CHAPTER 12.27

Oil and Tar Sands

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Despite great effort in developing alternative and renewable energies to mitigate greenhouse gas emissions, fossil fuels will remain a major mix of our energy strategy for many years to come because of their high-energy intensity and proven utilization with existing infrastructures, in particular considering the rapid increase in population of developing countries and steady improvement in quality of life. Unfortunately, the steady and increased consumption of conventional liquid fossil fuels (oils) will inevitably deplete these attractive high-value energy resources. For the security of future energy demand, we are forced to exploit unconventional fossil fuel resources, most notably shale gas, oil (tar) sands, and gas hydrates. With more than 300 billion barrels of ultimate potential recoverable reserve of heavy oil (bitumen) locked in place in oil sands of northern Alberta (Canada) alone, development of this vast energy resource would alleviate the pressure of depleting conventional liquid fossil fuels for a significant period, buying time to develop new technologies and materials for renewable energies, most notably solar energy. Although the largest and most mature (produced reserves) oil sands reserves are found in Canada, there are several other significant global oil sands deposits in Venezuela, the United States, Trinidad, Russia, Nigeria, Madagascar, and South-Eastern Europe (Romania and Albania). Of the major accumulations, the vast majority of the known initial in-place volumes occurs in Canada and Venezuela. Current estimates of global reserves are not readily available, although orders-of-magnitude assessments can be made from past reviews (Scott 1967; Walters 1974). At present, Canada produces approximately 2.5 million barrels of oil per day from oil sands reserves. This chapter provides an overview of the technologies used to unlock the oil sands energy resources, mainly focusing on minable oil sands where mineral processing technologies are heavily used, starting with an overview on oil sands resources and major properties of bitumen as they are highly pertinent to the processing technologies.

As shown in Figure 1, Alberta oil sands formation is a result of aerobatic biodegradation of conventional petroleum as it migrated updip from deeper sections of the pre-Cretaceous formation of the Western Canada Sedimentary Basin, to the Alberta Basin where it was trapped in the permeable sands of the Fort McMurray formation between the Devonian carbonate below and Cretaceous Clearwater Formation shale above. Based on the environment of sediment deposition, oil sands formation in Fort McMurray can be conveniently divided into three subsections: Lower (continental fluvial), Middle (tidal estuary), and Upper (tidal marine), with increasing content of marine clays in the formation. The biodegradation over millions of years led to the formation of heavy oil known as crude bitumen. On average, bitumen has an in situ viscosity >100 Pa·s and density of about 998 kg/m^3 (an API gravity <10°), which is similar to the density of water. It is important to note a power law dependence of bitumen viscosity to the temperature and roughly a linear decrease in bitumen density with increasing temperature. Such physical properties of bitumen require the bitumen recovery process to operate at elevated temperatures typically greater than 40°C and by air-assisted flotation as described in the following sections.

OVERALL PROCESSING OF MINABLE OIL SANDS

The processing flow sheet of minable oil sands is shown in Figure 2. The unit operations involved in the processing are described in more detail later in this chapter. Here, only the overall bitumen recovery process and connections between the unit operations are described. Oil sands ores typically contain about 10 wt % bitumen and 3–6 wt % of connate (formation) water, with the remaining being a mixture of silica sand and clays including kaolinite, illite, and small amounts of other clay minerals. After removing overburden in the mine, the ore is mined with electric or hydraulic shovels and transported to the slurry preparation unit by trucks. Economy of scale prefers using equipment that is as large as possible.

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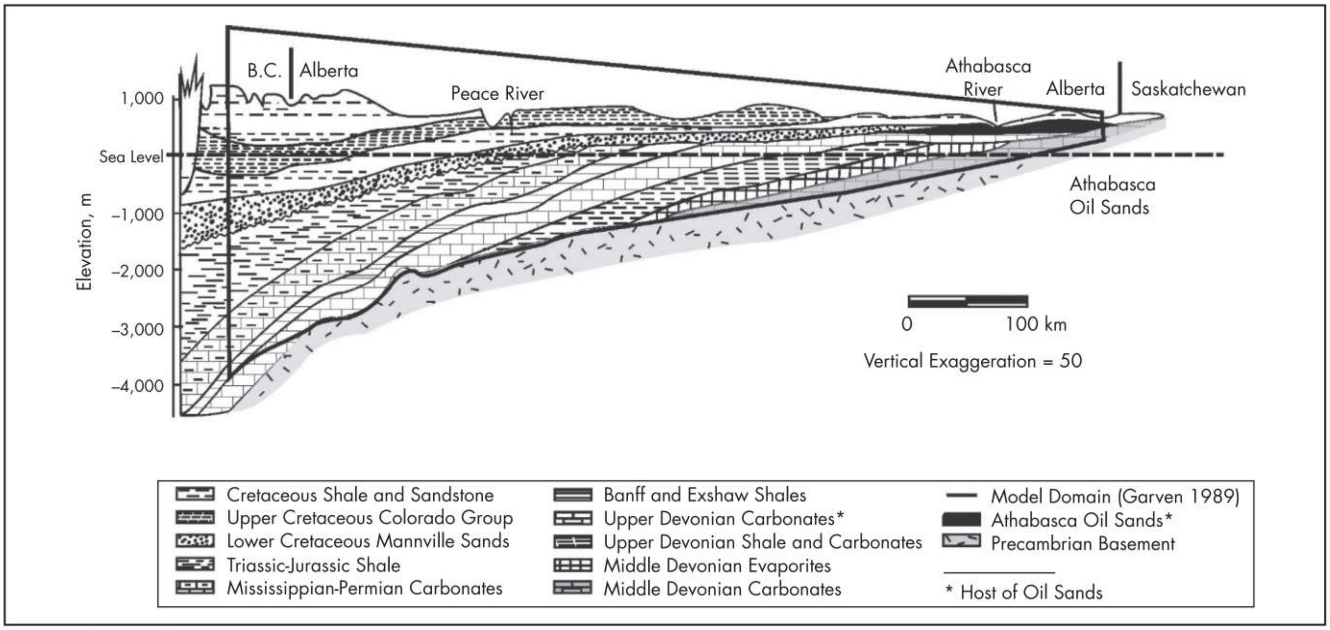


Source: Adams et al. 2004

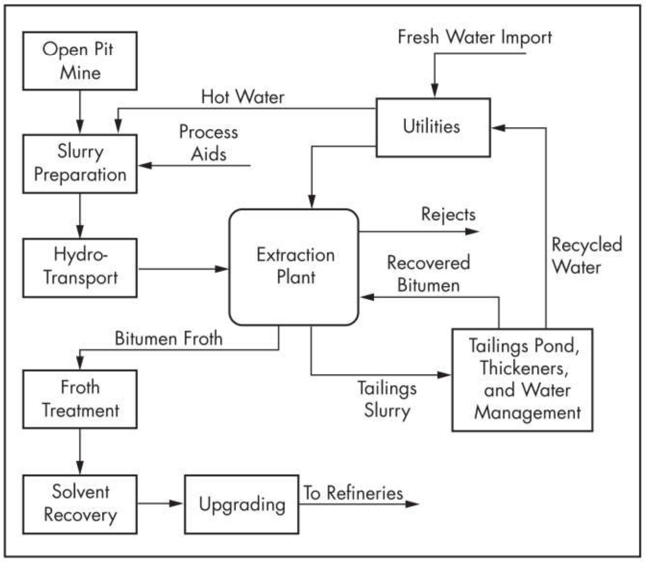
Figure 1 Geological formation and migration of crude oil

At slurry preparation the ore is crushed, screened, and mixed with hot water to produce slurry that is then fed to a slurry hydrotransport pipeline, which is a major innovation in the oil sands industry.

To enhance bitumen recovery, chemical process aids are often added at this point. Sodium hydroxide (caustic) is the most commonly used chemical to control the slurry pH, although sodium bicarbonate or carbonate can also be used as additives. For example, a mineral named trona and a commercial product called Geosol (mixtures of both sodium carbonate and bicarbonate) have been tested at large pilot-plant scale. In some cases, inorganic dispersants such as sodium silicate (liquid glass) and calcium chelating agents such as sodium citrate have also been tested either in laboratory or commercial operations.

Most of the ore conditioning takes place in the pipeline. *Conditioning* is a term used to cover all elementary processes needed to make bitumen separation feasible. Oil sands ore chunks (lumps) have to be ablated, bitumen washed off the solids (or liberated), and clay minerals dispersed. Bitumen droplets collide with dispersed air bubbles. Under favorable conditions, air bubbles and bitumen droplets form stable aggregates on collision. At temperatures well above 50°C, bitumen spreads over the air, totally engulfing air bubbles. At much lower temperatures, bitumen droplets attach themselves to the bubbles, similar to mineral grain attachment to air bubbles in conventional mineral flotation.

To separate the aerated bitumen from the slurry, the conditioned slurry is fed to primary separation vessels or cells in the extraction plant. The aerated bitumen floats to the top of the separation vessels to form a layer of bituminous froth, which is collected, deareated, and then sent to froth treatment to further remove entrained solids and water. The coarse solids in the slurry settle quickly to the bottom of the primary separation vessels, which are pumped, in most cases, to the tailing ponds. The middle layer, called *middlings*, contains mostly water and dispersed fine solids (clays) with some bitumen in the form of fine droplets that do not have sufficient time to report to the froth. This is usually caused by insufficient aeration, compounded by the attachment of bitumen to some hydrophobic solid particles, making the bitumen-carrying aggregate too heavy to float. To recover this bitumen, the middlings stream is sent to flotation cells, similar to those used in conventional mineral processing. Both column and mechanical flotation cells are used, depending on the configuration of the plant. In flotation, additional air is introduced under a high-shear environment to aerate this portion of bitumen, which is recovered in the form of a secondary froth, usually of much lower quality than the froth formed in primary separation vessels. This secondary froth is typically recycled to primary separation vessels while the underflow from flotation cells is sent to tailings.



Adapted from Masliyah et al. 2011

Figure 2 Overall flow sheet of minable oil sands processing

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The bituminous froth from the primary separation vessels typically contains about 60 wt % bitumen, 30 wt % water, and 10 wt % solids. Water contains dissolved salts, mostly originating from the ore, which contain various amounts of chlorides. Chlorides pose serious corrosion problems in downstream operations. Solids, in particular finely dispersed clays, deactivate upgrading catalysts by clogging catalyst pores. Both fine solids and small amounts of larger solid particles contribute to erosion of pump impellers, valves, and pipes. Before passing bitumen to downstream operations or transporting in pipelines to the market, the entrained solids and water must be removed to meet stringent upgrading or pipeline specifications. Removal of all those impurities takes place in the froth treatment operation.

Since the density of bitumen is very close to the density of water, in the froth treatment process, a light hydrocarbon solvent is added to the froth to provide a density difference between oil and water phases. Solvent addition also lowers the viscosity of the oil phase. Both of these factors enhance the oil–water-phase separation under gravity in inclined plate settlers, centrifuges, or hydrocyclones. The added solvent is then recovered in solvent recovery units by flash distillation and recycled to froth treatment. After stripping the solvent, the bitumen product is then fed to the on-site upgrading plant or sent to off-site refineries by pipelines after adjusting its viscosity either by solvent addition or by heating the bitumen.

Currently, two main technologies are used for froth treatment, depending on the type of solvent used. In naphthenic froth treatment, naphtha from a local upgrading plant is added at a solvent-to-bitumen ratio of about 0.7. In paraffinic froth treatment, a paraffinic solvent imported from outside is added at a solvent-to-bitumen ratio of about 2 for the low-temperature process and a lower value for the high-temperature froth treatment. The paraffinic solvent addition causes partial precipitation of asphaltenes in the diluted bitumen. The precipitating asphaltenes act as flocculant to bind water droplets and fine solids. The oil phase obtained from paraffinic froth treatment is very clean and dry, exceeding the pipelining or refinery specifications. The naphtha-based process produces diluted bitumen that requires addition of polymer demulsifiers and additional centrifugation to meet product specifications of water and solids content.

A utilities plant provides hot water for extraction, steam, and power for the whole integrated plant operations. The extraction plant uses mostly recycled water from tailings operations. Some fresh makeup water has to be imported from outside, usually from the Athabasca River. If there is an upgrading unit on-site, utilities use all low-cost hot gases produced by the upgrader in addition to the imported natural gas. Burning coke is also possible to provide needed energy but difficult to implement because of the high sulfur content of on-site coke.

A crucial part of the overall plant operation is water management. Tailings slurry waste from extraction is typically sent to tailing ponds, where coarse solids settle quickly on the beaches and fine solids settle slowly, forming a semifluid layer of so-called fine tailings toward the bottom of the pond. After several years, the fine tails consolidate only to some degree, forming what the industry calls *mature fine tailings*, or MFT. MFT typically contain approximately 30 wt % solids without further consolidation under natural tailings pond conditions. Nevertheless, sedimentation of solids in the pond leaves a layer of relatively clean water on top. This water is recycled to the extraction plant. Since fine solids take an extended time to settle, the water cools down to ambient temperature. As a result, the recycled water is in most cases cold, requiring reheating to about 80°C before it can be reused in slurry preparation. Therefore, there is a huge incentive to recover and recycle as much water as possible while it is still warm. This could be achieved by passing the whole tailings stream through a hydrocyclone with the warm overflow stream being recycled. Another option is to treat the flotation tailings in a thickener after proper dosing of flocculant to enhance solid–liquid separation that allows overflow warm water to be recycled quickly.

Regardless of the specific plant issues, it is always beneficial to recover as much warm water from the tailings for energy conservation (and thus lower operating costs and greenhouse gas emissions). Also, it is always beneficial to minimize the tailing ponds area. Public perception and regulatory requirements favor dry tailings disposal. Several technologies can be used to achieve this goal. One of them is flocculation of middlings followed by thickening to produce clarified warm water for recycle while generating high-settling-rate flocs. The sediments from the thickener are then mixed with coarse solids from the hydrocyclone to form nonsegregated tailings. Another is known as consolidated (or composite) technology (CT). In the CT process, the MFT is mixed with coarse sands mostly from hydrocycloned extraction tailings to achieve the right mix of fine and coarse solids. Gypsum is added to provide calcium ions needed to flocculate fine solids, allowing them to settle with the coarse sands to produce a nonsegregated sediment. This technology, capable of releasing substantial amounts of water quickly, is currently being used by a few companies, allowing reclamation of the tailings disposal sites a few years after placement. Dosing of gypsum has to be just right to avoid loading the recycle water with calcium, as calcium ions are known to be detrimental to the extraction plant operation.

Following atmospheric and vacuum distillation in the on-site upgrading plant, bitumen is fed to a fluid or delayed coker. Placing a coker at the front end of the upgrading plant allows bitumen feed of a lower quality than that required for a catalytic hydrotreatment unit. If the bitumen is sent off-site for further processing, substantially cleaner product is required. Therefore, plant-specific issues dictate the configuration of the upgrading unit, specifications for the froth treatment product, light hydrocarbon solvent recycle schemes, and many other parameters needed for plant design and operation. Most of the unit operations mentioned earlier in this chapter are discussed in substantially more detail later.

BITUMEN RECOVERY FUNDAMENTALS

For effective bitumen recovery from the oil sand–water slurry, the bitumen has to be *liberated*; that is, the oil sand must be dispersed in water and bitumen must be washed off the sand grains. Individual bitumen droplets formed by liberation collide with dispersed air, forming stable bitumen–air aggregates in a process called *aeration*. In *flotation*, aerated bitumen of sufficient buoyancy reports to the top of the separation vessel to form a layer of froth. Rates of all these elementary steps, including liberation, aeration, and flotation, depend on viscosities of all phases involved (and therefore on temperature) and interfacial tensions between all the phases. Water chemistry, especially pH and divalent ion content, and to a lesser extent the total salt content, also have a profound effect on all the

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elementary steps and therefore on bitumen recovery. The fundamental science governing these elementary steps involved in bitumen recovery is discussed next.

Bitumen Liberation

Bitumen liberation, or the separation of bitumen from sand grains in water, is the first essential step in bitumen recovery. It proceeds in two consecutive steps: bitumen recession on the sand surface and its separation from sand grains to form small droplets freely flowing in the slurry (Figure 3). The recession step is driven by an energy change relating to the replacement of bitumen–sand interface with sand–water interface, assuming the change in the bitumen–water interface when bitumen forms small droplets can be neglected. The governing formulae of the well-known Young's equation for bitumen on a solid surface in water is given by

$$\gamma_{B/S} - \gamma_{S/W} = \gamma_{B/W} \cos\theta \qquad \textbf{(EQ 1)}$$

where

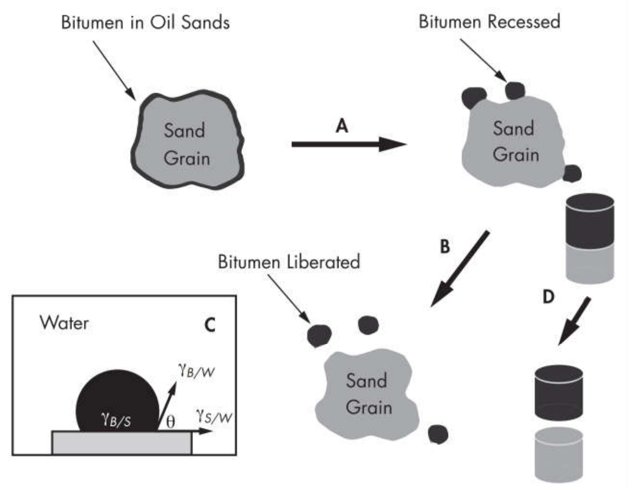
B, S, and W = bitumen, solid, and water, respectively; that is, $\gamma_{B/S}$, $\gamma_{S/W}$, and $\gamma_{B/W}$ are the bitumen–solid, solid–water, and bitumen–water interfacial tensions, respectively

θ = contact angle measured through the aqueous phase in the bitumen–solid–water system

It is important to distinguish the contact angle of water in two different systems: water–solid–bitumen and water–solid–air. The same contact angle value in these two systems does not indicate the same hydrophobicity of the solids. In other words, for a given solid, the contact angles measured in these two systems are almost always very different. Combining the thermodynamic analysis of the bitumen liberation process with Young's equation (1) yields

$$dG/dA = -\gamma_{B/W} \cos\theta \qquad \textbf{(EQ 2)}$$

where dG/dA represents the energy change during bitumen recession.



Note: Bitumen recession, A, and bitumen detachment, B (simplified in D), are determined by the aqueous contact angle, ˉ , of bitumen on a sand grain, C.

Source: Masliyah et al. 2011

Figure 3 Bitumen liberation from a sand grain in two subprocesses

Since $\gamma_{B/W}$ is always greater than zero, Equation 2 shows that spontaneous bitumen recession from a sand grain in water can only occur when $\theta < 90°$, pointing out that sand grains have to be hydrophilic for bitumen recession. In other words, the condition of Equation 2 indicates that the interaction between the sand and water must be stronger than the interaction between the sand and bitumen, $\gamma_{B/S} > \gamma_{S/W}$. The smaller the angle θ, the more negative is dG/dA, making bitumen easier to recede.

Bitumen recedes to form an approximately spherical droplet still attached to the sand grain via a "neck" unless the contact angle θ defined previously is zero. The neck diameter depends on the contact angle θ. The energy associated with the droplet displacement on solid in water is given by

$$dG/dA = \gamma_{S/W} + \gamma_{B/W} - \gamma_{B/S} \qquad \textbf{(EQ 3)}$$

Combining Equation 3 with Young's equation (1) yields

$$dG/dA = \gamma_{B/W}(1 - \cos\theta) \geq 0 \qquad \textbf{(EQ 4)}$$

Keeping in mind that $\gamma_{B/W} > 0$, the detachment energy is always greater unless $\theta = 0$. Therefore, for bitumen liberation to occur under static conditions, sand grains must be completely hydrophilic; that is, they must have a contact angle of zero, regardless of the bitumen–water interfacial tension. This is likely never to occur in practice, as even miniscule amounts of impurities adsorbing on sand would make $\theta > 0$. Therefore, bitumen droplets formed by recession have to be washed off the sand grains under the influence of hydrodynamic forces created in the hydrotransport slurry pipelines as practiced. To a lesser extent, the buoyancy of aerated bitumen and inertial forces can also play a role in bitumen detachment.

In practice, a small contact angle is always favorable. It increases the driving force for bitumen recession and makes energy required for detachment lower. Young's equation (1) suggests that to reduce the contact angle, one must reduce the bitumen–water interfacial tension ($\gamma_{B/W}$) and increase $\gamma_{B/S} - \gamma_{S/W}$, that is, increase the bitumen–sand interfacial tension and/or reduce the sand–water interfacial tension. The bitumen–sand interfacial tension cannot be easily changed in operation, whereas the exposure of sand to water on bitumen recession allows for the sand–water interfacial properties to be controlled. Increasing pH, for example, can reduce the sand–water interfacial tension, as it enhances hydrolysis and increases the charge of the sand surface, making the sand more hydrophilic at high pH, which is beneficial for bitumen liberation (Wang et al. 2010). Notably, increasing the temperature from 40°C to 80°C had little effect on contact angle. It is believed that at 40°C, bitumen is already fairly fluidlike so that the transfer of natural surfactant from the bulk bitumen to the bitumen–aqueous interface and bitumen globule formation occurred over the time span of the experiments.

The important role of wettability of sand in bitumen liberation is clearly reflected by difficulties in the processing of weathered ores (Ren et al. 2008). Researchers found that the weathering of oil sands ores led to a significant reduction of water wettability (an increase in the contact angle of water on solids from 42° to 65°) because of the contamination of solids by toluene-insoluble hydrocarbons on solid surfaces. Direct force measurements by atomic force microscopy (AFM) showed an increase in the adhesion force between

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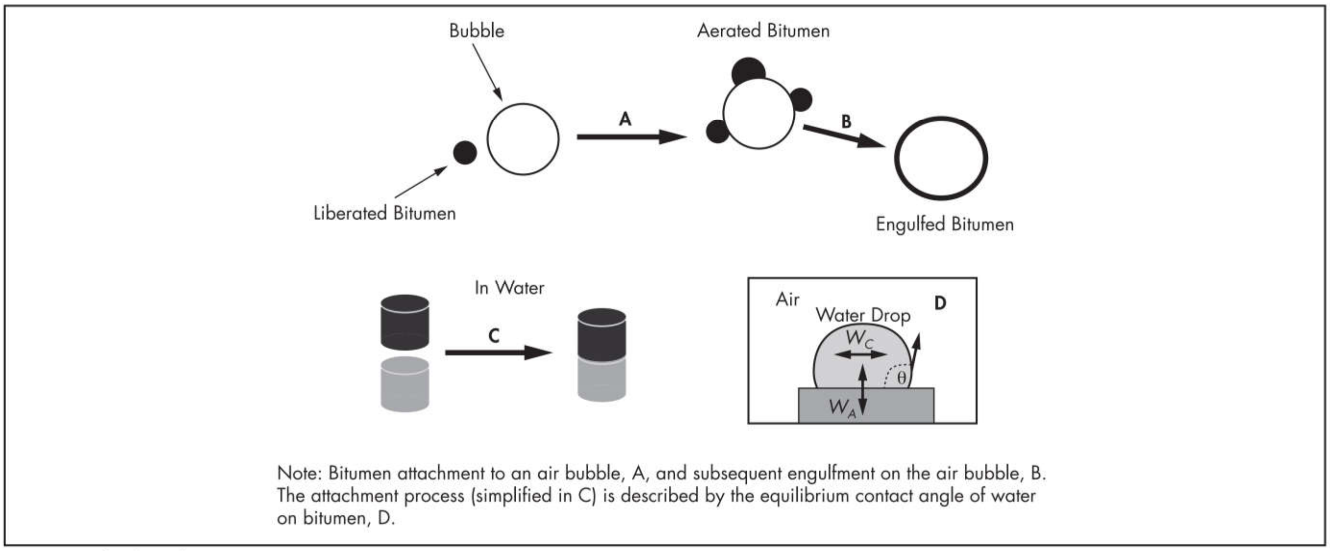

Note: Bitumen attachment to an air bubble, A, and subsequent engulfment on the air bubble, B. The attachment process (simplified in C) is described by the equilibrium contact angle of water on bitumen, D.

Source: Masliyah et al. 2011

Figure 4 Bitumen attachment and engulfment of an air bubble

bitumen and silica spheres on weathering of bitumen-coated sand grains. Poor liberation of bitumen from weathered oil sand ores was confirmed experimentally by bitumen recession experiments using bitumen-coated glass slides with and without artificial weathering (Ren et al. 2009). Slow bitumen liberation following artificial weathering is partially responsible for the poor processability of weathered ores, leading to low bitumen recovery and poor froth quality. Note that hot-water washing (at temperatures above 65°C) was able to restore the wettability of contaminated solids and hence improve the processability of weathered ores, further justifying the use of hot water in industrial oil sands extraction operations to ensure a robust processing condition.

In view of the observed significant role of surfactants, water chemistry is expected to influence bitumen liberation, as it affects the soluble surfactant concentration. A recent study using the AFM probe technique showed a significant increase in adhesion force between a silica particle and bitumen in the presence of divalent calcium and magnesium cations (Zhao et al. 2006). The presence of surfactants was found to alleviate the negative impact of divalent cations on bitumen liberation. A further study found that there was strong adhesion between bitumen and silica sand in simulated process water, whereas the addition of bicarbonate to the simulated process water could reduce the adhesion by more than tenfold, suggesting that bitumen liberation is much easier in the presence than in the absence of bicarbonate (Zhao et al. 2009). Bicarbonate is believed to scavenge calcium ions, so that the natural surfactant from bitumen remains effective, reducing the bitumen–water interfacial tension, whereas the sand surface remains hydrophilic by eliminating calcium cation bridging through scavenging of calcium ions with bicarbonate. Sodium bicarbonate addition also increases the pH of the slurry, which could contribute to enhancing bitumen liberation. It should be noted that thermodynamic analysis provides only the direction of liberation. To accurately predict the liberation process, one must consider the hydrodynamic conditions under which the liberation occurs.

Bitumen Aeration

Bitumen aeration is the process of bitumen attachment to air bubbles. It is another key step in bitumen recovery. The density of bitumen is similar to the density of water in that under its own buoyancy the bitumen would not float appreciably for industrial applications. Aeration reduces the apparent density of the bitumen–air mixture so that it is much lower than the density of the separation medium, enabling the aerated bitumen to float within a reasonable residence time to the top of the slurry in the separation vessel, where it can be recovered as bitumen-rich froth. Bitumen aeration can occur in either hydrotransport slurry pipelines or in flotation vessels. In some cases, aeration of bitumen has been found to assist in bitumen liberation (Lelinski et al. 2004).

The strength of the bitumen–air bubble attachment can be analyzed using interfacial energies. In bitumen–air bubble attachment described by A and C in Figure 4, the free energy change associated with air attachment is given by

$$dG/dA = \gamma_{B/A} - (\gamma_{B/W} + \gamma_{A/W}) \qquad \textbf{(EQ 5)}$$

Using Young's equation (1) for system D in Figure 4 leads to

$$dG/dA = \gamma_{A/W}(\cos\theta - 1) \qquad \textbf{(EQ 6)}$$

Clearly, when the contact angle θ is greater than zero, *dG/dA* is less than zero, that is, the bitumen–air bubble attachment is thermodynamically spontaneous. Equation 6 shows that the larger the contact angle, the more negative the *dG/dA*, and hence the more favorable it is for bitumen to attach to air bubbles. Increasing pH decreases the contact angle of water on bitumen, indicating less favorable attachment of air bubble to bitumen at higher pH, as shown by the less-negative value of *dG/dA* in Equation 6.

To understand how interfacial properties can be optimized for bitumen liberation and aeration, it is instructive to examine Young's equation (1) for bitumen–sand–water and for air–bitumen–water. Table 1 shows the desired trend of various interfacial tensions for this optimization. For practical

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Table 1 Desired change of interfacial tensions for better performance of bitumen liberation and aeration*

	$\cos\theta$	$\gamma_{B/S}$	$\gamma_{B/W}$	$\gamma_{B/A}$	$\gamma_{S/W}$	$\gamma_{A/W}$
Liberation	↑	↑	↓	—	↓	—
Aeration	↓	—	↑	↓	—	↑

Source: Masliyah et al. 2011

*Subscripts *B*, *S*, *A*, and *W* represent bitumen, solid, air, and water, respectively.

purposes, when the surface tension of bitumen is given, there is little room to change the interfacial tension of bitumen–sand. The only interfacial properties that can be adjusted are those of bitumen–water, sand–water, and air–water. Increasing the pH of the process medium would lead to hydrolysis of sand surfaces and ionization of both sand and bitumen surfaces, making both the bitumen and solids more hydrophilic. Increasing pH therefore would decrease the interfacial tension of the sand–water and bitumen–water interfaces, a condition that is favorable for bitumen liberation.

Increasing the pH of the process water also decreases the air–water interfacial tension, which is undesirable for bitumen aeration. It is evident that high pH is favorable for bitumen liberation, whereas a low pH is favorable for bitumen aeration. There is a clear conflict in the pH requirement, making caustic addition an important process variable. Current warm water–based oil sands extraction processes almost exclusively operate at pH values above 8.0 and below 9.0 as a compromise between bitumen liberation and aeration. Novel ideas are needed either to decouple these two subprocesses through a two-stage processing option or to maximize the air–water interfacial tension for aeration. An effective way to do this would be the use of fresh air bubbles where the air–water interfacial tension is at its maximum. In this respect, producing the bubbles in an area where contact between bitumen droplets and air bubbles could be made immediately would be beneficial. This is the concept behind the aeration technology used in modern flotation cells, such as the Microcell, the Jameson cell, and Canadian Process Technologies' cavitation-based cell.

From the perspective of molecular interaction, the thermodynamic condition of the contact angle of water on bitumen being greater than zero can be thought of as the cohesion of water being stronger than the adhesion of water to bitumen. The work of adhesion (W_A) is given by

$$W_A = \gamma_{A/W} + \gamma_{B/A} + \gamma_{B/W} \qquad \textbf{(EQ 7)}$$

whereas the work of cohesion (W_C) is

$$W_C = 2\gamma_{A/W} \qquad \textbf{(EQ 8)}$$

Inserting Equations 7 and 8 into Young's equation (1) leads to

$$\begin{aligned} dG/dA &= \gamma_{B/A} - (\gamma_{B/W} + \gamma_{A/W}) \\ &= (\gamma_{A/W} + \gamma_{B/A} - \gamma_{B/W}) - 2\gamma_{A/W} = W_A - W_C \end{aligned} \qquad \textbf{(EQ 9)}$$

Equation 9 shows that having $dG/dA < 0$ is equivalent to having $W_A < W_C$, which is identical to the contact angle being greater than zero. A stronger cohesion of water to itself than its adhesion to bitumen is illustrated in Figure 4D, where water molecules pull together to form a water droplet on the bitumen. Anything that weakens the work of adhesion of water on bitumen, such as increasing the hydrophobicity of bitumen, will enhance bitumen–air attachment and improve flotation.

The important role of bitumen surface hydrophobicity (measured by water contact angle on bitumen) in bitumen flotation is illustrated by Zhou et al. (2004). There is a correlation between bitumen recovery and water contact angle on bitumen surfaces: a higher contact angle value corresponds to a higher bitumen recovery. A critical contact angle value of 65° appears to exist. Interestingly, this critical contact angle value for effective bitumen recovery corresponds well with the value required for effective mineral flotation (Fuerstenau 2003).

After attaching to air bubbles, bitumen may spread quickly over the bubble, completely covering the bubble in a bitumen film and resulting in the formation of stable bitumen–air bubble composites. The extent and rate of bitumen spreading on an air bubble depends on the interfacial tension and the temperature of the system. The spreading process, shown in Figure 4B, can be predicted by the spreading coefficients $S_{B|W:A} = \gamma_{A/W} - (\gamma_{B/W} + \gamma_{B/A})$. Applying typical interfacial tension values for the system, the spreading coefficients are calculated to be 32.4 mN/m and 36.5 mN/m for pH 8.5 and 10.5, respectively, indicating the engulfment of bitumen on air bubbles in process water for both pH values. Using Young's equation, the spreading coefficient can be written as

$$S_{B|W:A} = \gamma_{A/W}(1 + \cos\theta) - 2\gamma_{B/A} \qquad \textbf{(EQ 10)}$$

The spreading condition of bitumen on an air bubble is therefore determined by $S_{B|W:A} > 0$, that is,

$$\cos\theta > \frac{2\gamma_{B/A}}{\gamma_{A/W}} - 1 \qquad \textbf{(EQ 11)}$$

Inserting typical values of $\gamma_{B/A}$ = 30 mN/m and $\gamma_{A/W}$ = 68 mN/m for process water into Equation 11 leads to a critical contact angle value of 97°. This value is greater than the contact angle values measured over the entire operating pH range. Therefore, bitumen is likely to spread on the air bubble on attachment in the warm/hot-water extraction process. This finding implies that bitumen–air bubble attachment is a critical step for bitumen flotation, provided that the temperature is sufficiently high so that bitumen viscosity is not a rate-limiting factor.

UNIT OPERATIONS

The process of bitumen extraction begins at the mine face. To expose the oil sands ore, the muskeg and overburden are first removed using shovels and trucks. The excavated land is used for either land reclamation or the construction of tailings dikes. Once exposed, the oil sands ore is extracted and processed to condition the oil sands ore for optimal bitumen recovery. Many of the unit operations are common with other mining activities. Since the first commercial operation, the objectives of oil sands extraction have remained the same, although the methods to satisfy the processing criteria have witnessed several important changes. With increased production rates, oil sands operators became more flexible and adaptable to the receding mine face and the increased distance between the mine and processing facility. Increased flexibility in the mining process allows the opportunity to blend oil sands ores to ensure that the minimum criterion for bitumen recovery is exceeded. Most oil sands producers today operate a shovel-to-truck-to-hydrotransport facility, recognized for its energy efficiency and flexibility with integrated operating systems shown in Figure 2. The unit operations involved in oil sands extraction are shown in Figure 5 and are discussed briefly in the following section.

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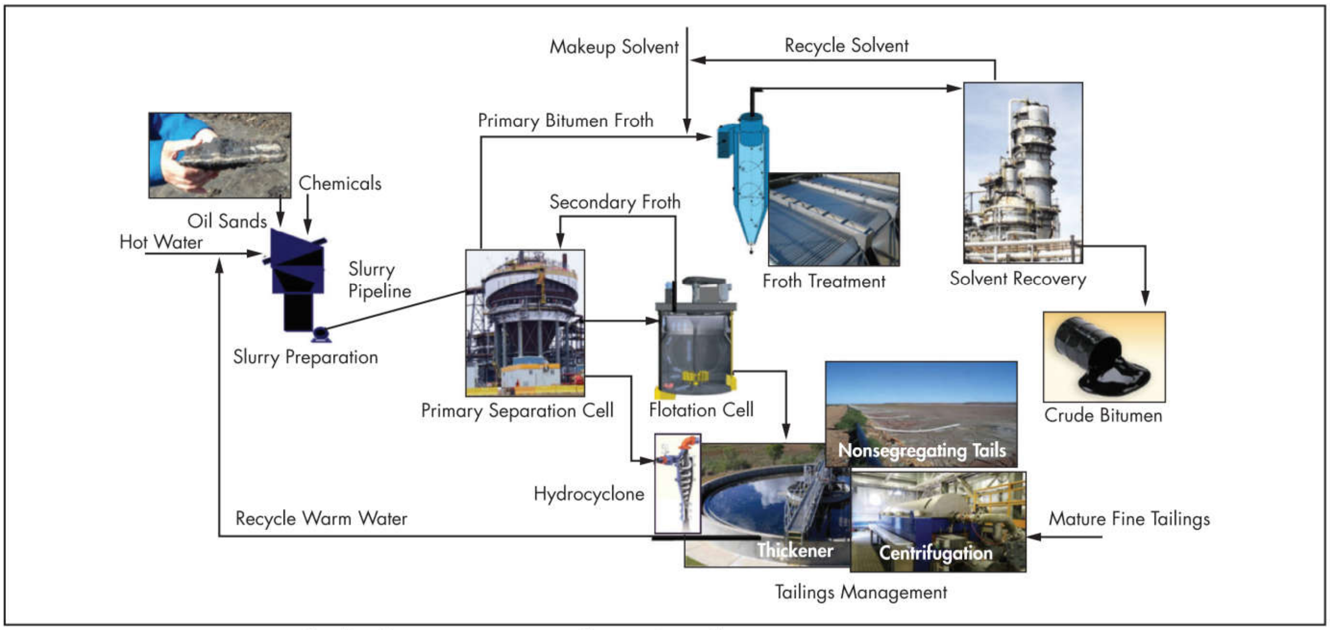


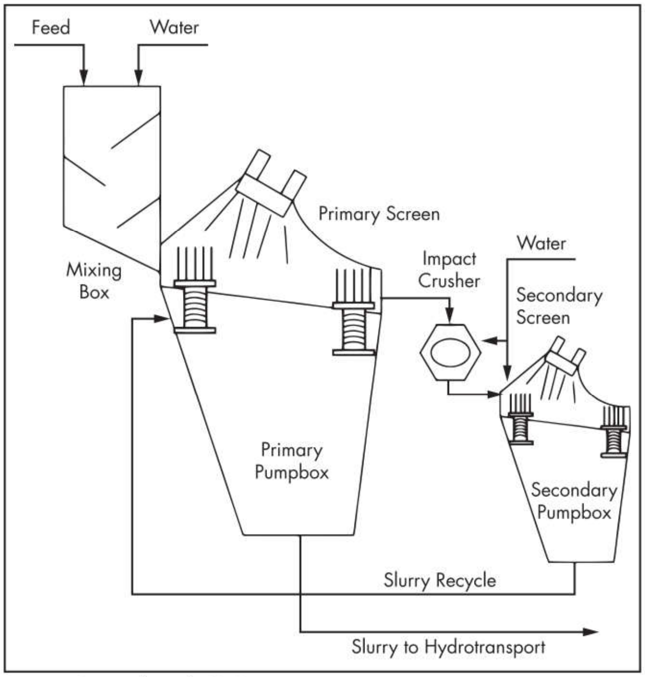
Figure 5 Unit operations involved in bitumen extraction from oil sands

Slurry Preparation

Mining of the oil sands ore typically uses a 100-t (metric-ton) bucket with large ton-capacity trucks used to move the oil sands ore to the preparation facility. The as-received oil sands ore from the mine site frequently contains large rocks and cohesive sediments that must be broken down and crushed to prevent damage to downstream processing equipment. The mined oil sands ore is therefore fed into a crushing plant where double-roll crushers reduce large lumps of oil sands ores to smaller lumps that are conveyed to a storage pile or surge bin, where the storage capacity can often provide approximately 30 minutes of continuous dry feed to the slurry preparation facility.

A typical example of a slurry preparation circuit is shown in Figure 6. The oil sands ore is mixed with process water through a baffled, inclined mixing box. The underflow slurry is then distributed onto a primary vibrating screen where coarse objects are separated from the oil sands slurry. The oversized objects are further reduced using an impact crusher with the product fed to a second screen on a secondary pumpbox and wetted with secondary wash water to improve the screening efficiency. The underflow from the secondary pumpbox is then recycled back to the primary vibrating screen, minimizing the loss of bitumen with oversized objects. Any oversized material from the secondary pumpbox is considered as waste and disposed of. The primary pumpbox underflow, on the other hand, feeds directly into the hydrotransport pipeline, continuing the process of lump ablation and bitumen liberation/aeration.

The oil sands slurry level in the primary pumpbox is maintained by the volumetric flow rate of the hydrotransport pipeline and the addition rate of process feedwater. The slurry preparation circuit produces pumpable oil sands slurry of density typically about 1,580 kg/m^3 and begins the sequence of oil sands lump ablation (size reduction) and bitumen liberation. To promote bitumen liberation, warm process water (normally >80°C) is added with pH-adjusting chemicals. As discussed earlier, warm water addition promotes a reduction in the bitumen viscosity, which improves the breakdown of large oil sands lumps and the flowability of bitumen on solids. Furthermore, operating in basic conditions at pH ≈8.5 creates favorable bitumen–water interfacial tensions and solids wettability to enhance bitumen-receding dynamics.



Source: Czarnecki et al. 2013

Figure 6 Slurry preparation circuit

A rotary breaker slurry preparation facility is an alternative to the previously discussed mixing box process. Rotary breakers were introduced by Suncor in the late 1990s at its Steepbank mine (Alberta, Canada). The crushed oil sands ore

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Courtesy of Shell Canada, as cited in *Oil Sands Magazine* 2018

Figure 7 ThyssenKrupp rotary breaker for a typical slurry preparation system

is agitated with warm water, forming a slurry that gradually slides along the inclined perforated drum. The rotary breaker is typically 4 m in diameter and about 20 m long, rotating slowly at ~10 rpm. Under slow rotation, the oil sands lumps are carried by lifters to the top of the drum before falling and impacting on the toe of the rotating drum. The digestion of large oil sands lumps allows slurry drainage into a pumpbox through 5.1- to 7.6-cm-diameter holes in the rotary breaker shell. Often the discharge from the rotary breaker is recycled to increase the slurry residence time and minimize the loss of bitumen with oversized material. An example of a rotary breaker is shown in Figure 7.

Hydrotransport

The oil sands slurry is discharged from the pumpbox and transported to the extraction facility via a hydrotransport pipeline, as shown in Figure 8. The objective of the hydrotransport pipeline is to (1) impart mechanical shear to further ablate lumps of oil sands ore, and (2) provide sufficient residence time that satisfies the requirements of bitumen liberation from the sand grains, bitumen–bitumen coalescence, and attachment of bitumen droplets to entrained air bubbles in the oil sands slurry.

Oil sands operators have to consider many factors when designing an oil sands slurry pipeline, such as the (1) maximum throughput; (2) operating flow conditions to prevent excessive pipe/pump wear and sanding; and (3) slurry flow residence time, which is often influenced by the locations of the mine site and extraction facility, and the operating temperature. Although maximum throughput is aligned to production capacity, the volumetric flow rate to achieve the desired throughput is directly related to the hydrotransport pipe diameter and slurry transport velocity. Predicting the slurry deposition velocity and reducing the potential for sliding bed flow in the pipeline are desirable to avoid excessive pipe wear and potential pipe blockage. The minimum operating velocities for oil sands slurries can be calculated using the two-layer model (Gillies et al. 1991), provided that the fines (<44 μm) content and the carrier fluid (water + fines) viscosity are known. Typical pipeline operating velocities are in the range of 3.0 to 5.0 m/s, and the pipe length is often a few kilometers. Hence, the oil sands slurry residence time is approximately 10–20 minutes.

Courtesy of Syncrude Canada Ltd.

Figure 8 Oil sands hydrotransport pipeline and primary separation vessel at Syncrude Aurora mine

Bitumen Recovery

Bitumen and water have an almost identical density; therefore, the potential for separation under gravity is very low. Attachment of bitumen to air bubbles in the slurry preparation phase, as practiced in mineral flotation, reduces the bitumen apparent density and promotes effective separation of bitumen from water and solids in the primary separation vessel. For most ores the naturally entrained air in the hydrotransport pipeline is sufficient to aerate the liberated bitumen for a recovery of up to 90%; however, operators can add additional air if deemed necessary.

The objectives of the extraction process are to maximize bitumen recovery, produce clean bitumen froth (bitumen-to-solids ratio of 6) with a bitumen recovery >90%, and discard the mined solids to the tailings ponds. To support the processing capacity of an oil sands mine, the primary separation vessels are typically between 20 m and 30 m in diameter and height to ensure a residence time >30 minutes. The cone angle of the primary separation vessel (PSV) is sufficiently steep (>55°) to prevent sand buildup and minimize the potential for plugging the underflow outlet. The bitumen extraction process

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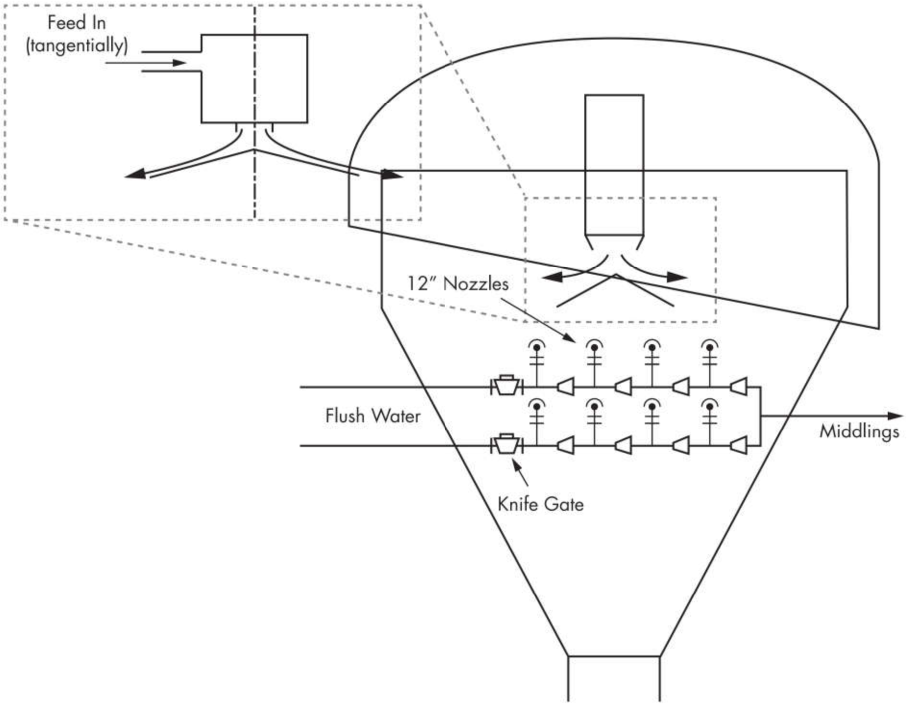

The radial distribution of the nozzles allows for a balanced withdrawal of the middlings from the PSV.
Inset: Radial feedwell increasing the tangential velocity of the slurry for even distribution within the PSV.
For a special feedwell design, see also Tyler et al. 2009.

Adapted from Czarnecki et al. 2013

Figure 9 Middlings withdrawal system positioned a few meters below the froth launder

begins as the oil sands slurry from the hydrotransport pipeline is fed into the PSV. To enhance bitumen separation from the oil sands slurry, process water is added to the oil sands slurry prior to being discharged just below the froth zone in the separation vessel. The oil sands slurry density in the feedwell is controlled to approximately 1,400 kg/m^3. The feedwell as shown in the inset of Figure 9 is designed to introduce the oil sands slurry into the separation vessel with minimal turbulence and disturbance on the separation zone. The tangential feedwell design generates a swirling flow that spreads evenly across the separation vessel as the oil sands slurry is discharged from the feedwell.

Once the oil sands slurry is fed to the separation vessel, the aerated bitumen droplets rise to form primary bitumen froth (1–2 m deep) that flows over the edge of the separation vessel into an insulated froth launder. The primary froth containing up to 40% by volume of air is deaerated with steam, and the deaerated bitumen froth containing 60 wt % bitumen, 30 wt % water, and 10 wt % solids is transferred to the froth treatment stage.

Most of the remaining bitumen is associated with the fines and clay particles that are either too heavy to float or not effectively aerated. This portion of bitumen is suspended in the slurry right below the froth, which is termed as middlings and removed from the separation vessel for further processing (secondary recovery). The middlings withdrawal system as shown in Figure 9 is designed to maintain a low-density suspension (~1,200 kg/m^3) that does not hinder the migration of aerated bitumen to the froth zone, while bitumen-loaded fines and clays are discharged to secondary separation by either flotation column or conventional mechanical flotation cells. In both flotation column and mechanical flotation cells, forced air is added to enhance aeration of fugitive bitumen and hence improve bitumen recovery. The bitumen froth from secondary separation is of much lower quality than the froth from primary separation vessels, containing more fine solids and water. The bitumen froth from the flotation circuit is therefore returned to the primary separation vessel to improve the froth quality. Bitumen recovery by primary separation and flotation is equivalent to a rougher–scavenger closed circuit in mineral processing. Cleaning as a common practice in mineral processing is hardly considered in bitumen extraction, due largely to difficulties in breaking the sticky bitumen froth.

The third exit stream from the primary separation vessel is the underflow consisting of a dense slurry of coarse solids that are transported via pipeline to the tailings pond. The bitumen concentration in the underflow is typically <0.5 wt % and is not currently considered for secondary separation. Hydrophilic particles that remain in the slurry from the flotation vessel are also transported to the tailings pond.

Proper operation of the primary separation vessel is achieved by controlling the withdrawal rate of the underflow stream based on its density, whereas dilution water is used to control the density and withdrawal rate of middlings. By considering the slip velocity of fluid particles, Masliyah and coworkers developed a materials balance model around a source zone that supplies solids to both the underflow and overflow (Nasr-El-Din et al. 1999). The concentration of light

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(oil or aerated bitumen) and heavy (solid) particles in the source zone is assumed to be uniform. If the downward fluid velocity is greater than the rise velocity of the light particles, the fluid can carry the light particles beyond the lower boundary (underflow). Otherwise, the light particles can only move beyond the upper boundary (overflow). Similar constraints govern the motion of heavy particles in the source zone. A further stipulation of the mathematical model is that light and heavy particles cannot enter the source zone from the lower (light) and upper (heavy) boundaries, respectively. The vertical velocity of the light particles at the upper boundary is given by

$$V_{lo} = V_{fo} + K_{lo} \qquad \textbf{(EQ 12)}$$

where

V_{fo} = vertical velocity of the fluid at the overflow
K_{lo} = generalized slip velocity

Similar equations can be derived for both heavy and light particles at the underflow and overflow boundaries. In addition to the slip velocities, one must define a withdrawal rate from either the underflow or overflow. For the overflow (o), the volumetric withdrawal rate (Q_o) is given by

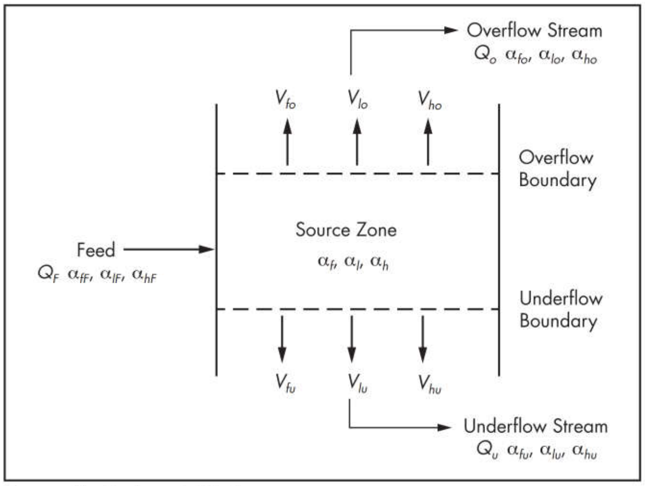
$$Q_o = -A[V_{lo}\alpha_l + V_{ho}\alpha_h + V_{fo}\alpha_f] \qquad \textbf{(EQ 13)}$$

where downward is taken to be positive and

A = cross-sectional area of the separator
α = volume fraction
l, h, and f = light particle species, heavy particle species, and fluid, respectively

The mathematical model describes the continuous separation of a bi-disperse suspension settling in a vertical settler and neglecting any lateral concentrations gradients. With the feed stream flow rate and composition defined, the model is used to describe the recovery of light and heavy particles as a function of the split ratio (Q_u/Q_F); see Figure 10.

With a high throughput, bitumen recovery in the primary separation vessel can be controlled by adjusting the middlings flow rate, the underflow withdrawal rate, or the flow rates of both streams. The typical residence time in the primary separation vessel is around 30 minutes but is highly dependent on variations in the feed stream flow rate and the quality of the oil sands ore. For low-grade ores, the residence time is often increased to account for the higher dilution ratio (water to oil sands ore), reduced attachment efficiency of bitumen droplets to flotation-sized air bubbles, and the increased hindrance of bitumen droplets navigating through the tortuous middlings layer. Typical operation performance indicators of the primary separation vessel include the bitumen froth–middlings interface level, the interface clarity, and the color of the bitumen froth. Good processing ores typically exhibit a sharp interface and shining dark bitumen froth. Although there is some instrumentation to monitor the performance of separation vessels, such as pressure or density profilers, often the most reliable performance indicator is obtained from the level of the froth–pulp interface imaged via sight glasses on the separation vessel. Sight glasses are installed in the shell of the vessel, providing plant operators with real-time information on the bitumen froth quality, clarity of the bitumen froth–middlings interface, and the depth of the bitumen froth layer. A possible challenge in running primary separation vessels is the gelation of the middlings layer because of high clay content combined with poor water chemistry, such as high divalent cation concentration.



Source: Masliyah et al. 2011

Figure 10 Vertical separation vessel used to construct a mathematic model that describes heavy and light particle separation in the source zone

Bitumen Froth Treatment

The processing objective in froth treatment is to reduce the water and solids content to meet the specifications for upgrading and/or refining of heavy bitumen. The bitumen froth containing typically 40 vol % air is too viscous to be efficiently pumped over long distances. As mentioned earlier, the bitumen froth is first deaerated prior to being fed to the subsequent froth treatment vessel as shown in Figure 11. Reducing the air content reduces the bitumen froth viscosity and increases its flowability. The air bubbles separate from the bitumen froth under buoyant force, with the separation process greatly enhanced by operating at elevated temperatures ~95°C. Through a steam deaerator, the air content in bitumen froth is reduced to approximately 5 vol %. After removal of air (deaeration), bitumen froth from the PSV typically contains 60% bitumen, 30% water, and 10% solids by weight, which remains of little value unless it is cleaned using so-called froth treatment to further reduce the water ~2.0 wt % and solids ~0.5 wt % contents so that the produced bitumen becomes suitable for upgrading and conversion to synthetic crude oil using cokers. However, much lower water and solids content are required when the diluted bitumen is transported for long distances to upgraders.

The separation of water and solids from bitumen is complicated by a weak driving force which results from an almost equivalent density of bitumen and water, and a d_{50} for the suspended water droplets and solids ranging from a few micrometers to hundreds of micrometers. To enhance the rate of separation, deaerated bitumen froth is cooled and diluted with a solvent (light hydrocarbon). The addition of a bitumen-miscible solvent significantly reduces the viscosity and density of the organic phase, assisting the separation of fine water droplets and solids by gravity. Currently, two distinctly different solvents (naphtha and paraffin liquids) are used, leading to two different froth treatment technologies known as naphthenic and paraffinic froth treatment processes.

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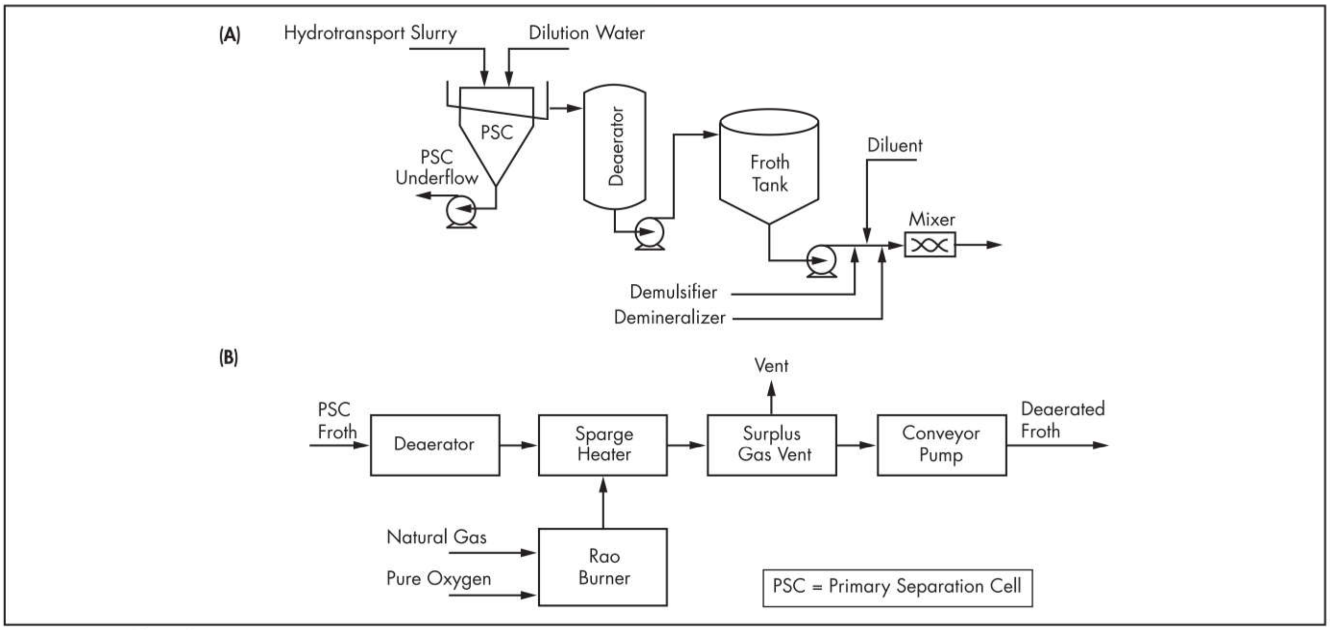

Source: Czarnecki et al. 2013

Figure 11 Typical process flow diagrams applied (A) to treat bitumen froth recovered from the primary separation vessel, and (B) expanding the sequence of steps encountered in the deaeration process via heating

In a typical naphthenic froth treatment process, shown in Figure 12, the operators dilute the bitumen froth with naphtha at a solvent-to-bitumen ratio of about 0.65–0.8 by weight. The source of naphtha is usually from an integrated upgrading plant, where a light hydrocarbon cut can be produced. Although the process provides improved separation of water and solids from bitumen, the naphthenic process requires a series of inclined plate settlers and centrifuges to achieve desirable separation rates and product quality. The complexity of the bitumen separation process is demonstrated by the process flow diagram of a commercial froth treatment plant (Figure 12).

Naphtha-diluted bitumen froth is first processed using scroll centrifuges to remove coarse solids, with a secondary separation of oversized solids achieved by pumping the diluted bitumen through a stack of Cuno filters. The remaining stream of diluted bitumen containing over-specification content of water and fine solids is then fed through a series of disc centrifuges and disc clarifiers to ensure that the water and solids contents are below the specifications of the feed to the upgrading processing plant. The fine solids and water from the disc centrifuges are further treated to recover naphtha in the naphtha recovery unit. To increase plant capacity, inclined plate settlers are installed to rapidly process a fraction of the diluted bitumen froth that immediately satisfies upgrading specifications. The underflow from the inclined plate separators is combined with the feed into the scroll centrifuges to minimize bitumen losses from the operation. The naphthenic froth treatment process is operated at atmospheric pressure and 75°–78°C.

During the naphtha separation process, any agitation resulting from pumping and mixing of the diluted bitumen can cause the formation of “tight emulsions,” with micrometer-sized water droplets (~3 μm) stabilized by hydrophobic fines (Figure 13) and asphaltenes. These solids-stabilized interfaces prevent the coalescence of water droplets and inhibit water dropout. The enhanced interfacial film stability is related to the particle wettability. Equation 14 describes the energy (ΔE) needed to detach a colloidal particle from a planar oil–water interface.

$$\Delta E = \pi r^2 \gamma_{\frac{o}{w}} (1 \pm \cos\theta)^2 \qquad \textbf{(EQ 14)}$$

With a constant oil–water interfacial tension (γ) and particle radius (r), the particle detachment energy is maximized when $\cos\theta = 0$ and minimized when $\cos\theta = -1$ and $+1$, depending on the type of emulsion, that is, water in oil (W/O) or oil in water (O/W). The conditions for minimal detachment energy correspond to complete particle wetting in either the oil phase (-1) or water phase ($+1$), whereas the maximum detachment energy is a consequence of equal partitioning of the particle in both the water and oil phases, as shown in Figure 13B. At this condition, solids-stabilized emulsions exhibit the greatest stability, which results from steric hindrance to compensate for the particle detachment energy.

To promote coalescence of solids-stabilized water droplets, chemical demulsifiers are added to the diluted bitumen at a concentration in the order of parts per million. Chemical demulsifiers are amphiphilic; hence they have a strong affinity to partition at the water–oil interface. The competitive adsorption of the demulsifier molecules at the water–oil interface disrupts the rigid particle networks, allowing the droplets to coalesce on contact. Simultaneously, demulsifier molecules continually adsorb onto the oily-contaminated solids, gradually lowering the particle hydrophobicity and consequently the particle detachment energy into the water phase. Such actions are favorable for increased rates of water separation.

The low-temperature paraffinic froth treatment process uses a paraffinic solvent at about 2:1 mass ratio, causing partial precipitation of asphaltenes. A “rigid” water–oil interface is characteristic in paraffinic froth treatment and is favorable for the sweep flocculation of water droplets by the precipitated

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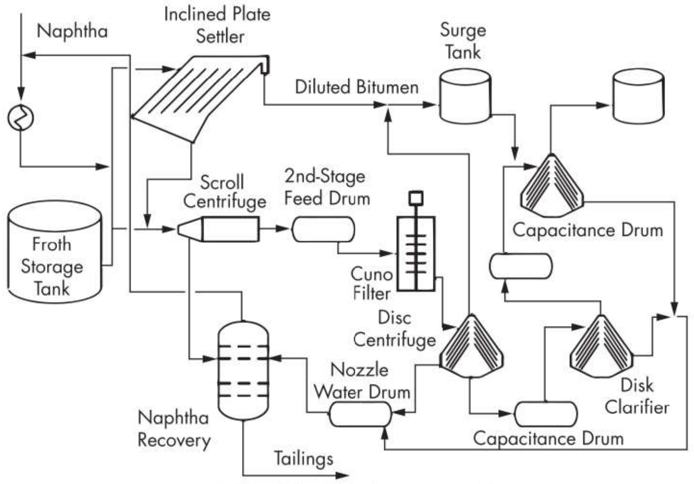
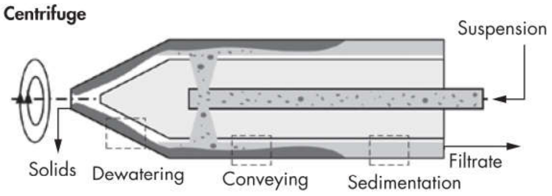


Typical Naphthenic Froth Treatment Plant

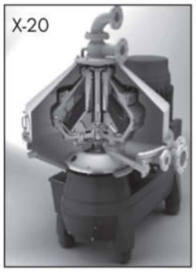
Scroll Centrifuge



Diluted bitumen froth is fed into the center of a rotating bowl and discharged through a scroll rotating in the same direction. The bowl rotating at ~800 rpm pushes the coarse solids to the bowl wall. The scroll rotating at a slightly lower speed pushes the coarse solids in the opposite direction to the liquid flow. The coarse solids are discharged to a hopper and the diluted bitumen froth recovered over a weir.

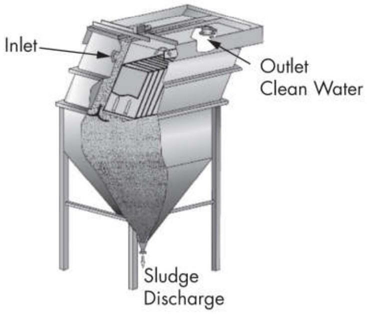
Adapted from Karsten Keller, DuPont

Cutaway of an Alfa-Laval Disc Centrifuge



The filtrate from the Cuno filter is centrifuged to separate the naphtha-diluted bitumen from water and fine solids (2–5 μm diameter). The feed enters through a central feed line and is discharged over the disc stack. Diluted bitumen is recovered through the top of the disc centrifuge as the high centrifugal forces (~2,500 g) push the fine solids and water to the outer edge of the disc stack. Water, fine solids, and some hydrocarbon are discharged through nozzles at the edge of the centrifuge. Typical disc centrifuge capacities exceed 100 m^3/h.

Inclined Plate Settler



Diluted bitumen froth flows down the feed chamber and up through the inclined plates. The narrow spacing between the plates reduces the settling distance for the solids, resulting in a higher unit capacity for a given settling area. The settled solids slide down the angled (~55°) plates and are discharged through a cone at the base of the settler along with water and some hydrocarbon emulsions. Clarified diluted bitumen froth is deaerated as the froth is recovered in the overflow launders. The bitumen product typically contains <2 wt % water and 1 wt % solids, suitable for upgrading without further processing.

Source: Czarnecki et al. 2013

Figure 12 Simplified process flow diagram of a commercial naphthenic froth treatment plant and an overview of the key processing units

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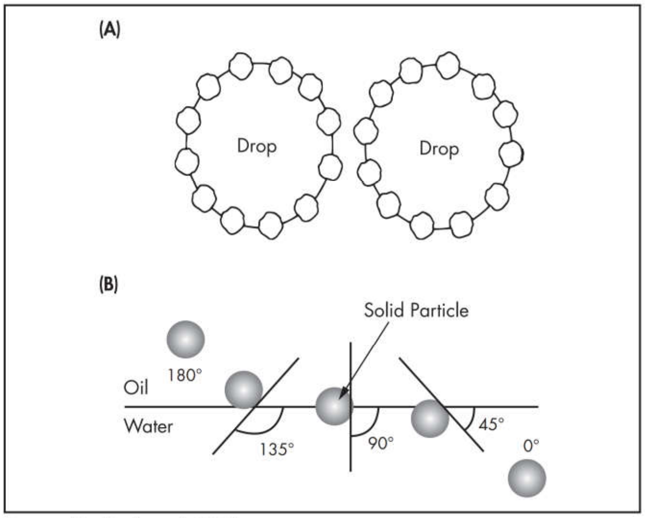
asphaltenes. The rapid settling of flocculated water droplets forms a sludge layer but leads to a virtually water- and solids-free diluted bitumen, producing a better-quality bitumen product than the naphthenic process with the water and solids contents typically <300 ppm and 700 ppm, respectively. The low water content and the partial rejection of asphaltenes mitigate corrosion concerns in downstream processing as well as facilitate higher conversion rates when treating the partially upgraded bitumen with hydrogen. The unit operations involved in a typical paraffinic froth treatment process are shown in Figure 14.



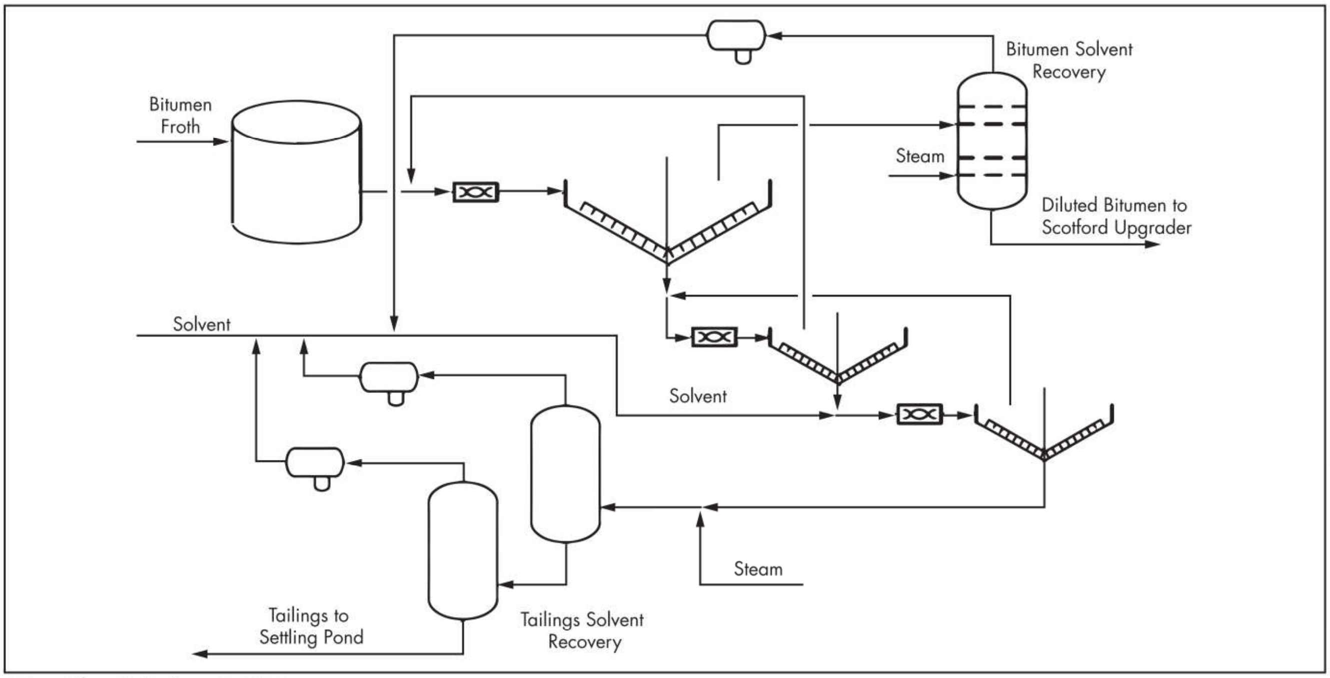
Source: Masliyah et al. 2011

Figure 13 (A) Particle-stabilized film preventing the coalescence of water droplets, and (B) influence of the particle wettability on the particle positioning at the oil–water interface

With enhanced separation driven by asphaltene precipitation, the inclined plate settlers and centrifuges used in the naphthenic froth treatment process can be replaced by large settling vessels. Three settling vessels are operated in a countercurrent flow configuration with fresh solvent blended with the underflow from the second separation vessel. The countercurrent flow ensures that the diluent-to-bitumen ratio increases from the first stage to the third stage. The final diluted bitumen product is removed from the first-stage overflow and the majority of the diluent recovered in a solvent recovery plant. Additional solvent is recovered from the tailings underflow from the third-stage separation vessel. Both solvent streams are recycled back into the third-stage settling vessel. The paraffinic froth treatment process is typically operated at atmospheric pressure and at 30°–32°C, although higher temperature operations are being used at other plants. The latter operations are referred to as high-temperature froth treatment.

Solvent Recovery

With both froth treatment processes requiring significant solvent loading, there is a need to recover and recycle the solvent back into the froth treatment process. The amount of solvent recovered is often a balance between several factors, including economics, availability, environmental impact, and transportability. Solvent recycle is achieved by passing the diluted bitumen (dilbit) through a series of process units that provide dilbit preheating, flash drums to recover the majority of the solvent, and finally fractionation. A typical process flow diagram for a naphtha solvent recovery unit is shown in Figure 15. The dilbit is first heated to a temperature between



Adapted from Birkholz et al. 1997

Figure 14 Paraffinic froth treatment process flow sheet from Albian Sands Energy

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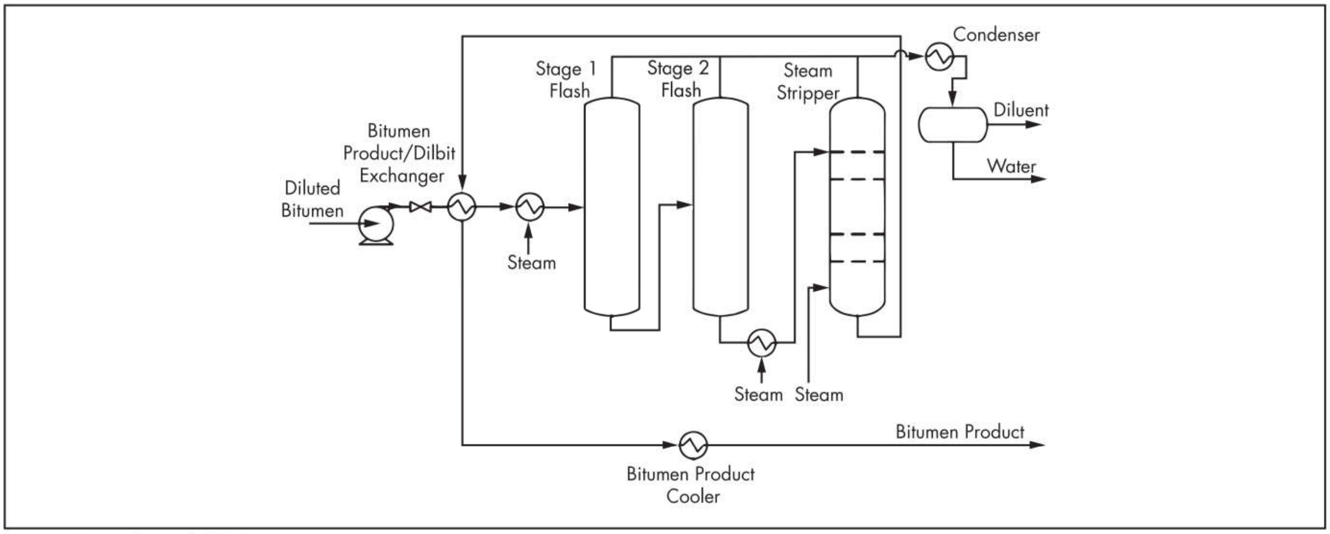

Source: Czarnecki et al. 2013

Figure 15 Naphtha-based diluent recovery unit process flow diagram

80°C and 100°C and then discharged into a flash drum or a series of flash drums. A steam stripper is then used to remove the heaviest fraction of naphtha to produce a dry bitumen product that meets the required specification for upgrading.

In paraffinic froth treatment, the product is already partially upgraded because of the loss of asphaltenes in the froth treatment process. Although solvent is recovered for recycle, the long-term stability of the bitumen is also a requirement, and this is achieved by either partial or complete removal of the paraffinic solvent to prevent further asphaltene precipitation. Since the same solvent is used in the froth treatment and bitumen transportation processes, the solvent recovery process in paraffinic froth treatment operations, as shown in Figure 16, has been designed to recover a fraction of the added solvent. The dilbit entering the solvent recovery unit contains approximately 70 wt % paraffinic (C_5/C_6) solvent. The feed stream is heated from ~33°C to the operating temperature via a sequence of heat exchanges with overhead vapor and diluted bitumen underflow from the solvent recovery unit, and a steam heater. The dilbit is then flashed in the solvent recovery unit column, and the solvent content in the bitumen product is reduced to approximately 25 wt %, suitable for pipeline transportation to the upgrading facility.

Although the majority of the added solvent is removed with the bitumen, a small portion is lost in the tailings underflow (with residual bitumen and solids) of the separation units. To further recover the solvent, the underflow streams are transferred to a tailings solvent recovery unit where the solvent content in the tailings is reduced below limits of no greater than 4 volumes of solvent to every 100 volumes of dry bitumen produced, set by the environmental regulator. A naphtha tailings solvent recovery unit is shown in Figure 17A. The hot tailings are initially diluted with hot water and distributed evenly across the flash vessel to flow down the column of shed decks, which provide countercurrent contact with the rising stripping steam added directly into the tailings pool at the bottom of the flash column. The recovered vapor from the flash vessel is sprayed with water to remove any entrained solids prior to three-phase separation of noncondensable vapors, water, and naphtha. Operating the flash vessel close to 100°C at atmospheric pressure, the solvent recovered is approximately 80% of the feed solvent.

For paraffinic solvent recovery, the flash vessel is specially designed to enable efficient solvent recovery from a feed stream that contains residual bitumen encapsulated by precipitated asphaltene flocs. The solvent recovery process from paraffinic froth treatment tailings (Figure 17B) begins by injecting steam directly into the froth treatment tailings such that the tailings temperature is well above the boiling point of the solvent. The tailings stream is subsequently sprayed into the flash vessel, which operates slightly above atmospheric pressure. Creating a fine mist increases the solvent–vapor surface area to enhance solvent mass transfer to the vapor phase. The recovered vapor separated with the solvent is recycled back to the froth treatment, and residual water and oil returned to the flash vessel. The falling mist is captured in an agitated liquid pool at the bottom of the flash vessel where continuous agitation of the liquid pool provides sufficient shear to break asphaltene flocs and particle aggregates, thus aiding the release of encapsulated bitumen. Further solvent is recovered as the underflow from the first flash vessel is fed to a second flash vessel that operates at a lower temperature and under a slight vacuum pressure. Because of the high asphaltene content, fine solids, and natural surfactants in the bitumen, there is a tendency of building up foams in the first flash vessel. To avoid excessive foaming and the potential carryover of unwanted solids, a secondary vessel (foam-breaking vessel) is operated under vacuum with the addition of chemical defoamers and asphaltene dispersants to collapse the foam before reinjection into the flash vessel. The two-step solvent recovery process as applied to treat the tailings is capable of recovering >99% of the feed solvent with ~95% of the solvent recovered in the first flash vessel.

Tailings Management

In the warm-water extraction process, the production of one barrel of crude bitumen results in approximately 3.3 m^3 of fresh tailings slurry, which is discharged to the tailings ponds. As the rate of oil production increases, industry has focused efforts on reducing the use of fresh water and increasing

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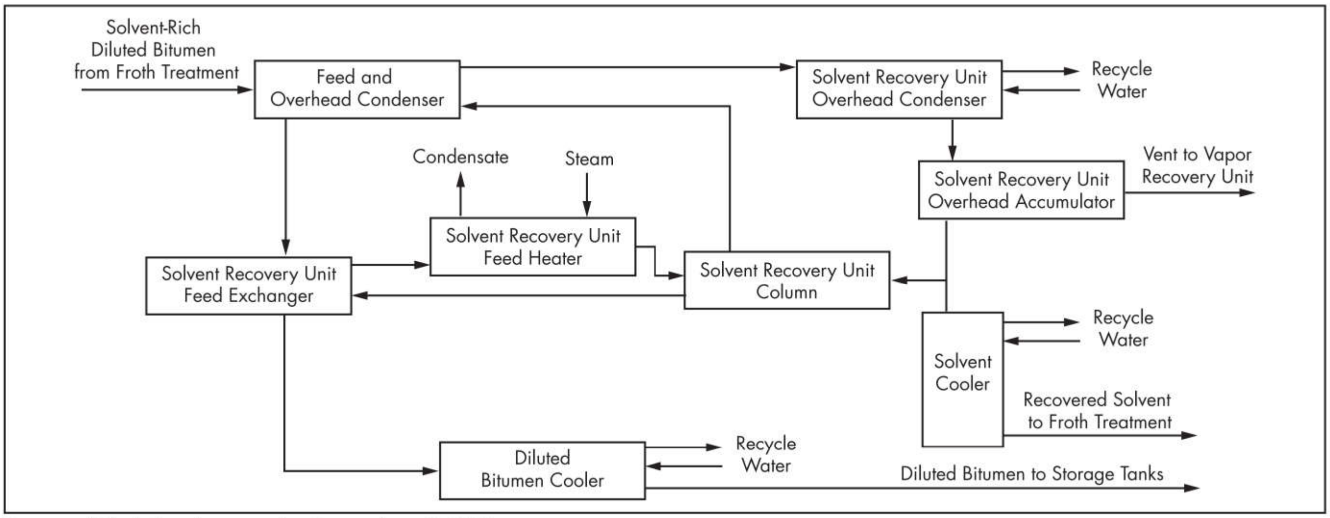
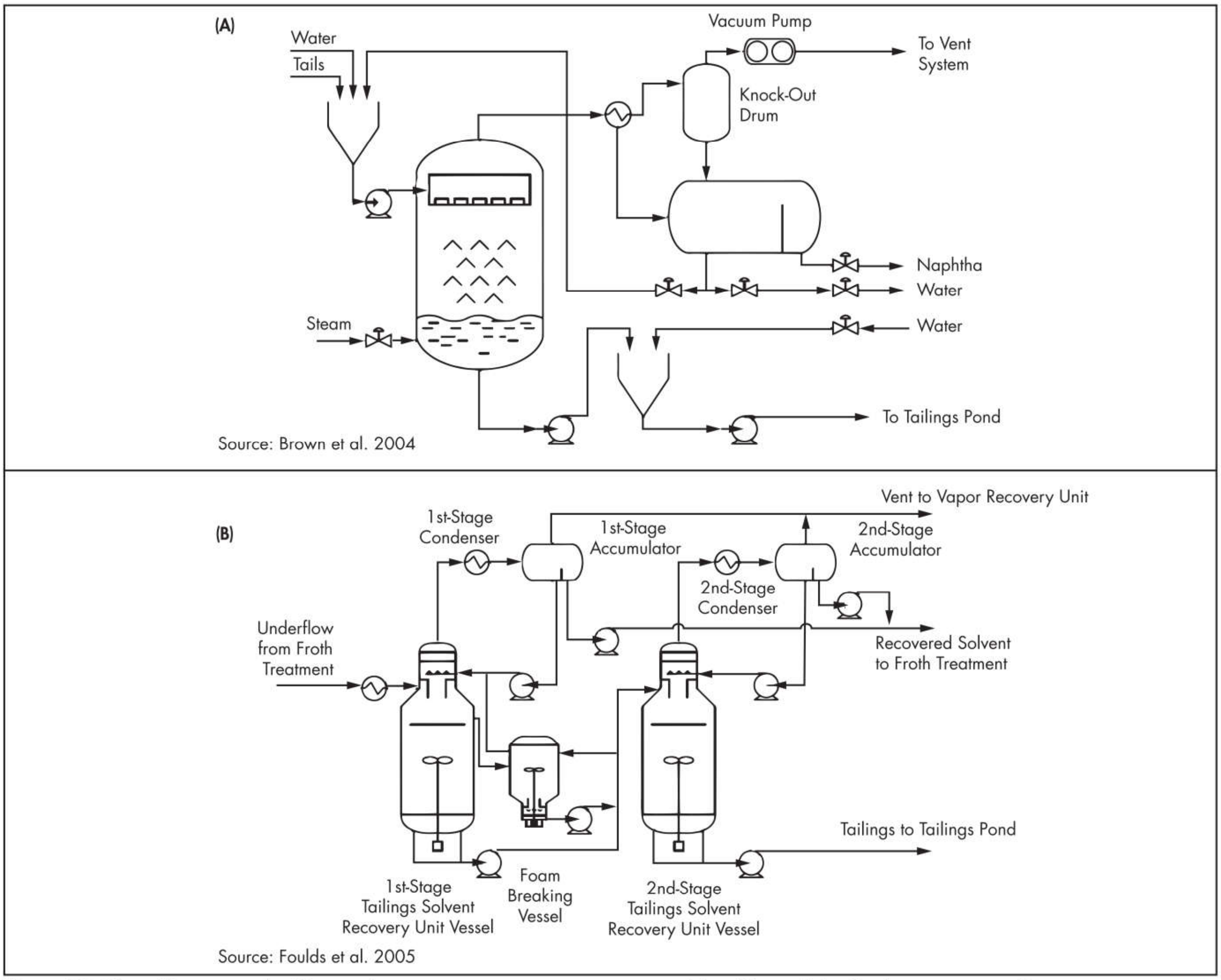


Courtesy of Shell Canada, as cited in Czarnecki et al. 2013

Figure 16 Paraffinic solvent recovery process flow diagram as operated by Albian Sands Energy



Source: Brown et al. 2004

Source: Foulds et al. 2005

Figure 17 Flow diagrams of tailings solvent recovery processes operated for (A) naphtha froth treatment tailings and (B) paraffinic froth treatment tailings

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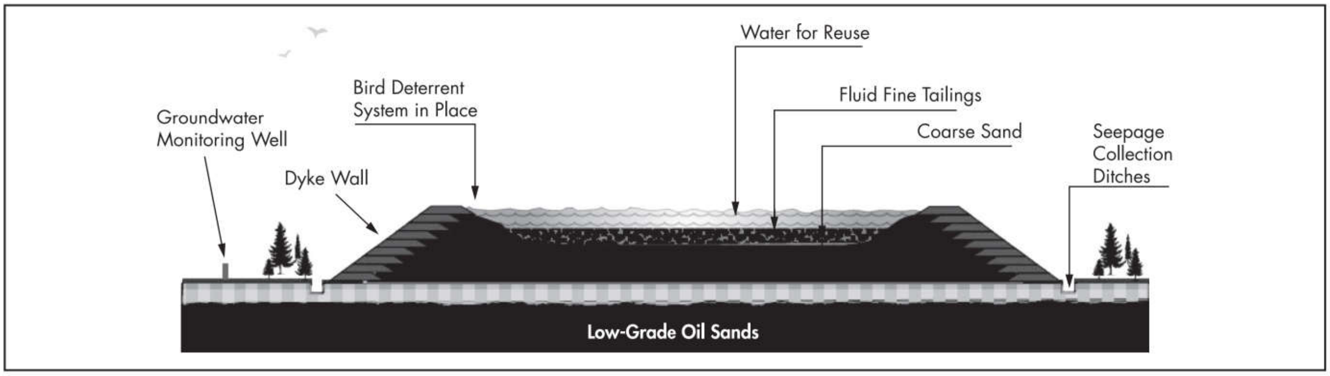
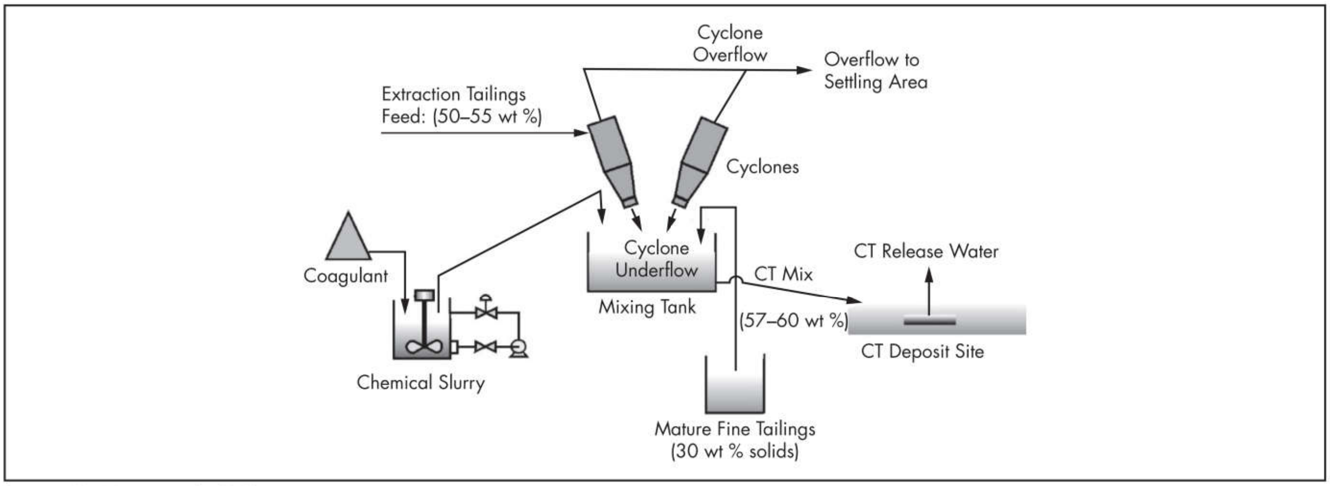


Source: Czarnecki et al. 2013

Figure 18 External tailings management facility



Source: MacKinnon et al. 2010

Figure 19 Typical CT process

energy conservation within the process. Both features rely on the rapid separation and recycle of water from the combined tailings streams received from the bitumen extraction and froth treatment stages.

Tailings ponds are contained by dikes that are formed using the overburden and interburden materials from the mining operation and from the extraction of coarse solids. As the whole tailings is discharged into the pond, the coarse solids (sands) segregate rapidly from the fines and contribute to the formation of sand beaches surrounding the tailings pond. The fine particles (silt and clays) settle along the beach as the slurry flows toward the pond water surface, where the runoff arrives as a thin slurry containing very fine solids. Following a short induction period, the fine particles begin to settle to form a zone of fluid fine tailings (FFT) in the pond. With the expansion of the oil sands industry, Alberta has witnessed the construction of tailings ponds that now occupy a total land area of more than 220 km^2. With the volume of FFT accumulating at a rate more than 20% of the volume of oil sands excavated from the mine, substantial efforts have been directed to enhance the settling rate of FFT and consolidation of MFT. FFT typically contains 85 wt % water, 13 wt % clays, and 2 wt % bitumen, with the FFT zone in the tailings pond often as deep as 40 m. After two or three years of gradual consolidation, MFT of ~30 wt % solids develops with very slow consolidation thereafter because of the relatively high compressive yield strength of the three-dimensional particle network. To avoid disturbance of the FFT during water removal, the tailings pond is usually operated with a 3-m-deep surface water zone. Figure 18 shows a typical tailings pond with the stratified tailings contained between dikes.

Environmental regulations stipulate that tailings ponds should be remediated and reclaimed within 10 years of the end of mine life. The long-term geological stability of the tailings ponds is linked to the compressibility, deformability, strength, and hydraulic conductivity of the tailings deposit. Improving the rate at which the tailings deposit meets geotechnical strength and stability calls for innovation. Tailings management innovation has allowed the industry to rapidly increase oil production during the last decade. The CT process outlined in Figure 19 and developed earlier has been used to enhance settling of FFT and densify MFT. In this process, fresh extraction tailings are first classified by hydrocyclones such that the coarse particles in the underflow of the cyclones are combined with reclaimed MFT from the tailings pond. The MFT feed stream is first treated with a coagulant, typically gypsum at 1,000 g/m^3, to promote the aggregation of the fine clay particles. The coarse particles from the hydrocyclone underflow are then blended with the treated MFT at a sands-to-fines (S/F) ratio of ~4. The mixture is discharged to a CT

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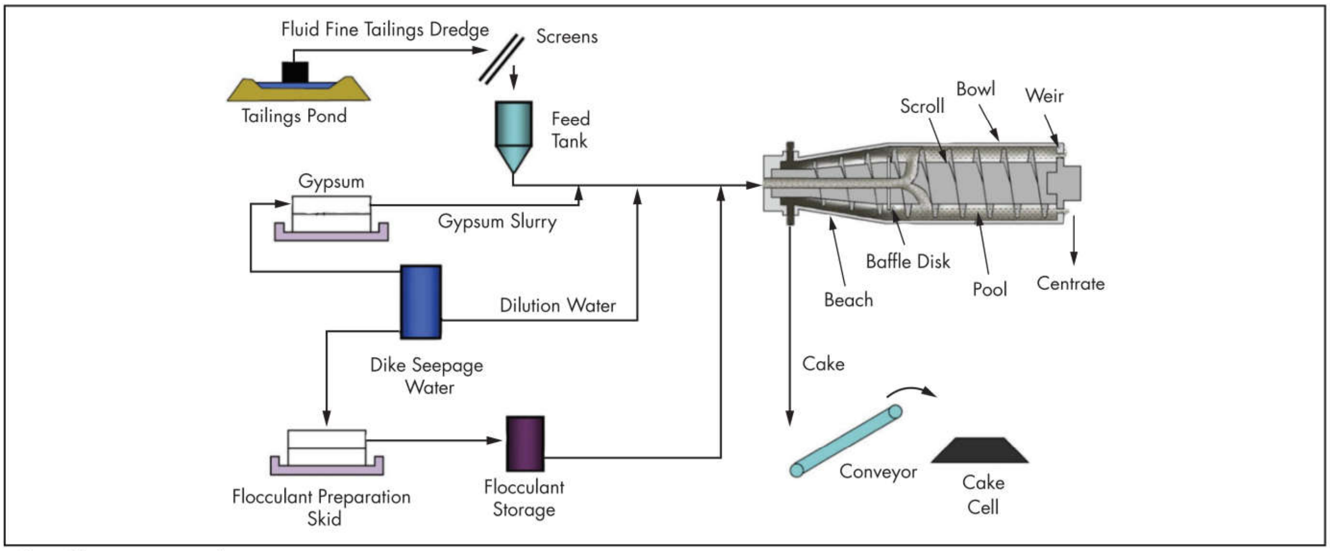
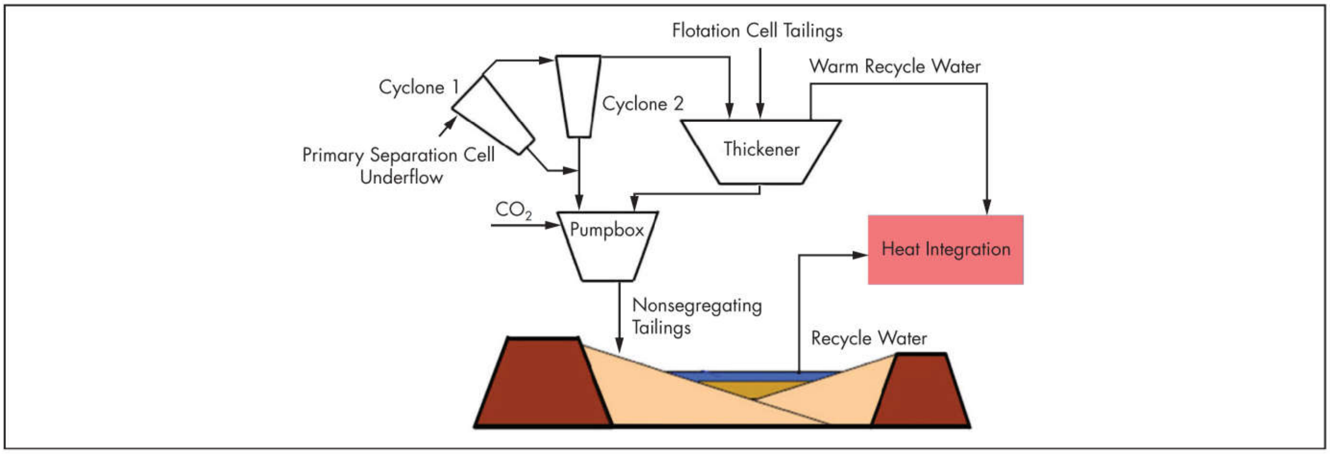


Adapted from Spence et al. 2013

Figure 20 Process diagram of decanter centrifuge for treating fluid fine tailings



Adapted from Chu et al. 2008

Figure 21 Process diagram of nonsegregating tailings process for treating fresh oil sands extraction tailings

tailings pond where the coagulated fines and the coarse sands settle at equivalent rates to quickly release the clarified water ready for recycle within a few days. After 30 days, the nonsegregating solids form a consolidated sediment of approximately 60 wt % solids, whereas further desiccation occurs over time. One of the downsides to the CT process is the continual buildup of calcium ions in the process water. Unless otherwise treated, a high concentration of calcium ions is detrimental to the processing of certain types of oil sands ores and can cause scaling in pipes and other processing equipment. The demand for coarse sands at an S/F ratio of 4 is another concern that may limit the potential of the CT process in oil sands tailings management.

A recent advance in treating MFT is by flocculation of MFT, followed by centrifugation as schematically shown in Figure 20. The centrifugation process has been commercially demonstrated (Gillies et al. 1991). In this treatment option, MFT is first dredged through a screen to remove coarse sands and debris that could potentially cause severe wear of the downstream centrifuge. The underscreen suspension stream, kept in a holding tank, is mixed with coagulant (gypsum) and further diluted if required prior to flocculant addition. The addition of gypsum is found to increase both the strength of the flocs and the throughput of the centrifuge. The flocculated MFT is sent to a decanter centrifuge to produce a centrifuge cake of solids content >55 wt % with a fines capture of 95%. With a centrifuge of 1-m bowl diameter, it is anticipated to treat 70 t of dry solids per hour (Spence et al. 2015).

There are incentives to treat FFT right after their production to avoid building large tailings ponds and additional materials handling of moving MFT, while utilizing the thermal energy in warm recycle water. To this end, the nonsegregating fresh tailings treatment process shown in Figure 21 represents another industry innovation. In this process, flotation tailings are flocculated using polymer flocculants for enhanced thickening in a specially designed thickener and rapid release of warm water. The underflow stream of primary separation cell is fed to a hydrocyclone to separate fine solids and fugitive

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bitumen from coarse sands, while fine solids and fugitive bitumen in the hydrocyclone overflow stream are fed to flotation cells for further bitumen recovery. The coarse solids in the underflow stream of the primary separation vessel are blended in the pumpbox with the underflow stream of the thickener. The mixture with added carbon dioxide (CO_2) is discharged as nonsegregating tailings (NST) to the tailings ponds where more water is released for recycle. The addition of CO_2 is to reduce the pH of NST, improve clarity of released water, and accelerate the release of water in the tailings pond for recycle. To form NST, the key is to control the ratio of fines to sand so that they fall in a nonsegregating regime of a solids mix.

Although technology has evolved to treat oil sands FFT, the challenge remains to reduce the cost of treatment and increase operational liability. For this reason, many technologies are currently under investigation or large-scale testing, including thin-lift drying, flocculation-assisted filtration, rim-ditch deposition, in-line filtration, and freeze–thaw cycles, to name just a few. Interested readers are directed to consult the Oil Sands Tailings Road Map (COSIA, n.d.).

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