Using Silicate and pH Control for Removal of the Rag Layer Containing Clay Solids Formed during Demulsification

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Initial processing of Athabasca oil sands obtained from surface mining yields stable water-in-bitumen emulsions. When the bitumen is diluted with naphtha to reduce its viscosity and density, nearly complete separation can be obtained with a suitable coalescer in the absence of clay solids. However, a rag layer forms between the clean oil and free water layers when clay solids are present. We show here that complete separation in this case can be obtained by (a) adding a small amount of sodium silicate during initial emulsion formation to make the solids less oil-wet, (b) removing the clean oil formed following subsequent treatment with a demulsifier and adding sodium hydroxide or sodium silicate with shaking to destroy the rag layer and form a relatively concentrated oil-in-water emulsion nearly free of solids, and (c) adding hydrochloric acid to break the oil-in-water emulsion.

1. Introduction

Stable water-in-oil emulsions, which form in processing Athabasca oil sands from surface mining, are problematic because of clay solids.[1–3] In our previous study, PR_5 [a polyoxyethylene (EO)/polyoxypropylene (PO) alkylphenol formaldehyde resin] was added to the diluted bitumen emulsion system as a coalescer.[4] PR_5 can accelerate the coalescence of water drops, and the system forms an upper clean oil layer and a lower bulk water layer. However, a "rag layer" containing preferentially oil-wet clay solids, oil, and emulsion develops in the middle of the sample and prevents the complete separation of oil, water, and clay solids. In the rag layer, clay solids are associated with oil components (e.g., asphaltenes) in diluted bitumen,[1–6] which will stabilize water-in-oil emulsions.[1–4] To break the rag layer and obtain complete separation, associated oil should be separated from clay solids. pH control is very important to such separation and to emulsion stability.[7] Bitumen

film thinned down and ruptured when increasing the pH to a high level (pH 11).[7] An increase of pH will also change the wettability of sand to be more water-wet, and bitumen can be separated from oil sands.

This paper focuses on reducing or eliminating the rag layer. Sodium metasilicate (Na_2SiO_3) and sodium hydroxide (NaOH) were used to separate the clay solids in the rag layer. Sodium metasilicate can enhance the dispersion of clay solids and minimize bitumen–clay coagulation.[8] Sodium hydroxide or sodium metasilicate can increase the pH and convert naphthenic acids in the oil to soaps, which can emulsify and separate oil from clay solids and form an oil-in-water emulsion. After removal of the free water layer containing the clay solids, hydrochloric acid (HCl) was added to the emulsion layer to break this oil-in-water emulsion and achieve final separation.

2. Materials and Methods

2.1. Materials. Samples of Athabasca bitumen from the flotation process were provided by Syncrude Canada Ltd. Diluted bitumen samples were prepared by diluting with naphtha with the ratio of 0.7 (naphtha/bitumen, w/w). The density of diluted bitumen with a dilution ratio of 0.7 is 821 kg/m^3, and the viscosity is 7.10×10^{-3} Pa s (50 °C). The diluted bitumen contains 1 wt % solids and <2 wt % water, which can be measured by centrifugation. Most of the solids and water can be removed by the centrifuge process, with a centrifugal acceleration of 3500g and a centrifuge time of 30 min.

Unless otherwise stated, the aqueous phase used here is synthetic brine with 2.5×10^{-2} M NaCl, 1.5×10^{-2} M NaHCO$_3$, 2×10^{-3} M Na$_2$SO$_4$, 3×10^{-4} M CaCl$_2$, and 3×10^{-4} M MgCl$_2$. The pH of synthetic brine is 8.3.

2.2. Water-in-Oil Emulsion Preparation. Emulsion samples (60 mL) were prepared by mixing 50 vol % brine and 50 vol % diluted bitumen in a glass tube (outer diameter of 48 mm, inner diameter of 44 mm, and length of 230 mm) with a six-blade turbine (Figure 1).[4] The stirring speed of the turbine was 3600 rpm, and

(1) Kotlyar, L.; Sparks, B.; Woods, J.; Raymond, S.; Le Page, Y.; Shelfantook, W. Distribution and types of solids associated with bitumen. *Pet. Sci. Technol.* **1998,** *16* (1 and 2), 1–19.
(2) Yang, X.; Wang, S. Investigation and characterization of fine solids isolated from a froth treatment plant. SPE/PS-CIM/CHOA 97788.
(3) Sztukowski, D.; Yarranton, H. Oilfield solids and water-in-oil emulsion stability. *J. Colloid Interface Sci.* **2005,** *285,* 821–833.
(4) Jiang, T.; Hirasaki, G. J.; Miller, C. A.; Moran, K.; Fleury, M. Diluted bitumen water-in-oil emulsion stability and characterization by nuclear magnetic resonance (NMR) measurements. *Energy Fuels* **2007,** *21* (3), 1325–1336.
(5) Sparksa, B.; Kotlyara, L.; O'Carroll, J.; Chung, K. Athabasca oil sands: Effect of organic coated solids on bitumen recovery and quality. *J. Pet. Sci. Eng.* **2003,** *39,* 417–430.
(6) Tu, Y.; Kingston, D.; Kung, J.; Kotlyar, L.; Sparks, B. Adsorption of pentane insoluble organic matter from oilsands bitumen onto clay surfaces. *Pet. Sci. Technol.* **2006,** *24,* 327–338.
(7) Basu, S.; Nandakumar, K.; Masliyah, J. On bitumen liberation from oil sands. *Can. J. Chem. Eng.* **1997,** *75,* 476–479.

(8) Li, H.; Zhou, Z.; Xu, Z.; Masliyah, J. Role of acidified sodium silicate in low temperature bitumen extraction from poor-processing oil sand ores. *Ind. Eng. Chem. Res.* **2005,** *44,* 4753–4761.
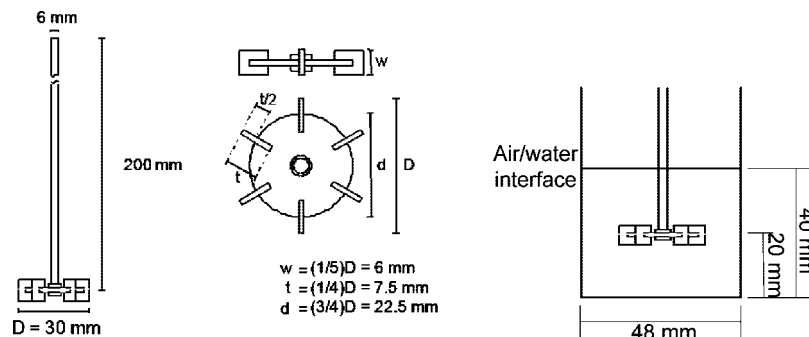
Figure 1. Sketch of the mixer and emulsion preparation.

Table 1. Emulsion Samples with Different Alkali at Different pH

sample	Na_2SiO_3 (M)	NaOH (M)	initial pH^a	equilibrium pH^b
1			8.3	8.0
2	1.0×10^{-4}		8.5	8.0−8.5
3		2.0×10^{-4}	8.5	8.0−8.5
4	2.0×10^{-4}		8.8	8.5
5		4.0×10^{-4}	8.8	8.5
6	1.0×10^{-4}	2.0×10^{-4}	8.8	8.5

a The initial pH of brine was measured with a pH meter without contacting diluted bitumen. *b* The equilibrium pH of brine was measured with pH test paper when the brine reached equilibrium with diluted bitumen.

Table 2. Emulsion Samples with Different Alkali at Different pH after Removing the Top Clean Oil Layer

sample	Na_2SiO_3 (M)	NaOH (M)	shaking	initial pH^a	equilibrium pH^b
7			without	8.5	8.0−8.5
8		2.0×10^{-4}	without	8.8	8.5
9			with	8.5	8.0−8.5
10		2.0×10^{-4}	with	8.8	8.5
11	1.0×10^{-4}		with	8.8	8.5

a The initial pH of brine was measured with a pH meter without contacting diluted bitumen. *b* The equilibrium pH of brine was measured with pH test paper when the brine reached equilibrium with diluted bitumen.

the mixing time was 10 min at the desired temperature. Different additives (e.g., Na_2SiO_3) were added to the brine prior to emulsion preparation. The initial pH of brine was measured with a pH meter without contacting diluted bitumen. The equilibrium pH of brine was measured with pH test paper when the brine reached equilibrium with diluted bitumen.

2.3. Water-in-Oil Emulsion Coalescence. PR_5 (200 ppm, on the basis of the total volume of the emulsion sample) was added to the emulsion samples immediately after the preparation. Afterward, all of the samples were shaken by hand at the same time for 1 min and then stored at 50 °C. The photographs and photomicrographs of the samples were taken at ambient temperature shortly after removing samples from the oven. After photography, the samples were put back into the oven for storage. One-dimensional T_1 weighted profile nuclear magnetic resonance (NMR) measurements of the samples were performed at 30 °C to obtain the water fraction profile of the whole sample in the vertical direction.[4] Water and oil have different NMR relaxation times T_1. On the basis of the T_1 differences of water and oil, the water fraction profile of the whole sample can be calculated from the NMR signal amplitude.[4]

In the experiment, NaOH or Na_2SiO_3 was added to the aqueous phase to change the pH before emulsion preparation. Sample 1 was prepared as a control without silicate. The initial pH of the brine measured by the pH meter was 8.3. The equilibrium pH of the brine separated from the emulsion after the addition of PR_5 was 8.0, which was measured by pH test paper. Sample 2 was prepared with 1.0×10^{-4} M silicate. The initial pH of the brine was 8.5. The equilibrium pH of the brine was between 8.0 and 8.5. Other combinations of alkali and pH (samples 3−6) were tried as shown in Table 1.

2.4. Clay Solids Separation from the Rag Layer. Emulsion samples were prepared with silicate at an initial pH of 8.5 as described in Section 2.2. PR_5 (200 ppm) was added to the emulsion samples immediately after the preparation. The top clean oil layer was removed 1 day after adding PR_5. After the clean oil layer was separated, five samples were prepared for comparison. Samples 7−11 were prepared as shown in Table 2. Pictures were taken 1 day later.

2.5. Separation of Oil-in-Water Emulsion. A total of 30 mL of an oil-in-water diluted bitumen emulsion was prepared with 20 vol % diluted bitumen and 80 vol % synthetic brine. PR_5 (200 ppm) was added to the diluted bitumen before emulsion preparation. Silicate (1×10^{-4} M) and NaOH (2×10^{-4} M) were added to the

synthetic brine to increase the initial pH to 8.8. Then, the emulsion sample was formed by shaking the bottle for 1 min at ambient temperature. Several drops of 1.0 M HCl were added to the samples immediately after emulsion preparation. The samples were put into the oven at 50 °C. The pH was measured by pH paper when the system reached equilibrium.

After finding the optimal separation conditions in each step (Sections 2.3−2.5), the entire three-step procedure was performed. A total of 60 mL of water-in-oil diluted bitumen emulsion was prepared with 50% diluted bitumen and 50% synthetic brine with 1×10^{-4} silicate at 50 °C, as described in Section 2.2. PR_5 (200 ppm) was added to 30 mL of emulsion sample immediately after preparation. The clean oil layer was removed 1 day after emulsion preparation. NaOH (2×10^{-4} M) was added to the aqueous phase to increase the initial pH to 8.8 with shaking. The emulsion and solid layers were separated 1 day later. A total of 0.15 mL of 1 M HCl was added to the emulsion layer to lower the equilibrium pH to 5.0.

2.6. Microscopy Observations. Slides were prepared by sampling from different positions of emulsion samples for making microscopy observations. In the observation of clay solid "skins" in the rag layer, the pH of the aqueous phase was increased from 8.5 to 9.5 by adding 0.1 M NaOH. The skins were observed for 10 min before adding NaOH. Then, NaOH was added at time zero. Photomicrographs of clay solids skins were taken as the function of time. In the observation of oil-in-water emulsions, the pH of the aqueous phase was decreased from 8.8 to 4.5 by adding 0.1 M HCl. The oil-in-water emulsions were observed for 10 min before adding HCl. Then, HCl was added at time zero. Photomicrographs of clay solids skins were taken as the function of time.

3. Results and Discussion

The separation procedure can be divided into three steps. The first step is emulsion coalescence and clean oil separation with PR_5 and silicate. The second step is clay solids separation from the rag layer by increasing pH and shaking. The last step is separation of the resulting oil-in-water emulsion by lowering the pH. Each step is studied to find optimal separation conditions.

3.1. Emulsion Coalescence and Clean Oil Separation. *3.1.1. Effects of Na_2SiO_3 and Shaking.* Figure 2 shows emulsion sample photographs and water fraction profiles measured with
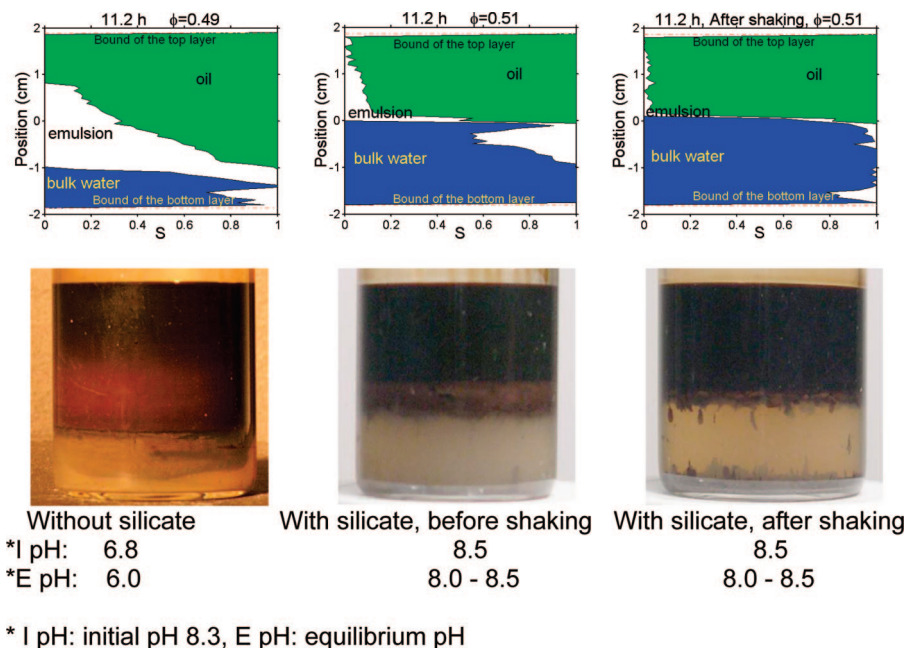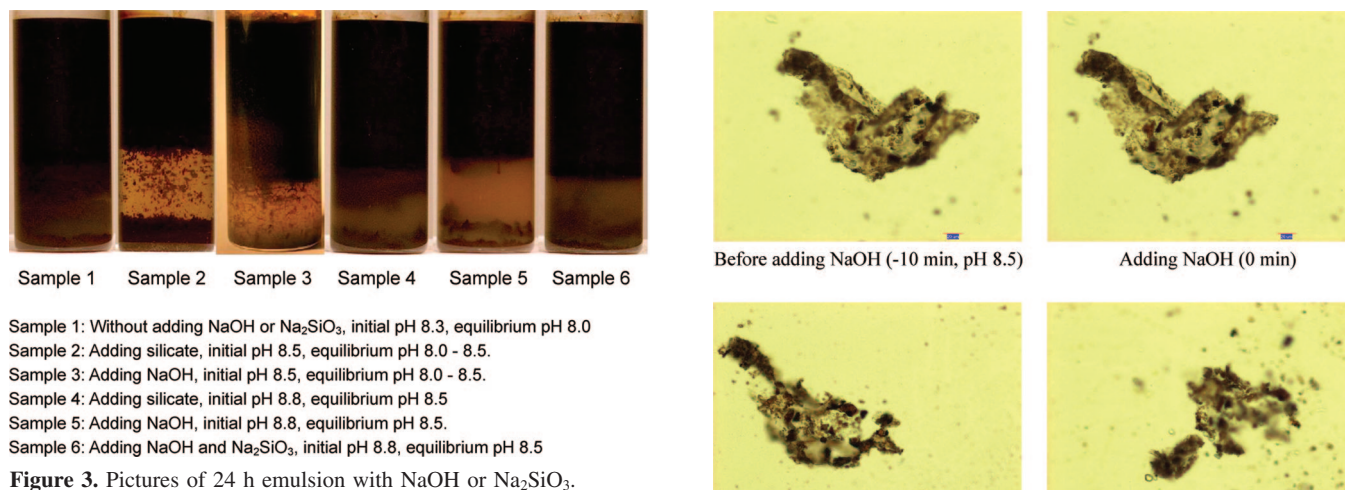
Figure 2. Water fraction profile of 11.2 h emulsion.

Sample 1: Without adding NaOH or Na$_2$SiO$_3$, initial pH 8.3, equilibrium pH 8.0
Sample 2: Adding silicate, initial pH 8.5, equilibrium pH 8.0 - 8.5.
Sample 3: Adding NaOH, initial pH 8.5, equilibrium pH 8.0 - 8.5.
Sample 4: Adding silicate, initial pH 8.8, equilibrium pH 8.5
Sample 5: Adding NaOH, initial pH 8.8, equilibrium pH 8.5.
Sample 6: Adding NaOH and Na$_2$SiO$_3$, initial pH 8.8, equilibrium pH 8.5

Figure 3. Pictures of 24 h emulsion with NaOH or Na$_2$SiO$_3$.

the 1D T_1 weighted profile method[4] of the emulsion samples 11.2 h after preparation. The first one is the sample without Na$_2$SiO$_3$ using diluted bitumen and 1% NaCl brine adding PR$_5$ (sample 2 in previous work[4]); the second one is the sample with Na$_2$SiO$_3$ before shaking using diluted bitumen and synthetic brine adding PR$_5$; and the third one is the second sample after shaking. In the profile figures, the red dashed lines represent the boundaries of the sample. The total height is a little less than 4 cm. The x axis S is the emulsified or free water saturation of the sample, and the y axis position is the position measured from the middle of the sample. Φ is water volume fraction in the total sample measured by NMR. In the profile figure, the green part is the clean oil fraction; the blue part is the bulk water fraction; and the white part is the emulsified water fraction. The upper part has oil and emulsified water, corresponding to the water-in-oil emulsion. If the water fraction is 0, it is separated clean oil. The lower part has bulk water and emulsified water, corresponding to the rag layer. If the water fraction is 1, it is separated free water. On the basis of the water fraction profiles and pictures of the samples, it is easy to find that the top is clean oil, the middle consists of an emulsion layer and a rag layer, and the bottom is mostly separated free water.
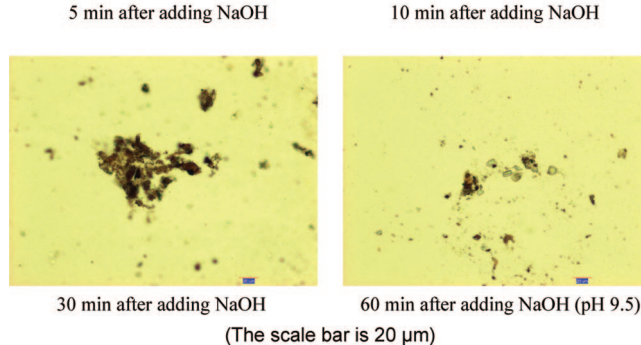

Figure 4. Clay solids skins with time when increasing pH from 8.5 to 9.5.

The separation results for the three samples are different. The sample without silicate does not reach complete separation. An emulsion layer with about 1.5 cm thickness lies under separated oil layer. A rag layer forms above the separated water layer with a thickness of about 0.5 cm. The sample with silicate before shaking also has a rag layer in the middle, but it has no obvious emulsion layer. After shaking, the thickness of the rag layer is reduced to 1−2 mm and more clay solids settle to the bottom.

Sample 7 Sample 8 Sample 9 Sample 10 Sample 11
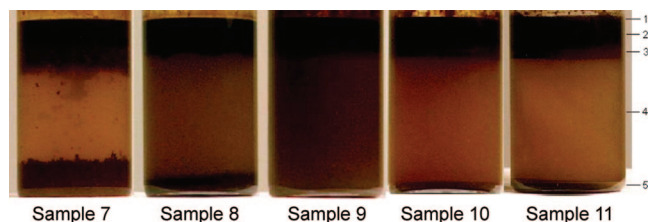
1. Top of the rag layer
2. Middle of the rag layer
3. Bottom of the rag layer
4. Water layer
5. Solids layer

Sample 7: Without adding NaOH or Na_2SiO_3, initial pH 8.5, equilibrium pH 8.0 - 8.5.
Sample 8: Adding NaOH without shaking, initial pH 8.8, equilibrium pH 8.5.
Sample 9: With shaking, without NaOH, initial pH 8.5, equilibrium pH 8.0 - 8.5.
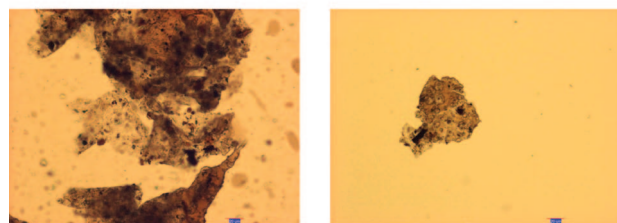Sample 10: Adding NaOH with shaking, initial pH 8.8, equilibrium pH 8.5.
Sample 11: Adding Na_2SiO_3 with shaking, initial pH 8.8, equilibrium pH 8.5.
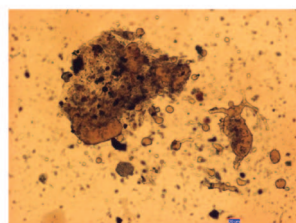
Figure 5. Pictures of 24 h emulsion after the top clean oil layer was removed.
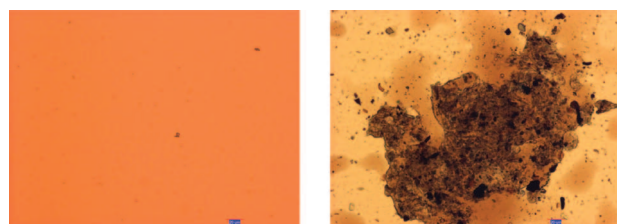
1. Top of the oil layer   2. Middle of the oil layer

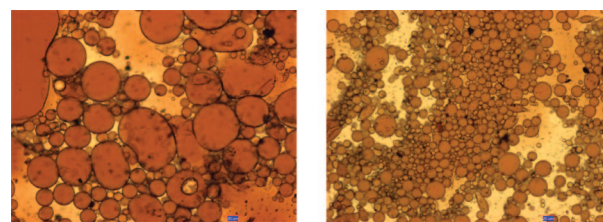3. Near oil/water interface   4. Water layer

5. Solids layer
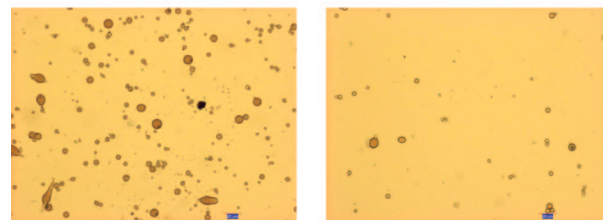(The scale bar is 20 μm)
(Equilibrium pH 8.0 − 8.5)

Figure 6. Emulsion (24 h) without changing pH or shaking (sample 7).

On the basis of the comparison of three samples, adding silicate with shaking can obtain a better separation and thinner rag layer.
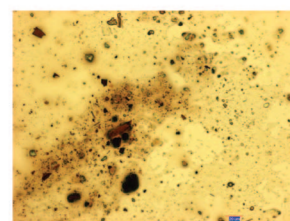
Most of the clay solids in Athabasca bitumens are kaolinite and illite.[9] The basal surface of kaolinite is negatively charged, while the edge surface of kaolinite is positively charged.[10] The positively charged edges of the solids will adsorb negatively charged components of the oil (e.g., naphthenic acid ions) and

(9) Mercier, P. H.; Patarachao, B.; Kung, J.; Kingston, D. M.; Woods, J. R.; Sparks, B. D.; Kotlyar, L. S.; Ng, S.; Moran, K.; McCracken, T. XRD-Derived Processability Markers for Oil Sands Based on Clay Mineralogy and Crystallite Thickness Distributions. *Energy Fuels* **2008**, *22*, 3174–3193.

1. Top of the oil layer   2. Middle of the oil layer

3. Near oil/water interface   4. Water layer

5. Solids layer
(The scale bar is 20 μm)
(Equilibrium pH 8.0 − 8.5)

Figure 7. Emulsion (24 h) with shaking, without adding NaOH (sample 9).

make that portion of clay solids preferentially oil-wet. The partially oil-wet clay solids can stabilize water-in-oil emulsion and retard emulsion coalescence.[1−4] The addition of PR_5 results in coalescence of water drops, but the clay solids contribute to the formation of rigid skins dispersed in water (Figure 6 has a microscopy picture of skins near the water-in-oil interface). They also entrap oil drops, which results in a rag layer having an intermediate density lying in the middle of the sample. If the anionic silicate ions can adsorb on the positively charged edges of the solids, the positively charged edges will become neutral or negatively charged. The surface charge will become more negative; negatively charged naphthenic acid ions will prefer not to adsorb onto the clay solids; and the surface of the solids will be more hydrophilic. As a result, some of the adsorbed oil on the solid surface can be replaced by water, and the density of the rag material will be greater than that of water, causing it to settle to the bottom.

3.1.2. Effects of pH. The results of the preceding section strongly suggest that adding silicate decreases the amount of rag layer formed, thereby improving the separation of oil and water phases. However, because brine compositions were different for the samples with and without silicate, the following experiments were performed to confirm the favorable effect of silicate and find the optimal pH.

Emulsion samples were prepared with synthetic brine and diluted bitumen with a dilution ratio of 0.7 at 50 °C, which is close to the practical operation condition. On the basis of the results of "bottle test" experiments, PR_5 is still the optimal coalescer for the new conditions.

(10) Tombácz, E.; Szekeres, M. Surface charge heterogeneity of kaolinite in aqueous suspension in comparison with montmorillonite. *Appl. Clay Sci.* **2006**, *34*, 105–124.
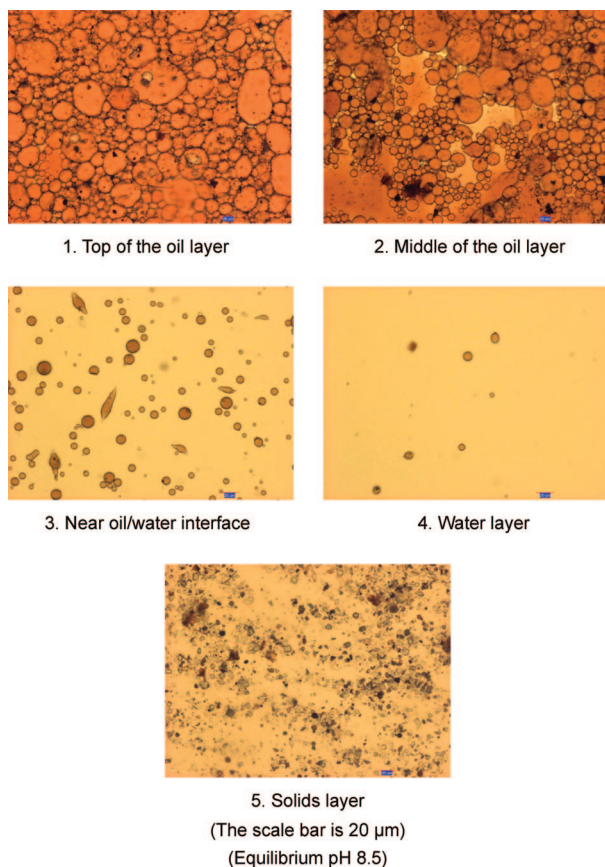
1. Top of the oil layer

2. Middle of the oil layer

3. Near oil/water interface

4. Water layer

5. Solids layer
(The scale bar is 20 μm)
(Equilibrium pH 8.5)

Figure 8. Emulsion (24 h) adding NaOH with shaking (sample 10).

Figure 3 shows pictures of the six emulsion samples prepared as described in Section 2.3. From Figure 3, we see that samples 2 and 3 have clearer aqueous phases than others. Sample 2 has more separated free water and a thinner rag layer. Therefore, sample 2 with silicate at an initial pH 8.5 has the best emulsion separation results.

3.2. Clay Solids Separation from the Rag Layer (Effects of pH and Shaking). From Figure 2, we see a rag layer containing aggregates of clay solids and oil in the middle of the sample. In this section, we show that a second step of the separation involving an increasing pH of the system can emulsify the oil to form an oil-in-water emulsion and separate oil from clay solids.

Figure 4 shows the photomicrographs of clay solids skins with time when increasing pH from 8.5 to 9.5 as described in Section 2.6. Before NaOH was added, the skins did not change in 10 min. After NaOH was added, the skins became smaller gradually and disappeared. Finally, only clay solids remained. Clay solids and the oil form rigid skins. Athabasca bitumen has a relatively high acid number (total acid number of 3.3 mg of KOH/g of oil).[11] With an increase of pH, additional naphthenic acids in the oil form soaps and separate the oil from clay solids. Therefore, an increasing pH can break the skins.

On the basis of the discussion in Section 3.1.2, sample 2 with silicate at an initial pH of 8.5 has the best emulsion separation results. In the second step, emulsion samples were prepared starting with sample 2 of Table 1. After the clean oil layer was separated, five samples were prepared as described in Section 2.4.
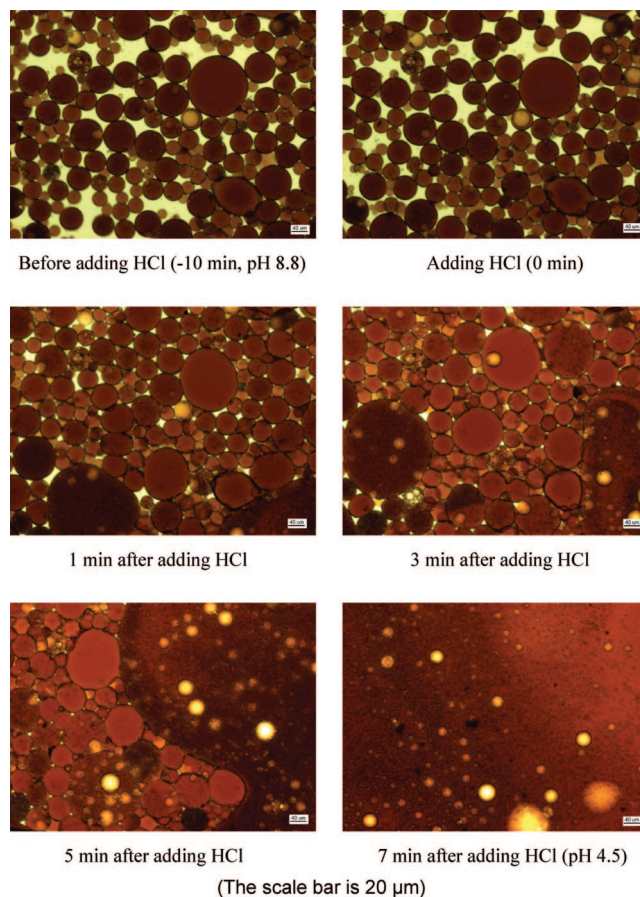
(11) Fuhr, B.; Banjac, B.; Blackmore, T.; Rahimi, P. Applicability of total acid number analysis to heavy oils and bitumens. *Energy Fuels* **2007**, *21*, 1322–1324.

Before adding HCl (-10 min, pH 8.8)

Adding HCl (0 min)

1 min after adding HCl

3 min after adding HCl

5 min after adding HCl

7 min after adding HCl (pH 4.5)
(The scale bar is 20 μm)

Figure 9. Oil-in-water emulsions with time when lowering pH from 8.8 to 4.5.

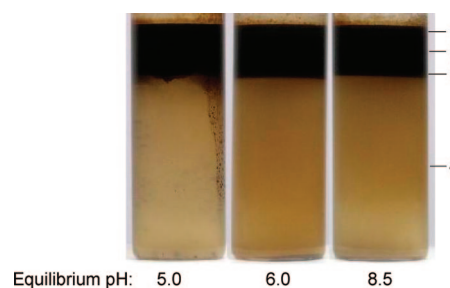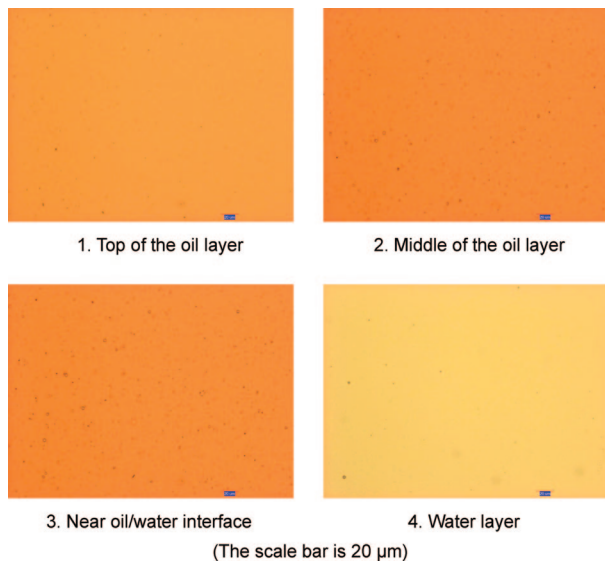Equilibrium pH: 5.0   6.0   8.5

Figure 10. Pictures of 24 h emulsion samples adding HCl.

Figure 5 shows photographs of the five samples after 1 day. All of them have a layer containing oil on the top and a solids layer at the bottom. The samples that were not shaken have loose solids layers. The samples that were shaken have more compact solids layers.

Figures 6−8 show photomicrographs obtained by sampling from the five different positions indicated in Figure 5. Sample 7 (Figure 6), which is not shaken, exhibits rigid skins in the rag layer. Sample 8 has similar results, although the pH was increased. In contrast, all three samples that are shaken exhibit oil-in-water emulsions at the two highest sampling positions. A few skins are seen in the lowest sampling position of sample 9, where nothing was added and pH remained at 8.5 (Figure 7). No skins are seen for samples 10 (Figure 8), where pH was raised to 8.8. Sample 11 has similar results to sample 10.

On the basis of a comparison of the five samples, increasing the pH alone can not separate oil from clay solids. Shaking alone can offer external energy and separate part of the oil from clay solids, but the skins of clay solids do not completely disappear.

Figure 11. Emulsion (24 h) adding HCl (equilibrium pH 5.0).
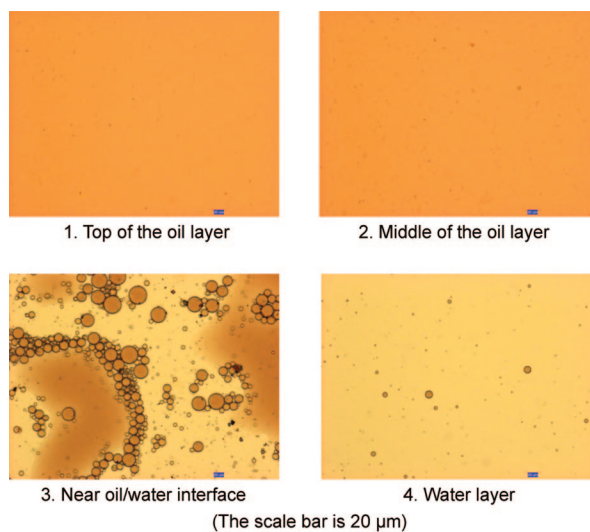
Figure 12. Emulsion (24 h) sample adding HCl (equilibrium pH 6.0).

Figure 14. Microscope pictures from different positions of the sample at pH 8.8.

Figure 15. Microscope pictures from different positions of the sample at pH 5.0.

A combination of increasing pH and shaking can separate the oil from clay solids and destroy all of the skins. After the top clean oil layer was removed, increasing the pH of emulsion samples using NaOH or Na_2SiO_3 (samples 10 and 11) has similar separation results. Therefore, increasing the pH to 8.8 with shaking is a good method for the separation of clay solids.

3.3. Separation of Oil-in-Water Emulsion (Effects of pH). In the second step of the separation procedure described in
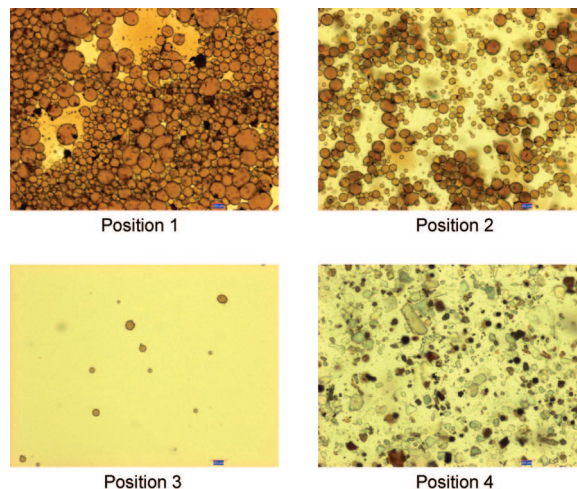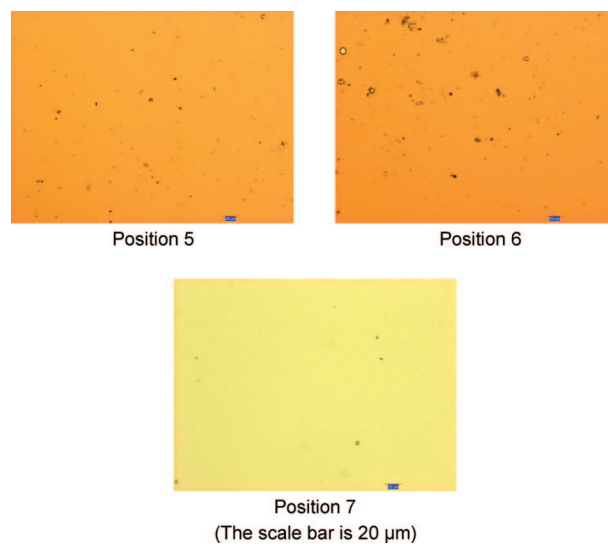
Section 3.2, increasing pH and shaking caused the formation of an oil-in-water emulsion. To break this emulsion, the pH of the aqueous phase needs to be lowered in a third step. In this section, experiments are described in which hydrochloric acid (HCl) was used to find the optimal pH for demulsification.

Figure 9 shows the photomicrographs of oil-in-water emulsions with time when lowering the pH from 8.8 to 4.5, as described in Section 2.6. Before HCl was added, the oil-in-water emulsions did not coalesce in 10 min. After HCl was
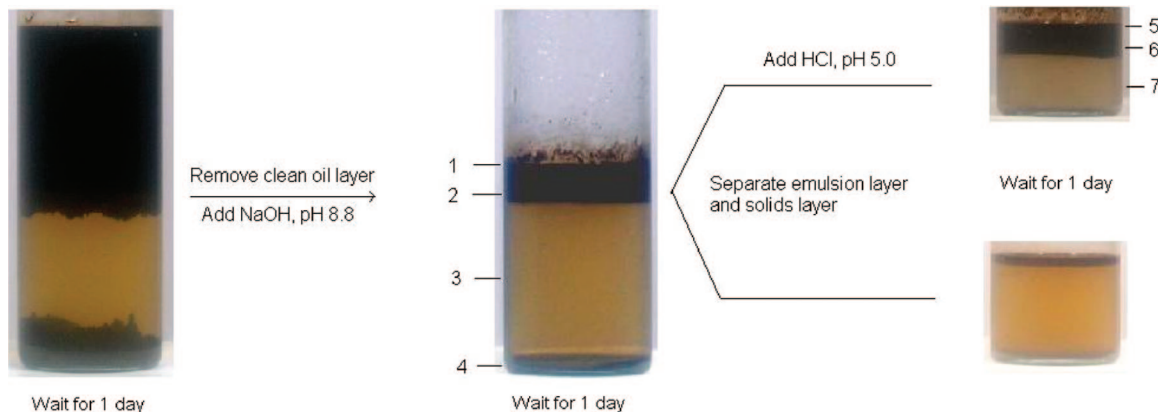

Figure 13. Pictures of the emulsion during the whole operation procedure.

added, the oil-in-water emulsions coalesced very fast and formed a continuous oil phase finally. With the decrease of pH, soaps will form naphthenic acids and destabilize the oil-in-water emulsions.

The following experiments were performed to find the optimal pH for oil-in-water emulsion coalescence, as described in Section 2.5. Figure 10 shows photographs of three samples after 24 h, having equilibrium pH values ranging from 5.0 to 8.5. As pH decreases, the water layer becomes more transparent.

Figures 11 and 12 show the photomicrographs of samples at equilibrium pH 5.0 and 6.0. At pH 6.0 (Figure 12), the top of the oil layer is clean oil. At the bottom of the oil layer is the oil-in-water emulsion with a relatively low oil concentration. At pH 8.5, the emulsion has a similar result to that at pH 6.0. At pH 5.0 (Figure 11), the top of the oil layer is clean oil but, in this case, the bottom of the oil layer is oil with a few drops of dispersed water. The water layer is also almost clean. Emulsion samples at pH 5.0 and 6.0 have different emulsion types. Thus, the original oil-in-water emulsion remains stable at pH 6.0 but not at pH 5.0.

This experiment shows that the oil-in-water emulsion can be broken at a low pH level, i.e., 5.0 or lower. The study of interfacial properties of emulsified bitumen droplets also shows that bitumen drops are unstable at low pH.[12] When the pH is low enough, all of the soap will form naphthenic acid. The system will prefer to form a water-in-oil emulsion. However, because the oil layer contains PR$_5$, water-in-oil emulsions are not stable in the absence of clay solids. Thus, clean oil and bulk water layers can be obtained.

Figure 13 shows the photographs for an experiment in which the entire three-step procedure was applied, as described in Section 2.5. Figures 14 and 15 show the photomicrographs at

the seven different positions indicated in Figure 13. On the basis of the photomicrographs, the results after steps 2 and 3 (positions 1−4 and 5−7, respectively) are similar to those of Figures 8 and 11, respectively, confirming that the same results are obtained when the steps are combined as when they are performed separately. Step 2 destroys the rag layer but forms an oil-in-water emulsion. Step 3 breaks the oil-in-water emulsion. After this three-step procedure, nearly all of the oil, water, and clay solids can be separated.

4. Conclusions

Stable water-in-oil emulsions form during processing of bitumen from Athabasca oil sands. In the absence of clay solids, the coalescer PR$_5$ produces complete separation into a clean diluted bitumen layer and a free water layer. However, when fine clay solids are present, separation is incomplete and a rag layer consisting of skins of solids, oil, and emulsion forms near the interface between these two layers. When a small amount of silicate is present in the water drops, the solid particles are more water-wet and the volume of the rag layer is smaller.

If the clean oil is removed after this initial demulsification step and sodium hydroxide is added to the remaining material with shaking to increase pH to 8.8, the skins making up the rag layer are destroyed, an oil-in-water emulsion forms, and nearly all of the solids are released to the aqueous phase. Finally, adding hydrochloric acid to reduce pH to 5.0 breaks the oil-in-water emulsion. This three-step procedure yields nearly complete separation of water, diluted bitumen, and solids.

(12) Moran, K. Roles of interfacial properties on the stability of emulsified bitumen droplets. *Langmuir* **2007**, *23* (8), 4167–4177.