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Ind. Eng. Chem. Res., **2008**, 47 (22), 8828-8839 • DOI: 10.1021/ie800601r • Publication Date (Web): 18 October 2008

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Rag Layers in Oil Sand Froths

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During the settling stages in some oil sands froth treatments, a rag layer (an undesirable mixture of dispersed oil, water, and solids) can form at the water–oil interface. To investigate rag layer formation, oil sand froths were diluted with mixtures of toluene and heptane and the diluted froths were centrifuged in steps of increasing rpm. The volumes of oil phase, rag layer, free water, and sediment were measured after each step. The data obtained from the experiments were used for material balances to determine the composition of the rag layers. The size and properties of the rag layer solids were also measured. Two mechanisms were found to influence rag layer formation: slow coalescence of emulsified water between 1500 and 3000 rpm (200–1000 times gravity); trapping of fine intermediate to oil wet solids at higher rpm and residence times. The main process factors affecting rag formation appear to be the type of diluent and asphaltene precipitation. As well, higher quality oil sand produced much smaller rag layers.

Introduction

A first stage in recovering bitumen from oil sands is water-based extraction; for example, the Clark hot water extraction process. Processing begins at the mine site where oil sands are mixed with hot water at approximately 95 °C, and the slurry is then pipelined to the extraction and upgrading plant site. Sodium hydroxide and steam are added as required to the slurry. During hydrotransport, the hot water and sodium hydroxide liberate natural surfactants and begin the process of separating bitumen from the sand grains. At the plant site, more hot water is added and the slurry is fed to a large separation vessel. In this vessel, under normal operation, the bitumen readily separates from the coarse sand grains. However, the density of the bitumen is almost the same as the surrounding water and it is aerated to obtain a bitumen-rich froth. A significant amount of water is collected in this primary froth. The coarse solids settle to the bottom of the separation vessel. The rest of the mixture is removed as a ‘middlings’ stream which is sent to a secondary separation vessel where it is aerated to produce a secondary froth.¹

The froth produced from a water-based extraction processes typically contains approximately 60 wt % bitumen, 30 wt % water, and 10 wt % solids with small concentrations of natural surfactants. The froth must be further treated to remove water and solids prior to upgrading. In the Syncrude and Suncor processes, the froth is diluted with naphtha to reduce the density and viscosity of the continuous oil phase and then centrifuged to accelerate the separation. In the Albion process, the froth is diluted with a paraffinic solvent and separated with gravity settling. The product of froth treatment is diluted bitumen which is then processed for solvent recovery and bitumen upgrading.

One issue in froth treatment is the buildup of material at the water–oil interface. This interfacial zone has two components: a hindered settling zone and a “rag” layer. The hindered settling zone is a layer of settling solids and water droplets. The size of this zone depends on the ratio of the feed rate to the settling rate as well as the geometry of the vessel.^{2,3} The hindered

settling zone will disappear if the feed is stopped. The rag layer typically consists of water droplets and solids suspended in a continuous oil phase. This material accumulates over time, does not easily separate, and persists for long times even if the feed is stopped. Rag layer formation is known to be problematic in heavy crude oils with an API gravity of less than 20⁴ and rag layers have been observed in froth treatment processes.^{3,5} In poor processing conditions, this rag layer can grow thick enough to overflow into the oil or water outlet streams. If the rag material enters the oil stream, it introduces water and fine solids which may cause corrosion and fouling in downstream processes. If it enters the water stream, oil recovery is reduced, necessitating further treatment. Note, the same problems can occur in conventional and heavy oil separation processes.

There are at least two possible mechanisms for rag layer formation. Rag layers can occur when the coalescence rate of the water droplets is lower than the accumulation rate.² Oil sand froths do contain emulsified water. For instance, in the Syncrude and Suncor processes, after centrifugation, the diluted bitumen product from the froth treatment process contains 2–3% emulsified water, even though demulsifying agents have been used.⁵ The coalescence rate of the emulsified water may be a significant factor in oil sand rag layer formation.

Another possible mechanism for rag layer formation is the accumulation of fine oil-wet solids which are held at the interface by interfacial tension forces. Oil sands contain a variety of clays.^{6,7} While pure phyllosilicate clays tend to be hydrophilic, asphaltenes and other oil constituents adsorb on their surfaces creating biwetted particles.^{8–10} Chen et al.¹¹ showed that biwettable fine solids adsorb at water–oil interfaces. These accumulated solids could present a barrier to settling materials. These solids also contribute to the stability of dispersed water droplets in the oil phase in froth treatment processes. Small asphaltene-coated emulsion droplets which are oil-wet are also expected to accumulate at the interface.

The mechanisms that determine rag layer build up in oil sands froth treatment are not yet well understood. Consequently, the response of rag layers to changes in process conditions or chemical additives is at times unpredictable. Since rag layers can ultimately shut down a process, there is an incentive to

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Table 1. Composition of the Oil Sand Samples

component	LQOS3, wt %	AQOS2, wt %
bitumen	5.5	10.4
water	1.1	3.4
solids	93.6	85.8
finest (<44 μm) ^a	30.4	27.6

^a Weight percent of fines in solids.

determine the factors that control rag layer growth. Hence, the two main objectives to this study are (1) to understand the mechanisms that cause the rag layer to grow in oil sands froth treatment and (2) to understand how operating conditions and oil sand quality affect rag layer formation.

Experimental Methods

Materials. Oil Sand Samples. Two oil sand samples, designated LQOS3 and AQOS2, were obtained from Syncrude Canada Ltd. The bitumen, water, and solids content of the oil sand samples were determined at the Syncrude Research Centre using Dean–Stark extraction, and the fines content of the solids was determined by laser light scattering analysis.¹² Fines are defined as solids less than 44 μm in diameter. Table 1 shows the composition of the two oil sand samples. On the basis of the Pow et al.¹³ criteria for oil sand quality, the LQOS3 is a low quality oil sand and the AQOS2 is an average quality oil sand.

Upon receipt, the oil sand sample pails were dated and any clay chunks in the samples were manually broken down to pea-size. Samples were transferred to plastic bags to prevent evaporation of the free water. Then they were mixed and homogenized by hand and transferred to a polyethylene pail. As recommended by Schramm and Smith,¹ the oil sand samples were stored in the dark in a freezer to minimize the effects of aging. The LQOS3 sample was of unusually poor quality and was far more consolidated than typical samples. It was ground and sieved to approximately half-centimeter size for the extraction experiments.

Other Materials. Athabasca coker-feed bitumen was obtained from Syncrude Canada Ltd. Commercial grade *n*-heptane (Conoco Phillips), reagent grade toluene (Univar), histology grade 2-propanol (EM Science), reagent grade sodium hydroxide (EM Science), anhydrous methanol (Fisher Scientific), Nitrogen (PRAXAIR Canada Inc.) and type 4A molecular sieves (Fisher Scientific) were used in this study. Reverse osmosis (RO) water was supplied from the University of Calgary water plant. The Karl Fischer titration reagent was Aqualine Complete 5 which was a mixture of iodine, sulfur dioxide, and imidazole (Fisher Scientific).

Asphaltenes were required for one experiment and were separated from Athabasca coker feed bitumen using a modified ASTM D4124 method. *n*-Pentane was added to bitumen in a ratio of 40 cm^3 per gram of bitumen, the mixture was sonicated for 45 min at room temperature and then left for 24 h. Most of the supernatant was decanted and filtered through Whatman filter paper number 2 (8 μm pore size). The residue in the beaker was diluted again with a 4:1 cm^3/g ratio of *n*-pentane to the original bitumen. After sonication and 24 h of equilibration, the mixture was filtered through the same filter paper. The filter cake (asphaltenes) was washed with *n*-pentane for 5 days and then dried in a fume hood overnight.

Oil Sand Extraction. Bitumen froth was extracted from oil sands using a Denver Cell extraction apparatus obtained from the Saskatchewan Research Council Pipeflow Technology Centre. The flotation was based on the Syncrude method.¹⁴ The

Table 2. Composition of LQOS3 and AQOS2 Froths^a

component	LQOS3, wt %	AQOS2, wt %
bitumen	9.7	44.6
water	59.8	29.5
solids	30.5	25.9

^a Data is the average of all assays for each oil sand's froth.

frozen oil sand was partially thawed and approximately 500 g of the sample was weighed and allowed to reach room temperature before the extraction. RO water was preheated to the desired temperature, usually 80 °C. Approximately 300 g of RO water and the 500 g oil sand sample were added to the Denver pot, and NaOH was added to the water if required for the experiment. Then the impeller was turned on to 2100 rpm for 5 min. After 5 min of mixing, 600 g of preheated water was added to the Denver pot, and the impeller speed was adjusted to 1200 rpm. At the same time, the Denver Cell pot was aerated with 300 cm^3/min of nitrogen injected through the impeller shaft. After another 5 min of mixing, the impeller and nitrogen flow were turned off, and all the froth was skimmed from the surface of the Denver pot.

The extraction experiments were conducted at 23, 50, and 80 °C for LQOS3, but they were only conducted at 80 °C for AQOS2. Some oil sands exhibit a maximum bitumen recovery and bitumen content in the froth when an optimum amount of NaOH is added during extraction. However, the maximum bitumen recovery for the LQOS3 sample occurred at zero or near zero NaOH addition. The AQOS2 extraction was not sensitive to NaOH addition and there was no clear optimum amount. Note, the processibility curves are provided in the Supporting Information. For the froth experiments presented in this study, the extractions were conducted at 0 and 0.04 wt % NaOH for LQOS3 and at 0 wt % NaOH for AQOS2.

Froth Composition Measurement. A subsample of froth obtained from the bitumen extraction experiment was assayed for oil, water, and solid contents. First a froth sample was dissolved in a 74% toluene/26% 2-propanol mixture. The bitumen content was determined gravimetrically after evaporating an aliquot to remove solvent and water. The water content was determined for another aliquot using a Karl Fischer Titrator (658 KF Processor and 655 Dosimat). The solid content was calculated by difference. The detailed procedure is reported elsewhere.¹² Table 2 shows the froth compositions for the two oil sand samples.

Measurement of the Onset of Asphaltene Precipitation. The mass fraction of inorganic solids in the bitumen and the onset of asphaltene precipitation were determined as described elsewhere.¹⁵ The yield of asphaltene precipitate is reported on a solids-free basis. Note, a solution of *X* vol % heptane and *Y* vol % toluene is denoted as Heptol *X/Y*. Figure 1 shows fractional asphaltene yields for different solvents at 23 °C on a solids-free basis. The Heptol 70/30 and Heptol 80/20 data were collected in this study, and the *n*-heptane data were taken from literature.¹⁶ The onsets were determined by extrapolating the yields to zero. The precipitation onsets in Heptol 80/20 and 70/30 occur at solvent mass fractions of approximately 0.76 and 0.9, respectively. No asphaltene precipitation was observed in Heptol 50/50.

Stepwise Centrifuge Tests. Romanova et al.¹⁷ assessed the effectiveness of froth treatment by centrifuging a 15 cm^3 test tube containing diluted froth for 5 min at 4000 rpm. The diluted froth usually separated into an oil layer, a rag layer, a water layer, and a sediment layer. The rag layer volumes were usually small, hence it was not possible to assess what factors might

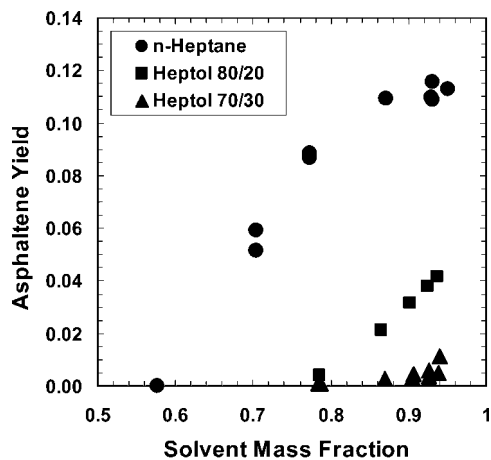


Figure 1. Asphaltene precipitation yields at 23 °C for *n*-heptane, Heptol 70/30, and Heptol 80/20. Data for *n*-heptane was taken from Akbarzadeh et al., 2005.

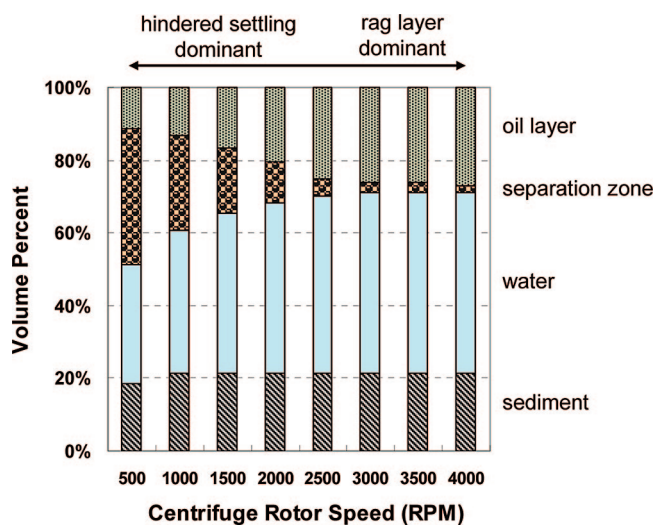


Figure 2. Volumes of the oil, rag, water, and sediment layers formed during a stepwise centrifuge test performed on the LQOS3 froth. Froth extracted at 23 °C with 0.04 wt % NaOH; froth diluted at 2.7 g/g heptane/bitumen at 60 °C.

have affected rag layer formation. In this study, the method was modified to include a series of centrifugation steps of increasing rotational speed, with the layer volumes being measured after each step. Both the hindered settling zone and the rag layer were present at low centrifuge speeds but, at higher speeds, differences in rag layer formation at different conditions were more easily discerned than at 4000 rpm alone. The centrifuge speeds ranged from 500 to 4000 rpm, equivalent to 26–1600 times gravity.

The gradual change in “separation zone” (hindered settling + rag layer) thickness as centrifuge speed increased is shown in Figure 2. Note that the separation zone shrinks significantly up to approximately 2500 rpm but only gradually at higher speeds. As will be discussed later (see Figure 10) and was confirmed with hindered settling calculations,¹⁸ the settling process was essentially over by approximately 3000 rpm (1000 times gravity) or less in all cases. In several experiments, samples from the interfacial zone were taken after the 1500 or 2000 rpm step. These centrifuge speeds were at a condition where hindered settling was nearly complete and the remaining interfacial zone was predominantly a loose rag layer which had

Table 3. Dilution Ratios and Onset of Asphaltene Precipitation for the Three Solvents Used in Stepwise Centrifuge Tests

solvent	dilution ratios (g solvent/g bitumen)	onset of precipitation (g solvent/g bitumen)
toluene	4.1 and 8.5	N/A
heptol 80/20	0.70 and 5.1	3.0 ± 0.3
heptane	0.66 and 2.7	1.5 ± 0.3

sufficient volume to provide a sample. For convenience, these samples will be referred to as a rag layer in all subsequent discussion.

To begin a test, the froth from a Denver Cell bitumen extraction was diluted with either heptane, Heptol 80/20, or toluene at the dilution ratios given in Table 3. For heptane and Heptol 80/20, the lower dilution ratio was below the onset of asphaltene precipitation and the upper ratio was above the onset of precipitation. The experiment was conducted at either 23 or 60 °C. A froth bottle that had been stored in a refrigerator was preheated for 20 min in a 60 °C water bath to reduce the viscosity of the sample. The froth was then mixed using a spatula and a sample was transferred to a test tube. The diluent was added at 23 °C to the test tube to obtain the desired solvent to bitumen ratio, and the test tube contents were mixed using a shaker table for 5 min. If the experiment was to be conducted in 60 °C, the test tube was preheated in a water bath for 15 min to reach the required temperature.

The test tube was then centrifuged at 500 rpm for 5 min. After centrifuging, the volumes of the oil, separation zone, water, and sediment layers were measured. For the 60 °C experiments, the test tube was then heated in a water bath for 5 min. For the 23 °C experiments, the test tube was left standing at ambient conditions for approximately 1 min. Note, preliminary experiments indicated that, at 23 °C, the separation zone layer volume changes only occurred while centrifuging and little or no change occurred with gravity settling. The test tube was then centrifuged for another 5 min at 1000 rpm, and the layer volumes again measured. The centrifugation and heating steps were performed a total of eight times. The centrifuge speed was increased 500 rpm each time to a final speed of 4000 rpm.

A number of variations were performed in the stepwise centrifugation tests to assess possible mechanisms for rag layer stability. These variations are presented in the results and discussion section. Two cases required preparation of other materials: (1) the addition of an emulsion to the froth; (2) the addition of fine solids to the froth. The preparation of the emulsion and the extraction of the fine solids are described below.

Emulsion Preparation. Following the same procedures described in stepwise centrifugation, a froth sample was diluted with toluene in a test tube but centrifuged only at 4000 rpm for 5 min. The oil phase was decanted with a pipet and transferred to a small glass bottle. About 5 vol% RO water was added slowly to the glass bottle and was homogenized using a CAT-520D homogenizer with a 17 mm flat rotor generator at 18000 rpm for 5 min.

Fine Solids Extraction. A froth sample was diluted with toluene and the test tube was centrifuged at 1500 rpm for 5 min. Oil was decanted using a pipet and the rag layer was removed with a small spatula. The recovered material was placed in a test tube, diluted with toluene, and sonicated until it was completely dispersed. The test tube was then centrifuged at 6000 rpm for 5 min, and the diluted bitumen and water was decanted with a pipet. The sonication and centrifuge steps were repeated until the supernatant was clear. The residue of fine solids was kept in toluene to maintain their wettability.

Rag Layer Composition Measurement. Rag layers from three diluted froths were examined: (1) from LQOS3 froth diluted with *n*-heptane to a ratio above the asphaltene precipitation point; (2) from AQOS2 froth diluted with *n*-heptane to a ratio above the asphaltene precipitation point; (3) from LQOS3 froth diluted with toluene. The LQOS3 samples were collected after the 1500 rpm centrifuge step and the AQOS2 sample was collected after 1000 rpm centrifuge step. The rag volumes for the AQOS2 froth at 1500 rpm were too small for the experiment. In each case, a minimum of 34 cm³ of rag layer material was collected from one froth sample for each composition measurement. The rag layer material is expected to contain oil, water, solids, and some precipitated asphaltenes. On the basis of the volume of the sample, the compositions are expected to be accurate to within 5 wt %.

The rag layer material was centrifuged at 6000 rpm for 5 min resulting in an oil, water, and sediment layers. The oil layer was decanted, and the mass of the oil (solvent + bitumen) was determined from the change in mass of the test tube. The oil was spread dropwise on Whatman glass microfiber 934-AH filter (1.5 μm pore size). The filter paper had been dried in an oven for at least an hour at 70 °C before it was weighed. After adding the oil, the filter paper was again dried in a fume hood and weighed, and the mass of bitumen was determined from the weight difference.

Water also was decanted, and its mass was determined by weight difference. Since the sediment settled below the water layer, it was assumed to consist of solids in a water-continuous phase. The mass of the water-filled sediment was determined. The sediment was then dried overnight at 80 °C at atmospheric conditions, and the dry weight was determined. The change of mass was assumed to be the water and was added to the previously determined mass of water.

For the heptane diluted rag layers, the dried sediment was dispersed in *n*-heptane by sonication and centrifuged at 4000 rpm for 5 min. The sonication and centrifuge steps were performed until the supernatant was clear. Then the sediment was dried overnight under vacuum at 60 °C and weighed. Since only maltenes are soluble in heptane, the change in mass was assumed to be maltenes. The same procedure was used for washing the dried sediment with toluene and, in this case, the change in mass was assumed to be asphaltenes. For the toluene diluted rag, there were no precipitated asphaltenes because they are soluble in toluene. Therefore, the above procedure was used except that the sediment was washed only with toluene, and the change in mass was assumed to be bitumen.

Micrographs of the Rag Layer. A froth sample from LQOS3 was diluted with *n*-heptane and centrifuged at 1500 rpm for 5 min. Small samples from four different layers from the top to the bottom of the rag layer were transferred using a small spatula to concave glass slides and then covered with glass slip covers. The micrographs were taken with a Carl Zeiss Axiovert S100 inverted microscope equipped with a video camera and Image Pro image analysis software. The size distribution of the emulsified water was determined using the image analysis software on several micrographs and counting at least 600 droplets for each distribution.

Size Distribution of the Rag Layer and Sediment Solids. Solid particles were obtained both from the rag layer and the sediment layers as described previously. The particle size and size distribution of solids were obtained with a Malvern model 2000 Mastersizer particle size analyzer that has a detection range from 0.020 to 2000 μm. Samples were prepared by adding

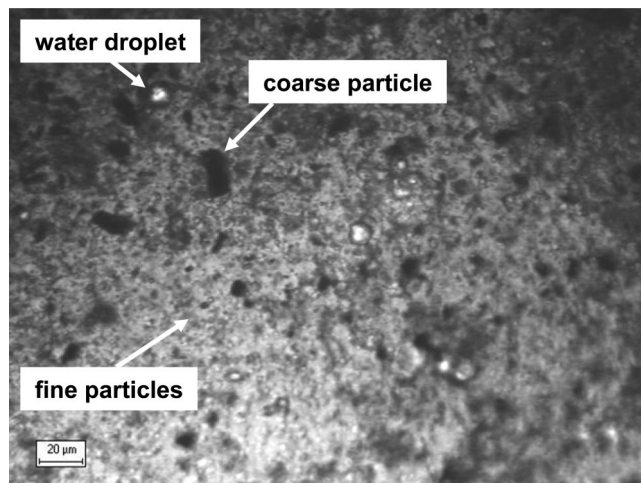


Figure 3. Micrograph of a sample from the top layer of the rag layer from an LQOS3 froth diluted with *n*-heptane at a ratio of 0.66 g/g heptane to bitumen at 23 °C.

approximately 0.2 g of solids to about 20 mL of RO water. Both sonication and heating (80 °C) were used to disperse solids in water.

Floatability of Rag Layer and Sediment Solids. The floatability of the rag layer solids was qualitatively assessed using a mixture of water and methanol. A layer of particles was spread on the surface of a mixture of water and methanol, the methanol content was stepwise increased, and the percentage of floating particles was measured at each step. Larger and more water-wet particles tend to sink at low methanol mole fractions while smaller and more oil-wet particles tend to float as the mole fractions of methanol is increased.

Rag Layer Solids. A glass dish containing a solution of methanol and RO water was placed on the stage of a Carl Zeiss Axiovert S100 microscope. A small cylinder was placed in the dish so that it enclosed a circular area at the methanol/water interface. A layer of solids was spread on the surface by adding droplets of toluene with dispersed solids. Upon evaporation of toluene a thin layer of fines remained on the water surface. Enough solids were added to cover just the surface of the hole. Then, methanol was added to the water to obtain the desired volume fraction and the mixture was mixed by a small magnetic stir bar for one minute. Images were captured with a video camera and analyzed using the Image Pro software. The amount of floating particles was determined from the ratio of the dark area divided by the total area of the hole. The details of the procedure are provided elsewhere.¹⁸

Sediment Solids. Some droplets of toluene with dispersed solids were transferred to the surface of pure RO water in a Petri dish. Almost all of the solids immediately sank. The remaining solids from the water surface were transferred to a small beaker. Both the beaker and the Petri dish were dried for 48 h under vacuum at 50 and 80 °C and the mass determined. Over 95 wt % of the solids sank into the water.

Description of Rag Layer

Micrographs were taken of material from the top and the bottom of the rag layer prepared from LQOS3 froth diluted at various conditions. Figure 3 shows the top layer of a froth diluted with *n*-heptane at a ratio of 0.66 g diluent per 1 g bitumen and centrifuged at 2000 rpm for 5 min. Note, at the S/B ratio of 0.66 g/g no asphaltenes precipitate. Emulsified water and solid particles were observed in all rag layers. The bottom

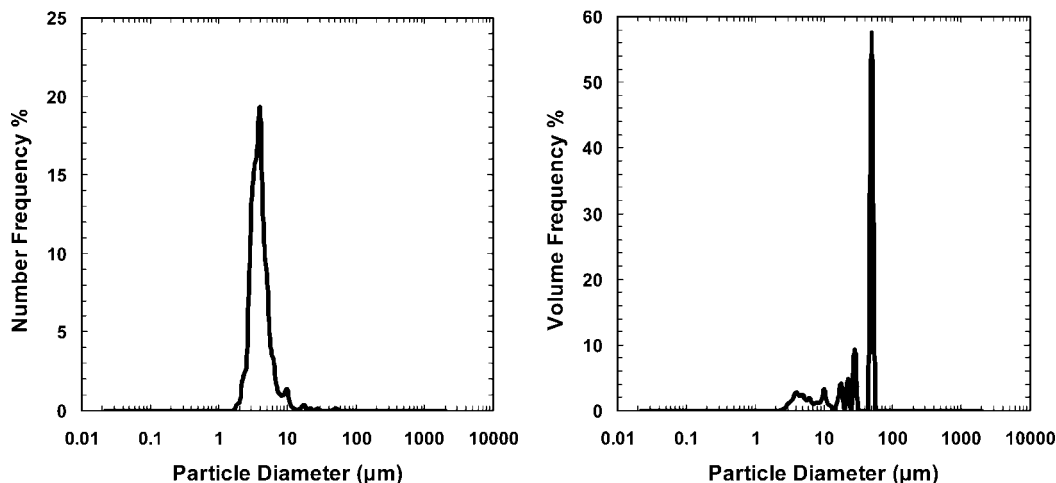


Figure 4. Number and volume frequency of emulsified water droplets in rag layer formed in LQOS3 froth diluted with *n*-heptane at a ratio of 0.66 g/g heptane to bitumen at 23 °C.

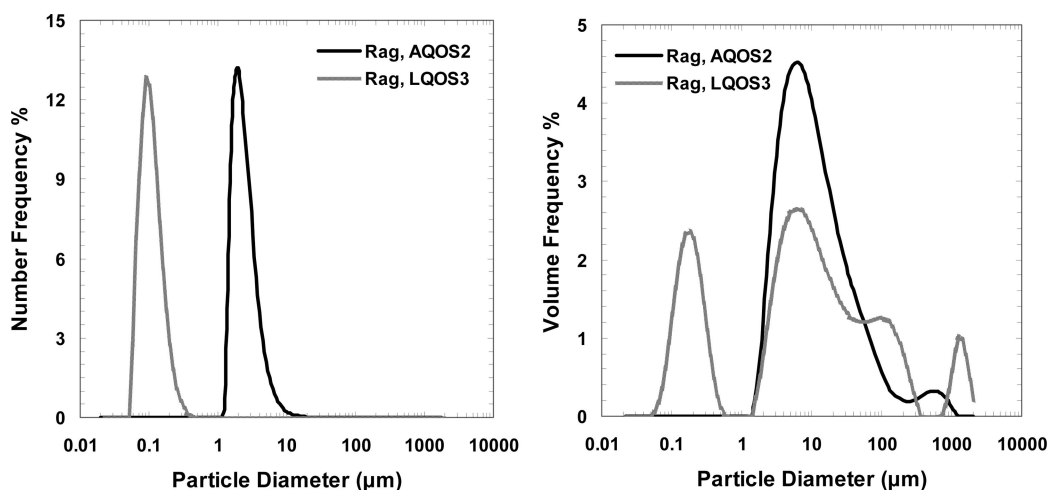


Figure 5. Number and volume frequency of solids in rag layer extracted from LQOS3 and AQOS2 froths diluted with *n*-heptane at a ratio of 0.66 g/g heptane to bitumen at 23 °C.

layer contained larger water droplets and some free water; it also contained more solid particles. In general, the particles were smaller in the upper layers of rag. These observations are expected within a settling process and are consistent with the observations of Chen et al.¹¹

Figure 3 is representative of the many micrographs examined in that they were all oil continuous and contained emulsified water and solid particles. No evidence of complex emulsions was detected from these measurements which were taken under normal light. The micrographs also showed that, after preparation on the microscope slide, fine particles and emulsified water droplets were scattered randomly in the oil phase. Any significant aggregation that may have occurred during settling was disrupted when the samples were collected. This observation suggests that the rag layer is a loose structure of layered materials at the interface rather than a consolidated matrix of fine solids and emulsion.

Emulsified Water and Particle Size Distributions. Figure 4 shows number and volume frequency of emulsified water in the rag layer formed in LQOS3 froth diluted with *n*-heptane. The average drop mean diameter is 6.2 μm . This distribution includes samples from several locations within the rag layer and is intended to indicate the average distribution of the whole rag layer. As noted previously, the drop size increases from the top to the bottom of the rag layer.

Figure 5 shows number and volume frequency of the solids extracted from rag layers in LQOS3 and AQOS2 froths diluted with *n*-heptane. The number mean diameter of the particles from the LQOS3 rag is 0.14 μm , much smaller than the mean diameter of 3.98 μm for the particles from the AQOS2 rag. The volume frequency distribution indicates that the main difference between the LQOS3 and AQOS2 particles is a significant amount of 0.05 to 0.5 μm diameter particles in the LQOS3 sample. The very fine particles in the LQOS3 are of interest because fine particles have been implicated in stabilizing water-in-oil emulsions,¹⁹ which would then contribute to rag layer growth. Indeed, larger rag layers are observed with the LQOS3 froth.

Figure 6 shows the size distribution of the solids extracted from sediment layers in LQOS3 and AQOS2 froths diluted with *n*-heptane. The size distributions for the two samples are similar although the AQOS2 sample contains a broader range of larger particles. The mean particle diameter for the sediment layers from LQOS3 and AQOS2 froths are 4.9 and 5.8 μm , respectively.

Floatability of Solids. Figure 7 shows the floatability of the rag layer solids from the LQOS3 froth. The solids float on water and do not sink until the liquid phase composition reaches 70 vol% methanol. The flotation of the solids depends both on their size and their wettability; that is, smaller more oil-wet solids will sink at higher methanol content. While the effects of size

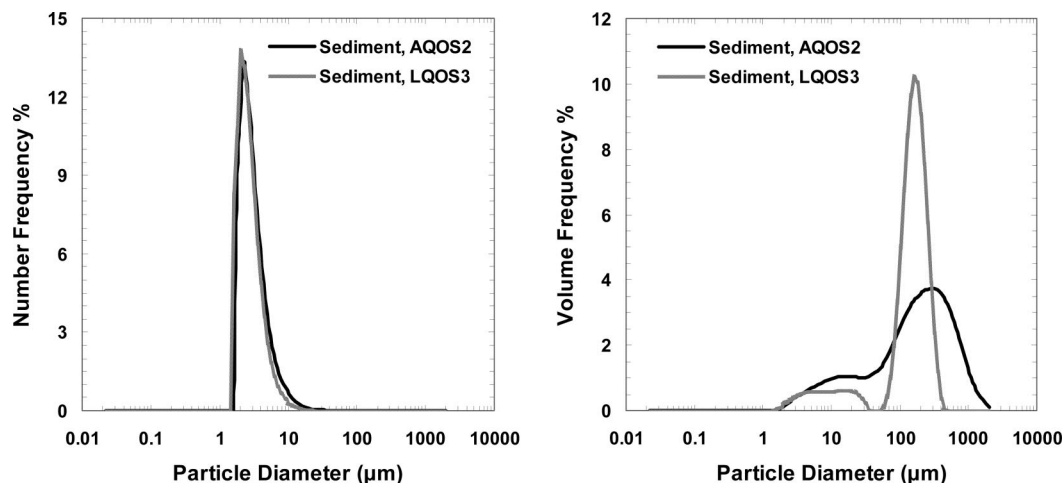


Figure 6. Number and volume frequency of solids in sediment layer extracted from LQOS3 and AQOS2 froths diluted with *n*-heptane at a ratio of 0.66 g/g heptane to bitumen at 23 °C.

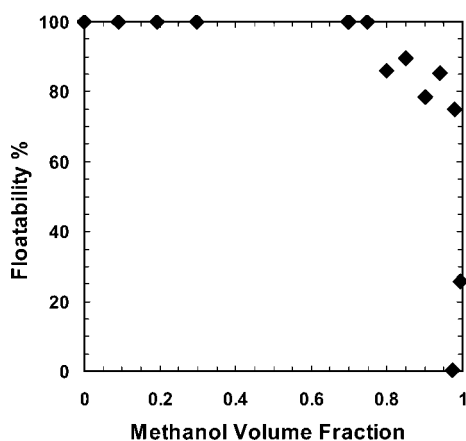


Figure 7. Floatability of fine rag layer solids.

and wettability cannot be separated in this test, the results are consistent with intermediate oil-wet particles. Sztukowski and Yarranton²⁰ found that fine solids from Athabasca oil sands bitumen are plate-like clay particles mainly composed of kaolin minerals. They also observed smaller quantities of nonclay minerals such as pyrite, quartz, and titanium oxide. Kotlyar et al.,^{8,21} studied bitumen-free solids from different grades of Athabasca oil sands. They reported the presence of mica, kaolinite, quartz, and feldspar in these solids and found that the majority of solids appear to be composed of noncrystalline inorganic components. Yan et al.¹⁰ found that asphaltenes tend to adsorb on kaolin clays to form intermediate oil-wet particles. Hence, it is not unexpected that the fine solids from an oil sands froth are intermediate oil-wet particles.

In contrast, over 95% of the coarse solids from the sediment layer settled immediately in water. These relatively large particles are probably water-wet silicates.⁸ The large contrast between the floatability of the rag layer and sediment solids is consistent with the observed settling behavior. The sediment tends to form very rapidly as the coarse water-wet solids settle almost unimpeded. The fine, possibly oil-wet, solids are unable to pass through the free-water layer and collect at the oil–water interface as part of the rag layer.

Rag Layer Composition. Rag layer compositions were measured for two LQOS3 and one AQOS2 froth samples. The froth samples were diluted with toluene and *n*-heptane for the LQOS3 sample. One AQOS2 sample was diluted with *n*-heptane for comparison. The dilution ratios in the froth

Table 4. Composition of Rag Layers from LQOS3 and AQOS2 Froths Diluted with *n*-Heptane or Toluene at 23°C^a

	heptane diluted LQOS3 (wt %)	toluene diluted LQOS3 (wt %)	heptane diluted AQOS2 (wt %)	naphtha diluted Gu et al., 2007 (wt %)
solvent	37.3	42.7	22.3	29.4
bitumen		12.4		15.0 ^b
maltenes	12.3		11.9	
asphaltenes	2.9		9.6	
water	32.1	38.3	45.9	43.2
solids	15.4	6.7	10.2	19.0

^a LQOS3 samples were centrifuged at 1500 rpm, and the AQOS2 sample was centrifuged at 1000 rpm. ^b Includes asphaltenes; the relative proportion of asphaltenes that were precipitated and dissolved in the rag layer was not determined.

treatment were 2.7 g/g heptane-to-bitumen, and 4.1 g/g toluene-to-bitumen. Note, some asphaltenes precipitated in the heptane diluted froth. The compositions are provided in Table 4 and are generally comparable to those reported by Gu et al.⁵ for a rag layer recovered from a naphtha diluted froth. The asphaltene content of the rag layer from the heptane diluted LQOS3 froth is lower than expected but some asphaltenes may have settled to the sediment.

Mechanisms of Rag Layer Formation

Two potential mechanisms for rag layer formation are discussed: a mechanical barrier and slow coalescence. If the froth contains oil-wet materials, they may accumulate at the interface and form a barrier that prevents water and solid particles from passing through. The emulsified water in froths is stabilized by a coating of asphaltenes,²² and hence the surface must be oil-wet. These droplets may not settle through the interface until they coalesce to large sizes or in effect coalesce with the free water layer. If the coalescence rate is slow, a rag layer may accumulate.

Mechanical Barrier. Proof of Concept. To test if accumulated solids could create a barrier at the interface, approximately 10 g/L of precipitated asphaltenes were dispersed in *n*-heptane and placed on top of a layer of RO water. Asphaltenes are oil-wet particles and do not readily settle into water. Hence, they accumulated at the water–oil interface. Water droplets were then pipetted into the oil phase and allowed to settle to interface. The droplets were on the order of 1 mm in diameter. The experiment was performed with

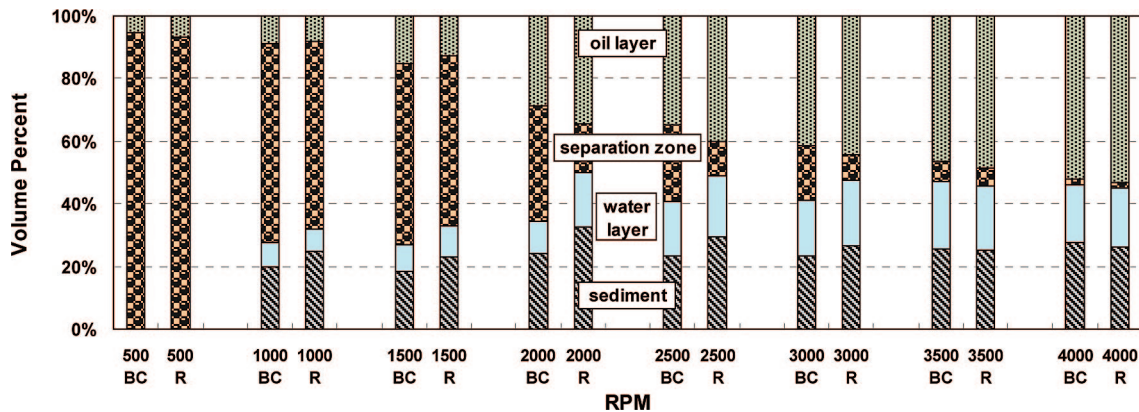


Figure 8. Comparison of rag layer formation from LQOS3 froth (8.5 g/g toluene to bitumen at 23 °C) in a base case stepwise test (BC) with a stepwise test on a sample redispersed after centrifugation at 6000 rpm for 5 min (R).

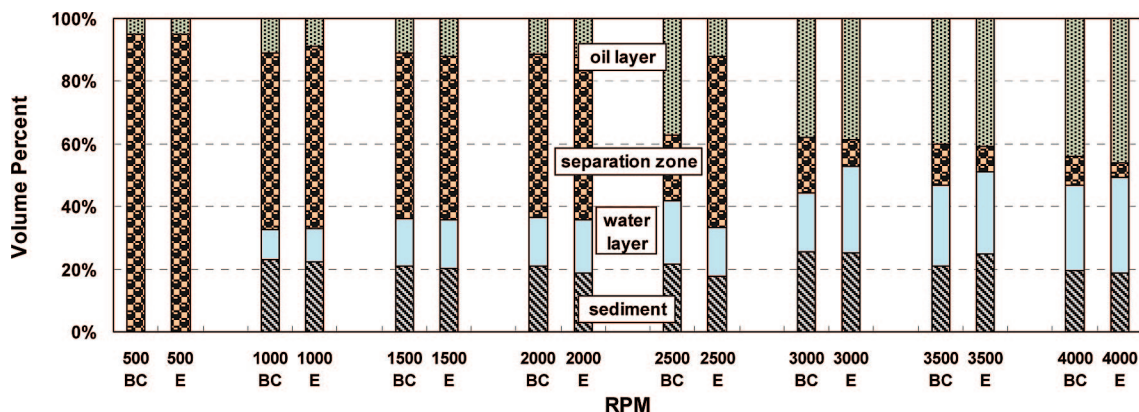


Figure 9. Comparison of rag layer formation from LQOS3 froth (8.5 g/g toluene to bitumen at 23 °C) in a base case stepwise test (BC) with a stepwise test on a sample with 5 vol % added emulsified water (E).

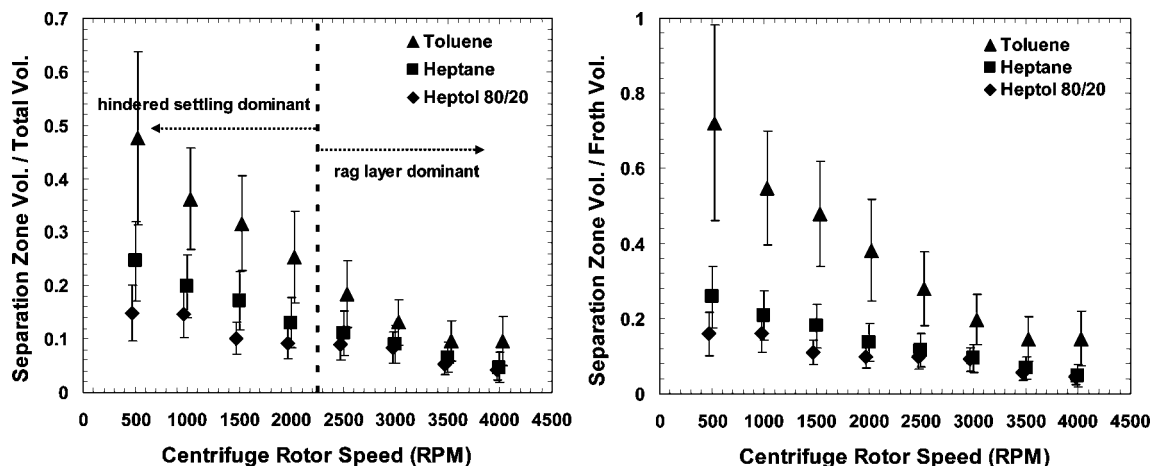


Figure 10. Rag layer volumes from LQOS3 froth for the three different solvents. The data for toluene, heptane and Heptol 80/20 were averages of 10, 10, and 11 trials, respectively, (toluene to bitumen ratios of 4.1 and 8.5 g/g, Heptol 80/20 to bitumen ratio of 0.70, heptane to bitumen ratio of 0.66 g/g, extraction temperatures of 23 and 80 °C, froth treatment temperatures of 23 and 60 °C, NaOH wt % of 0 and 0.04 wt %).

asphaltenes with coprecipitated solids (0.34 wt % fine solids) and with asphaltenes from which the solids had been removed. The results were the same in both cases. (Note, images of the experiment are included in the Supporting Information).

As water droplets were added, the water–oil interface did not rise indicating that the water did not pass through the interface. Even after water droplets equal in volume to the oil phase were added, the water–oil interface was unchanged. Over several hours the droplets near the interface coalesced but only rarely passed through the interface under normal gravity.

However, by applying a low centrifuge force (500 rpm for 5 min), the droplets readily passed through the interface.

A second experiment was conducted using the same procedure but with Heptol 50/50 as the solvent. In this case, the asphaltenes were dissolved in the solvent and no interfacial barrier was anticipated. As expected, the water droplets immediately passed through the interface into the free water layer.

These experiments demonstrate that relatively large water droplets will pass into the water phase unless a mechanical barrier is present. The results confirm that oil-wet solids can

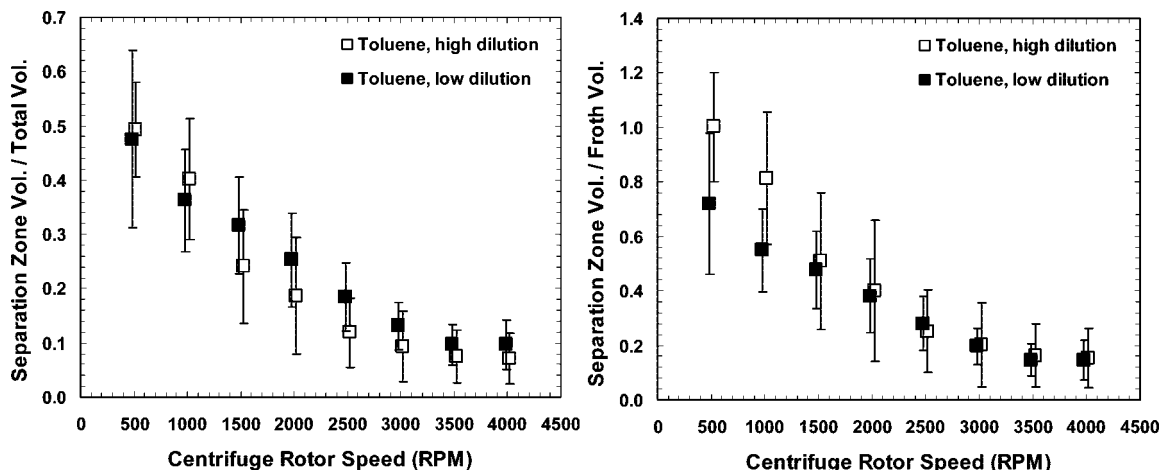


Figure 11. The effect of dilution ratio on rag volumes from LQOS3 froth diluted with toluene. The data at high and low dilution ratios were averages of 9 and 11 trials, respectively, (toluene to bitumen ratios of 4.1 and 8.5 g/g, extraction temperatures of 23 and 80 °C, froth treatment temperatures of 23 and 60 °C, NaOH wt % of 0 and 0.04 wt %).

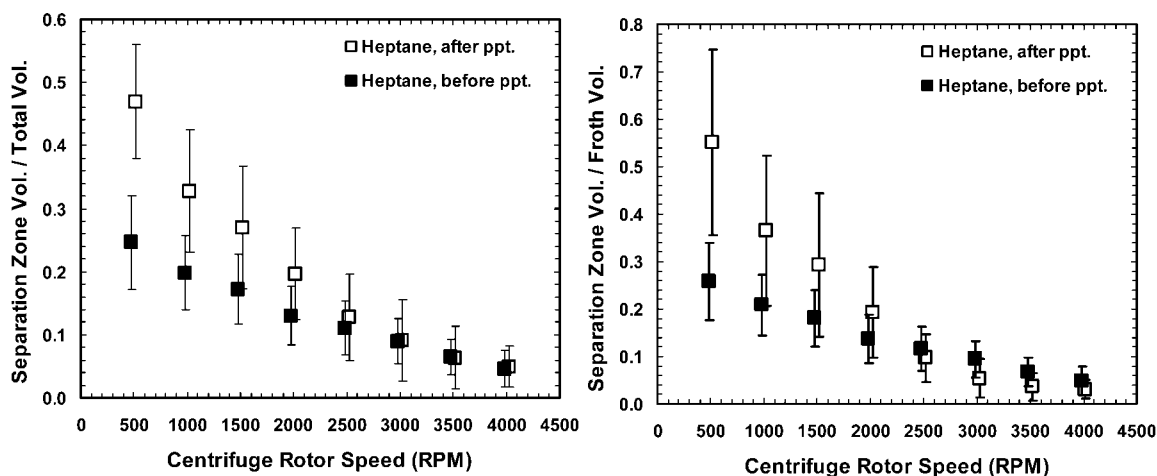


Figure 12. Rag volume and stability in LQOS3 froth diluted with *n*-heptane. The data above and below the asphaltene precipitation point were averages of 10 trials for each case (heptane to bitumen ratios of 0.66 and 2.7 g/g, extraction temperatures of 23 and 80 °C, froth treatment temperatures of 23 and 60 °C, NaOH wt % of 0 and 0.04 wt %).

form a mechanical barrier but the barrier may only be effective at normal gravity or very low centrifuge forces. Note, only relatively large droplets of water were examined. Small droplets of emulsified water are known to accumulate at the interface²³ and may act as a barrier as well.

Contribution of Fine Solids to Mechanical Barrier. Two experiments were conducted to investigate the effect of the quantity of fine solids on rag formation. In both experiments fine solids in the rag layer were extracted and stored in toluene in order to avoid a change in their wettability. However, the quantity of fine solids and the method for extracting the fines were different in both experiments.

In the first experiment, fines were extracted from rag layer by the following method. A sample of LQOS3 froth was diluted with toluene to 2.1 g/g solvent-to-bitumen ratio. The test tube was centrifuged to 4000 rpm for 5 min, and the rag layer was decanted. The rag layer was filtered using a glass microfiber filter 934-AH, 0.3 μm pore size, in a vacuum filter. The filtered rag which contained fine solids was kept in a capped glass to prevent drying. To perform the experiment, filtered rag layer material from two test tubes was added to diluted froth in another test tube. The amount of solids added to the sample by this method was approximately double the original mass of fine solids in the froth; that is, the amount of fines in the froth was

increased from approximately 3 to 9 wt % (undiluted basis). Then a stepwise centrifuge test was conducted and the rag that formed was compared with a similar case in which no fines were added to the test tube. No major differences in the volumes of the rag layers were observed between the two cases.

The second experiment was conducted by adding fine solids extracted from a sample of LQOS3 froth. The fine solids were kept in toluene to preserve their wettability. The solids content in the mixture of toluene and solids was determined as follows. The sample was centrifuged to 6000 rpm for 5 min, and the toluene was decanted from the test tube. While the whole sample was kept in a capped test tube in the refrigerator, a small portion of it was dried overnight in a vacuum oven at 60 °C. The solids content was determined by weight difference to be 52 wt %. Once the composition was known, a mass of wet solids was added to the froth with additional toluene so that the fine solids content in the undiluted froth increased from 3 to 22.7 wt % and the final dilution ratio was 8.3 g/g solvent per bitumen. Finally, a stepwise centrifuge test was conducted and the rag layer volumes were compared to a sample to which no fines had been added. Surprisingly, when fines were added, no rag layer formed at all.

It appears that in this case the addition of small amounts of fine solids has little effect but large amounts prevent rag layer

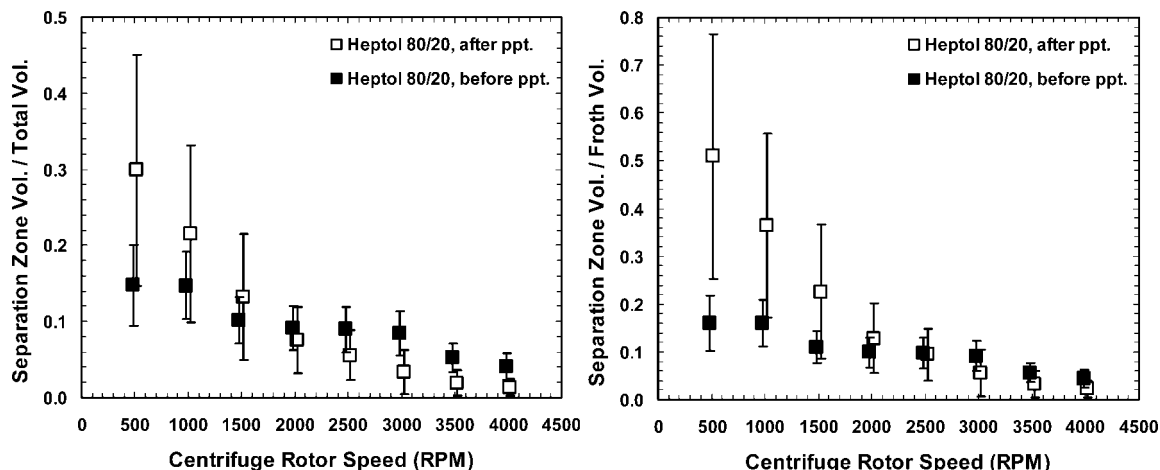


Figure 13. Rag volume and stability in LQOS3 froth diluted with Heptol 80/20. The data above and below the asphaltene precipitation point were averages of 10 and 11 trials, respectively, (Heptol 80/20 to bitumen ratios of 0.70 and 5.1 g/g, extraction temperatures of 23 and 80 °C, froth treatment temperatures of 23 and 60 °C, NaOH wt % of 0 and 0.04 wt %).

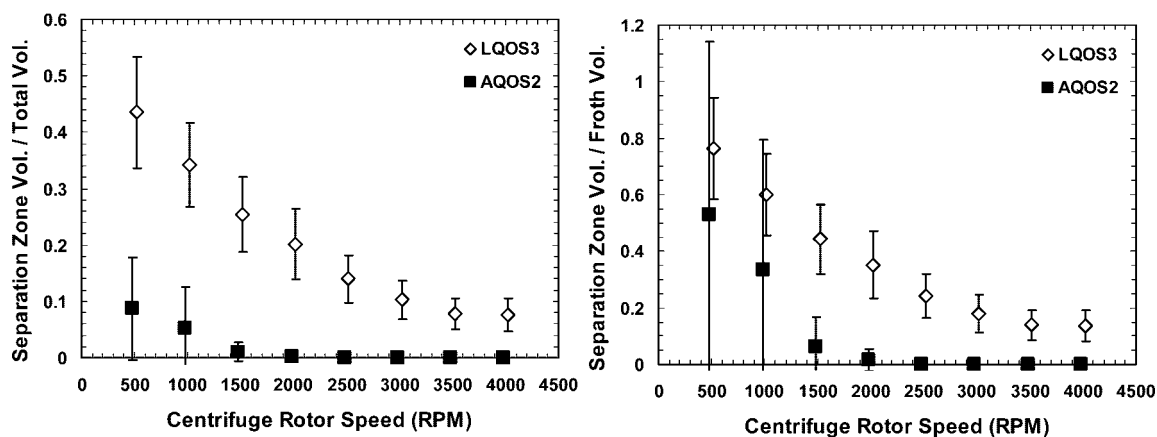


Figure 14. Comparing the rag formation in LQOS3 froth and AQOS2 froth diluted with toluene. The LQOS3 and AQOS2 data were averages of 9 and 2 trials, respectively, (toluene to bitumen ratios of 4.1 and 8.5 g/g, extraction temperatures of 23 and 80 °C, froth treatment temperatures of 23 and 60 °C, NaOH wt % of 0 and 0.04 wt %).

formation. A possible explanation is that adding large amounts of solids might accelerate coalescence. This effect has been observed in oil field emulsions.¹⁹ However, in general, fine solids are expected to stabilize emulsions and therefore increase rag layer growth.¹⁰ It is possible that the solids were altered when they were extracted from the froth. In summary, it appears that precipitated asphaltene can act as a barrier at the interface. The role of the fine solids is not clear, and it is possible in some cases that they may even prevent rag layer formation.

Effectiveness of Mechanical Barrier in Diluted Froth.

While it is clear that mechanical barriers can form at the interface, it is not clear how effective this barrier is in diluted froths. If the mechanical barrier is an important mechanism in rag layer accumulation, disturbing the interface with a small wire is expected to disrupt that barrier and allow some water through. In the following experiment, two samples of LQOS3 froth were diluted with n-heptane to a solvent ratio above the onset of asphaltene precipitation and a stepwise centrifuge test was conducted. The only difference between the two samples was that in one of them the rag layer was stirred with a small wire after each centrifuge step. It was found that mixing had no effect on the rag volume compared with the undisturbed rag layer. This experiment suggests that the mechanical barrier does not play a major role in rag formation.

Slow Coalescence. Let us define “weakly emulsified water” in a froth as relatively large droplets that coalesce easily and

“strongly emulsified water” as relatively small droplets that are slow to coalesce. If there is no strongly emulsified water in the froth and no mechanical barrier, then hindered settling is the only mechanism that is likely to contribute to the separation zone. In this case, the settling behavior of a redispersed diluted froth is expected to be the same as the original diluted froth. Since the mechanical barrier does not appear to be a significant factor, any differences in the settling behavior can be attributed to strongly emulsified water.

Proof of Concept. To determine if hindered settling was the only mechanism for rag formation, a stepwise centrifuge test of a redispersed froth was compared with the same test on a standard sample. The tests were performed on two samples of an LQOS3 froth diluted with 8.5 g/g toluene/bitumen. A stepwise centrifuge test was performed on the first sample as a control or “base case”. The second sample was centrifuged after dilution for 5 min at 6000 rpm to eliminate potential residual emulsified water. Then, the froth was redispersed on a shaker table for 5 min, and a stepwise centrifuge test was performed. The shaker table is capable of dispersing large droplets of water but does not supply sufficient energy to produce very small droplets. The frequency of droplets less than 2 μm in diameter was significantly lower in the redispersed froth (distributions are provided in the Supporting Information).

Figure 8 shows the results of these two experiments. In this figure, columns with “BC” are the base case and columns with

“R” are the redispersed froth. At low centrifuge speeds, the volumes of rag layer in both test tubes are the same; however, at intermediate speeds, the volumes of the redispersed rag layers are consistently smaller than the base case. At higher speeds, there is no clear difference between the two cases. The results indicate that there is strongly emulsified water in the original diluted froth and that this emulsified water appears to coalesce and pass through to the water layer at intermediate speeds. Most of this emulsified water is removed by 3500 rpm and therefore the final rag layer volumes are similar. This experiment suggests that although hindered settling seems to be the dominant effect at low centrifuge speeds, slow coalescence is a key mechanism in rag layer formation.

Confirmation. If reducing the emulsified water from the froth by coalescence can change the rag volume, adding it to the system should change the volume as well. In another experiment two LQOS3 froth samples were diluted to 8.5 g/g toluene-to-bitumen ratio. As with the previous experiment, the first sample underwent a stepwise centrifuge test and was labeled the “base case”. The second sample was first centrifuged to 4000 rpm and its oil layer was transferred to a small glass bottle. Then, 5 volume percent of water was emulsified into the oil with a homogenizer. The oil and emulsified water were then returned to the same froth sample which was first centrifuged at 4000 rpm. The test tube was redispersed, and the stepwise centrifuge test was conducted.

Figure 9 shows the results of this experiment. Columns with “BC” are again the base case and columns with “E” are the case with added emulsified water. Figure 9 shows that, at low centrifuge speeds, the rag layer volumes in both cases are almost the same. However, at intermediate speeds, the volume of the rag layer when emulsified water was added is significantly larger than the base case. There was a 20 vol % increase in rag volume at 2500 rpm from the base case to the emulsified water case. This increase is significantly larger than the typical variation in rag layer volumes; for instance, the difference in rag layer volume at 2500 rpm between the two base cases was approximately 10 vol %. The final rag volumes are similar. This experiment confirms that hindered settling is the dominant mechanism at low speeds but emulsion coalescence is also an important factor. For these diluted froths, coalescence appears to be accelerated at intermediate centrifuge speeds.

Note, an alternate explanation for the differences observed in Figures 8 and 9 could be scatter in the data. However, the average difference between rag layer volumes in the two base cases was 5.7%. The difference between the emulsified water cases and base cases were approximately 32% at intermediate centrifuge speeds. Hence, the differences between the base cases and the emulsified water cases are a result of the emulsion not scatter.

Stability of the Emulsions. The emulsions in the diluted froth tests appeared to destabilize at intermediate centrifuge speeds. To confirm this observation, the following experiment was conducted. Using the same method and sample specifications as in the previous experiment, an emulsion was made in the oil phase decanted from a diluted froth and a stepwise centrifuge test was conducted. As expected, the emulsified water began to break out at 1500 rpm; however, it did not completely break out until 6000 rpm, as shown in the Supporting Information. This result suggests that the other rag components in the original experiment, such as the solids, may weaken the emulsion.

Summary. The experimental data suggest that hindered settling, slow coalescence, and accumulation of oil-wet solids on the water/oil interface all contribute to the volume of the

settling zone. In the first seconds of centrifuging, coarse solids and large water droplets settle rapidly forming a visible sediment and free water layer. If there is sufficient water volume, a water–oil interface rises above the sediment layer. The majority of the fine solids, emulsified water, and asphaltene particles remain dispersed in the early seconds of centrifuging. At these low centrifuge speeds and settling times, hindered settling is the dominant factor and a significant settling zone is present.

At higher speeds and times, fine solids and emulsified water accumulate at the water–oil interface and the pressure and contact is sufficient to promote coalescence. Above the compacted interfacial zone, fine solids and emulsified water continue to settle. At still higher speeds and times, the majority of the particles are in close proximity, the settling zone is predominantly a rag layer, and slow coalescence becomes the dominant effect. Some emulsion droplets coalesce and enter the water phase while a relatively small amount of material still settles from above. Some precipitated asphaltenes, if present, and fine solids are also driven through the interface and end up in the sediment. Note, the continued settling of solids and some asphaltenes was evident from a rise in the sediment height in some cases and some discoloration when asphaltenes settled.

At high speeds and times, only very small fine solids, asphaltenes, and possibly water droplets remain at the interface. Micrographs confirmed that at these conditions only small particles were present. These particles are small enough that the centrifugal force cannot overcome the interfacial forces arising from their wettability. Hence, at the final stage, wettability dominates.

Effect of Process Variables

The effect of extraction temperature, amount of added NaOH, froth treatment temperature, type of diluent, dilution ratio, asphaltene precipitation, and oil sand quality were examined. Only diluent, asphaltene precipitation, and oil sand quality were found to have consistent and significant effects on rag layer formation.

Type of Solvent. Figure 10 shows separation zone volumes for three solvents: *n*-heptane, Heptol 80/20, and toluene. Data from both froth treatment temperatures are combined, and all of the data are below the onset of asphaltene precipitation. The error bars are based on a 90% confidence interval from the data from all of the trials included in the figure. Below 2500 rpm, the separation zone volume is significantly larger in toluene than in the other solvents. The type of solvent has a strong effect in the region where hindered settling is dominant. A likely explanation is that heptane and Heptol 80/20 promote flocculation, more rapid settling, and more compact rag layers. It is well-known that heptane induces flocculation of asphaltenes and asphaltene-coated water droplets.^{23,24} Above 2500 rpm, the rag layer volumes are also lower in the heptane dominated solvents than in toluene. A flocculated system is expected to settle into a more compact volume since the space between droplets and particles is lower.

Figure 11 shows the effect of the dilution ratio on separation zone layers formed in toluene. The initial layer volume is the same in both cases (the left plot). Up to 1500 rpm, the separation zone volume decreases at the same rate as would be expected in the hindered settling region. At 1500 rpm, the low dilution layer is larger. The right-hand plot shows that from this point on, the layer volume is proportional to the amount of froth material. In other words, the layer volume is now controlled by the amount of emulsified water and solids in the system; that is, it is a rag layer.

Asphaltene Precipitation. Figures 12 and 13 show the effect of asphaltene precipitation on separation zone volumes for heptane and Heptol 80/20 froths, respectively. In both cases, at low rpm, asphaltene precipitation significantly increases the layer volume. As expected, oil-wet asphaltene particles accumulate at the interface and contribute to the rag layer volume. These particles may contribute to a barrier at the interface or hinder coalescence. However, above 2500 rpm, the volume of the rag layers with precipitated asphaltenes are smaller than those without precipitation. At these centrifuge speeds, the asphaltenes may be forced through the interface releasing some trapped water at the same time.

Oil Sand Quality. Figure 14 compares separation zone volumes from the LQOS3 and AQOS2 froths diluted with toluene. Data from all of the dilution ratios are included in the averaging. Note, there was so little water in the AQOS2 froth that RO water was added to raise the separation zone above the sediment. Figure 14 shows that the layer volumes from AQOS2 froth are considerably smaller than from the LQOS3 froth. The same trends were found with the other solvents. The reason for this major difference is not known. However, the LQOS3 oil sand contains more fine solids than the AQOS2 oil sand, 28.5 versus 23.6 wt %. The LQOS3 froth contains more total solids than the AQOS2 froth, 30.5 versus 25.9 wt %. Also, as shown in Figure 5, the number frequency of fine solids in rag layers of each oil sand is different. The number mean diameter of the particles from the LQOS3 rag is 0.14 μm , much smaller than the mean diameter of 3.98 μm for the particles from the AQOS2 rag. It is likely that the larger quantity of very fine solids in the LQOS3 oil sand become part of the froth, contribute to emulsion stability, and to larger and more stable rag layers. Note that this observation contradicts the early result that added fine solids eliminated the rag layers. Again, it seems likely that the properties of the added solids were altered during their removal from the froth.

Conclusions

The formation of a separation zone under normal gravity or low centrifugal force at short settling times is mostly controlled by hindered settling. As more centrifugal force is used or at greater residence times, the rag layer volume is determined by the coalescence rate of the emulsified water. Once enough force is applied or time allowed for coalescence to occur, the remaining rag layer appears to consist of small oil-wet particles or asphaltene-coated water droplets; that is, wettability becomes the dominant mechanism.

The separation zone volume is sensitive to the type of solvent in that toluene produced the largest layer volumes while Heptol 80/20 and heptane produced much smaller volumes. The rag layers formed in heptane and Heptol 80/20 are more compact than in toluene, probably because the rag materials are more flocculated. Asphaltene precipitation increased the separation zone volume but decreased the ultimate rag layer volume.

Significantly larger rag layers were formed from the low oil sand quality froth compared to the average oil sand quality froth. The low quality oil sand contained more fine solids which could accumulate at the interface and possibly stabilize the emulsified water.

Acknowledgment

We thank the Consortium—Asphaltenes & Emulsions sponsors, Petrobras, Royal Dutch Shell, Schlumberger, and Syncrude Canada Ltd., for financial support. We thank Syncrude Canada

for supplying bitumen samples. We are also grateful to Elaine Baydak for assistance with the experiments.

Supporting Information Available: Processibility curves (extraction oil recovery and froth composition at different amounts of added NaOH) for the two oil sands; photographs of mechanical barrier experiments; stepwise centrifugation results for the effect of stirring rag layer; comparison of base cases from emulsion tests; comparison of drop size distributions of initial and redispersed froth; stability of homogenized emulsion. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Received for review April 14, 2008

Revised manuscript received August 12, 2008

Accepted September 8, 2008

IE800601R