotransport) usually with a smaller amount of NaOH added. During conditioning, the slurry is aerated and, ideally, the bitumen separates from the sand, and attaches to and spreads on the air bubbles. Water is added to the slurry, which is subsequently sent to a separation vessel. The bitumen-coated air bubbles are carried upwards to form a froth that is rich in bitumen. The froth also contains free water, emulsified water, and suspended solids[3, 4]. The froth is collected in two stages yielding a primary and a secondary froth. For high-quality oil sands, a typical primary froth composition is approximately 66 wt% oil, 25 wt% water, and 9 wt% solids. A typical secondary froth has lower oil content (approximately 24 wt%) and higher water and solids contents (59 wt% and 17 wt%, respectively). Poorer quality oil sand froths have lower oil content and higher water and solids contents[5].

Free water and coarse solids are relatively easily separated from the froth. However, the froth also contains fine solids and emulsified water droplets which are covered with surfactants (including asphaltenes) and non-surfactants [including ultra-fines (< 200 nm)][4, 6, 7]. The coated water droplets are of similar density to the bitumen under typical froth treatment conditions. The fine solids and emulsified water require further treatment to separate. There are currently two commercialized froth treatment processes in Alberta, termed the "Syncrude Process" and the "Albian Process."

In the Syncrude Process, the froth is diluted with naphtha to create a density difference between the bitumen and water and to reduce the viscosity of the bitumen. Surfactants are added to promote the flocculation and settling of the emulsified water. The dilute froth is centrifuged and the supernatant is distilled to recover the naphtha. Prior to distillation, the diluted bitumen product typically contains approximately 2% water and 0.5% fine solids. The "coker feed" bitumen product obtained after distillation typically contains approximately 1% fine solids.

In the Albian Process, a paraffinic solvent is added to the froth to reduce the bitumen density, decrease viscosity, and promote flocculation of the emulsified water and suspended solids. Some asphaltenes are also precipitated to achieve a product suitable to feed Shell's new Scotford Bitumen Upgrader. The water and solids are separated from the solution in a three-stage gravity settling process. A diluted bitumen product is obtained that, on the pilot scale, was free of water and solids. Some of the solvent is distilled off and a less dilute bitumen is transported to the refinery.

The main process objectives in oil sands design and operations are to maximize bitumen recovery (less asphaltene rejection for the Albian Process), minimize the water and solids content in the bitumen product, and minimize energy requirements. Some of the relevant factors are: mixing conditions for the conditioning step, process temperatures, the amount of additives such as NaOH, froth treatment solvent type, and the froth dilution ratio. Many of these factors depend on the quality of the oil sand being processed.

Most research has focused on bitumen recovery in the extraction process[8-11], since it contributes more to the overall bitumen loss. The effects of solvent type, dilution ratio, and temperature on froth treatment have also been evaluated[12]. However, extraction and froth treatment have not been considered together. The purpose of this work is to assess the effect of extraction conditions, including temperature, shear rate, and the addition of NaOH, on froth treatment and overall process performance.

TABLE 1: Oil sand composition.

Oil Sand	Quality	Bitumen (wt%)	Water (wt%)	Solids (wt%)	Fines (< 44 μm)* (wt%)
High	HQOS	14.3	1.2	84.4	4.1
	HQOS1	13.1	0.8	86.2	10.9
Average	AQOS	11.8	1.3	86.6	5.2
	AQOS1	9.5	1.9	88.6	29.5
	AQOS2	9.9	2.1	88.0	35.0
Low	LQOS	8.6	5.3	86.1	35.4
	LQOS1	6.6	7.3	86.1	33.7

*Fraction of fines in solids.

Experimental

Materials

Oil sand samples of different qualities were obtained from Syncrude Canada Ltd. Upon arrival, the oil sand was chopped, homogenized, and stored in the dark in a freezer to minimize aging effects, as recommended by Schramm and Smith[13]. The oil, water, and solids contents were determined by Dean-Stark extraction and the fines (< 44 μm) content was determined by laser light-scattering analysis at the Syncrude Research Centre using Syncrude's standard analytical methods[14]. The composition of the samples are given in Table 1.

Oil sands quality has historically been defined in terms of both the bitumen and the fines content. Ores with high bitumen and low fines content are more easily processed and usually yield a higher bitumen recovery. Low fines content often, but not always, correlates to high bitumen content[15]. Hence, the simplest criteria for oil sands quality is in terms of the bitumen content. Pow et al.[16] recommended the following definition of oil sand grades: 1) rich (12 – 14 wt% bitumen); 2) average (10 – 11 wt% bitumen); and, 3) lean (6 – 9 wt% bitumen). Following these criteria, the oil sands used in the study are deemed high, average, and low quality ores.

The sodium hydroxide (Fischer Scientific) used in the experiment was ACS reagent grade. The 2-propanol (EM Science), toluene (Univar), and n-heptane (Phillips 66 Co.) were of technical grade. The reagent for Karl Fischer titration was a pyridine-free reagent containing iodine, sulphur, imidazole, and 2-methoxyethanol (EM Science).

Extraction

Bitumen froth was extracted from the oil sand using a Batch Extraction Unit (BEU) or a Denver Cell following the Syncrude standard extraction procedure. The BEU is a low-shear laboratory approximation of the Clark Hot Water Extraction Process. It typically produces a froth similar to that obtained from the traditional commercial process (in the range of 50 to 80° C) with conditioning and separation stages. Froth was produced in two stages with the BEU: a "primary froth" and a "secondary froth." Typically, the primary froth bitumen recovery trends are used to scale up to plant operation. The Denver Cell is a higher shear flotation apparatus and produces a froth that is more similar to that obtained from a commercial process using hydrotransport conditioning (and particularly when the process temperature is below 50° C). The Denver Cell produces froth in a single stage and it is the trends in total flotation recovery that are used to scale-up to plant operation. A detailed description of the steps and variables involved in the BEU extraction is given elsewhere[12, 14, 17]. With the Denver Cell, froth was produced in one stage. The extractions were performed with both BEU and Denver Cell at both 80 and 50° C in order to compare methods. No additive was used in any of the extractions except sodium hydroxide which was added to maximize bitumen recovery for lower quality oil sands.

Subsamples of the primary and secondary froth from the batch extractions were collected and assayed for oil, water, and solids content as described elsewhere[12]. A Karl Fischer Titrator (Metrohm 658 KF Processor and 655 Dosimat, and later a 787 KF Titrino) were used to determine water content in samples. Only primary froth was used for froth treatment experiments because of the low amount of secondary froth produced. For high grade ores, this introduces very little bias. However, for average and low grade ores, where secondary froth may contribute significantly to the total froth yield, there may be some variance with commercial operations.

Froth Treatment

Two froth treatments were considered: 1) Aromatic Solvent (AS) Method—dilution with toluene followed by centrifuging; and, 2) Paraffinic Solvent (PS) Method—dilution with n-heptane followed by gravity settling. The AS Method approximates the Syncrude Process in the sense that all of the components are soluble in the solvent and separation is achieved through centrifugation. Toluene has slightly higher density, slightly lower viscosity, and is a better solvent for asphaltenes than the process naphtha. The PS Method approximates the Albian Process except that only a single stage separation is considered while the commercial process has three stages. Process temperatures of 23 and 60° C were evaluated for both methods. Residence times of 5 min and 8 hrs were considered for the AS Method, and 40 min and 8 hrs for the PS Method. The temperatures and residence times do not exactly correspond to commercial operating conditions, but were chosen to examine trends within a range of potential operating temperatures within the constraints of the experimental apparatus.

Preparation of the samples and froth treatment experiments were described in detail previously[12]. Briefly, a known mass of froth was combined and diluted with a known mass of given diluent and held at temperature for the specified residence time. For the AS Method, the sample was then centrifuged for 5 min at 4,000 rpm. The diluted froth separated into three layers: continuous oil phase, free water, and solids. At low dilution ratios, a rag layer of emulsified water and solids was sometimes observed between the oil and free water phases. For the PS Method, after gravity settling, the diluted froth separated into two layers: a continuous oil phase and a rag of emulsified water and solids.

For both methods, the water content of the continuous oil phase was measured by Karl Fischer titration. The water content is reported as a volume fraction in bitumen. Only water contents that were repeatable within a 90% confidence interval (± 5%) were used. The bitumen recovery was determined based on the mass of bitumen in the separated oil phase over the total mass of bitumen based on the original froth sample analysis.

Microscopic observations were performed to detect if solids were present in the oil phase. The solids content of the product bitumen was determined more rigorously for a limited number of froth treatments. Samples of froth diluted at the optimum solvent-to-bitumen ratios with solvents were shaken for 5 min and either centrifuged (AS Method) or left to settle (PS Method). Then, the oil phase was decanted and left overnight in a fumehood to evaporate the solvent. Asphaltenes and solids were then precipitated from the dried residue by adding 40 cm³ n-heptane per gram of residue. Note that solids are known to co-precipitate with the asphaltenes[18]. The solution was sonicated for 1 hr and left to settle for 24 hrs. The solution was filtered through Whatman 2 filter paper and the filter cake (asphaltenes and solids) was recovered and mixed with 4 cm³ n-heptane per gram of filter cake. The mixture was sonicated for 45 min and left to settle for 24 hrs. The solution was filtered through the same filter paper and left to dry for three days. After drying, approximately 2 g of asphaltenes with solids were placed in a glass with 200 cm³ of toluene, sonicated for 30 min to dissolve the asphaltenes, and centrifuged at 4,000 rpm for 6 min. The supernatant was decanted and the solids were left to dry in the fumehood overnight and weighed.

Results and Discussion

It was not practical to perform a parametric study on extraction and froth treatment operating conditions for more than one oil sand. Therefore, a relatively poor quality oil sand, LQOS1, was
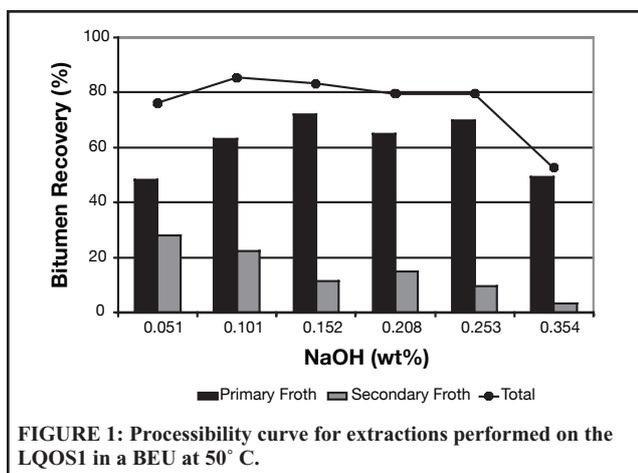
FIGURE 1: Processability curve for extractions performed on the LQOS1 in a BEU at 50° C.
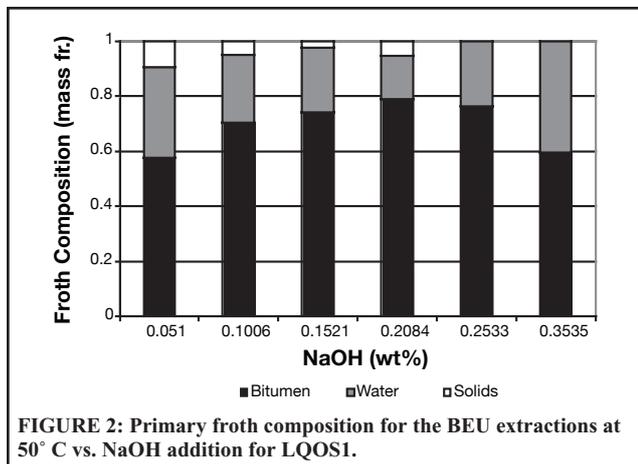
FIGURE 2: Primary froth composition for the BEU extractions at 50° C vs. NaOH addition for LQOS1.

chosen since extraction and froth treatment performance is expected to be more sensitive to operating conditions with a poor quality oil sand. The extraction performance of LQOS1 was compared with the extraction performance of a number of other oil sands to determine if it is a reasonably representative oil sand. Then the effect of extraction conditions on extraction, AS Method, and PS Method froth treatment, and overall process performance is evaluated for LQOS1.

Extraction

Effect of Oil Sand Quality

Extraction is commonly assessed using processability curves[8, 10, 12], plots of primary and/or total bitumen recovery vs. NaOH

addition. Figure 1 shows a processability curve for extractions performed on the LQOS1 by BEU at 50° C. In general, there is a maximum in bitumen recovery at a specific amount of NaOH added. The primary froth composition corresponding to the processibility curve in Figure 1 is shown in Figure 2. The oil content is maximized and the solids content minimized at the optimum amount of NaOH addition. The optimum NaOH addition depends on the oil sand, ranging from zero for some high quality ores to above 0.1 wt% for some poor quality ores[8, 19].

To determine if LQOS1 is a representative low quality oil sand, its extraction performance was compared with that of a variety of oil sands. Table 2 lists the primary froth composition, secondary froth composition, and bitumen recovery for seven different oil sands after extractions by BEU at 80° C without NaOH. Data on bitumen extractions from HQOS, AQOS, and LQOS were reported previously[12], but are included here for comparison. When bitumen is extracted with BEU at 80° C without NaOH, the total bitumen recovery (primary recovery + secondary recovery) normally decreases when the quality of oil sand decreases[12]. As expected, total bitumen recovery is 99%, 84%, and 67% for HQOS1, AQOS2, and LQOS1, respectively. The exception is AQOS1 where the total bitumen recovery was abnormally low (22%). The AQOS1 is likely an aged, oxidized oil sand[19, 20].

Table 3 shows bitumen recoveries and froth compositions for extractions by BEU at 80° C at the optimum addition of NaOH for different oil sands. As expected, the total bitumen recovery, primary bitumen recovery, and bitumen content in primary froth all increased at the optimum amount of NaOH. The behaviour of LQOS1 is consistent with expectations for a low quality oil sand.

Effect of Extraction Method and Temperature

Bitumen was extracted from LQOS1 by BEU and the Denver Cell at temperatures of 80 and 50° C, without NaOH and at optimum NaOH addition. The optimum NaOH amounts were determined from processability curves measured for each temperature and extraction method. As found in earlier work[21], the optimum NaOH amount is the same for BEU and Denver Cell extractions, increasing from 0.10 to 0.15 wt% as the temperature decreased from 80 to 50° C. Bitumen recoveries and froth compositions for these extractions are given in Table 4. While the data is somewhat scattered, some trends emerge.

In general, at higher shear rates (Denver Cell vs. BEU), bitumen recovery was higher, but the bitumen content in the froth was lower. The solids content of the Denver Cell froths was higher at optimum NaOH, but somewhat lower with no NaOH. However, when the solids from different froths were analyzed by particle size analysis, it was found that Denver Cell froth solids had a larger average surface area; that is, there were more fine solids. Note that with NaOH addition, less fine solids were observed for both BEU and Denver Cell froths. Overall, the higher shear rate Denver Cell

TABLE 2: Effect of oil sand quality on bitumen recovery and froth composition after BEU extraction without NaOH at 80° C.

Oil Sand	Froth	Bitumen Content (wt%)	Water Content (wt%)	Solids Content (wt%)	Bitumen Recovery (wt%)	Total Bitumen Recovery (wt%)
HQOS	Primary	68	20	12	84	98
	Secondary	49	26	25	14	
HQOS1	Primary	43	31	26	69	98
	Secondary	35	24	42	29	
AOQS	Primary	53	25	23	87	98
	Secondary	31	30	39	11	
AQOS1	Primary	30	61	8	9	22
	Secondary	27	60	14	13	
AQOS2	Primary	59	16	25	71	84
	Secondary	29	35	36	13	
LQOS	Primary	58	20	23	76	85
	Secondary	21	35	44	9	
LQOS1	Primary	51	27	20	42	67
	Secondary	23	36	29	25	

TABLE 3: Effect of oil sand quality on bitumen recovery and froth composition after BEU extraction at 80° C with optimum NaOH addition.

Oil Sand	Optimum Level of NaOH (wt%)	Froth	Bitumen Content (wt%)	Water Content (wt%)	Solids Content (wt%)	Bitumen Recovery (wt%)	Total Bitumen Recovery (wt%)
HQOS1	0.015	Primary	53	26	22	87	100
		Secondary	28	29	43	13	
AQOS1	0.020	Primary	76	24	ND	60	92
		Secondary	65	28	8	32	
LQOS	0.025	Primary	64	14	22	76	91
		Secondary	48	29	23	15	
LQOS1	0.100	Primary	65	35	ND	78	95
		Secondary	74	26	ND	17	

TABLE 4: Effect of extraction method and temperature on bitumen recovery and froth composition after extraction from LQOS1.

Extraction Method	Froth	Bitumen Content (wt%)	Water Content (wt%)	Solids Content (wt%)	Bitumen Recovery (wt%)	Total Bitumen Recovery (wt%)
BEU, 80° C, no NaOH	Primary	51	27	20	42	67
	Secondary	23	36	29	25	
BEU, 50° C, no NaOH	Primary	42	20	38	32	61
	Secondary	21	19	41	29	
Denver Cell, 80° C, no NaOH	Primary	18	65	16	63	63
Denver Cell, 50° C, no NaOH	Primary	32	51	17	100	100
BEU, 80° C, 0.10 wt% NaOH	Primary	65	35	ND	78	95
	Secondary	74	26	ND	17	
BEU, 50° C, 0.15 wt% NaOH	Primary	74	24	2	72	83
	Secondary	49	37	14	11	
Denver Cell, 80° C, 0.10 wt% NaOH	Primary	39	59	2	100	100
Denver Cell, 50° C, 0.15 wt% NaOH	Primary	43	49	7	97	97

achieved higher bitumen recovery at the expense of lower froth quality.

In most cases, bitumen recovery and froth quality both decrease as temperature decreases. A notable exception is Denver Cell extractions with no NaOH. Here bitumen recovery increased from 63% at 80° C to 100% at 50° C. It is not clear why recovery increased in this case. In most cases, the froth bitumen content increased as temperature decreased. In all cases, the froth solids content increased slightly as temperature decreased. Hence, decreasing temperature from 80 to 50° C decreases bitumen recovery while the effect on froth quality is ambiguous.
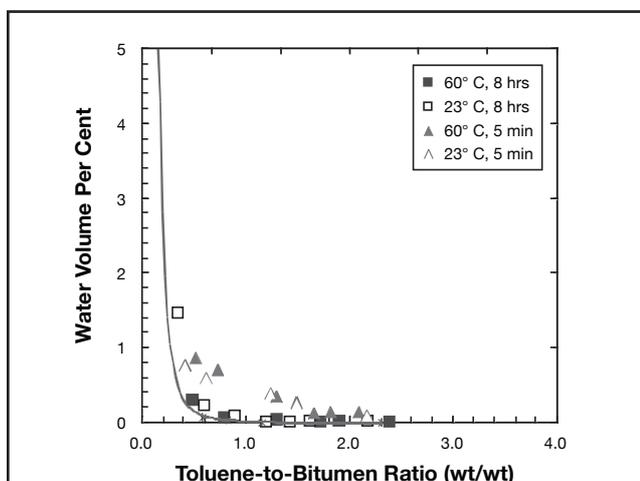
FIGURE 3: Water content in bitumen produced with AS Method at different toluene-to-bitumen ratios from LQOS1 by BEU (80° C, no NaOH addition during extraction).

AS Method Froth Treatment

Baseline Data

Froth treatment performance has been assessed based on the product quality; that is, the volume fraction of water in the bitumen product[12]. Figure 3 shows the effect of diluent ratio (toluene-to-bitumen or T/B ratio) on the residual water volume fraction for the AS Method and a LQOS1 froth. Note that the water volume fractions are based on the volume of bitumen, not bitumen plus diluent. In the AS Method, the residual water fraction decreased dramatically when sufficient diluent was added to decrease the diluted bitumen density below that of water. At the same time, the diluted bitumen viscosity decreased allowing a more rapid separation. Above an "optimum" dilution ratio, defined as the dilution ratio at which the water volume fraction decreases below 0.5 vol%, further dilution had little effect on the residual water volume

TABLE 5: Fine solids content in bitumen after different froth treatments at 23° C for LQOS1 primary froth extracted by BEU at 80° C.

NaOH Addition in Bitumen Extraction	Froth Treatment Method	Solvent-to-Bitumen Ratio (wt/wt)	Solids Content (wt%)
no NaOH	AS, 8 hrs	0.8	0.03
no NaOH	AS, 5 min	0.8	0.14
no NaOH	PS, 8 hrs	2.0	0.14*
no NaOH	PS, 40 min	3.5	0.19*
0.10 wt%NaOH (opt.)	PS, 40 min	1.5	0.01

*Average of two runs

TABLE 6: Optimum toluene-to-bitumen ratios for the AS Method.

Oil Sand	Extraction Conditions	Optimum T/B ratio (wt/wt)			
		60° C, 8 hrs	60° C, 5 min	23° C, 8 hrs	23° C, 5 min
HQOS	BEU, 80° C, no NaOH	0.4 ± 0.1	0.7 ± 0.1	0.5 ± 0.1	0.7 ± 0.1
HQOS1	BEU, 80° C, no NaOH	0.8 ± 0.1	1.8 ± 0.1	0.8 ± 0.1	1.8 ± 0.1
	BEU, 80° C, 0.015 wt% NaOH	0.8 ± 0.1	1.8 ± 0.1	0.8 ± 0.1	1.8 ± 0.1
LQOS1	BEU, 80° C, no NaOH	0.5 ± 0.1	1.2 ± 0.1	0.6 ± 0.1	1.3 ± 0.1
	BEU, 80° C, 0.1 wt% NaOH	0.5 ± 0.1	1.2 ± 0.1	0.6 ± 0.1	1.3 ± 0.1
	BEU, 50° C, no NaOH	0.5 ± 0.1	1.2 ± 0.1	0.6 ± 0.1	1.3 ± 0.1
	Denver Cell, 80° C, no NaOH	0.5 ± 0.1	3.0 ± 0.1	0.6 ± 0.1	3.2 ± 0.1
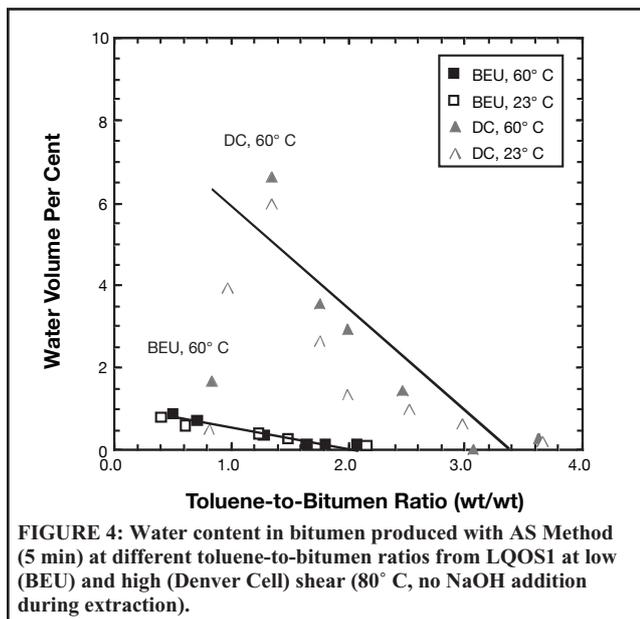
FIGURE 4: Water content in bitumen produced with AS Method (5 min) at different toluene-to-bitumen ratios from LQOS1 at low (BEU) and high (Denver Cell) shear (80° C, no NaOH addition during extraction).
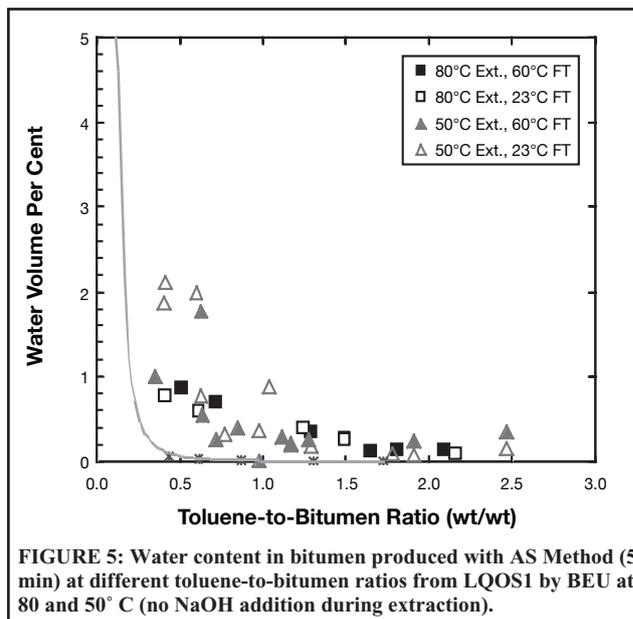
FIGURE 5: Water content in bitumen produced with AS Method (5 min) at different toluene-to-bitumen ratios from LQOS1 by BEU at 80 and 50° C (no NaOH addition during extraction).

fraction. In general, the solids content in the oil phase was observed to decrease as the water content decreased. No solids were observed in photomicrographs of the oil phase at or above the optimum toluene-to-bitumen ratios. However, Table 5 shows that at the optimum T/B ratio, the solids content is in fact 0.14 wt% at 5 min residence time, but only 0.03 wt% at 8 hr residence time. Optimum T/B ratios for froths from different oil sands are given in Table 6.

Figure 3 also shows that, in general, the optimum dilution ratio decreased at longer residence times and higher temperatures. It has also been shown that higher diluent ratios were required for poorer quality oil sands[12]. Note that the solid line in Figures 3 and 5 is provided as a comparative guideline. It is based on an ideal settling calculation[12] and corresponds to the best performance that has been observed for a high quality froth.

For the AS Method, the bitumen recovery was almost 100% at the optimum toluene-to-bitumen (T/B) ratio; that is, almost all bitumen reported to the oil phase. Most of the water coalesces to form a free water phase and little oil was trapped with the water and solids. Bitumen recovery does not appear to depend on the froth treatment temperature, the residence time (at least above 5 min), or the quality of ore[12].

Effect of Extraction Method, Temperature, and NaOH

Figure 4 shows the water content in the product bitumen produced using the AS Method and 5 min residence time for BEU and Denver Cell froths extracted from LQOS1 with no NaOH at 80° C. The water content at a given T/B ratio is higher for Denver Cell froth. The optimum T/B ratio for the Denver Cell froth is approximately 3.0 wt/wt, which is much higher than the ratio of approximately 1.2 wt/wt required for the BEU froth. Table 6 summarizes optimum T/B ratios for froths extracted using BEU at 80 and 50°

C and Denver Cell at 80° C with no NaOH. At long residence time, the optimum T/B ratio for the Denver Cell froth decreased to the same ratio as required for the BEU froth. The Denver Cell froth had higher solids content and more fine solids than the BEU froth. It is likely that the solids hinder settling or coalescence and therefore reduce the effectiveness of the Denver Cell froth treatment at short residence times.

Figure 5 shows the water content in bitumen produced using the AS Method and 5 min of residence time for BEU froth extracted from LQOS1 at 80 and 50° C with no NaOH added. The data are somewhat scattered, but extraction temperature appeared to have no significant effect on froth treatment performance. The same results were obtained at long residence time, as shown in Table 6.

The effect of NaOH addition was assessed for HQOS1 and LQOS1 froths extracted by BEU at 80° C, without NaOH and at optimum NaOH amounts. No difference in froth treatment performance was observed. Table 6 shows that the optimum T/B ratios are the same without NaOH and at optimum NaOH addition. Note that there was an insufficient amount of the unaged LQOS1 sample to perform the experiments required to compare Denver Cell froths from 50 and 80° C extractions, with and without NaOH.

In all cases, bitumen recovery was almost 100% at the optimum T/B ratios. Hence, for optimum T/B ratios with the AS Method, bitumen recovery does not appear to depend on the extraction or froth treatment conditions.

PS Method Froth Treatment

Baseline Data

Figure 6 shows the effect of diluent ratio on the residual water volume fraction for the PS Method and an LQOS1 froth. In the PS Method, the residual water fraction decreased dramatically when sufficient diluent was added to reach the precipitation point of asphaltenes; a heptane/bitumen (H/B) ratio of approximately
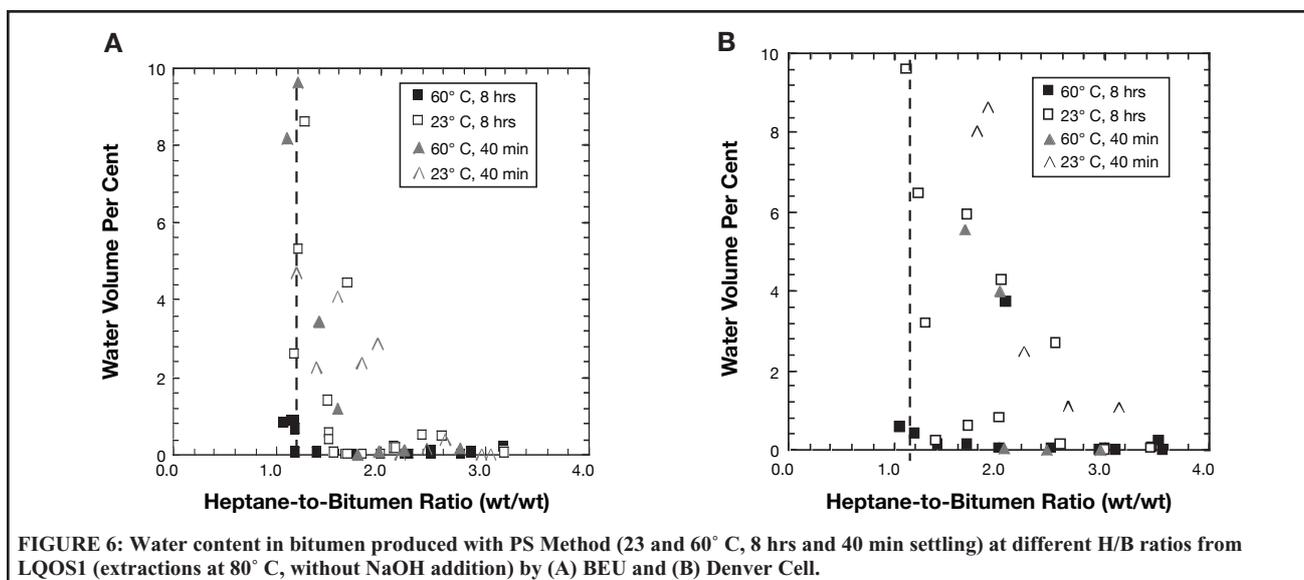
FIGURE 6: Water content in bitumen produced with PS Method (23 and 60° C, 8 hrs and 40 min settling) at different H/B ratios from LQOS1 (extractions at 80° C, without NaOH addition) by (A) BEU and (B) Denver Cell.

TABLE 7: Optimum heptane-to-bitumen ratios for the PS Method.

Oil Sand	Extraction Conditions	Optimum H/B Ratio (wt/wt)			
		60° C, 8 hrs	23° C, 8 hrs	60° C, 40 min	23° C, 40 min
HQOS	BEU, 80° C no NaOH	1.1 ± 0.1	1.2 ± 0.1	1.2 ± 0.1	1.2 ± 0.1
HQOS1	BEU, 80° C no NaOH	1.5 ± 0.1	2.2 ± 0.1	1.8 ± 0.1	2.5 ± 0.1
	0.015 wt% NaOH	1.2 ± 0.1	1.8 ± 0.1	1.2 ± 0.1	1.8 ± 0.1
LQOS1	BEU, 80° C no NaOH	1.2 ± 0.1	1.8 ± 0.1	1.5 ± 0.1	2.5 ± 0.3
	0.1 wt% NaOH	1.2 ± 0.1	1.4 ± 0.2	1.3 ± 0.2	1.4 ± 0.2
	BEU, 50° C no NaOH	1.2 ± 0.1	1.8 ± 0.1	1.5 ± 0.1	1.8 ± 0.2
	0.15 wt% NaOH	1.1 ± 0.1	1.1 ± 0.1	1.1 ± 0.1	1.1 ± 0.1
	Denver Cell, 80° C no NaOH	1.3 ± 0.1	2.2 ± 0.2	2.0 ± 0.5	3.0 ± 0.3
	0.15 wt% NaOH	1.1 ± 0.1	1.1 ± 0.1	1.1 ± 0.1	1.1 ± 0.1

TABLE 8: Bitumen recovery from LOQS1 froth at the optimum H/B ratio of the PS Method.

Oil Sand	Froth Extraction Conditions	Bitumen Recovery After Froth Treatment (wt%)			
		60° C, 8 hrs	23° C, 8 hrs	60° C, 40 min	23° C, 40 min
HQOS1	BEU, 80° C, no NaOH	72	66	81	64
	BEU, 80° C, 0.015 wt% NaOH	75	72	91	72
LQOS1	BEU, 80° C, no NaOH	78	77	72	70
	BEU, 80° C, 0.10 wt% NaOH	95	90	89	89
	BEU, 50° C, no NaOH	67	66	65	57
	BEU, 50° C, 0.15 wt% NaOH	70	69	69	62
	Denver Cell, 80° C, no NaOH	65	64	46	59
	Denver Cell, 80° C, 0.10 wt% NaOH	78	80	80	79

1.2 wt/wt. It is likely that flocculation becomes significant at this point allowing for more rapid settling. The water content was reduced to near zero above the optimum dilution ratio. Optimum H/B ratios are given in Table 7. Figure 6 also shows that, in general, the optimum dilution ratio decreased at longer residence times, but is relatively insensitive to temperature. It has also been shown that higher diluent ratios are required for poorer quality oil sands for both AS and PS Methods[12].

Bitumen recovery was less than 100% with the PS Method because asphaltenes were deliberately precipitated and diluted bitumen was lost to the rag layer. The rag layer is the sediment formed after gravity settling and consists of water droplets and solids surrounded by diluted bitumen. In general, bitumen recovery was lower for poorer quality oil sands, but improved at the optimum amount of NaOH. Bitumen recovery increases as froth treatment

temperature increases and at higher residence times, probably because a more compact rag layer is formed[12].

Effect of Extraction Method, Temperature, and NaOH

Effect of Extraction Shear

Figure 6 shows the water content in bitumen produced with the PS Method (23 and 60° C, 8 hrs and 40 min settling) from LQOS1 froth extracted by BEU (Figure 6a) and the Denver Cell (Figure 6b) at 80° C, without NaOH added. In general, froth treatment effectiveness is poorer for the Denver Cell froths. The difference was most pronounced at short residence times and lower temperatures. For example, at 23° C and 40 min residence time, the optimum
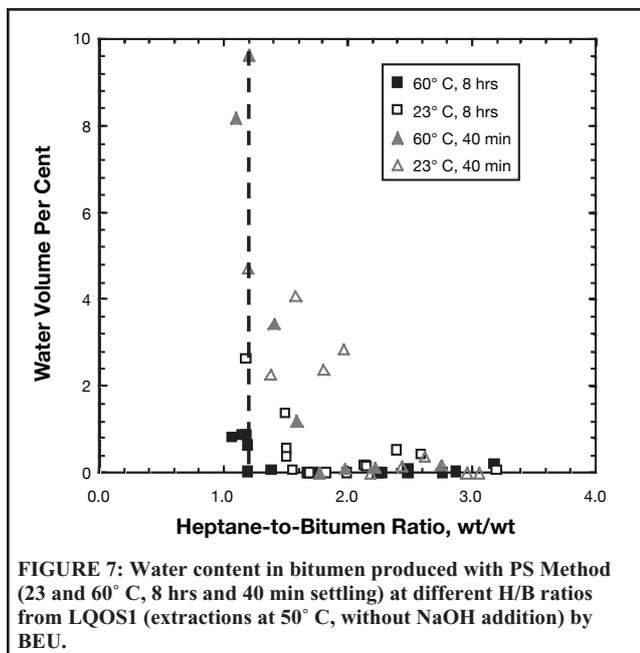
FIGURE 7: Water content in bitumen produced with PS Method (23 and 60° C, 8 hrs and 40 min settling) at different H/B ratios from LQOS1 (extractions at 50° C, without NaOH addition) by BEU.

H/B ratio was approximately 2.8 wt/wt for the BEU froth, but approximately 3.2 for the Denver Cell froth. At an 8 hr residence time and 60° C, the optimum H/B ratio was approximately 1.2 wt/wt for both froths.

Table 8 shows that bitumen recovery was less for Denver Cell froths than BEU froths at optimum H/B ratios. Hence, Denver Cell froths not only require higher H/B ratios, but have lower bitumen recovery than BEU froths. The poorer performance is likely related to the higher fines content of the Denver Cell froth. Fines are known to prevent coalescence of water droplets and may also inhibit the flocculation of water droplets and asphaltenes. Both factors could reduce settling efficiency. Also, less coalescence and more fines could lead to a thicker and less compact rag layer, trapping more bitumen.

Effect of Extraction Temperature

Figure 7 shows the water content in bitumen produced with the PS Method from LQOS1 froth extracted by BEU at 50° C without NaOH. There is no apparent difference in water content in bitumen for froth extracted at 50° C compared with that extracted at 80° C (Figure 6a). However, Table 8 shows that bitumen recovery is lower for froths extracted at the lower temperature. It appears that although similar settling can be achieved at a lower temperature, a less compact lag layer occurs resulting in lower bitumen recovery.

Effect of NaOH Addition During Extraction

Figure 8 shows the water content in bitumen produced after 8 hrs (Figure 8a) and 40 min (Figure 8b) of settling with the PS Method from LQOS1 froth extracted by Denver Cell, without and with NaOH. Froth treatment effectiveness was dramatically improved for froth produced with optimum NaOH at both low and high temperatures and short and long residence times. For example, at 23° C and long or short residence time, the optimum H/B ratio was reduced from approximately 3.0 to 1.2 when the extraction was performed with the optimum NaOH addition. Similar trends were observed for all the froths examined to date, including LQOS1 froth extracted by BEU at 80 and 50° C. Since the effect of NaOH was so significant, these experiments were repeated with another oil sand, HQOS1, and the same trends were observed for an HQOS1 froth extracted by BEU at 80° C. Note that the solids content of the product bitumen was also reduced to near zero when NaOH was used in the extraction, as shown in Table 5.

Optimum NaOH addition also improves the PS Method bitumen recovery (as shown in Table 8) for both LQOS1 and HQOS1 froths. A possible reason is the release of natural surfactants in bitumen when NaOH is used[22]. The natural surfactants may enhance coalescence of the water droplets in the froth leading to better phase separation and a smaller rag layer. To test this idea, photomicrographs of PS Method froth extracted without and at optimum NaOH addition were examined.

Figure 9 shows photomicrographs of LQOS1 froths at 23° C immediately after dilution with n-heptane. The froths were extracted by BEU at 80° C with no NaOH (Figure 9a) and with optimum NaOH addition (Figure 9b). Figure 9a shows an emulsion consisting primarily of 1 to 10 μm diameter droplets. Figure 9b shows much larger droplets and significant volumes of free water. The addition of NaOH in bitumen extraction clearly promotes the coalescence of the water droplets.

Why does NaOH addition in extraction not improve AS Method performance? Figure 10 compares the same froths after dilution with toluene. Figure 10a shows that, even without NaOH addition, relatively large droplets (greater than 20 μm diameter) are formed. Toluene promotes coalescence itself and the additional impact from NaOH addition appeared to be minimal (Figure 10b). Note that small droplets likely contribute most to residual water volumes and the differences in the number of small droplets would not be apparent in the photomicrographs. However, all of the AS Method froth treatment data suggests that there was little difference in treating froths with and without NaOH added during extraction. Therefore, it is reasonable to conclude that NaOH addition during extraction has little impact on coalescence and on AS Method froth treatment efficiency.
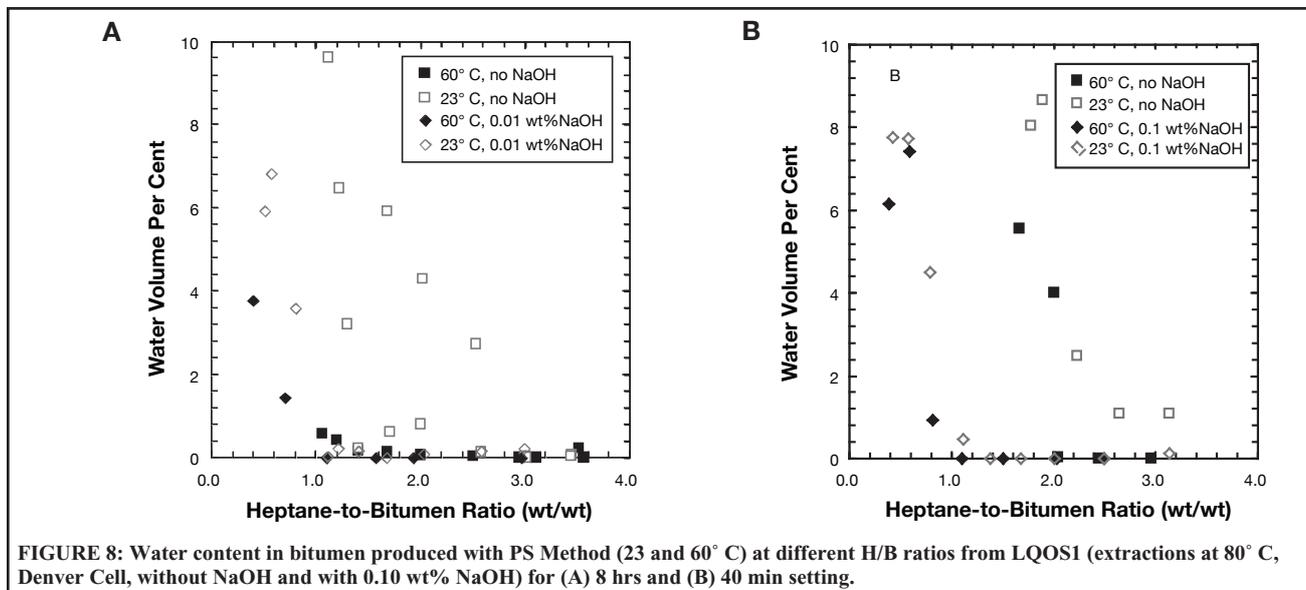
FIGURE 8: Water content in bitumen produced with PS Method (23 and 60° C) at different H/B ratios from LQOS1 (extractions at 80° C, Denver Cell, without NaOH and with 0.10 wt% NaOH) for (A) 8 hrs and (B) 40 min setting.
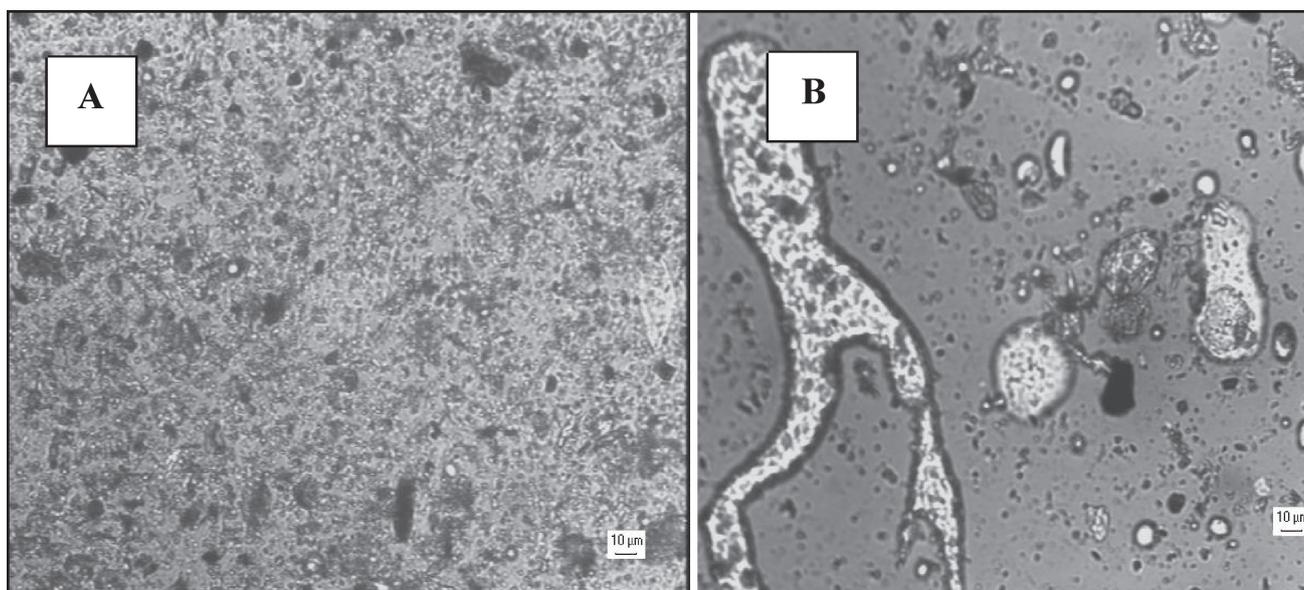
FIGURE 9: LQOS1 froths extracted by BEU at 80° C and diluted with n-heptane at an H/B ratio of 1 wt/wt at 23° C: A) no NaOH during extraction; and, B) 0.10 wt% NaOH during extraction.
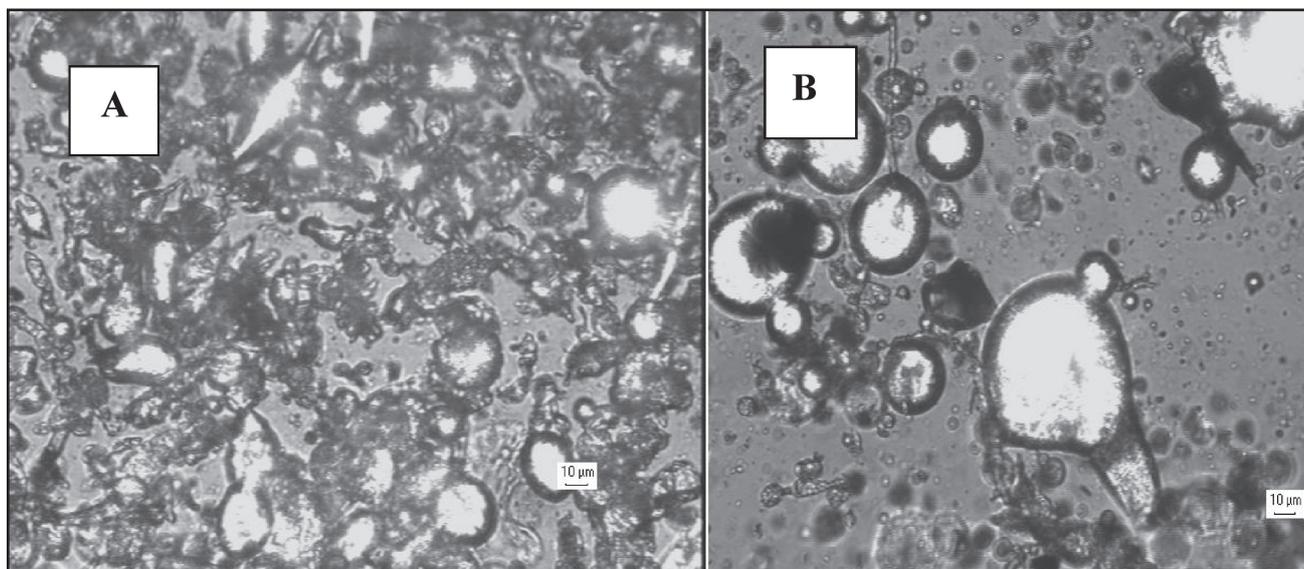
FIGURE 10: LQOS1 froths extracted by BEU at 80° C and diluted with toluene at a T/B ratio of 1 wt/wt at 23° C: A) no NaOH during extraction; and, B) 0.10 wt% NaOH during extraction.

TABLE 9: Optimum solvent-to-bitumen ratios, total bitumen recovery, and water content for different froth treatment conditions for LQOS1.

Froth Treatment	Bitumen Extraction	Optimum So/B Ratio (wt/wt)	Total Bitumen Recovery (wt%)	Water Content (wt%)
AS, 60° C, 5 min	BEU, 80° C, no NaOH	1.2 ± 0.1	67	< 0.5
AS, 60° C, 5 min	BEU, 80° C, 0.1 wt% NaOH (opt)	1.2 ± 0.1	95	< 0.5
AS, 60° C, 5 min	BEU, 50° C, no NaOH	1.2 ± 0.1	61	< 0.5
AS, 60° C, 5 min	Denver Cell, 80° C, no NaOH	3.0 ± 0.1	63	< 0.5
PS, 60° C, 40 min	BEU, 80° C, no NaOH	1.8 ± 0.1	48	~ 0.0
PS, 60° C, 40 min	BEU, 80° C, 0.1 wt% NaOH (opt)	1.4 ± 0.2	84	~ 0.0
PS, 60° C, 40 min	BEU, 50° C, no NaOH	1.8 ± 0.1	39	~ 0.0
PS, 60° C, 40 min	Denver Cell, 80° C, 0.1 wt% NaOH(opt)	1.1 ± 0.1	80	~ 0.0

Conclusions

Increasing shear extraction (Denver Cell) increases bitumen recovery in extraction but decreases froth quality. Reducing extraction temperature can decrease extraction bitumen recovery but may have little effect on froth quality. As is already well established, optimum NaOH addition maximizes bitumen recovery and froth quality. To see how these changes in extraction conditions affect combined extraction and froth treatment performance, optimum froth treatment solvent-to-bitumen ratio, total bitumen recovery, and product bitumen water content are summarized in Table 9 for representative cases.

The AS Method proved to be robust. Lowering the extraction temperature from 80 to 50° C and failing to add optimum NaOH had little effect on froth treatment performance. Total bitumen recovery was reduced because extraction bitumen recovery decreased. For froths extracted by the higher shear Denver Cell, higher solvent-to-bitumen ratios are necessary to obtain less that 0.5 wt% water in bitumen at short residence times. At long residence times, the optimum solvent-to-bitumen ratio was independent of the extraction method.

The PS Method was more sensitive to extraction conditions. Higher shear in extraction increased bitumen recovery. However, higher H/B ratios were required to achieve the same product quality. Lowering the extraction temperature from 80 to 50° C reduced bitumen recovery and led to higher optimum H/B ratios. The addition of the optimum amount of NaOH during extraction significantly improved froth treatment performance. Bitumen recovery was maximized and optimum H/B ratios reduced to 1.2 wt/wt in almost all cases. It appears that NaOH releases natural surfactant which promotes coalescence leading to more effective settling and higher bitumen recovery.

While the laboratory methods are only approximations of the commercial processes and cannot provide quantitative predictions, they are useful for examining trends. With this proviso, some process implications are that energy savings from reduced extraction temperature may be offset by lower bitumen recovery at least for low quality oil sands. Higher shear extraction may improve bitumen recovery but decreases froth treatment effectiveness. For paraffinic solvent-based froth treatments, the addition of NaOH in extraction may be required to obtain optimum froth treatment of low quality oil sands.

Acknowledgements

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