

Effects of Clay Wettability and Process Variables on Separation of Diluted Bitumen Emulsion[†]

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Initial processing of bitumen froth obtained using a water-based extraction process from Athabasca oil sands yields stable water-in-bitumen emulsions. When the bitumen is diluted with naphtha to reduce its viscosity and density, almost complete separation can be obtained with a demulsifier in the absence of clay solids. However, a “rag layer” persists between the oil and free water layers when clay solids are present. Effects of the naphtha/bitumen (N/B) ratio, demulsifier selection, and silicate dosage on the rag layer formation and product quality have been studied. Emulsions with a N/B ratio of 0.7 are more stable than those with a N/B ratio of 4.0. This can be partially attributed to the difference in viscosity and density affecting the sedimentation velocity. The residual water and solid contents in the oil layer decrease with the addition of silicate. This behavior is attributed to the effect of silicate on clay wettability. Clay solids have toluene-soluble organic contents, which vary as follows: in the oil layer > in the rag layer > in the bottom layer. This result indicates that the solids are the most water-wet in the bottom (water) layer and the most oil-wet in the oil layer. In the same layer, samples with a N/B ratio of 0.7 have a higher toluene-soluble organic content in solids than those with a N/B ratio of 4.0. At 80 °C with a N/B ratio of 4.0, emulsion adding 200 ppm of demulsifier PR₆ and 4 × 10⁻⁴ M sodium *m*-silicate had 0.3–1.5% water and 0.9% solids in the oil layer, with the water content decreasing with an increasing height above the rag layer.

1. Introduction

Stable water-in-oil emulsions, which persist in bitumen froth derived from surface mining of Athabasca oil sands, are stabilized by a combination of asphaltene and clay solids. Individually, asphaltene and oil-wet fine solids can stabilize water in diluted bitumen emulsions.^{1–3} However, when both are present, the capability of stabilizing such emulsions is greatest.³ Adding demulsifier PR₅ [a polyoxyethylene (EO)/polyoxypropylene (PO) alkylphenol formaldehyde resin] can result in nearly complete oil–water separation of asphaltene-stabilized emulsions in the absence of clay solids at room temperature.⁴ However, a “rag layer” containing solids and having intermediate density forms between the clean oil and free water layers when clay solids are present.⁴ This rag layer prevents further coalescence and the complete separation of the emulsified water.⁴

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Most of the clay solids in Athabasca bitumen are kaolinite and illite.⁵ Kaolinite in oil sands slurry has a heterogeneous surface charge⁶ and will present heterogeneous wettability with the adsorption of carboxylates or asphaltenes from bitumen, which is very important to the emulsion stability. Takamura et al. found that the carboxyl groups in bitumen can dissociate and form negatively charged sites on the bitumen/water interface.⁷ Adsorption of an anionic surfactant on a positive surface makes silica oil-wet and promotes its coagulation with bitumen.⁸ The positively charged edges of the kaolinite may adsorb negatively charged carboxylate components of the oil and make that portion of clay solids partially oil-wet. The partially oil-wet clay solids can adsorb at oil–water interfaces and retard water-in-oil emulsion coalescence. Masliyah et al. found that asphaltene-treated kaolinite can stabilize water-in-oil emulsions.⁹ Partially oil-wet clay solids also entrap oil drops and form aggregates, which results in a rag layer in the middle of the sample.¹⁰ Silicate has been used to change the wettability of clay in bitumen extraction.¹¹ A ξ -potential measurement

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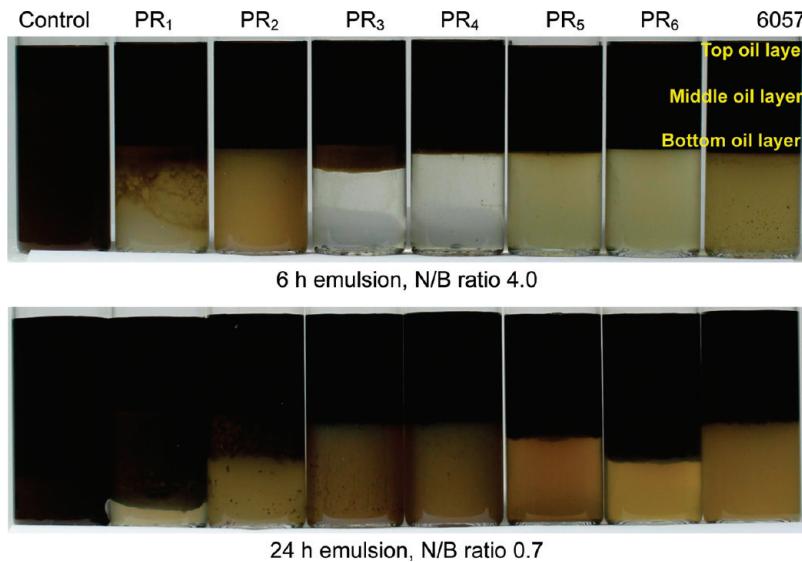


Figure 1. Emulsion (solids-free) separation adding 200 ppm demulsifiers PR₁–PR₆ and 6057 at pH 8.3.

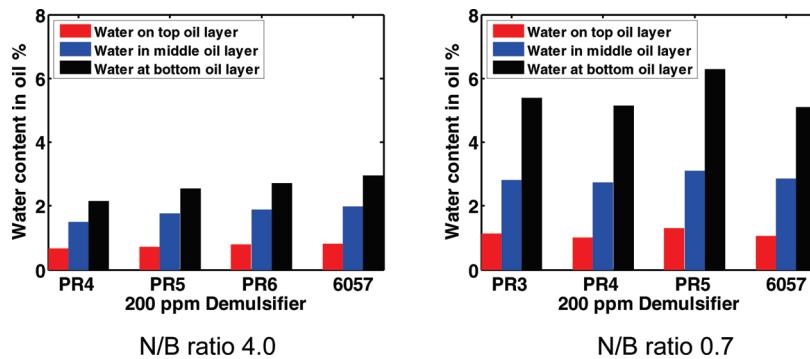


Figure 2. Water content in the oil layer (solids-free) adding 200 ppm demulsifiers.

was applied to characterize the wettability of clay.^{11–14} Experimental results confirmed that adding acidified sodium silicate can effectively minimize the coagulation between bitumen and clay.^{11–13} A contact-angle measurement is usually used to quantify the wettability change for the water–crude oil system.¹⁵ In our study, the clay size is too small to measure the contact angle directly. Thereby, we measured the toluene-soluble organic content of clay solids to characterize the wettability change.

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The solvent effect is also very important to the stability of diluted bitumen emulsion.^{16,17} If water was emulsified into already diluted bitumen, the stability decreased with the increase of the dilution ratio.¹⁶ The diluted bitumen film between water droplets in the drainage process becomes less stable with an increasing dilution ratio.¹⁷ The dilution ratio will also affect the physical properties of the oil phase, e.g., the viscosity and density of the oil, which will affect the sedimentation of water and clay solids.

To study the effects of clay wettability, demulsifier, and dilution ratio, bottle tests of emulsion separation were performed using sodium *m*-silicate and different demulsifiers with dilution ratios of 0.7 and 4.0. Residual water/solid content in the oil layer and solid distribution in different layers were measured by Karl Fischer (KF) titration and centrifugation to characterize the emulsion separation.

2. Experimental Section

2.1. Materials. Samples of bitumen froth (60% bitumen, 30% water, and 10% solids) and diluent naphtha were provided by Syncrude Canada Ltd. Diluted bitumen samples were prepared by diluting with naphtha to naphtha/bitumen ratios (N/B, w/w) of 4.0 and 0.7. Diluted bitumen with a N/B ratio of 4.0 has a density of 820 kg/m³ and contains 8.8 wt % water and 3.0 wt %

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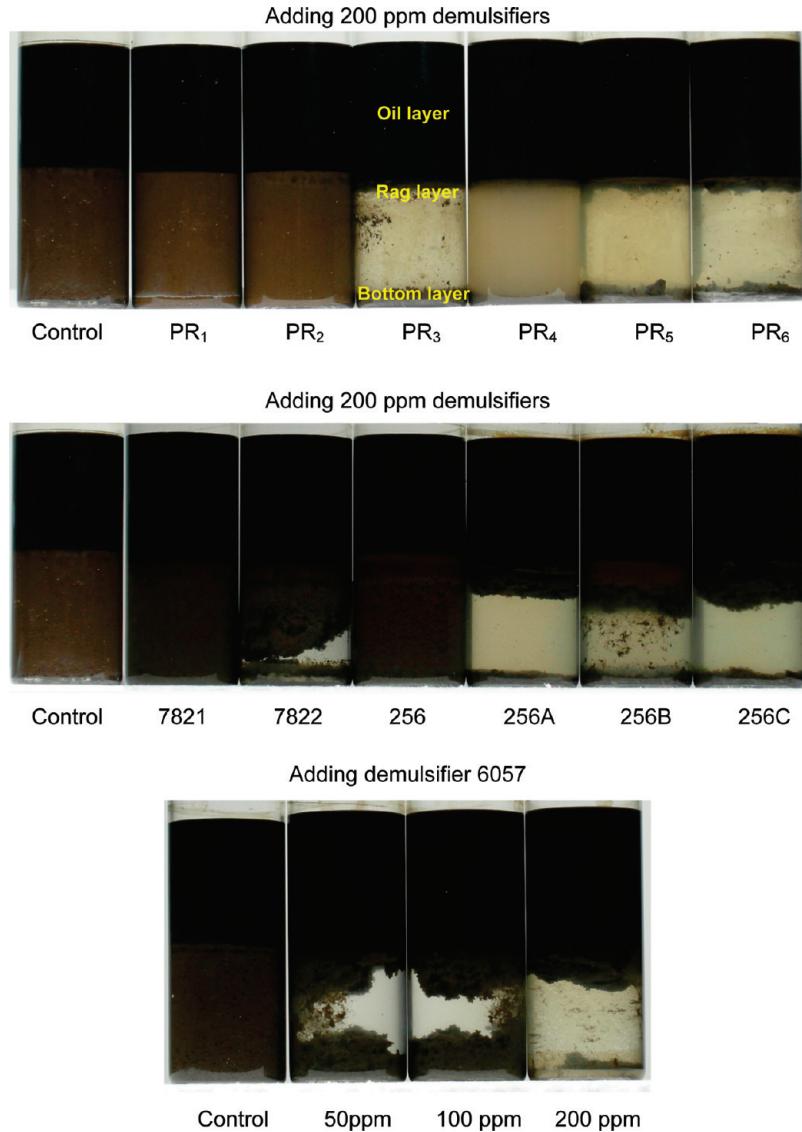


Figure 3. Emulsion (24 h; N/B ratio of 4.0) separation with demulsifiers.

solids, which was measured by centrifugation at 8000g for 30 min. Diluted bitumen with a N/B ratio of 0.7 has a density of 896 kg/m³ and contains 21.2 wt % water and 6.9 wt % solids. Solids-free diluted bitumen was prepared by centrifugation at 8000g for 30 min. Demulsifiers PR₁–PR₆ were from Nalco. Demulsifiers 7821, 7822, 256, 256A, 256B, and 256C were from Baker Petrolite. Demulsifier 6057 (activity of 54.6%) was also provided by Baker Petrolite.

Unless otherwise stated, the aqueous phase used here is synthetic brine with pH 8.3, which contains 0.025 M NaCl, 0.015 M NaHCO₃, 0.002 M Na₂SO₄, 3.0×10^{-4} M CaCl₂, and 3.0×10^{-4} M MgCl₂. The composition of synthetic brine is close to that of inorganic ions present in industrial process water for bitumen extraction. All of the salts in the synthetic brine were obtained from Fisher Scientific.

The KF reagent (around 5 mg of water/mL of reagent) was obtained from Sigma-Aldrich (product 36115-1L) and stored at temperatures lower than 15 °C. Methanol and toluene used as titration solvents were from EMD, Inc. The titration system used was Metrohm KF-701 Titroline.

2.2. Emulsion Sample Preparation and Separation. Emulsion samples were prepared by mixing 27.5 mL of brine and 35 mL of diluted bitumen (dilution ratio of 4.0) or 21 mL of brine and 41 mL of diluted bitumen (dilution ratio of 0.7) to obtain equal volumes of water and oil. Solids-free emulsion samples were

prepared by mixing 30 mL of brine and 30 mL of solids-free diluted bitumen (dilution ratios of 0.7 or 4.0). Emulsion samples were prepared in a glass tube (inner diameter, 44 mm; length, 230 mm) with a six-blade turbine.⁴ The stirring speed of the turbine was 3600 rpm, and the mixing time was 10 min at ambient temperature. For the samples with silicate, different amounts of silicate were added to the aqueous phase prior to emulsion preparation. The demulsifier (on the basis of the total volume of the emulsion sample) was added to the emulsion sample immediately after the preparation. Afterward, all of the samples were shaken by hand at the same time for 1 min. Then, the samples were placed in an oven set at 80 °C.

2.3. Solid Content and Distribution Measurement by Centrifugation. After partial separation of the emulsion, the oil layer (oil-continuous phase on the top with a small amount of water and solid), the rag layer (water-continuous phase with oil and solid skins in the middle), and the bottom layer (water layer with solid sediments in the bottom) were collected. Solids in different layers were collected by centrifugation at 8000g for 30 min. After centrifugation, water and oil were removed and the open centrifugation tube was put in the oven at 50 °C overnight for drying. The weight of solid after drying was measured, and the solid content in the oil layer was calculated on the basis of the original weight of the oil layer. Solid distribution was calculated on the basis of

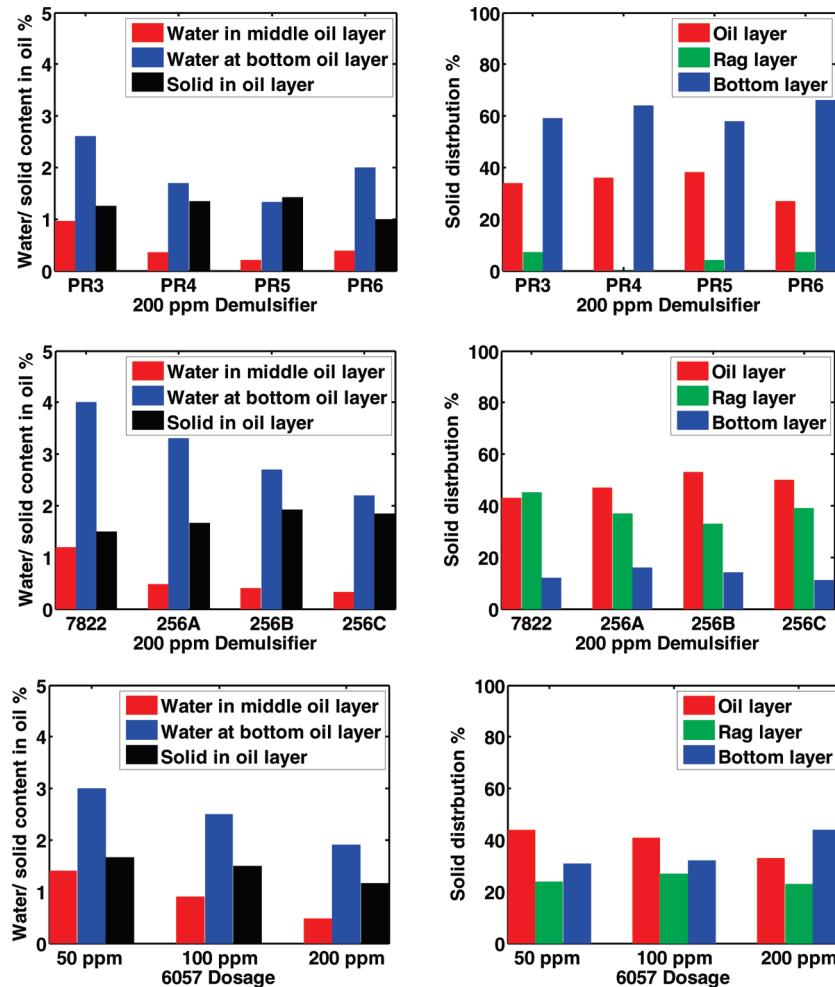


Figure 4. Water and solid contents in the oil layer and solid distribution in different layers adding demulsifiers, with a N/B ratio of 4.0.

the amount of solids in each layer and the total weight of solids obtained by centrifugation.

2.4. Water Content Measurement by KF Titration. Deionized water (25 μ L) was used to perform titer calibration of KF titration 3 times. A certain amount (< 1.0 mL) of the sample was injected into 25 mL of a toluene–methanol (toluene/methanol volume ratio was 3:1) mixture in the titration vessel. The water content was measured using KF titration.

2.5. Toluene-Soluble Organic Content Measurement. Solids in different emulsion layers were collected by centrifugation at 8000g for 30 min. After centrifugation, oil and water were removed and the open centrifuge tube was put in the oven (50 °C) overnight until the weight did not change. Then, the separated clay was treated with toluene several times until the supernatant toluene layer was colorless and transparent. Toluene was separated by centrifugation at 8000g for 30 min. After drying, the weight difference of solids before and after toluene treatment could be obtained. The toluene-soluble organic content of solids was calculated on the basis of the weight difference of solid and the total weight of solid before toluene treatment.

3. Results and Discussion

3.1. Solids-Free Diluted Bitumen Emulsion Separation. Figure 1 shows photographs of solids-free diluted bitumen emulsion samples with N/B ratios of 0.7 (24 h) and 4.0 (6 h) adding 200 ppm of demulsifiers PR₁–PR₆ and 6057 at 80 °C. The first sample is emulsion without any demulsifier as the control. The second to the eighth are emulsions adding 200 ppm

PR₁–PR₆ and 6057, respectively. The pH of the aqueous phase is 8.3.

At a N/B ratio of 4.0, emulsion samples adding 200 ppm PR₄, PR₅, PR₆, and 6057 have better separation than others. At a N/B ratio of 0.7, emulsion samples adding 200 ppm PR₃, PR₄, and 6057 have better separation results than others. No rag layer formed in the emulsion sample with these optimal demulsifiers. To compare the separation results, residual water content in the oil layer was measured in these samples, sampling from positions indicated in Figure 1.

Figure 2 shows bar diagrams of the residual water content in the oil layer using 200 ppm demulsifiers. Residual water content in the oil layer with a N/B ratio of 4.0 is lower than that with a N/B ratio of 0.7, even with a shorter separation time (6 h compared to 24 h). At both N/B ratios of 0.7 and 4.0, emulsion samples adding 200 ppm demulsifier PR₄ have the lowest residual water content (0.7–2.2% at a N/B ratio of 4.0 and 1.0–5.1% at a N/B ratio of 0.7) in the oil layer. The bottle tests and water content measurements reveal that solids-free diluted bitumen emulsion can reach almost complete separation adding an optimal demulsifier with no rag layer formed.

3.2. Diluted Bitumen Emulsion Separation with a Dilution Ratio of 4.0. *3.2.1. Emulsion Separation Adding Different Demulsifiers.* Figure 3 shows the photographs of 24 h diluted bitumen emulsion samples with a dilution ratio of 4.0 adding 200 ppm of demulsifiers at 80 °C. To study the effect of the demulsifier dosage, emulsions were prepared where the concentration

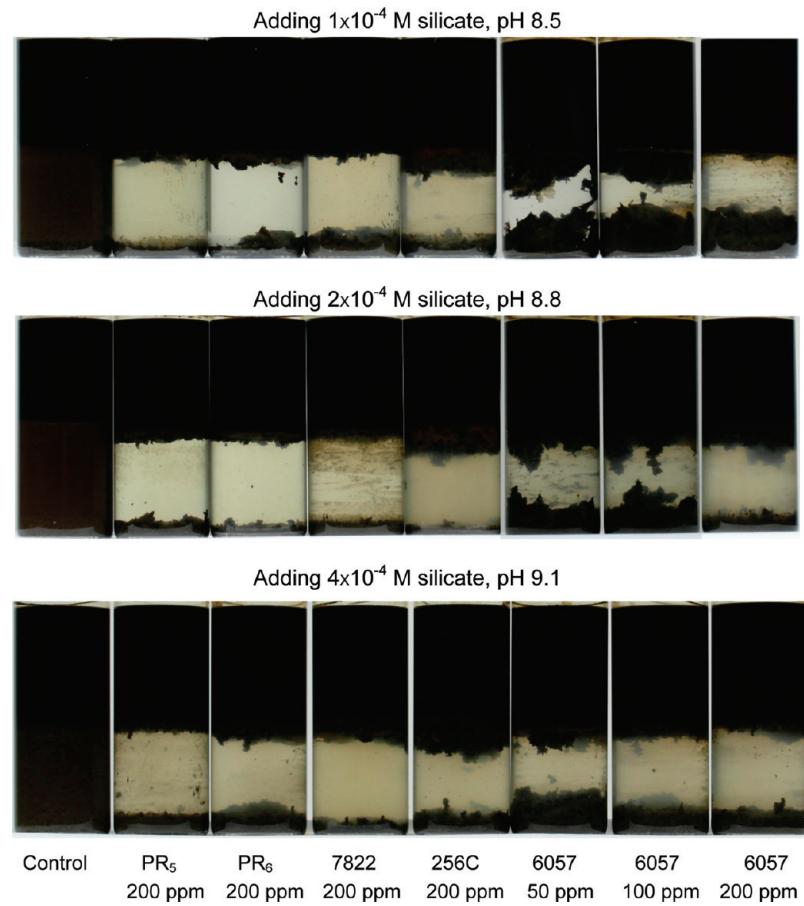


Figure 5. Emulsion (24 h; N/B ratio of 4.0) adding demulsifiers and silicate.

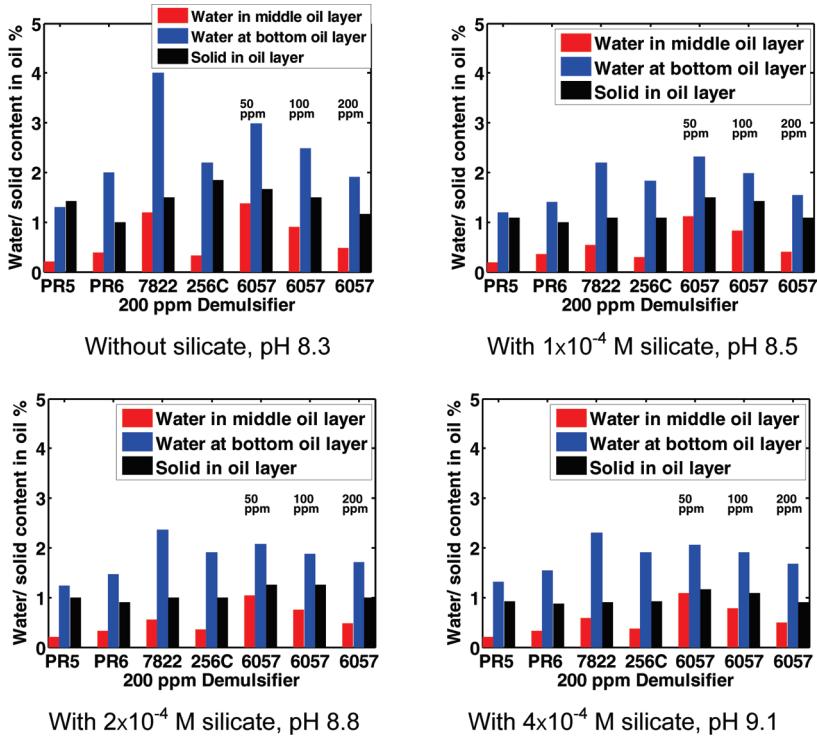


Figure 6. Water and solid contents in the oil layer adding demulsifiers with or without silicate, with a N/B ratio of 4.0.

of demulsifier 6057 ranged from 50 to 200 ppm. The pH of the aqueous phase was 8.3. The positions of sampling for the clay

solid distribution measurement are also shown in the figure. On the basis of bottle tests, emulsions adding 200 ppm demulsifiers

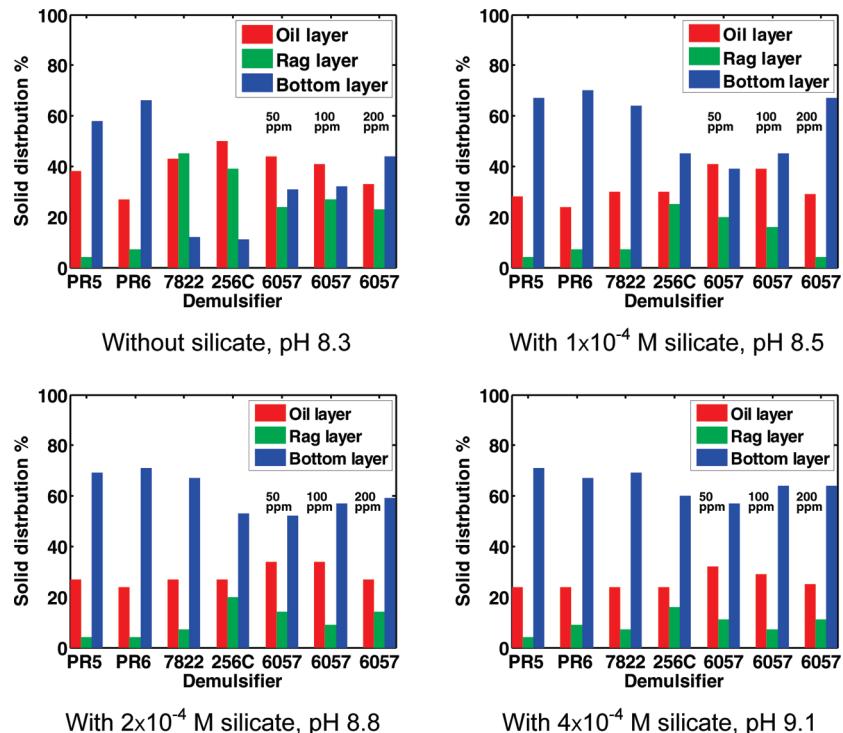


Figure 7. Solid distribution in different layers of emulsion samples adding demulsifiers with or without silicate, with a N/B ratio of 4.

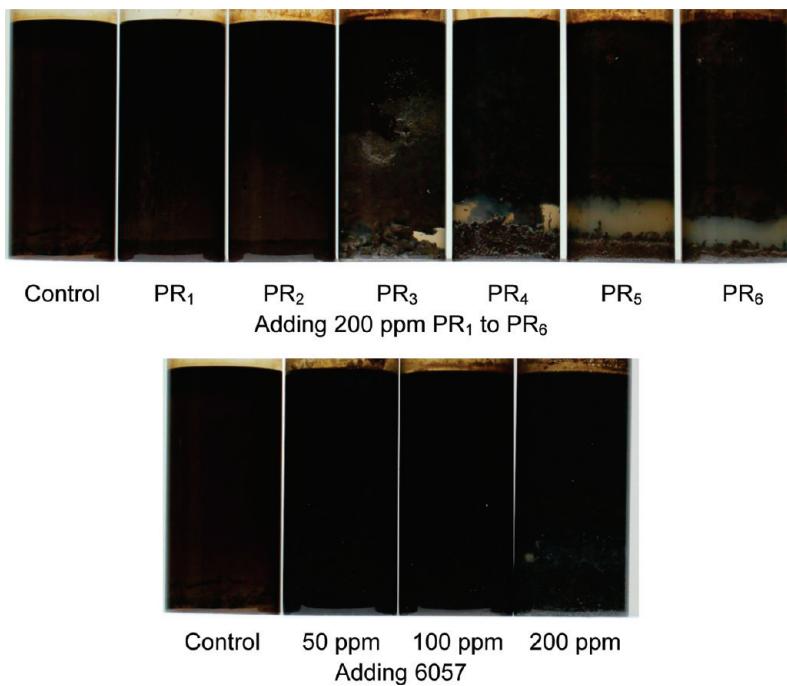


Figure 8. Emulsion (24 h; N/B ratio of 0.7) adding demulsifiers PR₁–PR₆ and 6057.

PR₃–PR₆, 7822, 256A–256C, and 6057 have better separation results than others. The top is the separated oil layer. A relatively thin rag layer lies in the middle of the sample. The bottom layer is separated water with solids.

Figure 4 shows bar diagrams of residual water/solid content in the oil layer and solid distribution in different layers using 200 ppm of demulsifiers PR₃–PR₆, 7822, and 256A–256C and 50–200 ppm of demulsifier 6057. Samples adding 200 ppm of demulsifiers PR₅, PR₆, 7822, 256C, and 6057 have lower residual water and solid contents in oil than other

samples. In samples adding 200 ppm demulsifiers of PR₃–PR₆, about 60% of the solid stays in the bottom layer. Solids in the rag layer ranges from 4 to 7%. The sample with demulsifier PR₅ has the lowest residual water in oil (0.2–1.3%). The sample with demulsifier PR₆ has the lowest residual solid in oil (1.0%).

3.2.2. Emulsion Separation Adding Demulsifier and Silicate. Figure 5 shows the photographs of 24 h diluted bitumen emulsion samples with a dilution ratio of 4.0 adding 200 ppm of demulsifiers (50–200 ppm for 6057) and 1×10^{-4} , 2×10^{-4} ,

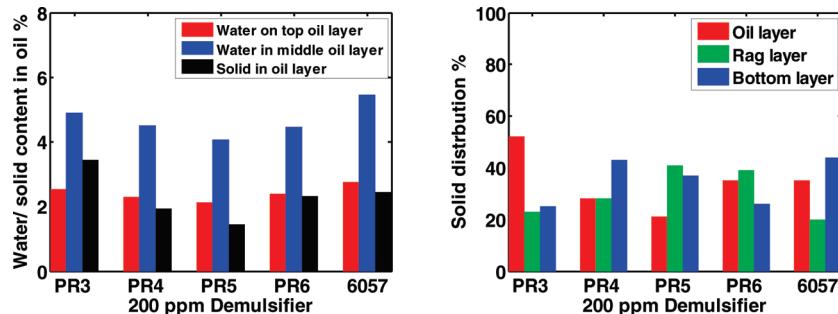


Figure 9. Water content and solid in the oil layer and solid distribution in different layers adding 200 ppm demulsifiers, with a N/B ratio of 0.7.

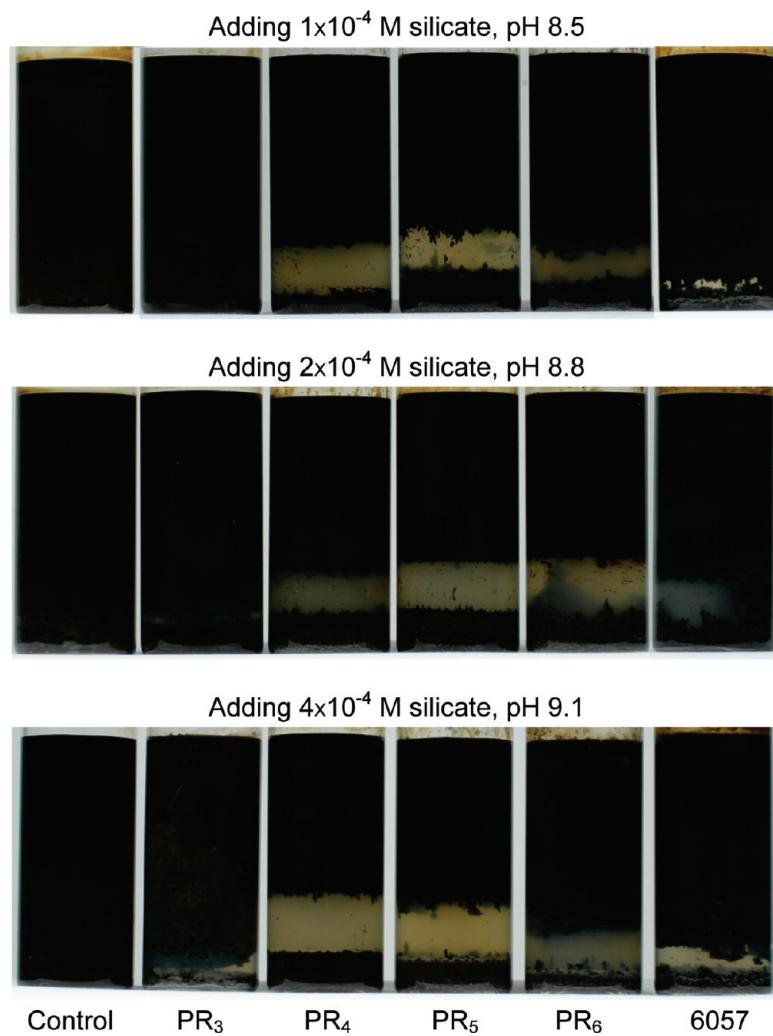


Figure 10. Emulsion (24 h; N/B ratio of 0.7) adding 200 ppm demulsifiers and silicate.

or 4×10^{-4} M sodium *m*-silicate (on the basis of the total volume of the aqueous phase) at 80 °C. The pH values of the aqueous phases are 8.5, 8.8, and 9.1, respectively. Here, demulsifiers PR₅, PR₆, 7822, 256C, and 6057 were used because they produce better emulsion separation from the results in section 3.2.1. On the basis of bottle tests, emulsion samples with silicate are better than those without silicate, as shown in Figure 3.

Figure 6 shows bar diagrams of residual water and solid contents in the oil layer adding demulsifiers with or without adding silicate as a comparison. In the oil layer, samples adding PR₅ have the lowest water content. The sample adding

PR₆ has the lowest solid content in the oil layer. The sample adding 200 ppm PR₆ and 4×10^{-4} M sodium *m*-silicate had 0.3–1.5% water and 0.9% solids in the oil layer. Residual water and solid contents in the oil layer are lower in the samples with silicate than those in the corresponding samples without silicate, especially for the samples adding demulsifiers 7822, 256C, and 6057. With an increasing concentration of silicate, residual solid content in the oil layer decreases for all of the samples.

Figure 7 shows bar diagrams of solid distribution in different layers of emulsions adding demulsifiers with or without silicate as a comparison. With silicate, about 25–30% of

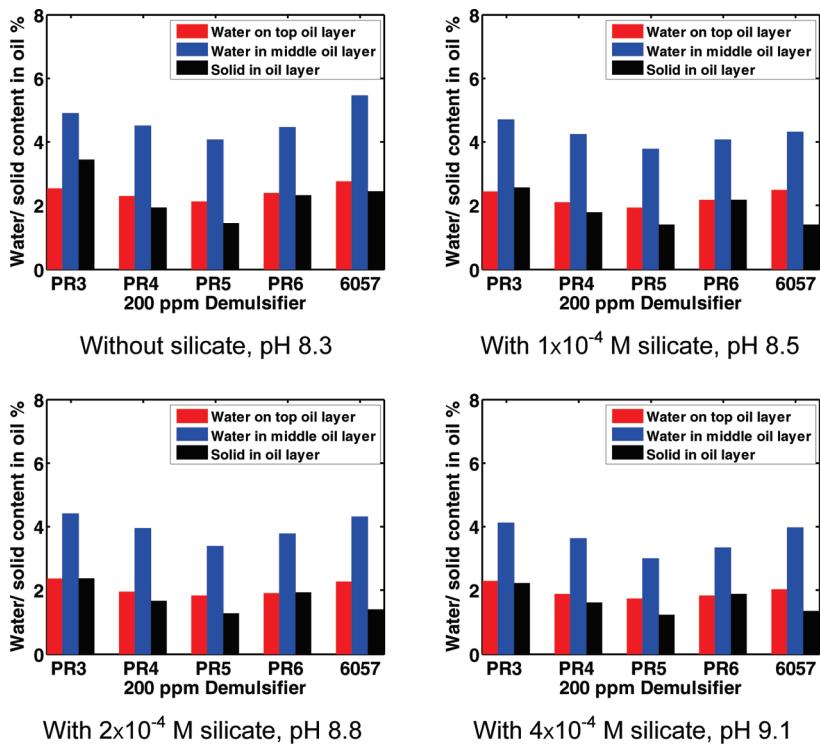


Figure 11. Water and solid contents in the oil layer adding 200 ppm demulsifiers, with a N/B ratio of 0.7.

the solids stay in the oil layer. Two thirds of the solids stay in the bottom layer. The sample adding 200 ppm of demulsifier PR₆ has the largest solid content in the combined rag and bottom layers and the smallest solid content in the oil layer.

3.3. Diluted Bitumen Emulsion Separation with a Dilution Ratio of 0.7. *3.3.1. Emulsion Separation Adding Demulsifiers PR₁–PR₆ and 6057.* Figure 8 shows photographs of 24 h emulsion samples (dilution ratio of 0.7) adding demulsifiers PR₁–PR₆ and 6057 at 80 °C. The pH of the aqueous phase without silicate is 8.3. The top is the separated oil layer. A rag layer lies in the middle. The bottom layer is separated water with solids. The rag layer is thick, and the borderline between the oil and rag layers is not very clear. On the basis of bottle tests, samples adding 200 ppm of demulsifiers PR₃–PR₆ and 6057 have better separation than other samples.

Figure 9 shows bar diagrams of the residual water/solid content in the oil layer and solid distribution in different layers adding 200 ppm of demulsifiers PR₃–PR₆ and 6057. Because the borderline between the oil and rag layers is not very clear, the top half of the sample is considered as the oil layer. On the top of the oil layer, emulsion samples adding demulsifiers PR₃–PR₆ and 6057 all have water contents larger than 2.0%. In the middle of the oil layer, water contents in samples are greater than 4.0%. All of the samples have more than 1.0% solids in the oil layer. About 20–50% of the solids stay in the oil layer. About 25–45% of the solids stay in the bottom layer. The sample adding demulsifier PR₅ has the lowest water and solid contents in the oil layer. Samples adding demulsifiers PR₃–PR₆ have more solids in the rag layer and fewer solids in the bottom layer with a N/B ratio of 0.7 compared to those with a N/B ratio of 4.0. In samples adding demulsifier 6057, solids in rag and bottom layers were less dependent upon the N/B ratio.

Residual water and solid contents in emulsions with a N/B ratio of 0.7 are higher than those with a N/B ratio of 4.0. The reason could be the viscosity and density difference of diluted

bitumen with N/B ratios of 0.7 and 4.0. At 80 °C, diluted bitumen after centrifugation with a dilution ratio of 0.7 has a density of 808 kg/m³ and a viscosity of 4.84×10^{-3} Pa s and diluted bitumen with a dilution ratio of 4.0 has a density of 748 kg/m³ and a viscosity of 8.1×10^{-4} Pa s. The density of brine is 975 kg/m³. The viscosity of diluted bitumen with a dilution ratio of 0.7 is about 6 times that with a dilution ratio of 4.0. Diluted bitumen with a dilution ratio of 4.0 has 1.4 times the density difference between oil and water compared to that with a dilution ratio of 0.7. On the basis of Stokes' law, for the same drop size, the sedimentation rate of water in diluted bitumen with a N/B ratio of 4.0 is 8.1 times faster than that with a N/B ratio of 0.7. A higher viscosity of oil and lower density difference between oil and water can slow the sedimentation of water and solid in oil. A higher sedimentation rate could result in lower residual water and solid contents in oil.

3.3.2. Emulsion Separation Adding PR₁–PR₆ and 6057 with Silicate. Figure 10 shows the photograph of 24 h emulsion samples (dilution ratio of 0.7) adding demulsifiers PR₃–PR₆ and 6057 with different amounts of silicate at 80 °C. The pH values of the aqueous phase with 1×10^{-4} , 2×10^{-4} , and 4×10^{-4} M silicates are 8.5, 8.8, and 9.1, respectively. On the basis of bottle tests, emulsion samples adding 200 ppm of demulsifiers PR₄–PR₆ are better than other samples.

Figure 11 shows bar diagrams of residual water/solid content in the oil layer using 200 ppm of demulsifiers PR₃–PR₆ and 6057. For all of the samples, as the added silicate concentration increases, residual water and solid contents in the oil layer decrease. After 4×10^{-4} M silicate is added, the top oil layer of emulsion samples has water contents around or less than 2.0% and, in the middle of the oil layer, water contents in samples are around or less than 4.0%. Residual solid contents in the oil layer are 1–2%. The sample with added demulsifier PR₅ has the lowest residual water and solid contents in the oil layer.

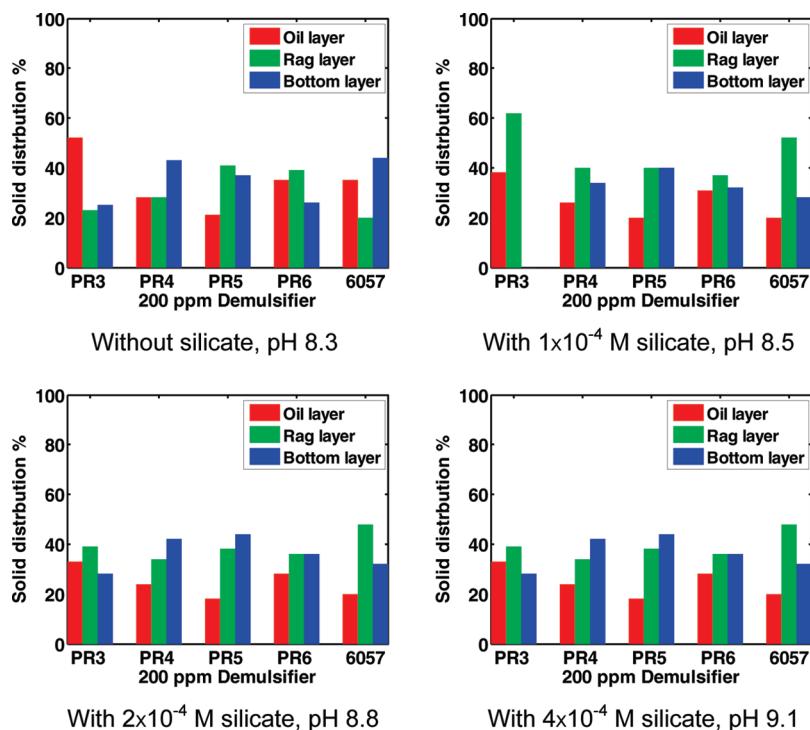


Figure 12. Solid distribution in different layers adding 200 ppm demulsifiers, with a N/B ratio of 0.7.

Table 1. Toluene-Soluble Organic Content of Solids in Different Layers of Emulsion

| emulsion sample | toluene-soluble organic content (% of solids) | | |
|---|---|-----------|---------------------------|
| | oil layer | rag layer | bottom of the water layer |
| N/B ratio of 4.0 and 200 ppm 6057 | 32 | 20 | 14 |
| N/B ratio of 4.0, 200 ppm 6057, and 4 × 10 ⁻⁴ M silicate | 29 | 20 | 15 |
| N/B ratio of 0.7 and 200 ppm 6057 | 37 | 28 | 20 |

Figure 12 shows bar diagrams of solid distribution in different layers using 200 ppm of demulsifiers PR₃–PR₆ and 6057. For all of the samples, as the added silicate concentration increases, less solid stays in the oil layer. With silicate, about 20–40% of the solids stay in the oil layer. About 30–50% solids stay in the bottom layer. The sample with added demulsifier PR₅ has the largest solid content in the combined rag and bottom layers and the smallest solid content in the oil layer. For the sample adding 200 ppm of demulsifier 6057, fewer solids stay in the oil and bottom layers but more solids stay in the rag layer.

On the basis of the separation results, samples adding demulsifiers PR₃–PR₆ have more solids in the rag layer and fewer solids in the bottom layer with a N/B ratio of 0.7 than those with a N/B ratio of 4.0. For all of the samples, residual water and solids contents in the oil layer of the sample with silicate are smaller than those without silicate and fewer solids stay in the oil layer.

3.4. Toluene-Soluble Organic Content in Solid at Different Layers in Emulsion. Table 1 shows solids distributions and toluene-soluble organic content of solids in different layers of partially separated emulsions with 200 ppm of demulsifier 6057 at 24 h after sample preparation at 80 °C. The pH of the aqueous phase without silicate is 8.3. The pH of the aqueous phase with 4 × 10⁻⁴ M silicate is 9.1.

For all of the samples, clay solids have toluene-soluble organic content, which varies as follows: in the oil layer > in the rag layer > in the bottom layer. Generally, clay solids in the emulsion sample have oil-wet sequence as follows: in the oil layer > in the rag layer > in the bottom layer. The results indicate that solids with a higher toluene-soluble organic content are more oil-wet. In the same layer, the sample with a N/B ratio of 0.7 has a higher toluene-soluble content of solids than that in a similar sample with a N/B ratio of 4.0.

4. Conclusions

For solids-free diluted bitumen emulsion, almost complete separation of oil and water could be achieved with optimal demulsifier and no rag layer formed. This reveals that solids in bitumen froth have a key effect on emulsion stability. Sodium *m*-silicate can change clay solids to be more water-wet, thereby minimizing the formation of the rag layer and, thus, allowing most of the water to separate from diluted bitumen emulsions containing fine solids when demulsifier is present. Emulsion samples adding silicate have better separation than those without silicate. The residual water and solids contents in the oil layer of the samples with silicate are smaller than those without silicate.

A comparison of separation results shows that emulsions with a dilution ratio of 4.0 are less stable than those with a dilution ratio of 0.7. In emulsion samples with a dilution ratio of 4.0, residual water and solid in oil are lower and the rag layer is almost eliminated. The reason could be the viscosity and density difference of diluted bitumen with N/B ratios of 0.7 and 4.0. On the basis of Stokes' law, for the same drop size, the sedimentation rate of water drops in diluted bitumen with a N/B ratio of 4.0 is 8.1 times faster than that with a N/B ratio of 0.7. It is recommended to break the rag layer in emulsion at a dilution ratio of 4.0. Emulsion at 80 °C with a N/B ratio of 4.0 adding 200 ppm of demulsifier PR₆ and 4 × 10⁻⁴ M sodium *m*-silicate had 0.3–1.5% water and 0.9% solids in the oil layer.

Clay solids in the emulsions have toluene-soluble organic content as follows: in the oil layer > in the rag layer > in the bottom layer. This result indicates that the solids in the oil layer are the most oil-wet and those in the bottom (aqueous) layer are the least oil-wet. In the same layer, a sample with a N/B ratio of 0.7 has a higher toluene-soluble

organic content in solids than a similar sample with a N/B ratio of 4.0.

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