

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/263946907>

# Froth Treatment in Athabasca Oil Sands Bitumen Recovery Process: A Review

ARTICLE *in* ENERGY & FUELS · NOVEMBER 2013

Impact Factor: 2.79 · DOI: [10.1021/ef4016697](https://doi.org/10.1021/ef4016697)

---

CITATIONS

5

---

READS

168

## 2 AUTHORS, INCLUDING:



[Feng Rao](#)

Universidad Michoacana de San Nicolás de H...  
10 PUBLICATIONS 53 CITATIONS

[SEE PROFILE](#)

# Froth Treatment in Athabasca Oil Sands Bitumen Recovery Process: A Review

Feng Rao and Qi Liu\*

Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta, Canada T6G 2 V4

**ABSTRACT:** Bitumen froth treatment is an integrated process step in the Athabasca oil sands bitumen recovery operations. Its objective is to separate mineral solids and water from the bitumen froth. The bitumen froth is diluted with naphthenic or paraffinic solvents to lower its viscosity to facilitate the separation; therefore, bitumen froth treatment is the removal of inorganics (mineral particles and water droplets) from a bitumen organic solvent solution. The micrometer sized mineral particles (mainly clays) and water-in-oil emulsion droplets are the most difficult to remove from the bitumen froth. Research has been carried out that has led to an understanding of the formation, stabilization and properties of the water-in-oil emulsions in the bitumen organic solvent solution. It is known that the water-in-oil emulsions are formed by water entrained into the bitumen froth during the water-based extraction process and stabilized by natural surfactants in bitumen (especially asphaltene) and fine mineral particles. In fact, the fine mineral particles are the main detriments in stabilizing the water-in-oil emulsions, for the emulsified water droplets were found to be easy to destabilize and remove in the absence of fine mineral particles. Effective removal of the fine mineral particles and water droplets requires both (1) that the fine mineral particles form larger aggregates and (2) that the water-in-oil emulsions can be destabilized. Different demulsifiers have been studied in froth treatment, but the focus was more on the “surfactant-stabilized” water-in-oil emulsions. Therefore, this approach can only partly contribute to item (2). No efforts were made to aggregate the fine mineral particles. Therefore, it was proposed that a possible approach for the effective bitumen froth treatment would be to develop and use process aids that can both aggregate the fine mineral particles and destabilize the water-in-oil emulsions. Several other potential directions to improve bitumen froth treatment have also been pointed out based on the literature review.

## 1. THE ORIGIN OF BITUMEN FROTH TREATMENT

The first commercial process for the exaction of bitumen from Athabasca oil sands was developed by Karl Clark, working with Alberta Research Council in the 1920s. Today, all of the oil sands producers utilizing the surface mining technique, such as Syncrude Canada Ltd., Suncor Energy Inc., and Albian Sands Energy Inc., etc., use a variation of the Clark Hot Water Extraction (CHWE) process. Figure 1 presents schematically the CHWE process. The oil sands ores are mined using open pit surface mining technology, crushed to break the lumps, and mixed with water (50–80 °C). The formed slurry is transported using hydrotransport pipelines to primary separation vessels (PSV) where bitumen is recovered by flotation as a bitumen froth.<sup>1</sup> The transporting pipelines also serve the purpose of conditioning the oil sands so that they are ready for separation in the PSV. Typically, the recovered bitumen froth consists of 60 wt % bitumen, 30 wt % water, and 10 wt % mineral solids.<sup>2,3</sup> Some typical bitumen froth compositions are given in Table 1. An alternative bitumen extraction process, mainly suitable for deep-buried oil sands deposits, is the in situ technology, such as the steam-assisted gravity-drainage (SAGD) technique. In the SAGD technique, steam is injected into upper horizontal wells to heat the oil sands, and the mobilized bitumen drains into the lower horizontal wells where it is produced. The fluid recovered from SAGD is also a mixture of bitumen, water and mineral solids, called bitumen emulsion. Some typical compositions of SAGD bitumen emulsions, which are obtained after being treated through a water and sand rejection process, are given in Table 2.<sup>6</sup>

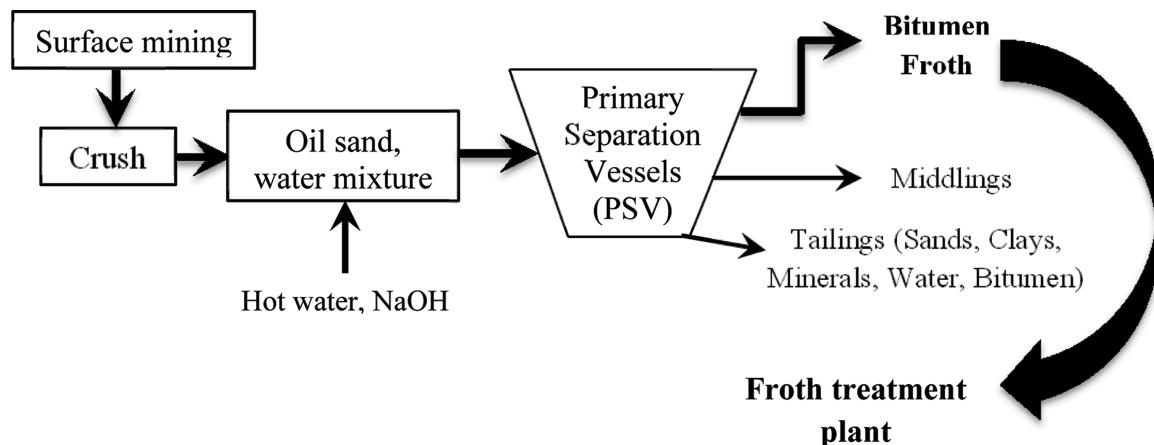
Water and mineral solids contained in either the in situ bitumen emulsion or the surface mined bitumen froth are contaminants that are detrimental for downstream processes such as pipeline transport, upgrading, and refining. Therefore, the bitumen product is required to contain less than 0.5 vol % total mineral solids and water and must have a viscosity of less than 350 cP.<sup>3,4</sup> The contaminating effects of solids are easy to understand, as they block and poison catalysts in downstream oil production processes. The contaminating effects resulted from water is due to the dissolved salts, mostly sodium chloride, which is carried to the downstream upgrading operations, creating serious corrosion problems. These salts come from the oil sands feed and accumulate in the process water as the water is recycled. After the upgrading with hydrogen, the chloride salts are converted into hydrochloric acid<sup>5</sup> and becomes corrosive.

Froth treatment plants have been built to purify the bitumen froth, as well as to remove contaminants from bitumen emulsions produced in SAGD process.<sup>6,7</sup> Two types of diluents, namely naphtha and paraffin, are used to lower the density and viscosity of bitumen emulsions to facilitate the purification. Based on the diluents, froth treatments were classified into naphthenic froth treatment (NFT) process and paraffinic froth treatment (PFT) process. Figure 2 schematically presents a typical two stage NFT process in industrial operations. As can

Received: August 20, 2013

Revised: October 29, 2013

Published: October 29, 2013



**Figure 1.** Schematic presentation of the surface mining and flotation process for the extraction of bitumen from oil sands.

**Table 1. Compositions of Some Typical Bitumen Froths<sup>2,3</sup>**

bitumen froth sample	bitumen (wt %)	water (wt %)	solids (wt %)
#1	47.7	39.2	13.1
#2	58.8	30.9	10.2
#3	44.2	36.5	19.3
#4	68.3	20.2	11.3

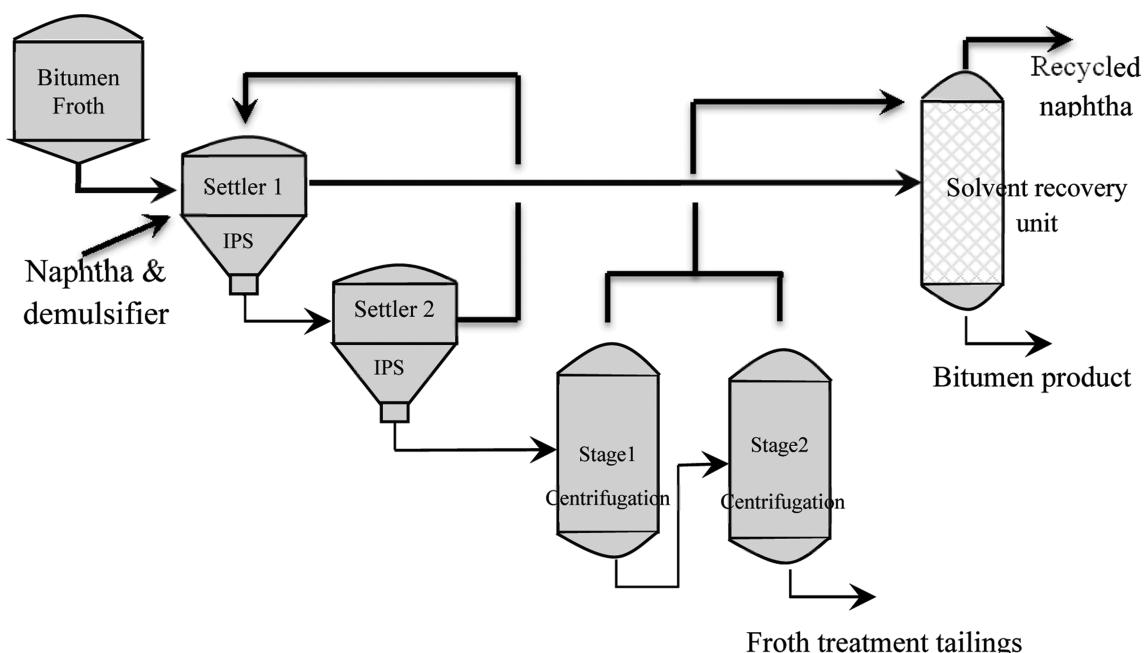
**Table 2. Compositions of Some Typical In Situ Bitumen Emulsions from SAGD<sup>6</sup>**

in situ bitumen emulsion sample	bitumen (wt %)	water (wt %)	solids (wt %)
#1	82.5	17.3	0.2
#2	66.3	33.3	0.4
#3	69.1	30.3	0.6
#4	90.7	8.3	1.0

be seen, a diluent (in this case, naphtha) is added to the bitumen froth in order to decrease its viscosity and to liberate

the hydrocarbon components from the inorganic contaminants (mineral solids and water). Multistage centrifugation (with centrifugal forces up to 2500 G) and the addition of demulsifiers are applied for the removal of solids and water-in-oil emulsions from the diluent-bitumen solutions. The treated bitumen froth can still contain on average 2–5 wt % water and 0.5–1 wt % solids.<sup>3</sup>

In view of the importance of the bitumen froth treatment in Alberta oil sands operations, the emergence of the two distinctively different bitumen froth treatment methods (i.e., NFT versus PFT), the need to develop effective solvent recovery processes from the froth treatment tailings, and more importantly, the general perception that the entire bitumen froth treatment process is more of an "art", a trial-and-error process rather than a science, it is felt that a literature review on the current status on the industrial operation and academic research on bitumen froth treatment is necessary. This housekeeping effort was carried out with an objective to identify gaps for future research and development work.



**Figure 2.** Schematic representation of a typical two stage naphthenic bitumen froth treatment process.

## 2. STABILITY OF WATER DROPLETS IN DILUENT–BITUMEN SOLUTION

On the basis of size distribution, water droplets in diluted bitumen were classified into three types: (I) emulsified water, with water droplet sizes less than 10  $\mu\text{m}$  in diameter, (II) dispersed water, with droplet sizes between 10 and 60  $\mu\text{m}$ , and (III) free water, with droplet sizes larger than 60  $\mu\text{m}$ .<sup>6</sup> The settling characteristics of the water droplets are summarized in Table 3. The type I water cannot be removed from the oil

**Table 3.** Size Distribution of Water Droplets in Diluted Bitumen<sup>6</sup>

water droplets	size distribution	settling characteristics
type I: emulsified water	<10 $\mu\text{m}$	cannot be removed
type II: dispersed water	10–60 $\mu\text{m}$	require time or centrifugation for settling
type III: free water	>60 $\mu\text{m}$	settle instantly

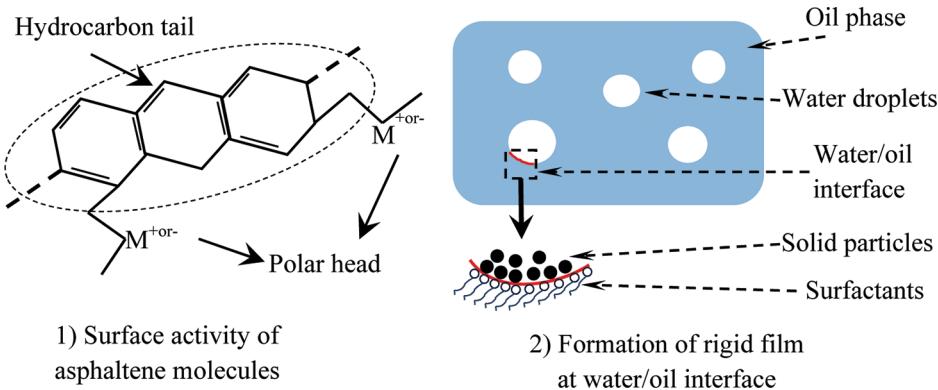
phase unless larger droplets are formed through coalescence or aggregation.<sup>6</sup> A new emulsification mechanism—the budding mechanism—was proposed for the formation of micrometer-sized water droplets. It asserts that these micrometer-sized water droplets are formed through budding (area concentration) of dispersed or free water, rather than by agitation.<sup>8</sup> However, no follow up studies have been carried out either by the original researchers or by other researchers. The formation mechanisms and the implications of such water-in-oil emulsification mechanisms on oil sands operations are interesting areas that can be studied further.

It is generally understood that micrometer-sized water-in-oil emulsions are strongly stabilized by native crude oil surfactants, which prevent droplet coalescence by forming a rigid film. Asphaltenes, resins, waxes, and small solid particles (clays or siderite) are generally considered to be responsible for the stability of water droplets.<sup>9</sup> The Athabasca bitumen contains on average about 17 wt % saturates, 40 wt % aromatics, 26 wt % resins, and 17 wt % asphaltenes. Both asphaltenes and resins have hydrophobic and hydrophilic parts, which give them surfactant character. For instance, asphaltenes are composed of polycyclic (aromatic and naphthenic) molecules with aliphatic side chains and doped with some metals and polar heteroatoms (such as nitrogen, oxygen, and sulfur). These can function as hydrocarbon tails and polar heads, respectively, as schematically

presented in Figure 3. These surfactants, together with the hydrophilic clay particles, form a rigid film at the water–oil interface. This film contributes to a variety of problems such as high stability of the water-in-oil emulsion, high viscosity of bitumen for pipelining, as well as high-coking propensity and catalyst poisoning during bitumen upgrading and refining.<sup>10,11</sup>

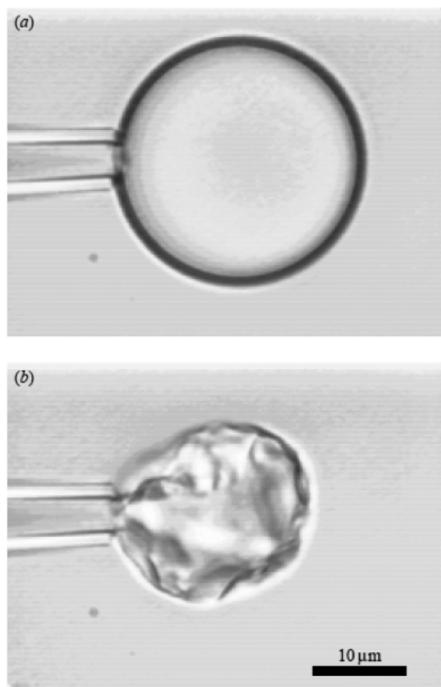
Much research has been conducted on the rigid oil–water film in diluent–bitumen solution. Alvarado et al.<sup>12</sup> investigated the effect of di- and monovalent metal cations on the water droplet stability in bitumen solutions. They showed that the stability improves when the aqueous phase contains calcium ions in contrast with solutions containing sodium ions exclusively at the same ionic strength. Eley et al. showed that the most stable emulsions exist when the asphaltenes are near the precipitation point.<sup>13</sup> However, resins alone cannot stabilize such emulsions.<sup>14</sup> However, Ese et al.<sup>15</sup> showed that the addition of resins into asphaltene monolayers caused the opening of the rigid asphaltene structure and that the presence of demulsifiers had the same effect. According to Yarranton et al.,<sup>16</sup> asphaltenes are able to stabilize emulsions by forming a monolayer at the water–oil interface when asphaltene concentration is below 0.2 wt %. However, others claim that asphaltenes can be adsorbed at the water–oil interface in the form of monolayer even at a concentration up to 0.4 wt %.<sup>17</sup> Neuville et al.<sup>18</sup> performed hanging droplet measurements to investigate the formation of surface active species coming from bitumen at the bitumen–water interface ( $\text{pH } 2.7, T = 90^\circ\text{C}$ ). They observed the existence of two different endogenous surfactants (called A and B types) adsorbing at bitumen–water interface. Their competition for the bitumen–water interface leads to sequential adsorption.

On this topic, Czarnecki and colleagues have carried out fundamental studies and reported significant results.<sup>5,19–21</sup> They designed a washing experiment to study the asphaltene that was involved in stabilizing the water-in-oil emulsion. The emulsion formed (which they called the first emulsion) was centrifuged to create a clean supernatant. In the next step, water was blended into the supernatant to form the second emulsion that contained 10% water. They found that as the amount of water used to make the first emulsion increases, the stability of the second emulsion decreases. Therefore, for a given quantity of diluent–bitumen solution, the total amount of water-in-oil emulsions that could be stabilized was more or less fixed. After calculating the volume of oil/water interfacial layers and knowing the quantity of asphaltene in the system, they



**Figure 3.** Schematic representation of perceived surface active structure of asphaltene and its role in stabilizing water droplets in diluent–bitumen solution.

concluded that if asphaltenes are involved in stabilizing the emulsion, it can only be a small subfraction of the total asphaltene content of the oil. They used the colloidal particle scattering (CPS) force measuring technique to study the interaction force between emulsified water droplets in diluent-bitumen solutions and showed that the interaction between water droplets belonged to the (repulsive) steric layer force, rather than the (attractive) van der Waals forces or electrostatic interactions. This steric force is originated from the rigid films at the water–oil interfaces. They employed the micropipet technique to study directly the interfacial properties of individual, micrometer-sized water droplets and showed the existence of the rigid cortical structure of the water droplet, as noted in Figure 4. They calculated the resistance of the rigid film on the water droplets to coalescence and reported that it was equivalent to about 10 000 G acceleration.

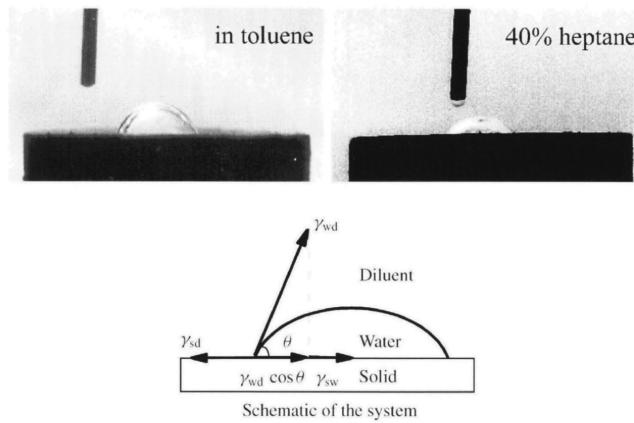


**Figure 4.** Deflation of a water droplet by micropipet. The rigid film is revealed as the droplet area is reduced (reproduced from ref 19, by permission of the Royal Society, copyright 1999).

In the absence of fine mineral particles in the diluent-bitumen solution, it is found that nearly complete oil–water separation of asphaltene-stabilized water-in-oil emulsions could be obtained with the addition of a demulsifier. The effects of fine mineral particles on the formation of rigid films on water droplets were then investigated by measuring the wettability of the mineral particles in various diluents. Obviously, the fine mineral particles would remain in the organic phase without being involved in the rigid films formation if they are highly oil-wet or hardly water-wet. Otherwise, the fine mineral particles would stay in the organic/water interfacial region to form rigid films on the water droplets. Jiang et al.<sup>22,23</sup> utilized kaolinite with sodium naphthenate in toluene–brine mixture as the model system for the wettability study of solids in the bitumen froth. They reported that kaolinite is naturally water-wet in toluene–brine mixtures. After adding sodium naphthenate, kaolinite becomes oil-wet due to the adsorption of naphthenate on kaolinite surface. However, the wettability of

kaolinite in the presence of naphthenate was altered to more water-wet by increasing pH and by the addition of silicate and surfactants. This alteration was attributed to an increase in the negative charge on kaolinite surfaces, which reduced the adsorption of naphthenate.

Chen et al.<sup>24</sup> carried out a fundamental study to analyze the effects of solids wettability on their function to stabilize water-in-oil emulsions. They concluded that (1) fine mineral particles were more water-wettable with increasing alkane components in the organic phase, as shown in Figure 5. The weaker



**Figure 5.** Wettability of fine mineral particles in diluent–bitumen solution in the presence and absence of alkane component (reprinted from ref 24, by permission of Taylor and Francis, copyright 1999).

interactions of the apolar molecules (alkane) with the mineral solids seem to be responsible. (2) The wettability of water on fine solids remained unchanged by washing the solids with heptane but increased significantly by toluene washing. An inversion in partition from the organic to the aqueous phase was observed in the latter case. The stronger dissolving power of toluene for organic matter (surfactants) made the fine solids more water-wettable by removing the adsorbed natural surfactant from the fine mineral particle surfaces.

### 3. NAPHTHENIC FROTH TREATMENT (NFT) AND PARAFFINIC FROTH TREATMENT (PFT)

There are two major technologies used for bitumen froth treatment in Athabasca oil sands industries. Their features are compared in Table 4. In conventional naphthenic froth

**Table 4. Features of NFT Process and PFT Process**

	NFT process	PFT process
diluents	naphtha	paraffinic solvents
solvent/bitumen (S/B) ratio	low (0.6–0.75 w/w)	high ( $\geq 1.5$ w/w)
contaminants in product	high (1–2 wt % water, 0.5 wt % solids)	low ( $\approx 0$ )
dissolution of asphaltene	yes	no
energy consumption	high	low
sacrifice of hydrocarbon components	no	yes
applied projects (company)	most projects in Athabasca oil sands industry	few projects such as Albion (Shell) and Kearl Lake (Imperial Oil)

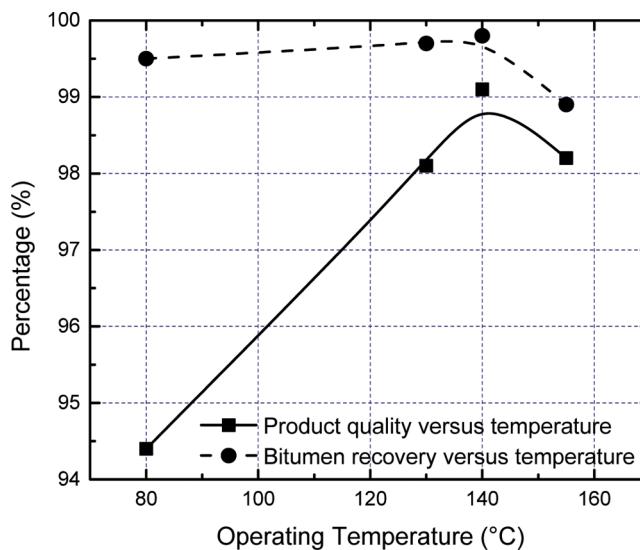
treatment (NFT), the solvent naphtha is used at relatively low solvent-to-bitumen ratio. The separation is enhanced by the addition of chemicals (demulsifiers) to destabilize the water-in-oil emulsions. Typical diluted bitumen products from this process contain 1–2 wt % water and about 0.5 wt % mineral solids. Because of the relatively high level of these inorganic contaminants, the diluted bitumen is usually not suitable for pipelining or refining. The diluted bitumen is therefore upgraded at high temperature to produce synthetic crude oil by means of a coker unit.

The second technology is the paraffinic froth treatment (PFT) process developed in the 1990s. The diluted bitumen product obtained through the PFT process has levels of inorganic contaminants that are almost 2 orders of magnitude lower than those from the NFT process. The content of asphaltenes, which are heavier molecules contributing to the high viscosity in the bitumen, are also lowered, thus improving the bitumen product quality. Mixing paraffinic solvent at required solvent-to-bitumen ratio (S/B) results in the formation of aggregates composed of emulsified water droplets, fine mineral particles and precipitated asphaltenes. The aggregated contaminants are easy to separate in conventional settlers and thus require less energy.<sup>25</sup> However, because paraffinic solvents cannot dissolve asphaltene, most of the asphaltene is precipitated in the PFT process and rejected to the froth treatment tailings, leading to a lower bitumen recovery than the NFT process.

**3.1. Effects of Demulsifier and Temperature on Naphthenic Froth Treatment (NFT).** In order to remove the emulsified water droplets from diluent–bitumen solution, physical methods, such as centrifugation, sonication, and usage of high-voltage electric fields, and chemical methods, such as the addition of demulsifier or emulsion breakers, were applied in the NFT process. Blends of surfactants, such as amines, copolymers of ethylene oxide, and propylene oxide, were used as demulsifiers. Stasiuk and Schramm<sup>26</sup> studied the addition of certain combinations of surfactants and solvents on nascent froth formation during flotation recovery of bitumen from Athabasca oil sands. They found that the addition of surfactants with high hydrophilic–lipophile balance (HLB) (e.g., Alcopol O, which has a HLB of 20) caused a significant reduction in water content without sacrificing bitumen recovery. The elastic properties of three copolymers of different composition at air/water and crude oil/water interface were studied by Sztukowski et al. and correlated to their demulsification efficiency.<sup>9</sup> They proposed that the interactions of native surface-active molecules in bitumen with copolymers containing hydrophilic polyethylene oxide and hydrophobic silicone moieties are the driving force leading to the destabilization of the water droplet film.<sup>9</sup> Zhang et al.<sup>27</sup> studied the monolayer characteristics of mixtures of asphaltene and a polymeric demulsifier using a Langmuir interfacial trough at air–water and heptol–water interfaces through measurements of the pressure–area and relaxation isotherms (“heptol” refers to solvent mixtures of heptane and toluene with varying ratios). The monolayers were also characterized by atomic force microscope (AFM) imaging and contact angle measurements. They found that the presence of polymeric demulsifier in an asphaltene monolayer can reduce the mechanical strength of the asphaltene monolayers as indicated by reduced rigidity with increasing demulsifier content. Sun et al.<sup>28</sup> studied the influences of two commercial demulsifiers, one with a straight chain and the other with branch chains, on the dilational viscoelasticity of an oil–water

interfacial film containing surface-active fractions from crude oil. They found that the molecular size of the surface-active fractions was an important factor influencing the reciprocity of demulsifiers and surface-active fractions at the oil–water interface. Peng et al. synthesized a novel magnetic demulsifier for water removal from diluted bitumen emulsion.<sup>29</sup> The demulsifier was synthesized with a surface-active ethyl cellulose (EC) grafted on magnetic nanoparticle surfaces, called M-EC. The M-EC was added to diluted bitumen froth, and after the application of a magnetic field, the water droplets were removed together with the M-EC. Their laboratory results showed a more than 90% removal of the original water from the diluted bitumen froth. Additionally, the application of M-EC nanoparticles to Syncrude commercial naphthenic plants showed a water removal rate of greater than 80%.

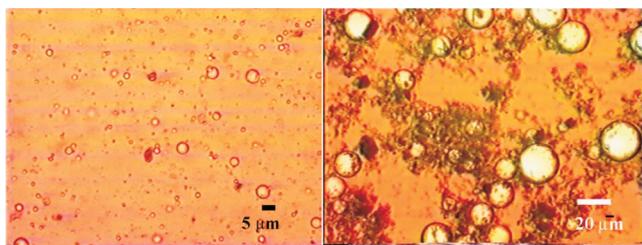
In naphthenic froth treatment (NFT) process, better diluted bitumen quality could be achieved by increasing the operating temperature from 80 to 140 °C.<sup>4,30</sup> However, high temperature operation is unstable due to equipment limitations, which lowers froth treatment performance. As noted in Figure 6, the



**Figure 6.** Changes of product quality (hydrocarbon content) and bitumen recovery as a function of temperature in NFT process.

product hydrocarbon content increased from 94.3 to 99% as the operation temperature was increased from 80 to 140 °C. Meanwhile, the recovery was almost flat over this temperature range, with a slight drop when the temperature was higher than 140 °C. The hydrocarbon content in the froth also dropped by about 1 percentage point when the temperature was above 140 °C. This was probably caused by the instability of the equipment.

**3.2. Effects of Solvent Ratio and Energy Input on Paraffinic Froth Treatment (PFT).** For paraffinic froth treatment (PFT), Long et al.<sup>3,6,31,32</sup> systematically studied the stability and settling characteristics of water-in-bitumen froth emulsion diluted with an aromatic solvent (toluene) and an aliphatic solvent (*n*-hexane) at various solvent to bitumen mass ratios (S/B), as well as the impact of temperature. They employed a Zeiss light microscope (Axiotech<sup>vario</sup>) to visually observe the settling and the characteristics of water–mineral–asphaltene aggregates. Figure 7 shows two micrographs of two diluted bitumen emulsions with low and high S/B ratios from their study. The main conclusions are (1) when bitumen



**Figure 7.** (a) Micrograph of *n*-hexane-diluted bitumen emulsion with S/B = 0.7. (b) Micrograph of *n*-hexane-diluted bitumen emulsion with S/B = 1.8 (reprinted from ref 3, with permission from Elsevier, copyright 2002).

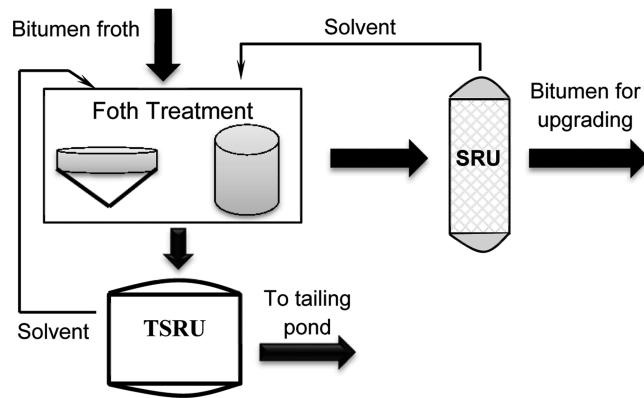
emulsions are diluted with aliphatic solvents at solvent-to-bitumen ratios above a certain value (e.g., 1.5 for hexane), water droplets, mineral solids, and precipitated asphaltene tend to form clusters that are much larger than the individual components; (2) the effective aggregate density was higher for the C5 and C6 aliphatic solvent system ( $\approx 1.0$  g/mL) than for the C7 solvent system ( $\approx 0.87$  g/mL); (3) raising the mixing temperature (e.g., from 50 to 120 °C), of bitumen emulsion and solvent leads to larger aggregates and results in a significant increase in the settling rate of the aggregates.

Furthermore, Zawala et al. studied the effects of mixing speed and duration on the formation of mineral solids, asphaltene, and water aggregates in PFT. They found that the mixing energy input (mixing speed and duration) during PFT at elevated temperature (about 80 °C) could help the formation of high density aggregates of contaminants in bitumen froth. By increasing the mixing energy, the mineral solids content in the aggregates can be increased from a few percent up to about 70 wt % without significant changes in the average aggregate size.<sup>33</sup>

**3.3. Equipment and CFD Model Studies in NFT and PFT.** During NFT, high efficiency equipment is required to enhance the removal of mineral solids and water droplets. Madge et al.<sup>34–37</sup> proposed a novel NFT process that uses an arrangement of hydrocarbon cyclones and inclined plate settler (IPS) to perform the removal of solids and water from the bitumen froth. The elimination of centrifuge equipment through the use of hydrocarbon cyclone and IPS provides cost and energy savings in comparison to the conventional process that uses centrifuges to achieve bitumen dewatering and demineralization. They also intended to develop computational fluid dynamics (CFD) models on the function of these devices. However, it seems that more elaborate boundary conditions than the simple no slip condition have to be defined. Interestingly, Kirpalani and Matsuoka<sup>2</sup> proposed another CFD model that incorporates the irregular (fractal) structure of aggregates by considering the aggregates as porous liquid-filled solids that are fractal in nature. They found that their results had good agreement with the experimental data of Long et al. in the PFT process.<sup>3</sup>

#### 4. SOLVENT RECOVERY FROM FROTH TREATMENT TAILINGS

After froth treatment, the used solvent (either naphtha or a paraffinic solvent) is recovered in the solvent recovery unit (SRU) and tailings solvent recovery unit (TSRU). Figure 8 schematically shows the flow of the solvents and the solvent recovery units in a bitumen froth treatment plant. As the SRU is a mature technology in the oil industry, this review will be focused mainly on the tailings solvent recovery unit (TSRU).



**Figure 8.** Schematic diagram of solvent recovery in bitumen froth treatment plant.

The water and mineral solid fraction obtained after separation in bitumen froth treatment is commonly referred to as froth treatment tailings. These tailings typically contain approximately 2 wt % hydrocarbon solvent, 4.5 wt % bitumen, 17 wt % mineral solid particles, and 76.5 wt % water. It is desirable both economically and environmentally to recover the hydrocarbon solvent from the froth treatment tailings prior to disposal. Most of the research regarding TSRU were presented in Canadian and U.S. patents, and Table 5 gives a chronological summary of the developments in this area. As can be seen from Table 5, in all patents, a recovery vessel was used to separate the solvents from the mineral solids and water by vaporizing the solvent from the tailing slurry. The methods to vaporize the solvents were different in the different patents, ranging from high temperature, low atmospheric pressure, or particular internal structures etc.

#### 5. INDUSTRIAL OPERATIONS

When Suncor started the first commercial oil sands operation, they chose naphtha as a diluent in the bitumen froth treatment. The naphtha was produced from their on-site refinery and contained slightly higher concentrations of aromatic and olefins than would hydrotreated naphtha. In the second commercial oil sands venture, Syncrude selected hydrotreated naphtha as the diluent, in order to meet the environmental restrictions on light hydrocarbon emissions. Using hydrotreated naphtha as a diluent, a higher diluent-to-bitumen ratio (than the initial Suncor naphtha) is required to achieve comparable process performance. This is because the hydrotreated naphtha has lower aromaticity, which results in relatively higher hydrocarbon phase viscosity. In most oil sands projects in the Athabasca region, naphtha at a solvent-to-bitumen mass ratio (S/B) of 0.6–0.75 is still used to reduce the bitumen viscosity with subsequent removal of the mineral solids and water from the bitumen froth using inclined plate settlers, hydrocyclones, and centrifuges. After the bitumen froth treatment, the supernatant is distilled to recover the naphtha. Prior to distillation, the diluent bitumen product typically contains approximately 2% water and 0.5% fine solids. The “coker feed” bitumen product obtained after distillation typically contains approximately 1% fine solids due to the removal of the solvents.

The paraffinic froth treatment (PFT) process, a relatively new process, is used in fewer commercial projects than the naphthenic froth treatment (NFT) process. However, many companies in the Athabasca region, such as Suncor, Shell, and Syncrude,<sup>36</sup> have designs and plans of PFT plants in the near

Table 5. Summary of TSRU Patents

patent	inventor	issued date	description	applied solvent
Canadian patent No. 1,027,501	M. Simmer	1978/03/07	Recovery of naphtha from hot centrifuge tailings by introducing the tailings into a vacuum flash vessel maintained at a subatmospheric pressure to vaporize the naphtha.	naphtha
Canadian patent No. 2,173,559 U.S. patent No. 6,712,215	A. F. Scheybeler	1996/04/04 (filed) 2004/03/30	The recovery of solvent from tailings which comprises directing a stream of tailings and saturated steam through a nozzle and discharging the combined stream of tailings and saturated steam against an impaction target.	naphtha
Canadian patent No. 2,227,035	W. Brown et al.	2004/03/09	Recovery of solvents by introducing the tailings into a vacuum flash vessel maintained at subatmospheric pressure to vaporize the solvents and some water. Steam is then introduced into the residual tailing pool for vaporizing residual solvents and water.	naphtha, paraffin
Canadian patent No. 2,353,109	G. A. Foulds et al.	2005/12/06	The tailings stream is introduced to a vessel that is wherein the temperature and pressure are such that the solvent is (a) vapor; (b) a pool of liquid and solids is maintained in the vessel; (c) the pool is agitated; (d) the solvent is recovered as an overhead vapor stream; (e) the solvent depleted remainder of the stream is removed from the bottom of the vessel.	paraffin
Canadian patent No. 2,227,045 U.S. patent No. 6358404	F. King et al.	2006/11/28 2002/03/19	Recovery of solvents by the tailings into a steam stripping vessel maintained at atmospheric pressure, and distributing the tailings over said shed decks. Steam is introduced below the shed decks for vaporizing the solvents and water.	naphtha, paraffin
Canadian patent No. 2,587,166 Canadian patent No. 2,613,873 Canadian patent No. 2,614,669	K. Sury	2008/10/07 2008/10/28 2008/12/30	The recovery of paraffin by introducing the tailings into a TSRU, and distributing the tailings over the internals in TSRU. An inert gas or steam is introduced below the internals and above the liquid pool for vaporize the solvents. In another aspect, the process comprises introducing the tailings into a first TSRU and then into a second TSRU operated at a lower pressure. In another aspect, internals are optionally present and steam or inert gas is injected in the liquid pool.	paraffin
U.S. patent No. 20110278202	K. Moran	2010/05/12 (filed)	An apparatus and a method include introducing tailings into a recovery vessel so that they form a tailing pool, introducing an amount of steam directly into the tailing pool, mixing the tailings and maintaining for a residence time.	naphtha, paraffin
U.S. patent No. 20120043178	J. Kan	2011/10/28 (filed)	Utilizing nozzles for forming fine solvent-containing hydrocarbon droplets from tailing feed stream. Heat from the vessel atmosphere or from steam flowing countercurrent to the falling hydrocarbon droplets is used to vaporize the solvents.	naphtha, paraffin
Canadian patent No. 2,454,942	J. Sharpe et al.	2012/05/08	A process for separating tailings into a recovered solvent component and a solvent recovered tailings component which comprise discharging and returning a portion of the solvent recovered tailings component to the solvent recovery apparatus as a returned solvent recovered tailings component.	naphtha, paraffin

Table 6. Bitumen Recovery and Water Content at Different Froth Treatment Conditions for a Low Quality Oil Sands Ore<sup>36,37a</sup>

froth treatment	bitumen extraction	optimum diluent/bitumen weight ratio	total bitumen recovery (%)	water content (wt %)
NFT, 60 °C, 5 min	BEU, 80 °C, no NaOH	1.2 ± 0.1	67	<0.5
NFT, 60 °C, 5 min	BEU, 80 °C, 0.1 wt % NaOH (optimum)	1.2 ± 0.1	95	<0.5
NFT, 60 °C, 5 min	BEU, 50 °C, no NaOH	1.2 ± 0.1	61	<0.5
NFT, 60 °C, 5 min	Denver Cell, 80 °C, no NaOH	3.0 ± 0.1	63	<0.5
PFT, 60 °C, 40 min	BEU, 80 °C, no NaOH	1.8 ± 0.1	48	≈0
PFT, 60 °C, 40 min	BEU, 80 °C, 0.1 wt % NaOH (optimum)	1.4 ± 0.2	84	≈0
PFT, 60 °C, 40 min	BEU, 50 °C, no NaOH	1.8 ± 0.1	39	≈0
PFT, 60 °C, 40 min	Denver Cell, 80 °C, 0.1 wt % NaOH (optimum)	1.1 ± 0.1	80	≈0

<sup>a</sup>Abbreviations: NFT, naphthenic froth treatment process; PFT, paraffinic froth treatment process; BEU, batch extraction unit.

future. At Albion's oil sands plant north of Fort McMurray, bitumen froth is processed with paraffinic diluents, followed by a three-stage gravity settling. Some of the solvent is distilled off and the resulting dilute bitumen product is transported to the refinery. The introduction of pure saturated light paraffinic solvents at Albion has resulted in a dramatic reduction in the water, mineral solids and chloride content of the diluted bitumen product. However, these positive effects are mostly accompanied with sacrifices on bitumen recovery due to the loss of asphaltenes which are insoluble in the paraffinic solvents.

Romanova et al.<sup>38–40</sup> simulated the NFT process and the PFT process by investigating the factors such as process temperature and the amount of additives such as NaOH in bitumen extraction, solvent type, and the froth dilution ratio in

froth treatment in laboratory tests. Some of their results are summarized in Table 6. They concluded that (1) the NFT process proved to be robust. Lowering the extraction temperature from 80 to 50 °C and changing the NaOH dosages had little effect on the subsequent bitumen froth treatment performance. For bitumen froth extracted by Denver flotation cell (higher shear than primary separation vessel, PSV), higher solvent-to-bitumen ratios (3:1) are necessary to obtain less than 0.5% water in bitumen at short residence times (5 min). At longer residence times (40 min), the optimum solvent-to-bitumen ratio was independent of the machinery used in extraction. (2) The PFT process was more sensitive to the bitumen extraction conditions. Higher shear in extraction increased overall bitumen recovery. However, higher paraffin/

bitumen ratios were required to achieve the same product quality. Lowering the extraction temperature from 80 to 50 °C reduced overall bitumen recovery (to 39%) and caused an increase in the optimum paraffin/bitumen ratios (1.8:1). The addition of NaOH during extraction significantly improved froth treatment performance for both NFT and PFT. In addition, they stated that many of those factors depend on the quality of the oil sands ores being processed.

## 6. RESEARCH OPPORTUNITIES

**6.1. Mechanism and Fundamental Studies.** Although the studies on bitumen forth treatment have been carried out for decades, the water emulsions stabilized by solid particles in bitumen froth is still the primary factor affecting the bitumen froth quality in the Athabasca oil sands industries. Most of the reported research were concerned with the nature of the water droplets in the bitumen froth. More research should be focused on methods to eliminate the water droplets from the bitumen froth. This research could be

- increasing the diffusion and mobility of the water droplets without increasing temperature, to encourage the coalescence of water droplets.
- developing effective technologies to induce coalescence of the water droplets, such as functional demulsifiers and high efficiency sedimentation equipment.
- investigating methods that prevent solid particles from getting involved in the formation of the rigid films on water droplets. It has been observed that it is much easier to eliminate water emulsions in the absence of fine mineral solids.
- developing novel collectors for the mineral solids and water droplets. Soluble polymers or partially soluble polymers that can act as both flocculants (for solid particles) and demulsifiers (for water droplets) in the diluent-bitumen solution may be promising collectors for the mineral solids and water.
- because only a subfraction of asphaltenes are believed to be involved in stabilizing the water emulsions, it is reasonable to separate the different asphaltene fractions and to study their effects in the formation of water-in-oil emulsions. However, this work would be quite challenging because of the complexity of asphaltene (e.g., even the definition of asphaltene fractions is not available).
- more studies on the possible “budding mechanism” of water-in-oil emulsion formation and the implications on oil sands bitumen extraction.

## 6.2. Pilot-Scale or Industrial-Scale Tests.

- In the paraffinic froth treatment (PFT) process, a high solvent-to-bitumen (S/B) ratio leads the removal of mineral solids and water contaminants. As a high S/B ratio both lowers viscosity and precipitates asphaltene, it is interesting to decouple these effects on the removal of mineral solids and water.
- Further systematic studies of operating parameters in bitumen extraction process, such as the dosages of NaOH, etc., on the efficiency of paraffinic froth treatment (PFT) and naphthenic froth treatment (NFT) processes, may be carried out to take a holistic approach to the extraction-froth treatment as an integrated operation rather than treating them separately.

## ■ AUTHOR INFORMATION

### Corresponding Author

\*E-mail: qi.liu@ualberta.ca.

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

The authors are grateful to Dr. Weibing Gan of Teck Metals Ltd. for his encouragement to initiate this review and for his comments and suggestions that have greatly improved this manuscript.

## ■ REFERENCES

- (1) Clark, K. A.; Pasternak, D. S. Hot water separation of bitumen from Alberta bituminous sand. *Ind. Eng. Chem.* **1932**, *24*, 1410–1416.
- (2) Kirpalani, D. M.; Matsuoka, A. CFD approach for simulation of bitumen froth settling process-Part I: hindered settling of aggregates. *Fuel* **2008**, *87*, 380–387.
- (3) Long, Y.; Dabros, T.; Hamza, H. Stability and settling characteristics of solvent-diluted bitumen emulsions. *Fuel* **2002**, *81*, 1945–1952.
- (4) Shelfantook, W. E. A perspective on the selection of froth treatment process. *Can. J. Chem. Eng.* **2004**, *82*, 704–709.
- (5) Czarnecki, J. *Encyclopedic Handbook of Emulsion Technology*; J. Sjöblom: New York, 2001; pp 497–514.
- (6) Mullins, O. C.; Sheu, E. Y.; Hammami, A.; Marshall, A. G. *Asphaltenes, Heavy Oils, and Petroleumics*; Springer: New York, 2007; pp 511–547.
- (7) Sharma A. K.; Raterman M. F. Optimizing feed mixer performance in a paraffinic froth treatment process. U.S. Patent No. US 20090321322A1, 2009.
- (8) Dabros, T.; Yeung, A.; Masliyah, J.; Czarnecki, J. Emulsification through area contraction. *J. Colloid Interface Sci.* **1999**, *210*, 222–224.
- (9) Sztukowski, D. M.; Jafari, M.; Alboudwarej, H.; Yarranton, H. W. Asphaltene self-association and water-in-hydrocarbon emulsions. *J. Colloid Interface Sci.* **2003**, *265*, 179–186.
- (10) Peramanu, S.; Pruden, B. B.; Rahimi, P. Molecular weight and specific gravity distributions for Athabasca and Cold Lake bitumens and their saturate, aromatic, resin, and asphaltene fractions. *Ind. Eng. Chem. Res.* **1999**, *38*, 3121–3130.
- (11) Groenin, H.; Mullins, O. C. Molecular size and structure of asphaltenes from various sources. *Energy Fuels* **2000**, *14*, 667–684.
- (12) Alvarado, V.; Wang, X.; Moradi, M. Role of acid components and asphaltenes in Wyoming water-in-crude oil emulsions. *Energy Fuels* **2011**, *25*, 4606–4613.
- (13) Eley, D. D.; Hey, M. J.; Symonds, J. D. Emulsions of water in asphaltene-containing oils 1. Droplet size distribution and emulsification rates. *Colloids Surf.* **1988**, *32*, 87–101.
- (14) Gafanova, O. V.; Yarranton, W. The stabilization of water-in-hydrocarbon emulsions by asphaltenes and resins. *J. Colloid Interface Sci.* **2001**, *241*, 469–478.
- (15) Ese, M. H.; Sjöblom, J.; Djuve, J.; Pugh, R. An atomic force microscopy study of asphaltenes on mica surfaces. *Colloid Polym. Sci.* **2000**, *278*, 532–538.
- (16) Yarranton, H. W.; Hussein, H.; Masliyah, J. H. Water-in-hydrocarbon emulsions stabilized by asphaltenes at low concentrations. *J. Colloids Surf.* **2000**, *228*, 52–63.
- (17) Daniel-David, D.; Pezon, I.; Dalmazzone, C.; Noik, C.; Clausse, D.; Komunjer, L. Elastic properties of crude oil/water interface in presence of polymeric emulsion breakers. *Colloids Surf. A* **2005**, *270*, 257–262.
- (18) Neuville, M.; Rondelez, F.; Cagna, A.; Sanchez, M. Two-step adsorption of endogenous asphaltene surfactants at the bitumen–water interface. *Energy Fuels* **2012**, *26*, 7246–7242.
- (19) Yeung, A.; Dabros, T.; Czarnecki, J.; Masliyah, J. On the interfacial properties of micrometer-sized water droplets in crude oil. *Proc. R. Soc. Lond. A.* **1999**, *455*, 3709–3723.

- (20) Czarnecki, J.; Moran, K. On the stabilization mechanism of water-in-oil emulsions in petroleum systems. *Energy Fuels* **2005**, *19*, 2074–2079.
- (21) Czarnecki, J.; Tchoukov, P.; Dabros, T. Possible role of asphaltenes in the stabilization of water-in-crude oil emulsions. *Energy Fuels* **2012**, *26*, 5782–5786.
- (22) Jiang, T.; Hirasaki, G. J.; Miller, C. A.; Ng, S. Effects of clay wettability and process variables on separation of diluted bitumen emulsion. *Energy Fuels* **2011**, *25*, 545–554.
- (23) Jiang, T.; Hirasaki, G. J.; Miller, C. A.; Ng, S. Wettability alteration of clay in solid-stabilized emulsions. *Energy Fuels* **2011**, *25*, 2551–2558.
- (24) Chen, F.; Finch, J. A.; Xu, Z.; Zarnecki, J. Wettability of fine solids extracted from bitumen froth. *J. Adhesion Sci. Technol.* **1999**, *13*, 1209–1224.
- (25) <http://canmetenergy.nrcan.gc.ca/oil-sands/404>
- (26) Stasiuk, E. N.; Schramm, L. L. The influence of solvent and demulsifier additions on nascent froth formation during flotation recovery of bibumen from Athabasca oil sands. *Fuel Process. Technol.* **2001**, *73*, 95–110.
- (27) Zhang, L. Y.; Xu, Z.; Masliyah, J. H. Langmuir and Langmuir–Blodgett films of mixed asphaltene and a demulsifier. *Langmuir* **2003**, *19*, 9730–9741.
- (28) Sun, T.; Zhang, L.; Wang, Y.; Zhao, S.; Peng, B.; Li, M.; Yu, J. Influence of demulsifiers of different structures on interfacial dilational properties of an oil–water interface containing surface-active fractions from crude oil. *J. Colloid Interface Sci.* **2002**, *255*, 241–247.
- (29) Peng, J.; Liu, Q.; Xu, Z.; Masliyah, J. Novel magnetic demulsifier for water removal from diluted bitumen emulsion. *Energy Fuel* **2012**, *26*, 2705–2710.
- (30) Kan J.; Andersen N.; Strand C.; Thomas R.; Erker G. *The 1997 Froth Treatment Pilot Test Program*, Syncrude division report WRC 98–07; Syncrude: Fort McMurray, Alberta, January 1998.
- (31) Long, Y.; Dabros, T.; Hamza, H. Structure of water/solids/asphaltenes aggregates and effect of mixing temperature on settling rate in solvent-diluted bitumen. *Fuel* **2004**, *83*, 823–832.
- (32) Angle, C. W.; Long, Y.; Hamza, H.; Lue, L. Precipitation of asphaltenes from solvent-diluted heavy oil and thermodynamic properties of solvent-diluted heavy oil solutions. *Fuel* **2006**, *85*, 492–506.
- (33) Zawala, J.; Dabros, T.; Hamza, H. A. Settling properties of aggregates in paraffinic froth treatment. *Energy Fuels* **2012**, *26*, 5775–5781.
- (34) Madge, D. N.; Romero, J.; Strand, W. L. Hydrocarbon cyclones in hydrophilic oil sand environments. *Miner. Eng.* **2004**, *17*, 625–636.
- (35) Madge, D. N.; Romero, J.; Strand, W. L. Process reagents for the enhanced removal of solids and water from oil sand froth. *Miner. Eng.* **2005**, *18*, 159–169.
- (36) Madge, D. N.; Garner, W. N. Theory of asphaltene precipitation in a hydrocarbon cyclone. *Miner. Eng.* **2007**, *20*, 387–394.
- (37) Garner W. N.; Madge D. N.; Strand W. L. Bituminous froth inclined plate separator and hydrocarbon cyclone treatment process. U.S. Patent No. US 7438807B2, 2009.
- (38) Romanova, U. G.; Yarranton, H. W.; Schramm, L. L.; Shelfantook, W. E. Investigation of oil sands froth treatment. *Can. J. Chem. Eng.* **2004**, *82*, 710–721.
- (39) Romanova, U. G.; Yarranton, H. W.; Schramm, L. L.; Shelfantook, W. E. The effects of oil sands bitumen extraction conditions on froth treatment performance. *J. Can. Pet. Technol.* **2006**, *45*, 36–45.
- (40) Romanova, U. G.; Yarranton, H. W.; Schramm, L. L. Towards the improvement of the efficiency of oil sands froth treatment. *Can. Int. Pet. Conf.* **2003**, 1–5.