Advancements of fluid fine tailings treatment technologies through fundamental research

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Abstract

Fluid fine tailings (FFT) management is one of the main challenges that oil sand developers continue to face. Syncrude Canada Ltd, independently or in collaboration with Canada’s Oil Sands Innovation Alliance (COSIA) member companies, has developed various technologies to accelerate FFT dewatering to meet progressive mine closure and reclamation objectives. One of the technologies is FFT clay treatment that targets the problematic clays in FFT. The basis of this step-out technology is the use of a polymeric flocculant to enlarge the effective size of clays and a collector to change the clay surfaces from hydrophilic to hydrophobic. In this way, the treated FFT dewater very fast. An effective, easy to use collector is key to the success of this technology. Collectors are chemical compounds added to FFT that change the clay hydrophobicity, promote aggregation of clay particles and assist in FFT dewatering. Theoretically, it is possible to directly use a cationic collector or a combination of a metal ion and an anionic collector to make the negatively charged FFT clays hydrophobic. Building on this concept, several process technology scenarios have been developed and tested. This paper demonstrates how fundamental research provides a simple and cost-effective method for screening collectors for operational FFT clay treatment.

Keywords: oil-solids attachment, collectors, hydrophobic, ether amine, quaternary amine, dodecylamine, metal ions, alkyl carboxylic acid, carboxylate, sulphonate, sulphate, FFT, clay flotation

1 Introduction

Oil sands that are geologically different from conventional petroleum resources consist of sand and clay deposits impregnated with high molar mass viscous oil, referred to as ‘bitumen’. Depending on the depths of the ore bodies, the oil sands can either be mined by surface mining followed by hot water-based bitumen extraction or treated in situ using steam assisted gravity drainage technology. At Syncrude Canada Ltd operations, the oil sand ore is open pit mined using electrical shovels and transported with heavy haulers to slurry preparation. The ore is crushed, pre-screened to reject the large rocks and debris, and slurried with hot water in the slurry preparation tower. The slurry is pumped to the extraction plant through hydrotransport pipelines where bitumen is liberated from the sands as a result of turbulent in-line conditioning. In the extraction plant, bitumen froth is separated from sands and clays that form the tailings.

After a centrifugal treatment of bitumen froth to further remove water and solids, the bitumen is sent to Upgrading to produce the final product, Syncrude Sweet Premium. In the past, the tailings were directly pumped into tailings settling basins. While the coarse sands settle out rapidly to form beaches, the silt, clays and water run off the beach to the tailings pond and settle very slowly to form fluid fine tailings (FFT). If untreated, the FFT may take decades to consolidate. After clarification in the tailings ponds, about 87% of the tailings water is recycled to Utilities, where it is reheated and returned back to the slurry preparation and bitumen extraction processes. FFT is currently stored in tailings ponds. With years of accumulation, FFT volume management is one of the main challenges that oil sand developers face (Alberta Energy Regulator 2017).
Syncrude is taking a multipronged approach to manage FFT that includes three main tailings technologies: composite tailings (CT), water capping, and centrifugation. In the CT process, coarse tailings from the bitumen extraction plant are processed with several packs of cyclones. The cyclone underflow is mixed with gypsum as coagulant and FFT that is dredged and pumped from the tailings pond. The non-segregated CT product with greater than 60% solids and SFR (sand to <44µm fines ratio) of 3–4 is pumped to a deposition area where it dewatered and consolidates with clear water release. Water capping of FFT uses a layer of combination of fresh and oil sand process-affected water to cap the FFT in the bottom in a mined-out pit, in which consolidation of FFT may occur. Centrifugation of FFT involves pre-treatment of FFT with a polymeric flocculant and gypsum and liquid-solids separation with a number of decanter centrifuges. The centrifuge cakes with 50–55% solids are trucked to a deposition area for further consolidation, while the centrate from the decanter centrifuges is returned to the tailings pond (Spence et al. 2013).

In addition to the three main technologies outlined, Syncrude R&D, independently or in collaboration with Canada’s Oil Sands Innovation Alliance (COSIA) member companies, has been investigating other FFT treatment technologies to meet progressive mine closure and reclamation objectives. These include thickening (Cymerman et al. 1999; Xu & Cymerman 1999; Yuan & Shaw 2007, 2008; Yuan & Lahaie 2010), accelerated dewatering (ADW) of deep deposit with perimeter ditching, co-mix of Kc clay overburden and FFT, FFT filtration, and FFT clay treatment.

It is known that the negatively charged clays in FFT are problematic to dewatering due to their high affinity for water (i.e. hydrophilic), small particle sizes and large specific surface areas. To accelerate FFT dewatering, Syncrude R&D conceived the FFT clay treatment project by targeting the problematic clays in FFT. The theory of this novel technology is to use a polymeric flocculant to increase the effective size of clays and a collector to change the clay surfaces from hydrophilic to hydrophobic. A flocculant-collector combination recipe was developed for FFT clay treatment. Collectors are chemical compounds added to FFT that change the clay hydrophobicity, promote aggregation of clay particles and assist in FFT dewatering.

The process of FFT clay treatment can take two paths. One approach is to remove clays from FFT by flotation followed by natural desiccation of the clay froth. As the clay froth repels water (i.e. hydrophobic), the clay froth dewatered and desiccates rapidly, resulting in >95% solids in three days in the lab. The other approach is to treat the entire FFT stream first with a flocculant and then with a collector. The treated FFT is subjected to liquid-solids separation (e.g. centrifugation, filtration and sedimentation in a deposition cell).

Syncrude has successfully conducted lab concept-proof tests, small pilot tests and field pilot tests for FFT clay treatment using dodecylamine (DDA) as collector. DDA is one of the most popular collectors used for non-metallic mineral flotation in the mineral processing industry (Laskowski et al. 2008; Zhang et al. 2008). DDA needs to be prepared in water of >35°C and dissolved in hydrochloric acid before being added to FFT slurry. It was demonstrated in the field pilot tests in 2017 that operating the complex DDA preparation system was quite challenging (i.e. liquid DDA corrosion to pump, high water temperature required and HCl safety issues). Therefore, it is necessary to explore more effective, easier to use, and less or non-toxic collectors for FFT clay treatment. Theoretically, it is possible to directly use a cationic collector or a combination of a metal ion and an anionic collector to make the negatively charged FFT clays hydrophobic. Both approaches were investigated in the project. This paper demonstrates how fundamental research provides a simple and cost-effective method for screening collectors for operational FFT clay treatment (Li et al. 2018).

2 Experimental

2.1 Materials

2.1.1 Chemicals

The following hydrolysable metal cations (2 and 3 valences) were used in this project: Ca²⁺, Mg²⁺, Mn²⁺, Cd²⁺, Ni²⁺, Co²⁺, Pb²⁺, Fe²⁺, Cr³⁺, Zn²⁺, Fe³⁺, Al³⁺.
All of the above cations were used as chloride salts except for Pb\(^{2+}\) in Pb (NO\(_3\))\(_2\) for solubility reasons. The inorganic salts were prepared in deionised water for use in the tests as clay activators.

Table 1 lists the major collector/surfactants evaluated in this project (Li et al. 2018). The collectors include the fatty/carboxylic acids, alkyl sulphonates, alkyl sulphates, primary amines, quaternary amines and ether amines. Hexadecane was used for oil-solids attachment tests described in the methodology.

### Table 1 Summary of collectors/surfactants evaluated in this project

<table>
<thead>
<tr>
<th>Category</th>
<th>No. of C</th>
<th>Structures</th>
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<td>Lauric</td>
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<tr>
<td></td>
<td>16</td>
<td>CH(_3)(CH(<em>2))(</em>{14})COOH</td>
<td>Palmitic</td>
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<tr>
<td></td>
<td>18</td>
<td>CH(_3)(CH(<em>2))(</em>{16})COOH</td>
<td>Stearic</td>
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<td></td>
<td>16</td>
<td>CH(_3)(CH(<em>2))(</em>{3})CH=CH(CH(<em>2))(</em>{7})COOH</td>
<td>Palmitoleic</td>
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<tr>
<td></td>
<td>18</td>
<td>CH(_3)(CH(<em>2))(</em>{7})CH=CH(CH(<em>2))(</em>{7})COOH</td>
<td>Oleic</td>
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<tr>
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<td>18</td>
<td>H(_3)(CH(<em>2))(</em>{3})CH=CH(CH(_2))CH=CH(CH(<em>2))(</em>{7})CO(_2)H</td>
<td>Linoleic</td>
</tr>
<tr>
<td></td>
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<td>Linolenic</td>
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<td>Sodium dodecyl sulphonate</td>
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<td>Alkyl sulphate</td>
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<td>Sodium dodecyl sulphate</td>
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<td>16</td>
<td>CH(_3)(CH(<em>2))(</em>{15})OSO(_3)Na</td>
<td>Sodium n-hexadecyl sulphate</td>
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<td>CH(_3)(CH(<em>2))(</em>{17})OSO(_3)Na</td>
<td>Sodium n-octadecyl sulphate</td>
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<td>12</td>
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<td>Lauric or dodecylamine (DDA)</td>
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<td>16</td>
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<td>CH(_3)(CH(<em>2))(</em>{14})CH(_2)-NCl-CsH(_5)</td>
<td>CPC</td>
</tr>
<tr>
<td></td>
<td>18</td>
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<td>ODBA</td>
</tr>
<tr>
<td>Ether amine</td>
<td>14</td>
<td>R-O-(CH(_2))(_3)-NH(_2)</td>
<td>Tomamine PA-14, ether monoamine</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>R-O-(CH(_2))(_3)-NH-(CH(_2))(_3)-NH(_2)</td>
<td>Tomamine DA-14, ether diamines</td>
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<td>CH(_3)(CH(<em>2))(</em>{12})CH(_3)</td>
<td>Hexadecane</td>
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</table>

#### 2.1.2 Fluid fine tailings

Both FFT and recycled process water (RCW) in 20 L pails were obtained from Syncrude Mildred Lake site. The solids content in FFT was determined by drying method as 31.6% by wt. The FFT had a typical <44µm fines content of 90–100%.
2.2 Methodology

2.2.1 Zeta potential measurement
To screen which metal cations are better for activating the negatively charged FFT solids, zeta potential of FFT solids in water under different water chemistry conditions were measured using a zeta potential analyser from Brookhaven Instruments Corporation (Holtsville, NY, USA). It was noted that precipitates formed when preparing stock solutions of inorganic salts in process water, probably due to much higher ionic concentrations in the process water. To minimise measurement errors due to precipitation, the salt stock solutions were prepared in deionised water, and the zeta potentials were measured in deionised water with 1 mM (milli‐mole/L) NaCl electrolyte concentration at pH = 8.0–8.2 (similar to process water pH). The FFT solids were taken from the FFT suspensions diluted with the RCW. The metal cations that give less negative or more positive zeta potentials of the solids were regarded as better cations for activating the solids (Li et al. 2018).

2.2.2 Oil-solids attachment tests
To select which collectors are better for rendering the solids hydrophobic, a common method is to conduct contact angle measurement, solids-bubble attachment tests, or induction time measurement. However, it would be difficult to run such tests for the small sizes of FFT solids. Instead, a simple method of estimating attachment of the solids to oil droplets was developed to evaluate the efficacy of the chemical recipes to cause FFT solids to attach to hydrophobic oil droplets.

The oil-solids attachment test procedure is described as following. For each test, 40 ml diluted FFT containing 0.4–0.5 wt % solid content was put in a 115 ml glass jar. A given amount of chemicals (e.g. 1 mM metal cations and/or collector solution) was added to the jar and mildly stirred, followed by adding 10 ml oil (hexadecane). While water soluble collectors were added directly into the water phase, the collectors that were difficult to dissolve in water, were added in the oil phase. The mixture was then shaken manually for 30 seconds. The prepared mixture was then poured into a 50 ml graduated cylinder for settling. The location of the interface with time was recorded. The hydrophobicity of the solids was evaluated by the stability of the oil-in-water emulsion and the interface rise velocity: the larger the volume of the emulsion zone or the slower the rise velocity of the interface or the less the solids remained in the water, the more hydrophobic the solids are. Figure 1 gives a typical good oil-solids attachment showing a stable solids oil-in-water emulsion on the top (Li et al. 2018).

Figure 1  A typical good oil-solids attachment showing a stable solids oil-in-water emulsion on the top
2.2.3 Flotation tests
A 2 L Denver flotation cell was used for the flotation tests. To maintain consistency with work previously undertaken in related projects, the original FFT containing 31.6 wt % solids was diluted to 12.5 wt% by adding process water. The prepared feed was mixed by agitation at 1,000 rpm for two minutes. During agitation, the required chemicals were added into the slurry. For the verification flotation tests, 800 g/t SNF 3338 flocculant was first conditioned for 0.5 minutes. Then 650 g/t or 1,000 g/t collector was added and mixed for 2 minutes. Compressed air was injected at a flow rate of 1 L/min into the flotation cell. The froth samples were collected for 15 minutes. The collected froth was weighed and left in a container for natural drying in the laboratory environment for 24 hours. The weight and solids content of the remaining flotation tailings were measured. The solids recovery in the froth was then calculated.

3 Results and discussion
This section describes the test results of new collectors and how a fundamental research method was used for collector screening.
To make the negatively charged clay minerals in FFT hydrophobic, two basic approaches were adopted:
- Direct use of a cationic collector.
- Use of a combination of a metal cation to activate clays and an anionic collector.

3.1 Direct use of a cationic collector
In addition to DDA as clay collector, it was found that ether amines and quaternary amines are more effective cationic collectors than DDA. These were proved by both the fundamental oil-solids attachment tests and the clay flotation verification tests. Figure 2 shows the concept of directly using a cationic collector to render clays hydrophobic. As shown in Figure 2, the head of the cationic collector can be adsorbed on the negatively charged clay surfaces at tailings pH of 8.0–8.2, while the tails of the collector render the clay hydrophobic.

Figure 2 Concept of directly using a cationic collector to render clays hydrophobic

3.1.1 Oil-solids attachment tests
Oil-solids attachment test is a fundamental research method to quickly determine if a collector can render a mineral hydrophobic. The oil-solids attachment tests were conducted using hexadecane (i.e. oil) in which the collector is dissolved to mix with FFT solids in process water (natural pH = 8.0–8.2). If the solids are rendered hydrophobic and truly attach to the oil droplets, they will form stable oil/solid/water three-phase contact and oil-in-water emulsion. Since the oil has a lower density (770 kg/m³) than water, the emulsion containing the hydrophobised solids will be carried over to the top, like flotation tests.
Figure 3 shows the oil-solids attachment tests with quaternary amine collectors compared with DDA at the dosage of 0.5 mM. With the exception of CTAB with C-16, the trend of capability to render FFT solids hydrophobic is obvious for the C-12 quaternary amines with different function groups as shown here:

where:

DPC = dodecylpyridinium chloride.
BDDA = benzyltrimethyldecylammonium chloride.
DTAC = dodecyltrimethylammonium chloride.
DDAHCl = acidified dodecylamine (DDA) with hydrochloric acid.
CTAB = cetyltrimethylammonium bromide or hexadecyltrimethylammonium bromide.

It appeared from this trend that the presence of aromatic rings in the molecules increased hydrophobicity on the FFT solids.

Figure 4 shows the oil-solids attachment tests with quaternary amine DPC and Tomamine ether amines DA-14 and PA-14 at the dosage of 0.5 mM. Tomamine DA-14 is an ether diamine with a structure of \( CH_3-(CH_2)_{13}-O-(CH_2)_3-NH-(CH_2)_3-NH_2 \), while Tomamine PA-14 is a monoamine with a structure of \( CH_3-(CH_2)_{13}-O-(CH_2)_3-NH_2 \). It is clear in Figure 4 that DA-14 is as good as DPC, but slightly better than PA-14.
Figure 4  Oil-solids attachment tests with quaternary amine DPC and ether amines DA-14 and PA-14

Figure 5 shows the oil-solids attachment tests with ether amines DA-14 and quaternary amine DPC at the dosage of 0.5 mM compared with no chemical (base test). It is seen that when no collector was used, a small number of solids also entered into the upper oil phase. However, the solids could not form oil/solid/water three-phase contact and oil-in-water emulsion. This is clearly different from the other two tests with DA-14 and DPC in which there is no clear oil phase. These tests proved again that DA-14 and DPC are good collectors for FFT clays.

Figure 5  Oil-solids attachment tests with DA-14 and DPC compared with no chemical (base test)

3.2 Use of a combination of a metal cation and an anionic collector

Activation of anionic collector adsorption onto negatively charged solids by hydrolysed metal cations depends on the formation of mono metal hydroxyl ions (MOH⁺) onto the solid surfaces, thereby providing positive charge sites on the solids to induce and attract the adsorption of anionic collectors on the solids. Therefore, metal cations that could reduce the negativity of solids zeta potentials in a larger degree or turn the solids surfaces to positive charges would favour for the solids to adsorb an anionic collector. Figure 6 shows the concept of using a combination of a metal cation and an anionic collector to render clays hydrophobic. In this model of adsorption, metal ions or mono metal hydroxyl ions are added and adsorbed on clays, which neutralise the negative charges of clays. The adsorbed sites of metal ions or mono metal hydroxyl ions work as the anchors for adsorbing the anionic collectors. The metal ions are called activators in mineral processing.
3.2.1 Zeta potential measurement

Figure 7 shows the zeta potentials of FFT solids in the presence of different hydrolysable metal cations. For Fe$^{3+}$ and Al$^{3+}$, zeta potentials of the solids reversed the sign from negative to positive, increasing the concentration above 0.7–0.8 mM. At the tested pH values (8.0–8.2), both Fe and Al ions would be in the form of Fe(OH)$_3$ and Al(OH)$_3$ precipitates at concentrations higher than 0.8 mM, based on solubility products of Fe(OH)$_3$ and Al(OH)$_3$ precipitates. It was possible that the FFT solids were coated by these precipitates, due to the surface precipitation. Therefore, the measured zeta potentials could be similar to, or the same as, those of Al(OH)$_3$ and Fe(OH)$_3$ precipitates (Li et al. 2018).

For other ions in Figure 7, the formation of metal hydroxide precipitates at concentration of 10 mM were higher than pH >9. Therefore, these ions were present in the ionic states at tailings pH 8.0–8.2, and no charge reversals were observed for adding these ions into the slurry with increasing the concentration, except Fe$^{2+}$. The capability of decreasing the negativity of the solid surface charges by the tested metal cations can be ranked based on zeta potentials as follows: Fe$^{2+}$ > Zn$^{2+}$ > Ni$^{2+}$ > Mn$^{2+}$ > Ca$^{2+}$ > Mg$^{2+}$.
According to the zeta potential measurements, it is expected that Fe\(^{2+}\) could have the strongest power to activate the FFT solids on which an anionic collector could be most favourably adsorbed. In other words, at the same concentration, adding Fe\(^{3+}\), in combination with anionic collector, could make the FFT solids the most hydrophobic, thereby increasing FFT solids recovery into the froth product.

### 3.2.2 Oil-solids attachment tests

To test the above hypothesis, that is, the role of hydrolysed metal cation in activating anionic collector adsorption on FFT solids, similar oil-solids attachment tests were conducted using diluted FFT. In this series of tests, the metal cation was first mixed with the diluted FFT slurry before mixing with the anionic collector and the oil. The anionic collectors include alkyl carboxylic acids/carboxylate, alkyl sulphonate and sulphate categories.

Figures 8 and 9 show the oil-solids attachment tests with different metal cations at the dosage of 1 mM and C-18 oleic acid at the dosage of 3 mM. C-18 oleic acid belongs to the carboxylate category of anionic collectors.

**Figure 8** Photos of oil-solids attachment tests with different metal cations and C-18 oleic acid

**Figure 9** Oil-solids attachment tests with different metal cations and C-18 oleic acid

Based on the results in Figures 8 and 9, the capability of metal cations in inducing FFT solids attaching to oil droplets, or activating solid hydrophobisation, can be ranked as follows: Fe\(^{2+}\) > Zn\(^{2+}\) > Pb\(^{2+}\) > Ni\(^{2+}\) > Co\(^{2+}\) > Al\(^{3+}\) > Fe\(^{3+}\) > Ca\(^{2+}\) > Mg\(^{2+}\) > no chemical
It is shown that Fe$^{2+}$ is the strongest in activating the anionic collector adsorption and rendering the FFT solids hydrophobic, which is consistent with the zeta potential measurement results in Figure 7.

To verify the reproducibility of the sequence shown in Figure 8, further tests were carried out using another anionic collector, C-12 fatty acid. A similar sequence was obtained, further confirming the trend of hydrolysed metal cations in activating FFT solids hydrophobisation by adsorbing carboxylic collector. The only difference shown here is that C-18 oleic acid is relatively stronger than C-12 fatty acid in collecting capacity as C-18 oleic acid has a longer carbon chain length than C-12 fatty acid.

With respect to the alkyl sulphonate and sulphate collectors, Figure 10 shows the oil-solids attachment tests with C-12 sulphonate or C-12 sulphate in the presence or absence of Fe$^{2+}$. The purpose of the tests was to expand the application of anionic collectors to the alkyl sulphonate and alkyl sulphate categories.

![Figure 10 Oil-solids attachment tests with C-12 sulphonate or C-12 sulphate with or without Fe$^{2+}$](image)

It is clear, in the absence of Fe$^{2+}$, the C-12 sulphate at 0.1 mM cannot make the FFT solids hydrophobic. In the presence of 1 mM Fe$^{2+}$, both C-12 sulphonate and C-12 sulphate at 0.1 and 0.5 mM dosages can render the FFT solids hydrophobic. It is noticed that in the presence of 1 mM Fe$^{2+}$, the effective dosage of alkyl C-12 sulphonate or C-12 sulphate is only 0.1–0.5 mM compared with C-18 oleic acid or C-12 fatty acid at 3 mM. Although the dosages of the anionic collectors need to be optimised, C-12 sulphonate or C-12 sulphate shows a stronger collecting capacity than the carboxylate collectors.

In addition to using metal cations as activator, a number of cationic polymers were tested to check if they have the same function as the metal cations. It was found that only a few cationic polymers at a high dosage together with the anionic collectors could render the FFT solids hydrophobic. As the cationic polymers are more expensive and potentially more toxic than metal cations such as Fe$^{2+}$, this option is not attractive although technically it is possible to make the FFT clay hydrophobic.

### 3.3 FFT clay flotation verification tests

Based on the chemical screening test results obtained from the oil-solids attachment tests, FFT clay flotation verification tests were conducted at Syncrude R&D Centre. Figures 11 and 12 show the flotation verification test data with the quaternary amine DPC and the ether diamine Tomamine DA-14 compared with the existing collector DDA.
Figure 11  Comparison of solids recoveries in froth in FFT clay flotation with DDA, DPC and DA-14

Figure 11 shows the comparison of solids recoveries in froth in FFT clay flotation with DDA, DPC and DA-14, where the flocculant SNF3338 of 800 g/t was conditioned with the diluted FFT at 12.6% solids prior to adding the collectors. At the same collector dosage of 650 g/t, as seen in Figure 11, the solids recovery in froth was significantly increased from 78% with DDA to 90% with DPC, and to 98% with DA-14. When the collector dosage was increased to 1,000 g/t, the solids recovery in froth was increased to 94% with DPC. However, the solids recovery with DA-14 was maintained at 98% at the dosage of 1,000 g/t. The ether amine DA-14 performed better than the quaternary amine DPC at the same dosage.

Figure 12  Comparison of solids content in tailings in FFT clay flotation with DDA, DPC and DA-14

Figure 12 shows the comparison of solids content in tailings in FFT clay flotation with DDA, DPC and DA-14. At the same collector dosage of 650 g/t, the solids content in tailings was decreased from 2.9% with DDA to 1.2% with DPC, and to 0.2% with DA-14 respectively. When the dosage was increased to 1,000 g/t, the solids content in tailings was decreased to 0.8% with DPC. However, the solids content in tailings was maintained at 0.2% at the DA-14 dosage of 1,000 g/t.
In summary, the FFT clay flotation tests verified the findings from the oil-solids attachment tests. It was proved that the quaternary amines and the ether amines are more effective collectors than the existing collector DDA in rendering the FFT solids hydrophobic.

The other advantages of using ether amines and quaternary amine DPC over DDA are that both ether amines DA-14 and PA-14 are liquid at ambient temperature and easy to disperse in RCW to form stable emulsions, while DPC is completely soluble in RCW. Ether amines and quaternary amine DPC can be easily prepared and applied in commercial FFT clay treatment. No heat and acid are needed in preparation of ether amines and quaternary amines. Furthermore, the liquid ether amines can be added as neat liquid without any preparation.

With respect to using the combination of a metal ion and an anionic collector in clay flotation, research work for optimising chemical recipes and dosages is still under way. Benefits of this option are that both Fe²⁺ and alkyl sulphate, sulphonate and carboxylate collectors are non-toxic, soluble in RCW, and much cheaper than cationic collectors.

### 3.4 Highlights of FFT clay treatment technologies

As mentioned earlier, to accelerate FFT dewatering, Syncrude R&D conceived the FFT clay treatment project to render FFT clays hydrophobic. Syncrude has successfully conducted lab concept-proof tests, small pilot tests and field pilot tests using DDA as collector. The flocculant-collector recipe and the related technologies for FFT clay treatment have been developed and patented by Syncrude (Yuan et al. 2018a, 2018b). This section highlights the process technologies for FFT clay treatment. The processes can be classified into Processes A, B and C as follows:

A. Clay flotation from FFT followed by desiccation of the clay froth.

B. Clay treatment for the entire FFT stream followed by physical separation (e.g. filtration, centrifugation and sedimentation in a deposition cell).

C. In situ or near in situ.

For Process A, Figure 13 depicts the lab clay flotation and froth desiccation tests, where the raw FFT is diluted and conditioned with a flocculant first and then a collector. When the treated FFT is aerated, the clay froth is generated from the flotation cell. The hydrophobic clay froth dewateres and desiccates rapidly, resulting in >95% solids in three days.

![Raw FFT](image1.png) ![Fresh froth](image2.png) ![>95% solids in 3 days](image3.png)

**Figure 13** Lab clay flotation and froth desiccation tests using DDA as collector

Figure 14 shows the clay froth dewatering and desiccation tests in a flume of 7.32 × 0.61 × 0.31 m. The pilot clay flotation tests were conducted using Syncrude EXP2000 pilot plant facilities and the same chemical recipe as the lab clay flotation tests. As shown in Figure 14, the flume was filled with a thickness of 0.61 m clay froth generated and pumped from the froth launder of flotation machines. The clay froth segregated after 5 hours with the hydrophobic froth on top and the clear release water at the bottom of the flume. After
decanting the clear water from the flume in the next three days, the froth was left in the flume for monitoring the natural desiccation. The entire froth deposit in the flume desiccated to 95–98% solids in three months.

Figure 14  Pilot clay flotation and froth desiccation tests in a flume of $7.32 \times 0.61 \times 0.31$ m

For Process B, that is, clay treatment for the entire FFT stream followed by physical separation (e.g. filtration, centrifugation and sedimentation in a deposition cell), the lab filtration test in Figure 15 shows that even under a very low pressure of 138 kPa (i.e. 20 psi), the flocculant-collector recipe resulted in significantly faster filtration rate than the flocculant alone. Building on this idea, a field test cell of $100 \times 100 \times 10$ m with a layer of 0.5 m sand filter was designed as an underdrain system for the 2017 field tests. Figure 16 demonstrates the field test cell with the 0.5 m sand filter before (on the left) and during cell filling with the treated FFT using the flocculant-collector recipe (on the right). In the 2017 field test, the raw FFT was slightly diluted to about 28% solids and mixed with a flocculant in an inline dynamic mixer and then mixed with a collector in another inline dynamic mixer. The treated FFT stream was pumped to fill the $100 \times 100 \times 10$ m deposition cell. The clear water was released and simultaneously pumped out of the deposition cell. The consolidation of the deposit in the test cell is being monitored for a few years. As seen in Figure 16, a steel spill box was installed to manage and pump out the underdrained and precipitate water during the deposit monitoring period.

Figure 15  Lab filtration tests of FFT treated with different chemical recipes
Advancements of fluid fine tailings treatment technologies through fundamental research

Figure 16 The field test cell of 100 × 100 × 10 m with a layer of 0.5 m sand filter before (left) and during filling with the treated FFT using the flocculant-collector recipe (right)

The initial deposit sampling data showed that the treated FFT with the flocculant-collector recipe had dewatered from initial 28% solids to 50–53% solids just one month after completing the field pilot tests. This result exceeded expectation of about 45% solids.

Process C, in situ or near in situ FFT clay treatment technology is still under development (Yuan & Lorentz 2018).

4 Conclusion

Based on the test data, the following conclusions can be drawn:

- Fundamental research, such as oil-solids attachment, provides a simple and cost-effective method for screening collectors for FFT clay treatment.
- It was found that ether amines DA-14 and DP-14 and quaternary amines DPC are more effective collectors for FFT solids than primary amines dodecylamine (DDA).
- Ether amines and quaternary amines are much easier to use in commercial scale than DDA. This is because no heat and acid are needed in preparation of ether amines and quaternary amines. Furthermore, the liquid ether amines can be added as neat liquid without any preparation.
- The combination of a metal ion (e.g. Fe^{2+}) and a non-toxic anionic collector showed promising potential in the oil-solids attachment tests. Process optimisation and clay flotation verification tests are ongoing.
- More effective and easy to use collectors for FFT clay treatment provide oil sand developers with another technology option to efficiently manage the fluid fine tailings.

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