Report

Validation of Titanium Corporation’s Solvent Extraction Technology to Recover Bitumen from Fine Fluid Tailings and Improve the Settling and Consolidation of Fine Fluid Tailings

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Executive Summary

Oil sands Fluid Fine Tailings (FFT) are a major concern for regulators and industry operators. The industry currently has 1,100 Mm^3 of legacy fluid fine tailings requiring treatment within the next 10 years and is expected to produce an additional 60-80 Mm^3 per year for the next 30 years which will also require treatment. The role of bitumen in tailings is the subject of much debate within the oil sands industry. One of the challenges is that bitumen content is difficult to separate from other influences such as clay content or process history. Titanium Corporation's (Titanium) previous R&D research demonstrated that their technology is capable of removing bitumen from froth treatment tailings. They have also gathered some evidence which indicates that the cleaned froth treatment tailings settles faster and require less chemical treatment in thickening experiments. In this study, Titanium intends to investigate the application of their bitumen removal process to provide clean FFT for use towards a "reclamation ready" surface after mine closure. NAIT's Centre for Oil Sands Sustainability (COSS) is committed to assist businesses validate near-market-ready technologies that have strong potential to enhance the economic and environmental sustainability of the oil sands industry.

COSS, in collaboration with Titanium, Alberta Innovates and NSERC has investigated the residual bitumen removal conditions on FFT and evaluated the impact of the bitumen removal from FFT on flocculation and consolidation. Two types of FFT, FFT-1 with high bitumen to solids ratio and FFT-2 with low bitumen to solids ratio, were used in this study to investigate the optimal bitumen removal conditions with a solvent (Jet B) the Titanium's technology.

Titanium's technology can effectively remove bitumen from the FFT. The cleaned FFT improves the flocculation performance by reducing the flocculant dosage required and increasing the final sediment density. Cleaned FFT showed faster consolidation after the first month than the raw FFT. Measurements of solids content, clay content, and particle size distribution showed insignificant differences between cleaned and raw FFT indicating that the differences in performance are primarily due to a different bitumen content.

The study provides a directional indication that removing bitumen using Titanium's process can produce quantifiable benefits in tailings treatment by reducing the flocculant dosage required. Consolidation impacts of cleaning were minimal, with the benefits seen only at higher void ratios. It appears that Titanium's treatment of FFT may increase the mobility of bitumen and organic matter. Therefore, it is not recommended for Titanium to treat FFT that will be placed in an aquatic environment. The improvements to flocculated solids content and suitable drying rate indicate that the technology is suitable for use in tailings processes targeting a final upland ecosystem (tailings drying).

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1. Introduction

Oil sands extraction in Alberta employs the Clark Hot Water Extraction process (CHWE), which produces fine fluid tailings (FFT) at a rate of 0.1 m^3 per tonne of processed sand (Masliyah, 2007). These tailings are stored in large ponds, and covered an area of about 77 square kilometers by 2013 (Alberta Canada, 2013). The CHWE process relies on both the dilution of the ore and elevating the pH to promote bitumen recovery and decrease slurry viscosity; however, this processing results in fine tailings that have poor settling and consolidation behavior (Mikula, et al., 1996). There are currently 1,100 Mm^3 of fluid fine tailings stored in tailings ponds (Alberta Energy Regulator, 2016). This fluid inventory poses significant risks as the fluid is primarily stored behind man made dykes which have the potential for failure and have been recognized as a global concern (UN environment, 2017). Government regulations, such as the Alberta Energy Regulator Directive 85 (Alberta Energy Regulator Directive 085, 2017) outline requirements for tailings ponds closure, which put significant business pressure on oil sands mine operators. As a result, oil sands companies and their suppliers are continually looking for improvements in tailings technology. The goals of these technologies are to treat the tailings such that they can be placed in their final location in the closure landscape on a trajectory towards reclamation (Alberta Energy Regulator Directive 085, 2017).

Titanium Corporation's (Titanium) previous R&D experience has demonstrated that their technology is capable of removing bitumen from froth treatment tailings. They have also gathered some evidence which indicates that the cleaned froth treatment tailings settles faster and requires less chemical treatment in thickening experiments. The overall objective of this study is to validate the Titanium technology's ability to remove bitumen from fluid fine tailings (FFT) using solvent addition and to evaluate if the bitumen removal provides a long term benefit for the reclamation of FFT and for mineral recovery.

This project will first test what conditions are required for their technology to work on FFT. The data obtained from this project can help Titanium to better understand the process conditions and the key factors to impact the efficiency of extraction. This knowledge will be valuable for Titanium to further refine and optimize their technology at a large scale.

The second objective is to validate that the removal of bitumen can enhance FFT consolidation and final remediation. It is expected that removal of bitumen can benefit FFT treatment, and expedite water release. In this project, cleaned FFT (after bitumen removal) and uncleaned FFT (no bitumen removal) will be treated with the same flocculant following the same procedure for comparison. The properties net water release, and strength gain over time, are the key performance indicators that will be used to evaluate the impact of bitumen removal on FFT treatment. In addition cleaned and uncleaned FFT without flocculant will be compared using seepage induced consolidation (SIC) testing to evaluate the longer term performance of the material. This data will determine whether there is a benefit obtained from Titanium's technology, in working toward a "reclamation ready" surface after mine closure.

In summary, the specific objectives include:

1. Determining the bitumen extraction conditions for FFT using Titanium's process
2. Evaluating the response of the resulting "cleaned" FFT in terms of the change in settling rate.
3. Evaluating the response of the resulting "cleaned" FFT to flocculant addition in terms of the solids content in the floc and flocculant dosage.
4. Comparing strength gain over time for unflocculated cleaned FFT, uncleaned FFT and flocculated uncleaned FFT
5. Evaluating the long term settling performance of "cleaned" FFT in terms of seepage induced consolidation testing and standpipe testing.

In this study, two types of FFT were used to evaluate the bitumen extraction efficiency using Titanium's process. The first type of FFT contained more bitumen and solids contents but less fines and clays. The second type of FFT contained less bitumen and solids contents but very high fines and clays. Jet B was used as the bitumen extraction solvent according to Titanium's process. The project included two phases: Phase 1 – determination and optimization of FFT cleaning process, and evaluation of cleaned FFT on settling, preliminary flocculation, drying, and consolidation tests; and Phase 2: investigation of solvent to feed ratio change on FFT flocculation performance.

2. Experimental

All of the detailed experimental procedures are in the Standard Operating Procedure (SOP) section in Appendix A. This section describes the experimental process.

2.1 Equipment and Instruments

The following equipment and instruments were used during the project:

Equipment: volumetric pipets (100 mL), glass funnel, 1 or 2 L of glass beaker, upstand mixer, two 20 L of metal cans, centrifuge Nalgene bottles, 20 L of plastic pail, D&S kettles, condenser, water trap, heat sleeve, heating bowl, rheostat, spatulas, rods with rubber policeman, balance, oven, clarity wedge, Phipps & Bird PB-700 Gang mixer, and Eberbach Shaker table.

Instruments: Avanti J-26XP Centrifuge, METTLER TOLEDO's Thermal Gravimetric Analyzer (TGA), HORIBA's LA-300 Particle Size Distribution Analyzer (PSD), DVIII Brookfield rheometers.

2.2 Bitumen extraction using Jet B solvent

The FFT samples were mixed with Jet B solvent on a shaker table, followed by centrifugation to separate the solvent layer (Jet B containing bitumen and rag layer if it existed) from the sediment layer (water and solids). The solvent layer was then removed using a pipet and the sediment layer was named "washed FFT".

2.3 Distillation of Jet B

The washed FFT was distilled 2-3 times to remove the residual Jet B. Each distillation took ~1.5 hours. The temperature of the heating mantle was set to 180-200°C. Water was added between each distillation round to maintain water content and to avoid drying out the clays. Based on some investigation, this was the most effective method of removing the Jet B solvent.

2.4 Dean and Stark analysis

The sediment layer collected from distillation process was conducted a standard D&S process using toluene to obtain the information on bitumen, solids, and water.

2.5 Flocculation test

Flocculation tests were conducted using a Phipps & Bird PB-700 Gang mixer with an adjustable paddle. An electronic motor control system regulated the variable speed of the paddle from 1-320 rpm, and was displayed via a digital readout. To start the testing, 300 g of FFT was introduced into a 10 cm diameter by 8 cm high metal cup. This cup was placed in the jar tester and a 76 mm by 25 mm paddle was inserted into the FFT ~7 mm above the bottom of the cup, centered in the cup. The stirring speed was set to 320 rpm and the polymer was added in increments for the "titration test" or one-dose for the dosage curve test. The optimal dosage determined during the titration test was when the flocs were formed and release water was observed. The one-dose test used the optimal dosage of the titration test as a dosing starting point and then increased and/or decreased the dose to cover the polymer dosage range. The dosage that resulted in the highest solids content in the flocs was considered the optimal dosage of the one-dose test. Once the floc structure was observed by the operator, the stirring speed was slowed to ~50 rpm. During slow mixing, when a gel structure was observed that broke up into large flocs and released water the polymer addition was stopped. The flocs were then mixed at low speed for a few seconds more until a structure of distinct flocs with released water appeared.

2.6 Settling test

For settling experiments, 1 L graduated cylinders were filled with cleaned, unflocculated FFT; cleaned and flocculated FFT samples; flocculated, uncleaned FFT samples; and raw (uncleaned, unflocculated) FFT samples were placed on a bench for 35 weeks. The height (h) of the mud line, i.e. a clear supernatant-sediment interface, was monitored as a function of settling time. The settling curves were constructed by plotting normalized mud line height, h/H as a function of settling time (t), where H represents the initial height of the slurry. These curves were built by taking measurements over 35 weeks. At the end of testing, the columns were dismantled and the solids contents were determined for: the water phase, the top, the middle and the bottom of the sediment.

3. Results and Discussion

3.1 Characterization of Raw FFT

Two types of raw FFT were characterized by Dean and Stark (D&S) (Dean & Stark, 1920), methylene blue index (MBI) (Currie, et al., 2014) (Kaminsky, 2014), and particle size distribution (PSD) analysis at COSS. The results of the analysis are presented in Table 1. The water chemistry of raw FFT was tested and the results are shown in Table 2. The representative PSD figure is shown in Figure 1 and Figure 2. FFT-1 was from a tailings pond containing a portion of froth treatment tailings and FFT-2 was from a typical FFT pond. FFT-1 contains more bitumen and is also very odorous leading to Health, Safety, and Environment (HSE) concerns. FFT-2 is a more “typical” FFT. The FFT-1 sample was also tested on x-ray fluorescence (XRF) analysis at COSS (Table 3).

Table 1. The average results of FFT Characteristics from Dean and Stark (D&S), Methylene blue (MB), and particle size distribution (PSD) Testing.

Item	FFT-1	FFT-2
Bitumen content (wt%)	7.81	1.23
Solids content (wt%)	32.09	24.68
Water content (wt%)	60.04	73.64
Bitumen/Solids Ratio	0.24	0.05
MBI (meq/100 g solids)	10.6	14.1
Fines content (%)	49.2	84.2

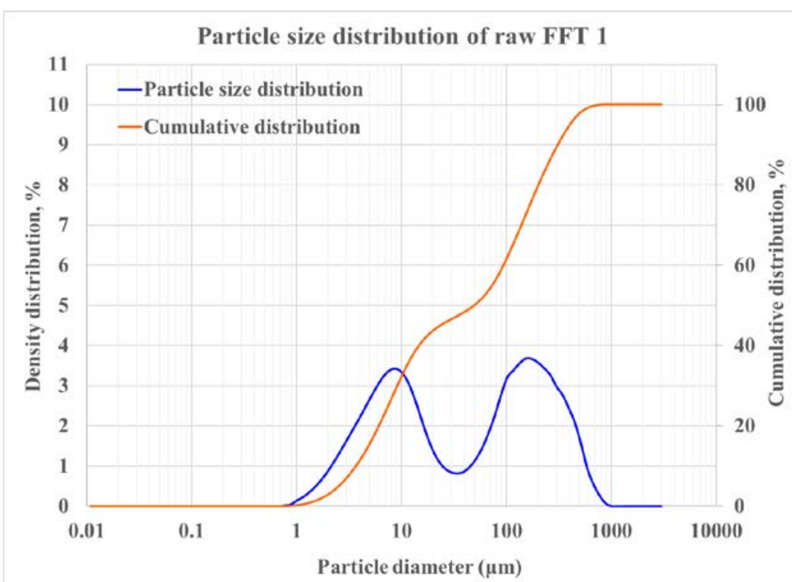


Figure 1. Particle size distribution of FFT-1 tailings.

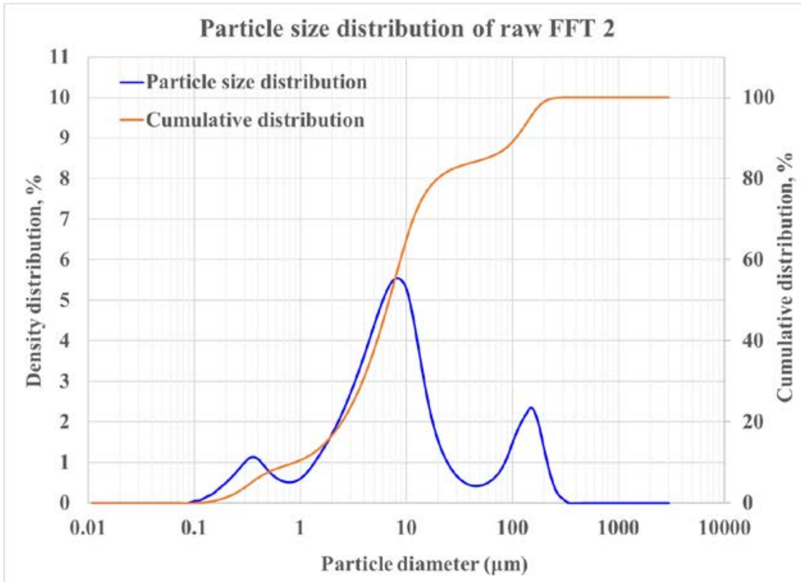


Figure 2. Particle size distribution of FFT-2 tailings.

Table 2. The water chemistry analysis results of raw FFT.

Sample	Total dissolved solids	Conductivity	pH	Total hardness as $CaCO_3$	Total alkalinity
	Mg/L	µs/cm		Mg/L	Mg/L
Raw FFT-1	2110	3400	8.20	160	1200
Raw FFT-2	-	2900	8.20	399	-

Table 2 continued.

Sample	Cation (mg/L)							Anions (mg/L)					
	Na	K	Ca	Mg	Ba	Sr	Fe	Cl	HCO_3	SO_4	CO_3	OH
Raw FFT-1	709	17.3	31.7	19.0	0.68	1.15	0.02	411.3	1500	2.7	<0.50	<0.50
Raw FFT-2	306	23	51	19	-	-	-	138	393	-	0	-

Table 3. XRF results of FFT-1.

Formula	Percentage (wt%)
	FFT-1
SiO2	48.16
Fe2O3	20.31
Al2O3	11.80
ZrO2	6.00
TiO2	5.74
K2O	3.08
CaO	2.00
Br	1.33
Ru	0.41
MgO	0.36
MnO	0.31
SrO	0.21
ZnO	0.10
Na2O	0.10
CuO	0.05
NiO	0.04

3.2 Phase 1 – Characterization and Evaluation of Cleaned FFT with One-stage Washing

3.2.1 Determination of the bitumen extraction conditions using Jet B

FFT-1 with high bitumen content was originally chosen for this study. The bitumen extraction process comprised three stages (Figure 3): washing to generate “washed FFT” by separating bitumen from the FFT sample, distillation to generate “cleaned FFT” by removing the residual Jet B from the washed FFT, and evaluation to characterize the cleaned FFT using D&S process in order to obtain the quantity of components. The bitumen to solids ratio before and after the bitumen extraction process was the key performance indicator (KPI) to evaluate the efficiency of the bitumen removal.

The washing stage included four main steps as shown in Figure 3: mixing raw FFT and Jet B, shaking the mixture to extract the bitumen from the solid phase into the solvent (Jet B) phase, centrifuging the mixture and separating the solid phase from the solvent phase (Diluted Bitumen). Three conditions were evaluated in order to optimize the bitumen extraction efficiency (Table 4): solvent (Jet B) to feed (FFT) ratio (S/F), shaking time and centrifuge time.

Bitumen recovery percentage (wt%) was the indicator to determine the optimal conditions. Optimization was limited to the number of conditions that could be tested within a 3 week period.

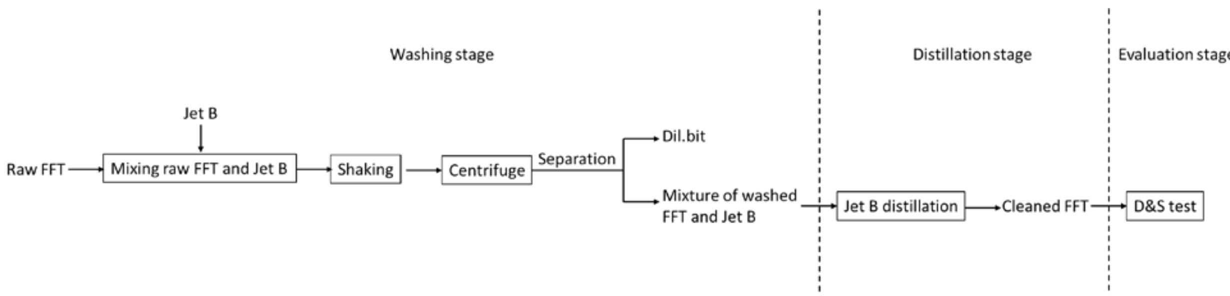


Figure 3. Bitumen extraction process with a single stage washing using Jet B solvent.

Table 4. Experimental conditions for bitumen extraction.

S/F (w:w)	1	0.5	0.25	0.1
Shaking time	15 min		30 min	
Centrifuge time	30 min		45 min	
Washing cycle	1		2	

Determination of solvent to feed ratio (S/F)

Four S/F ratios were tested to find the optimal S/F ratio as shown in Table 4. The bitumen recovery was determined by three types of calculations: (1) S/F ratio calculation based on the sediment data using D&S method to obtain the bitumen content in the sediment; (2) S/F ratio calculation based on the Diluted Bitumen data using D&S method to obtain the bitumen content in the Diluted Bitumen; (3) S/F ratio calculation based on removing the Jet B solvent by drying in the fume hood for 2 days to obtain the bitumen content in the Diluted Bitumen. All the tests were duplicated. Figure 4 shows that the S/F ratio of 0.5 obtained from the cleaned FFT-1 produced the highest bitumen recovery value. Both higher and lower S/F ratios produced lower bitumen recovery.

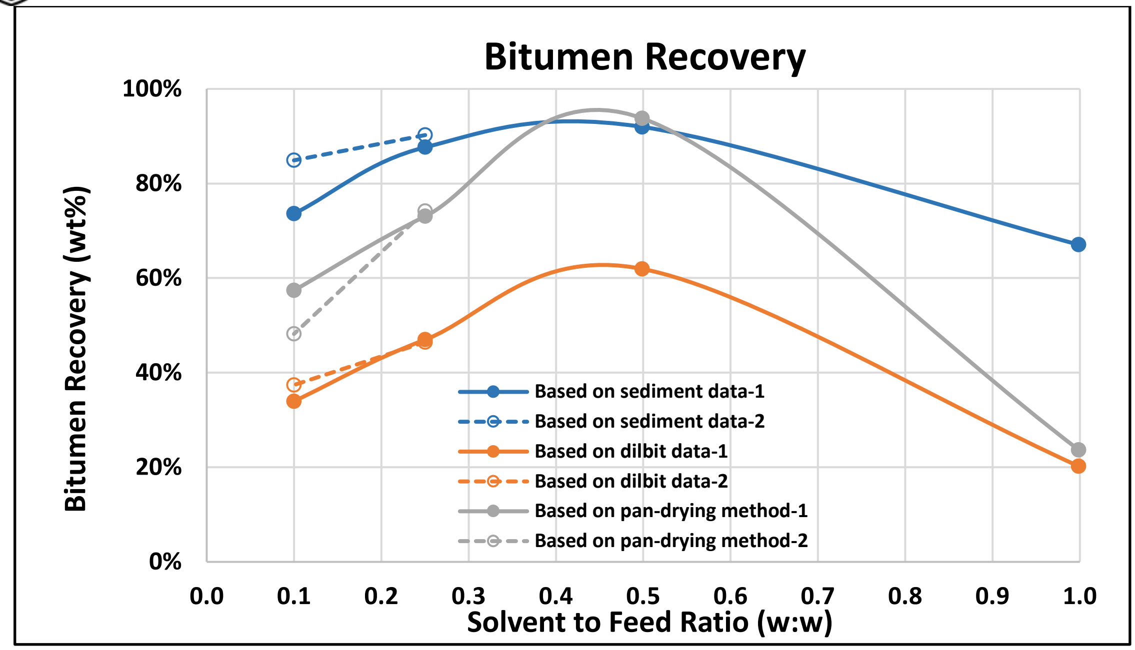


Figure 4. The comparison of the bitumen recovery percentage of FFT-1 using different solvent to feed ratios.

Determination of extraction (shaking) time

Two shaking times were tested to identify the optimal extraction condition: 15 minutes and 30 minutes. The higher bitumen recovery was the indicator used to determine the optimal shaking time. Figure 5 shows that at 30 minutes of shaking time, bitumen recovery increased compared with 15 minutes shaking time.

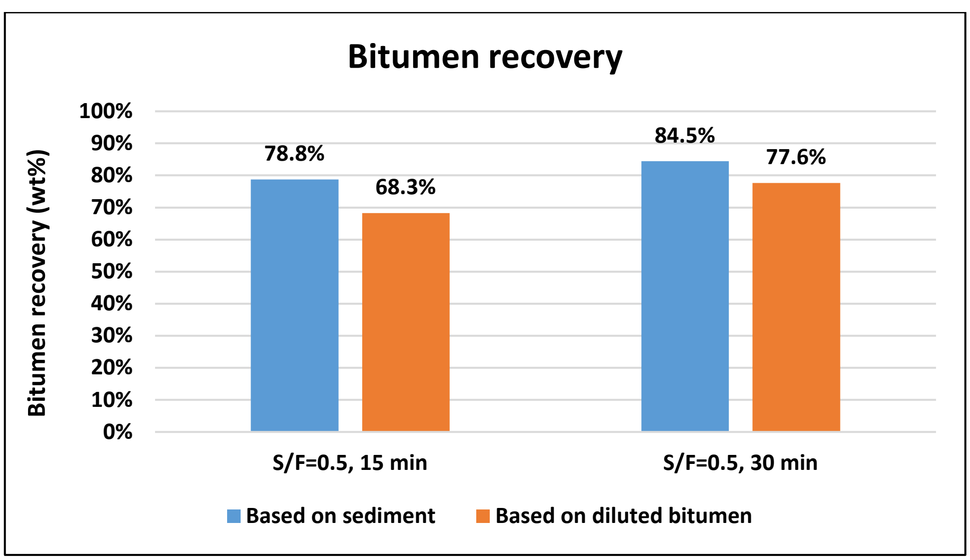


Figure 5. Comparison of bitumen recovery of FFT-1 using different extraction (shaking) time.

The total hydrocarbon (bitumen and Jet B) recovery values were calculated and compared as shown in Figure 6. The condition with S/F ratio of 0.5 and 30 minutes shaking time produced the highest total hydrocarbon recovery based on both sediment and Diluted Bitumen calculations.

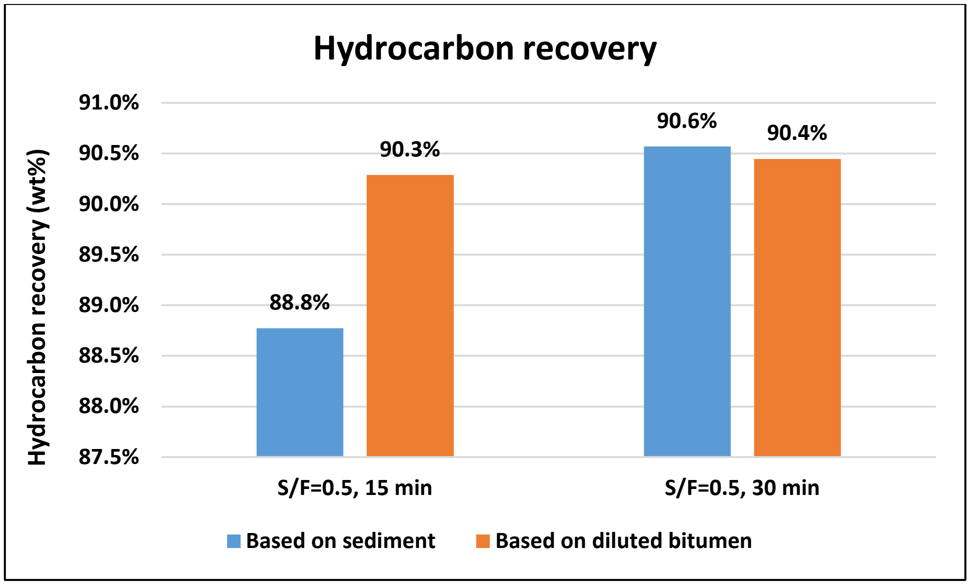


Figure 6. Comparison of total hydrocarbon recovery of FFT-1 using different S/F ratios and extraction (shaking) time.

Determination of centrifuge time

Two centrifuge times were tested to determine the optimal separation condition: 30 minutes and 45 minutes. The better separation of solvent phase and sediment phase was the indicator to determine the optimal centrifuge time. The samples centrifuged for 45 minutes showed a sharper phase interface (Figure 7) which made separating the layers easier.

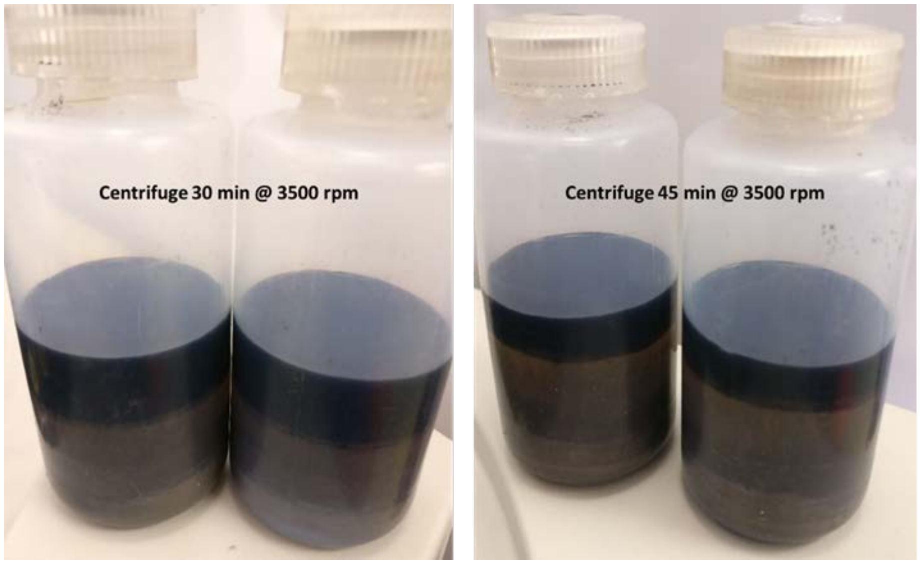


Figure 7. Photos of mixture of FFT-1 and Jet B after separation with different centrifuge time.

3.2.2 Characterization of cleaned FFT-1

The process of mixing through shaking and separation through centrifugation one time was named the "one-stage washing" method. The washed FFT was then distilled with one-round distillation to remove the residual Jet B in the sediment to generate cleaned FFT. Based on D&S results, the cleaned FFT-1 had a bitumen to solids ratio (B/S) of 0.04 which was greatly decreased compared with uncleaned FFT-1 with B/S of 0.24 (Table 5). The D&S test is able to provide the components contents of bitumen, solids and water. The calculated Jet B content was determined by subtracting the total contents of bitumen, solids, and water from 100% and the calculated Jet B content was 0.35 wt%. This was a rough approximation which assumed that all closure errors in the D&S were due to Jet B. The raw FFT-1 was sent to MAXXAM for the water analysis and the results are shown in Table 6. The water chemistry of raw FFT-1 and cleaned FFT-1 were comparable as expected.

Table 5. Characterization of cleaned FFT-1 using Jet B solvent.

	Raw FFT-1	Cleaned FFT-1 with single washing stage
Bitumen content (wt%)	7.81	1.46
Solids content (wt%)	32.09	36.28
Water content (wt%)	60.04	61.91
Jet B content (wt%)	--	0.35
Bitumen to solids ratio (B/S)	0.24	0.04
MBI of solids (meq/100 g)	10.6	10.6

Table 6. Water chemistry of two batches of cleaned FFT-1 compared with raw FFT-1.

Sample	Total dissolved solids	Conductivity	pH	Total hardness as $CaCO_3$	Total alkalinity
	Mg/L	µs/cm		Mg/L	Mg/L
Raw FFT-1	2110	3400	8.20	160	1200
Cleaned FFT-1	2470	3380	8.32	160	1000

Table 6 continued.

Sample	Cation (ppm)							Anions (ppm)				
	Na	K	Ca	Mg	Ba	Sr	Fe	Cl	HCO_3	SO_4	CO_3	OH
Raw FFT-1	709	17.3	31.7	19.0	0.68	1.15	0.02	411.3	1500	2.7	<0.50	<0.50
Cleaned FFT-1	725	18.0	40.9	13.6	1.08	1.26	0.01	426.3	1200	4.0	3.4	<0.50

In summary, the bitumen extraction conditions are as follows:

- Solvent (Jet B) to feed (FFT) ratio – 0.5:1
- Shaking time of the mixture of FFT and Jet B – 30 minutes
- Centrifuge time to separate the solvent phase and sediment phase: 45 minutes
- One-round distillation to remove the residual Jet B in FFT.

This bitumen extraction condition was named “one-stage washing” method**.**

3.2.3 Evaluation of bitumen removal of FFT-1 using one-stage washing on the settling test

3.2.3.1 Settling of raw and cleaned FFT-1 with one-stage washing

The cleaned FFT-1 samples were evaluated by 1-L settling tests. Figure 8 and Figure 9 show the photos of settling tests of raw FFT-1 and cleaned FFT-1, respectively. The raw FFT-1 settled faster resulting in a lower normalized mudline height throughout the 35-week settling, but the cleaned FFT-1 produced more release water during the settling tests. Both FFT samples produced clear released water. The total volume of the cleaned FFT-1 increased during the settling test and a significant amount of bubbles were observed within the sediment from the first week of settling, while the total volume of the raw FFT-1 stayed constant and no bubbles were observed in the sediment (Figure 10). The volume of fluid was ~950 mL at the onset of settling and increased to ~1100 mL by then end of week 8. This volume gain is attributable to the volume of gas formed. It is hypothesized that this was due to gas generation from microbial activity. Dissolved organic matter – residual bitumen and Jet B in this case – is generally considered a labile substrate for soil microbial activity (Haynes, 2005). Bacteria are known to break down these substrates to form methane, CO_2 and other gases. If we assume that each mole of gas produced is at atmospheric pressure at 23°C and contains 1 mole of carbon this is equivalent to 0.006 moles of carbon metabolized or approximately ~0.6 g of toluene. This just goes to show that a very small amount of solvent remaining in the system can have a large impact on the amount of gas generated. With the observation of these bubbles forming, extra effort was put into cleaning and removing the residual organics from the slurry and so a second stage of washing and a longer distillation time were added when cleaning the next batch of material.

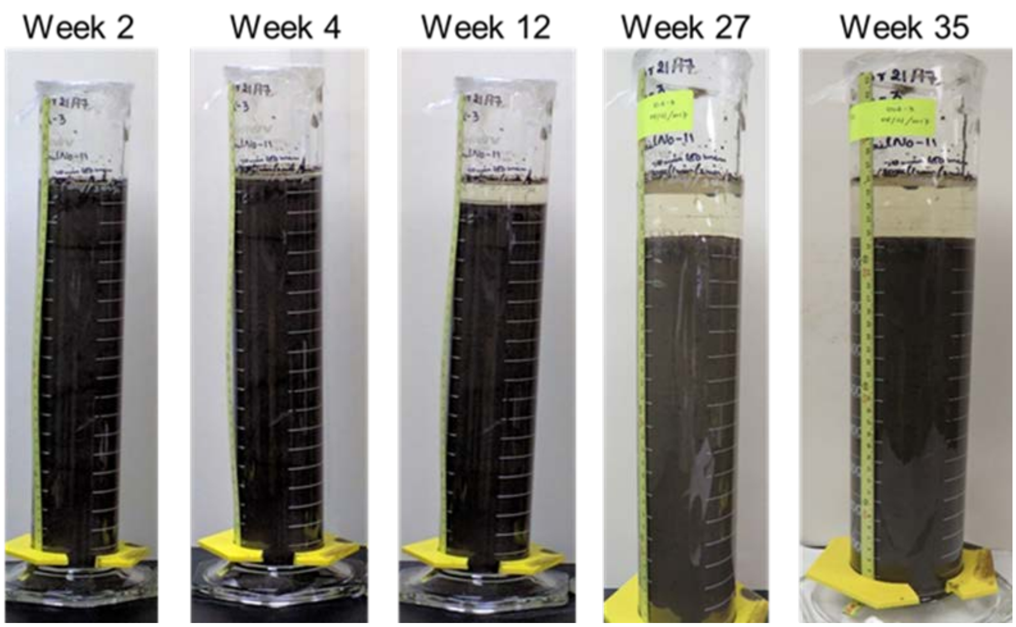


Figure 8. The photos of settling tests of raw FFT-1.

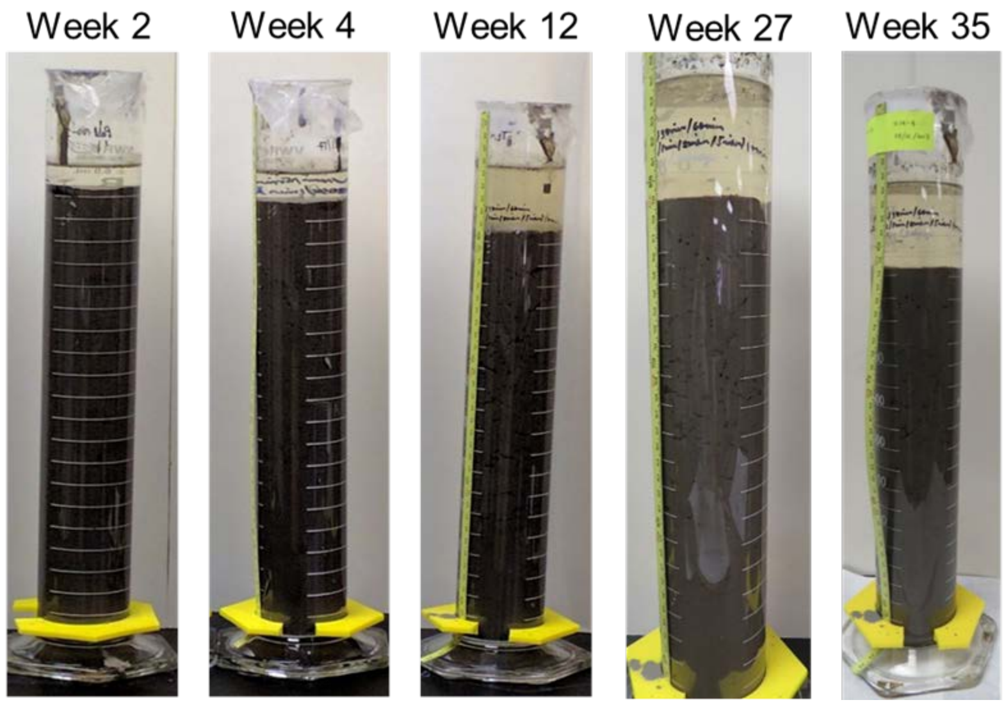


Figure 9. The photos of settling tests of cleaned FFT-1 with 1-stage washing process.

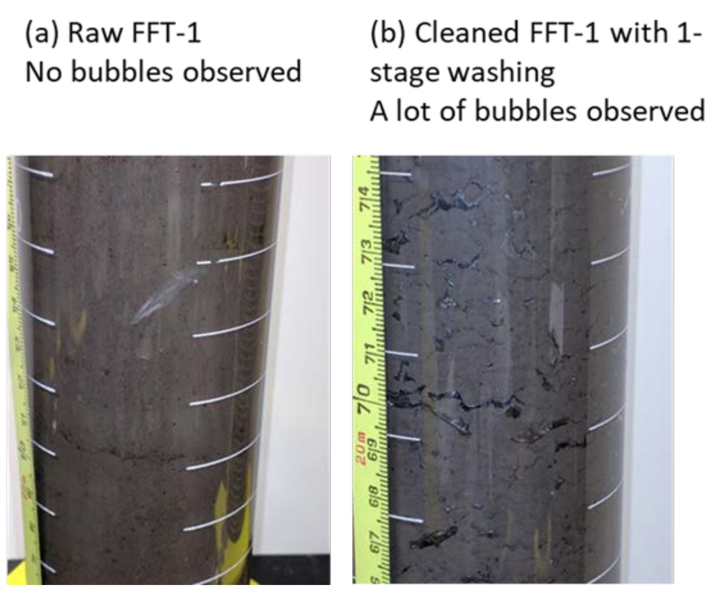


Figure 10. Photos comparison of raw FFT-1 and cleaned FFT-1 with 1-stage washing during the settling tests.

The settling curves of raw and cleaned FFT-1 in triplicates are shown in Figure 11. The normalized mudline height in the settling curve was calculated according to Equation 1. The settling curves show that raw FFT-1 settled faster than the cleaned FFT-1 and both were still settling after 35 weeks. The mudline height (or volume) of cleaned FFT-1 increased during the settling tests due to the gas generation. Although the volume of the sediments of cleaned FFT-1 samples increased during the settling tests, the cleaned FFT-1 produced more released water than the raw FFT-1 samples as shown in Figure 12. This was possibly because the clay's surface, after cleaning, were more hydrophobic and homogenously covered by the residual Jet B and bitumen so that less water was absorbed on the clays surface. Alternatively it could be due to a drop in pH caused by the presence of excess CO_2 in the pore fluid, as has been proposed by several researchers studying the influence of microbes on tailings consolidation.

Equation 1. Normalized mudline height calculation

$$Normalized\ mudline\ height = \frac{h}{H}$$

Where h is the mudline height at time t and H is the initial mudline height at time zero.

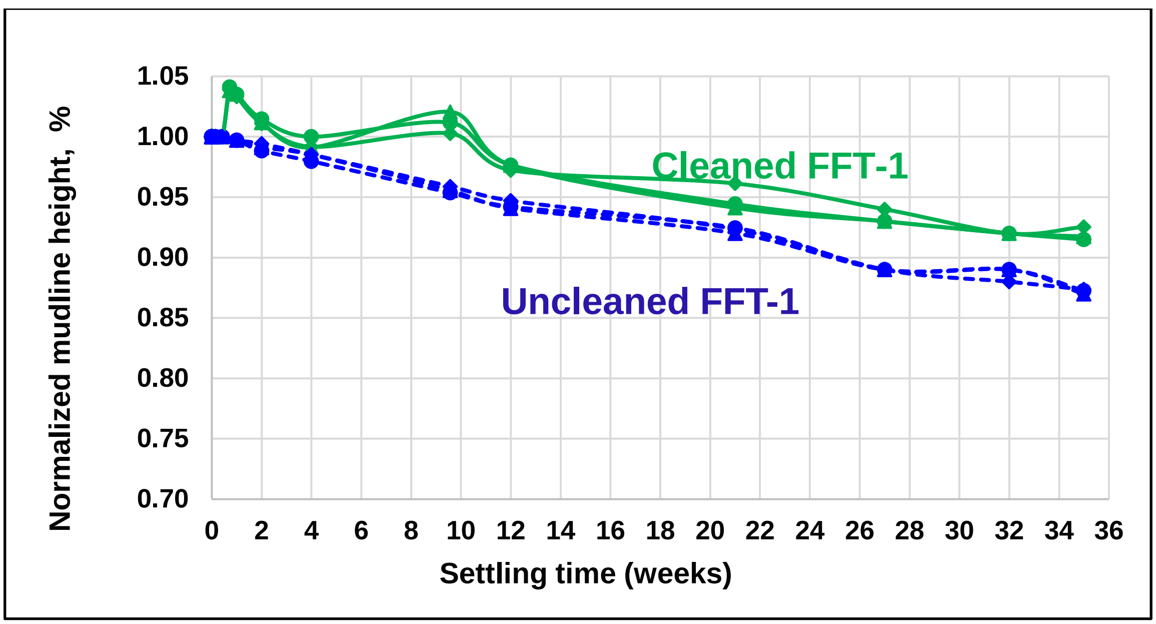


Figure 11. Settling curves of raw FFT-1 and cleaned FFT-1 with 1-stage washing.

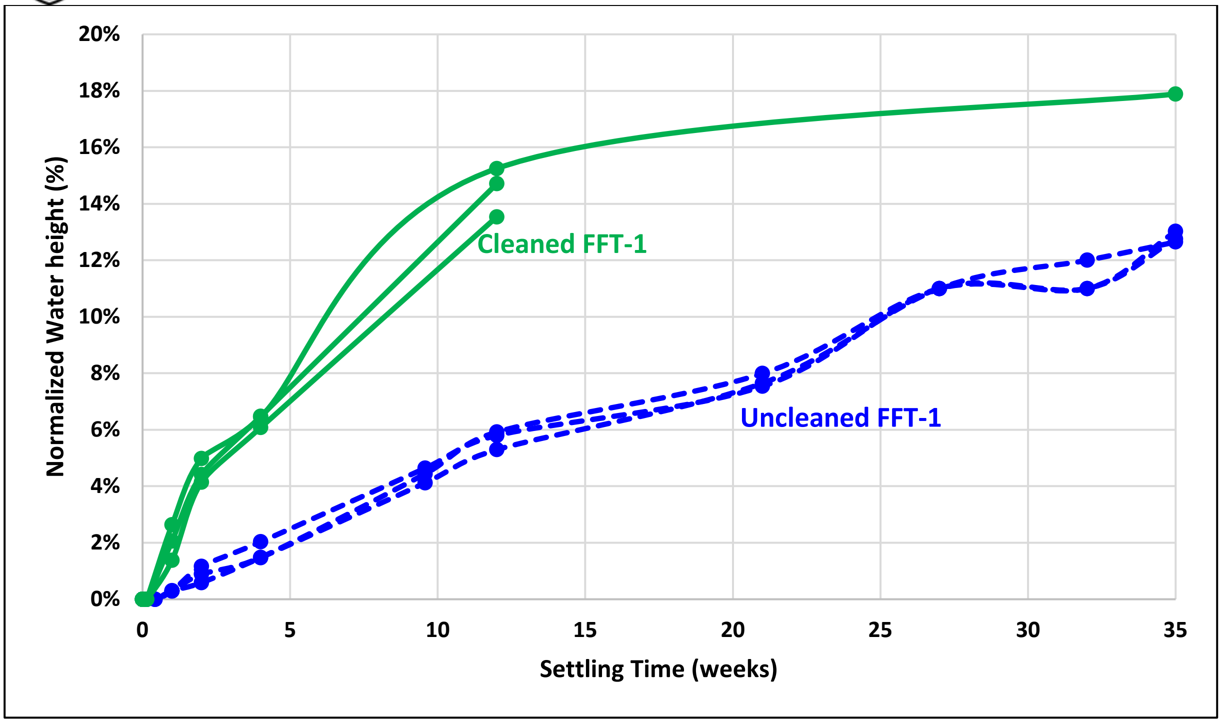


Figure 12. The change of normalized water height of raw FFT-1 and cleaned FFT-1 with 1-stage washing.

3.2.3.2 Settling of flocculated raw and cleaned FFT-1 with one-stage washing

The raw FFT-1 and cleaned FFT-1 samples were flocculated using polymer A3338 and settled in a 1-L graduated cylinder for the settling test as shown in Figure 13 and Figure 14. The dosage of A3338 used for raw FFT-1 was 1140 g/tonne solids and the dosage of A3338 used for cleaned FFT-1 was 911 g/tonne solids, which was 200 g/tonnes solids less than the raw FFT-1 required. The dosages for both raw and cleaned FFT 1 were determined by the titration flocculation method. The flocculated raw FFT-1 settled faster resulting in a lower normalized mudline height throughout the 35-week settling than the flocculated cleaned FFT-1 and the unflocculated FFT-1 samples. Both flocculated FFT-1 samples produced clear released water. It was observed that the volume of flocculated cleaned FFT-1 with 1-stage washing expanded after 8 weeks settling which was not observed in flocculated raw FFT-1. This was likely due to microbial activity. Both flocculated raw FFT-1 and flocculated cleaned FFT-1 showed pore structures in the sediment though evidence of gas pockets were observed in the flocculated cleaned FFT-1 where the pores appeared to contain water in the flocculated raw FFT-1 (Figure 15).

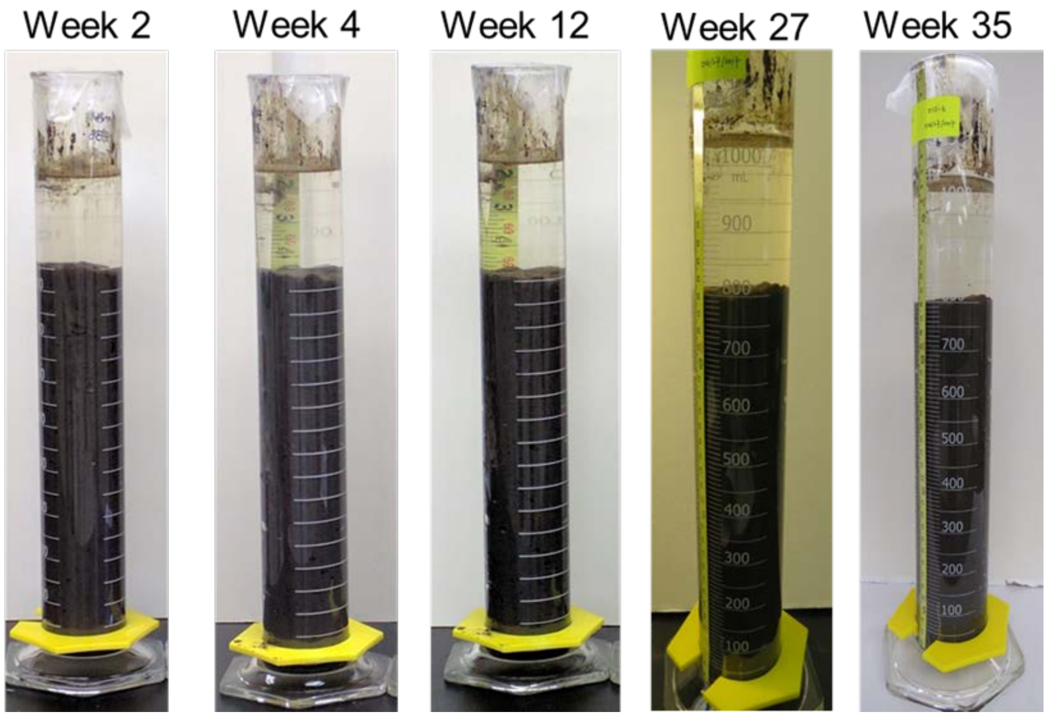


Figure 13. The photos of settling tests of flocculated raw FFT-1.

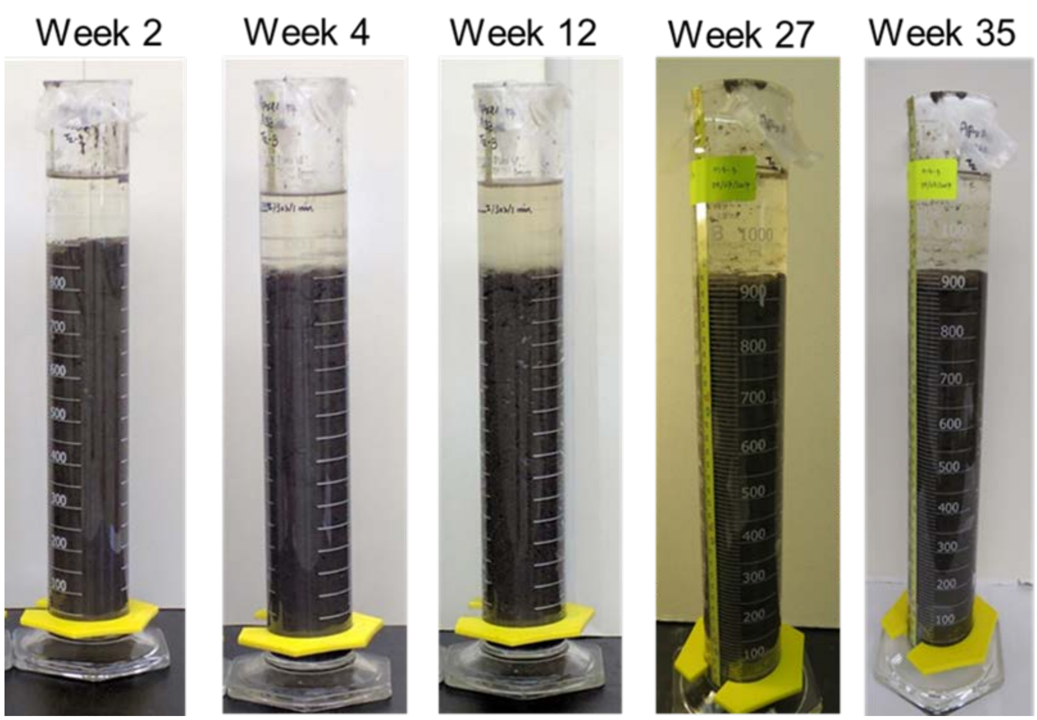


Figure 14. The photos of settling tests of flocculated cleaned FFT-1 with 1-stage washing process.

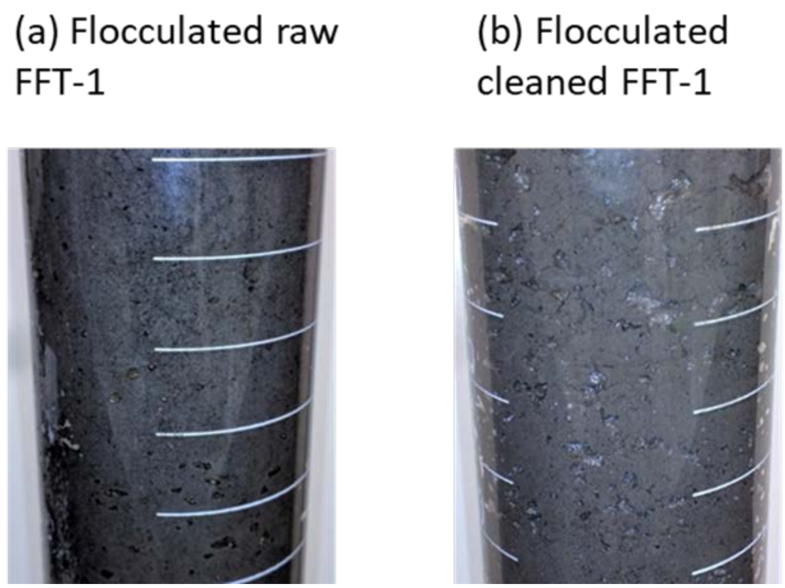


Figure 15. Photos comparison of flocculated raw FFT-1 and flocculated cleaned FFT-1 with 1-stage washing during the settling tests.

The settling curves of flocculated raw and flocculated cleaned FFT-1 in triplicate are shown in Figure 16. The settling curves show that flocculated raw FFT-1 settled faster than the cleaned FFT-1. The mudline height (or volume) of cleaned FFT-1 increased after 8 weeks settling due to the gas generation. The released water produced by the flocculated cleaned FFT-1 was less than that produced by the flocculated raw FFT-1 (Figure 17), but the flocculated FFT-1 released more water than the corresponding unflocculated FFT-1 samples. The residual hydrocarbons, possibly Jet B, and subsequent microbial activity might impact the flocculation performance which highlights the need to enhance hydrocarbon removal in the cleaned FFT.

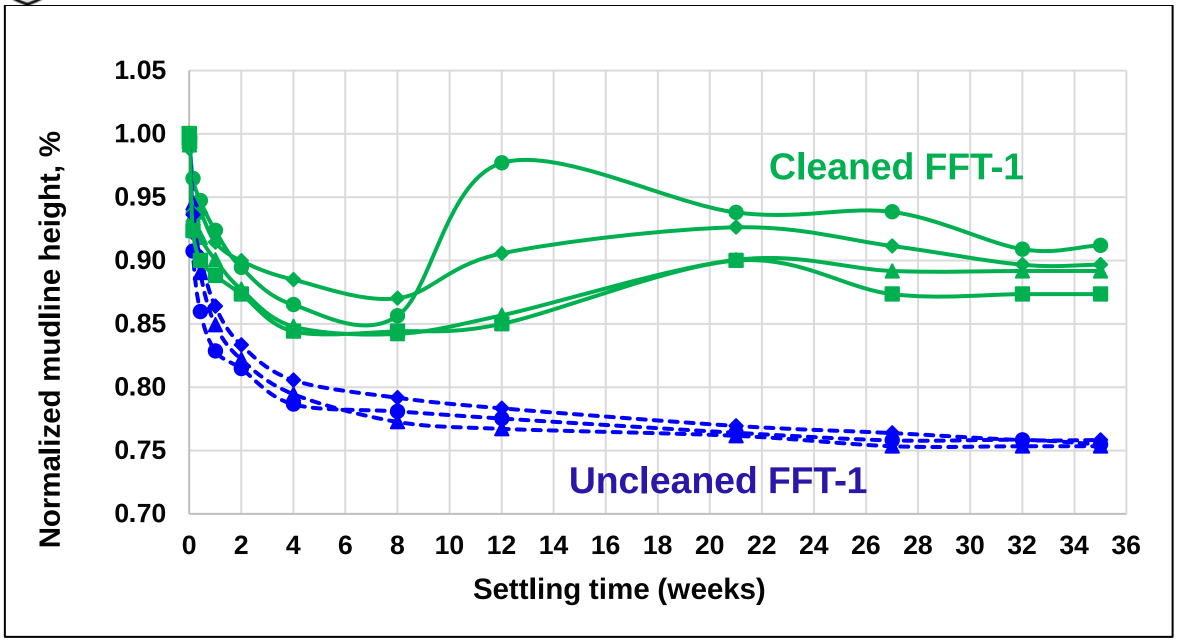


Figure 16. Settling curves of flocculated raw FFT-1 and flocculated cleaned FFT-1 with 1-stage washing.

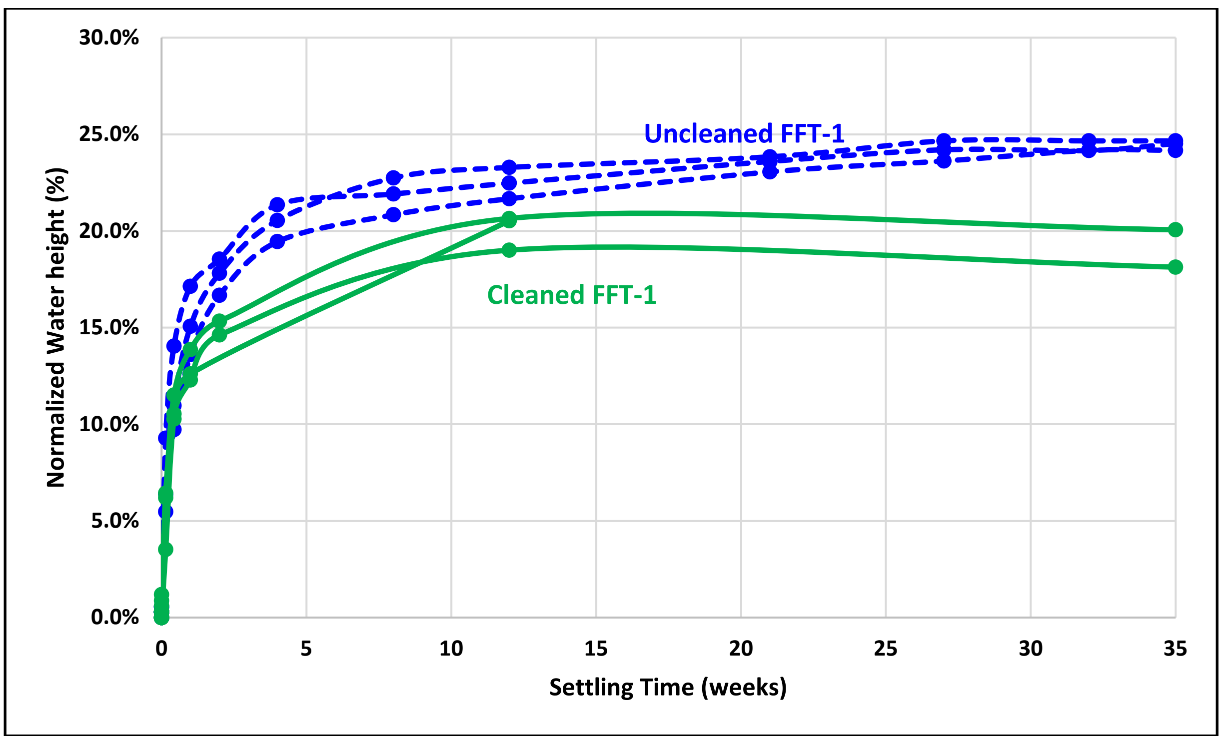


Figure 17. The change of normalized water height of flocculated raw FFT-1 and flocculated cleaned FFT-1 with 1-stage washing.

3.2.3.3 Column dismantling results of undiluted raw and cleaned FFT-1 with one-stage washing

The settling columns were dismantled after 35 weeks of settling. A subsample of the release water from each column was dried to determine the total solids content of the water. The sediment from each column was divided into three layers: top layer, middle layer and bottom layer. Each layer of the sediment was tested on the static yield stress using a Brookfield DVIII HB rheometer. A subsample of each layer was dried to determine the total solids plus bitumen content of the sediment.

The flocculated tailings produced a lower total solids plus bitumen content in the release water than the unflocculated tailings (Figure 18). The flocculated cleaned tailings produced the lowest total solids content and the most consistent results.

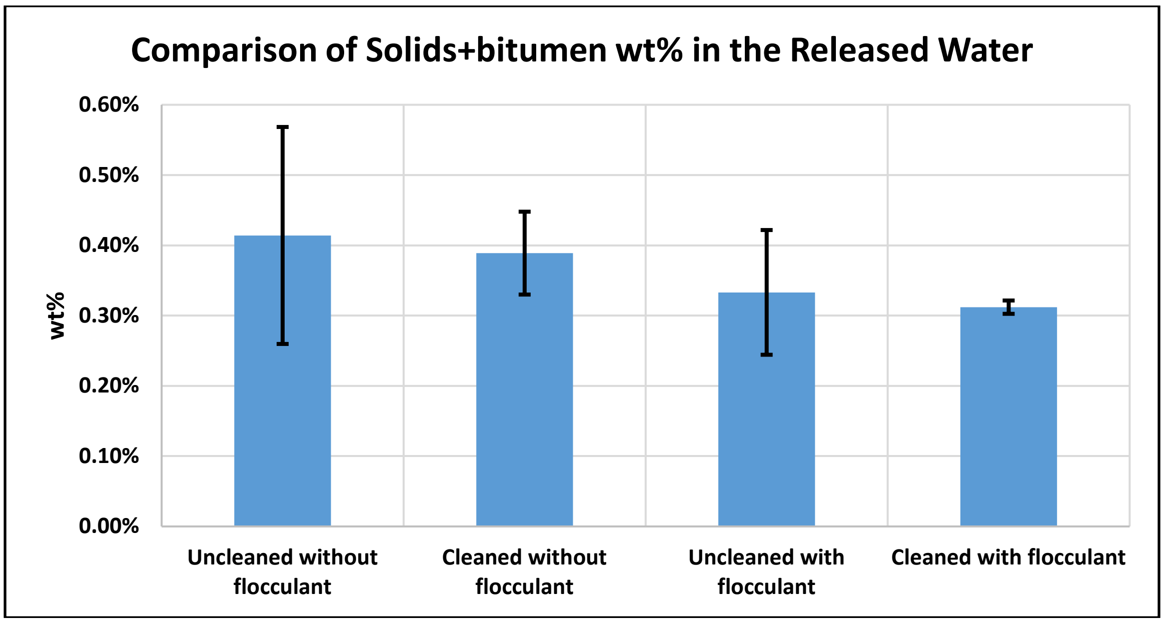


Figure 18. The solids plus bitumen content in the released water of undiluted FFT-1 after 35 weeks settling (error bar: standard deviation).

The total solids plus bitumen content in each sediment layer were measured and shown in Figure 19. All the raw and cleaned FFT-1 with and without flocculation produced similar total solids plus bitumen contents. The bitumen% in the raw and cleaned FFT were determined by D&S and it was assumed that all the bitumen were homogeneously distributed in the sediment after settling tests. The solids% in the each layer sediment was then calculated by subtracting the bitumen content from the total solids plus bitumen content and the values are shown in Figure 20. The cleaned FFT-1 therefore produced a sediment with a higher solids content than the uncleaned FFT-1 samples.

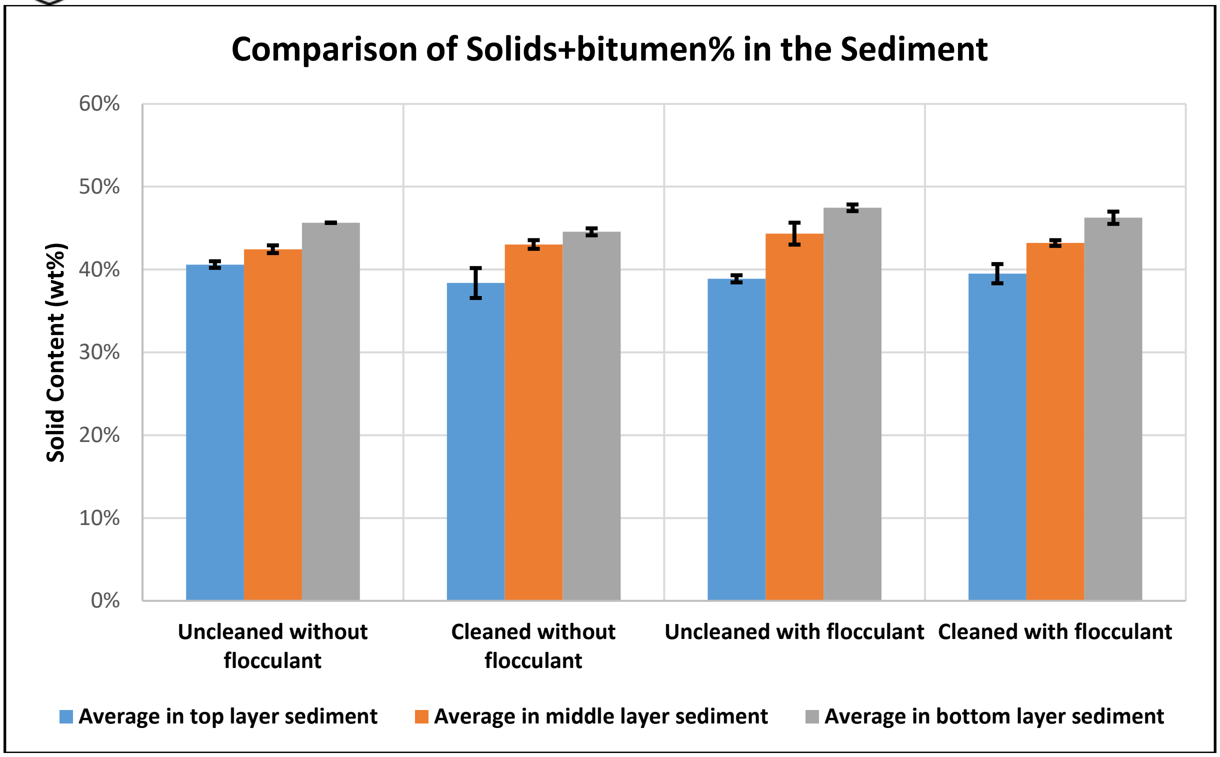


Figure 19. The solids plus bitumen content in the sediment of undiluted FFT-1 after 35 weeks settling (error bar: standard deviation).

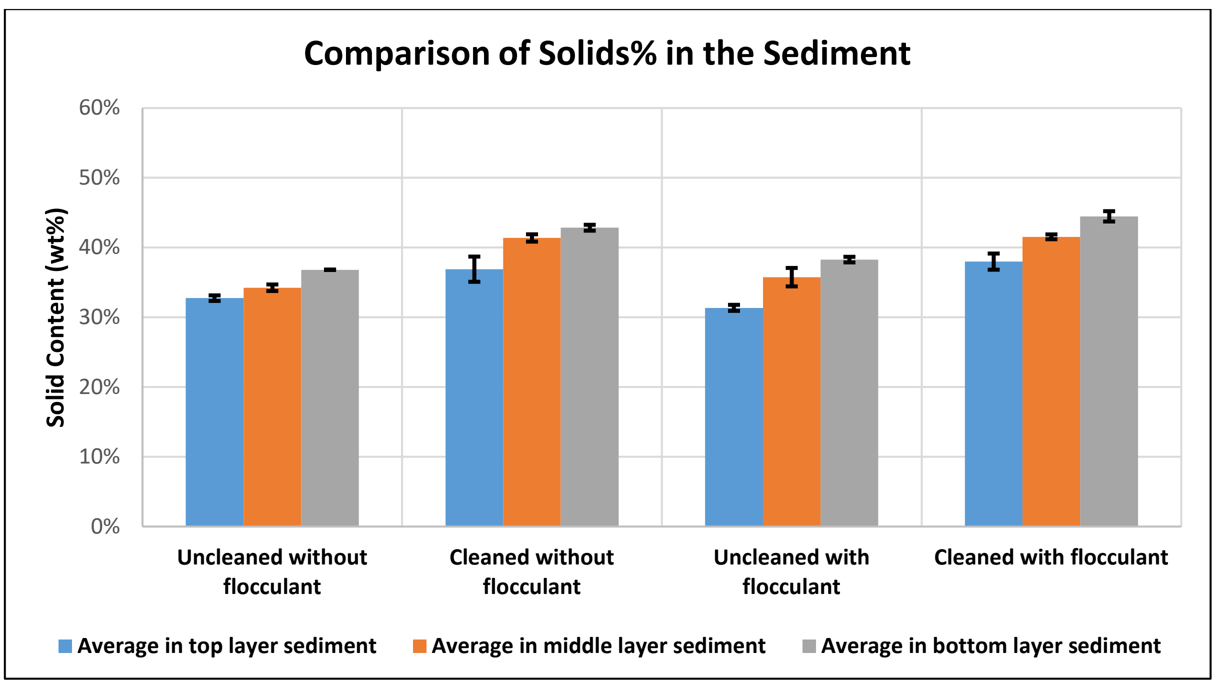


Figure 20. The solids content in the sediment of undiluted FFT-1 after 35 weeks settling (error bar: standard deviation).

The static yield stress of flocculated FFT-1 is shown in Figure 21. The static yield stress of unflocculated samples were under-range of the Brookfield DVIII HB rheometer. The static yield stress for both raw and cleaned flocculated FFT-1 were comparable.

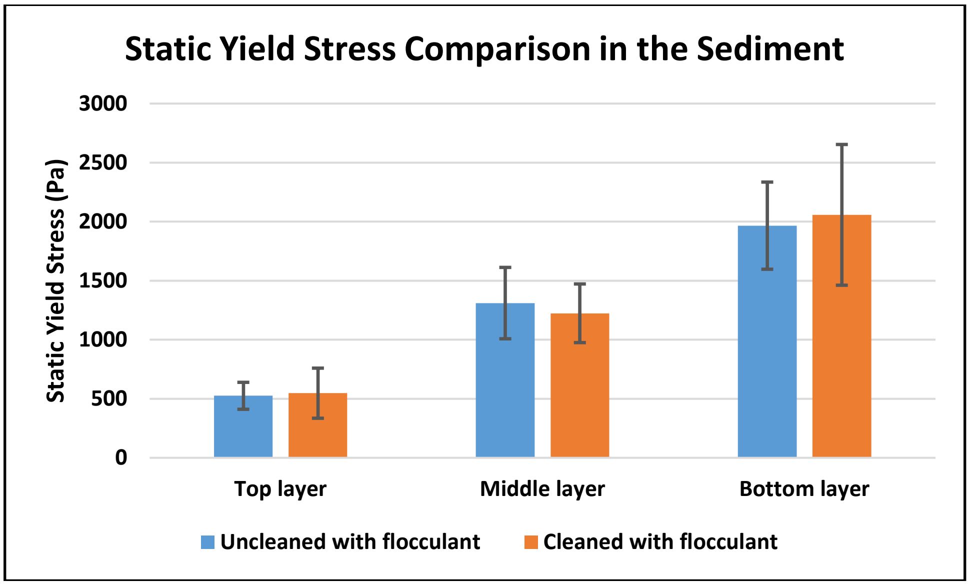


Figure 21. The static yield stress in the sediment of flocculated undiluted FFT-1 after 35 weeks settling (error bar: standard deviation).

3.2.3.4 Settling of diluted raw and cleaned FFT-1 with one-stage washing

The FFT was diluted to approximately 10 wt% solids in order to simulate a thickening process. It was then run through the settling test in the lab. Thickened tailings technology involves rapid settling of fines which could not be provided by undiluted FFT and sedimentation of suspended fines producing recyclable water (BGC Engineering Inc., 2010). Dilution allows the FFT to have a period of free, unhindered settling where flocculant impacts can be more readily assessed. The raw and cleaned FFT-1 were diluted using process effluent water (PEW) and allowed to settle in a 1 L graduated cylinder. Figure 22 and Figure 23 show the photos of settling tests of diluted FFT-1 and cleaned diluted FFT-1, respectively. The diluted raw FFT-1 settled faster resulting in a lower normalized mudline height throughout the 35-week settling (Figure 24). Both diluted FFT samples produced clear released water. The diluted cleaned FFT-1 showed significantly less bitumen floating at the surface of the water than was observed from the raw material, demonstrating that the bitumen was effectively removed from the FFT-1. Bitumen flotation on top of the water was not seen in the undiluted FFT-1. It is suspected that the diluted condition allowed residual bitumen to more readily segregate from the tailings during settling whereas in the undiluted material the bitumen was unable to separate. Unlike the undiluted cleaned FFT-1 samples, no swelling or gas pockets were observed in the diluted cleaned FFT-

1 samples. It is likely that microbial activity still occurred but the diluted nature of the FFT allowed the gas to be easily released without impacting the settling.

Figure 22. The photos of settling tests of diluted raw FFT-1 (10 wt%).

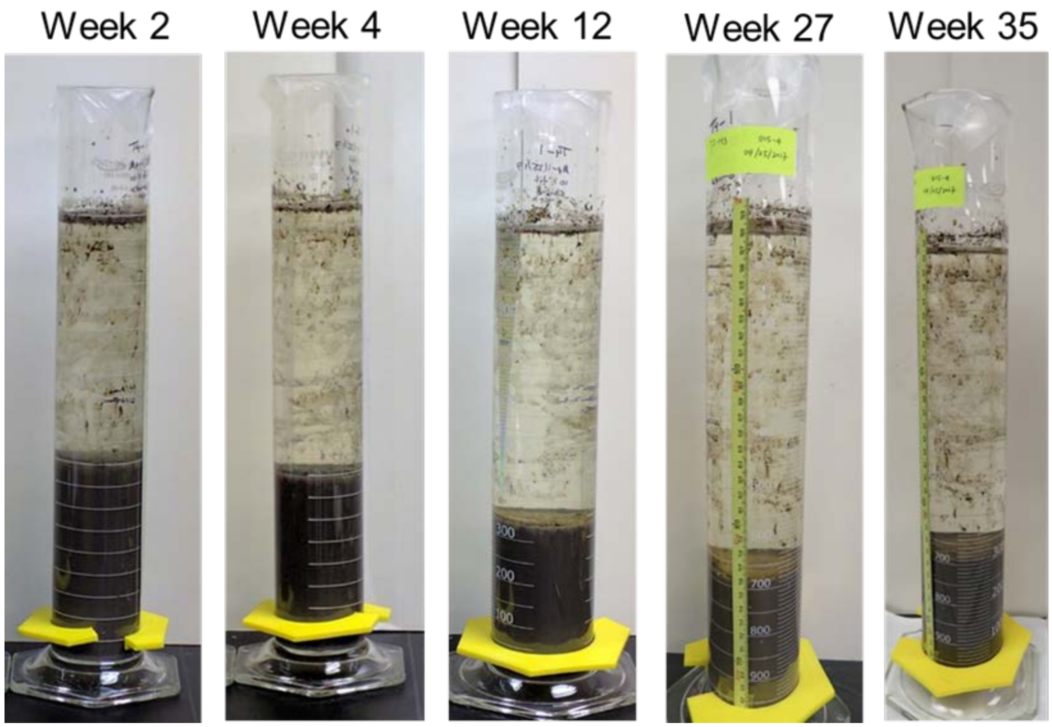


Figure 23. The photos of settling tests of diluted cleaned FFT-1 (10 wt%).

The settlement rates of diluted cleaned and uncleaned FFT-1 at the free settling zone (0-30 seconds of settling) were calculated (Table 7) according to the Equation 2. The diluted cleaned FFT-1 showed lower settlement rates than the diluted uncleaned FFT-1.

Equation 2. Settlement rate

$$Settlement\ rate\ \left(\frac{m}{h}\right) = \frac{settling\ height\ change\ (cm) \times 3600}{time\ (seconds) \times 100}$$

Table 7. The settlement rate of diluted cleaned and uncleaned FFT-1 at the free settling zone.

Sample	Settlement rate (m/h)			
	Test #1	Test #2	Test #3	Average
Diluted uncleaned FFT-1	3.12	2.88	2.04	2.68
Diluted cleaned FFT-1	0.72	1.08	0.6	0.8

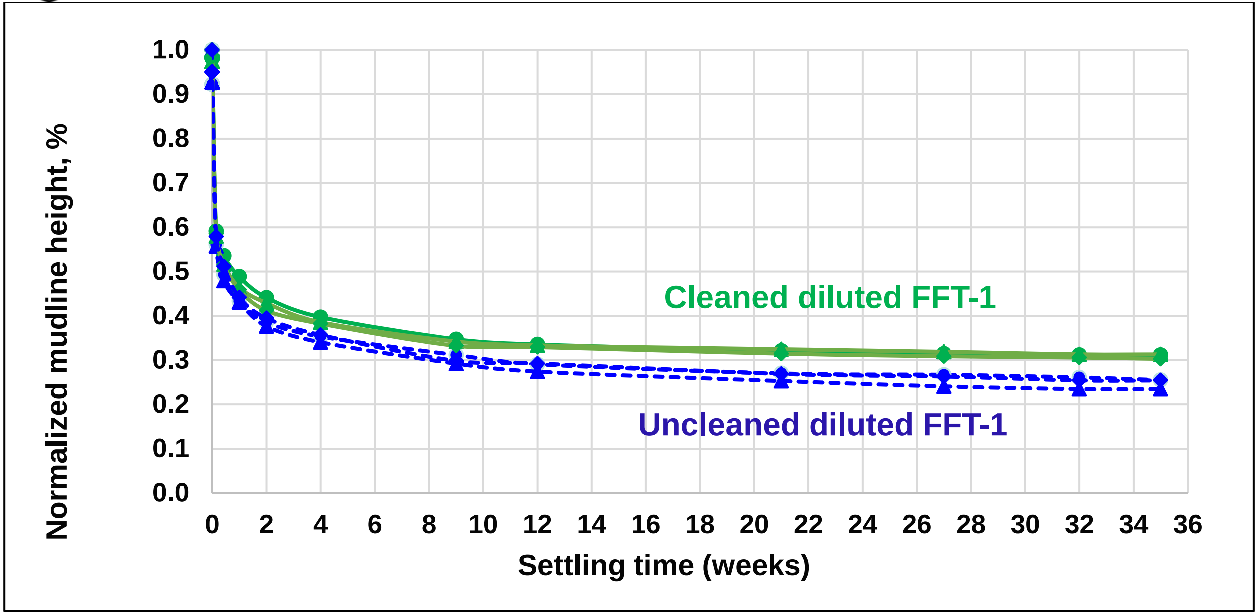


Figure 24. Settling curves of diluted FFT-1 and cleaned diluted FFT-1 with 1-stage washing.

A T-Test with two samples assuming unequal variances were used to analyze the whether diluted raw and cleaned FFT-1 samples were statistically significantly different between the final normalized mudline heights after 35-week settling. The alpha value was set at 0.05 for the T-Test, so if the p-value was less than 0.05, there was a statistically significant difference. The p-value was 0.003 which is less than 0.05. So the final normalized mudline heights obtained by diluted cleaned FFT-1 were statistically significantly higher than that obtained by diluted uncleaned FFT-1.

3.2.3.5 Settling of flocculated diluted raw and cleaned FFT-1 with one-stage washing

The diluted raw FFT-1 and diluted cleaned FFT-1 were treated with a flocculant (polymer A3338) and settled in a 1-L graduated cylinder. Figure 25 and Figure 26 show the photos of settling tests of flocculated diluted FFT-1 and flocculated diluted cleaned FFT-1, respectively. The flocculated diluted raw FFT-1 produced darker supernatant than the flocculated diluted cleaned FFT-1 water in the first four weeks of settling, and then the supernatant water of both types of samples became clear.

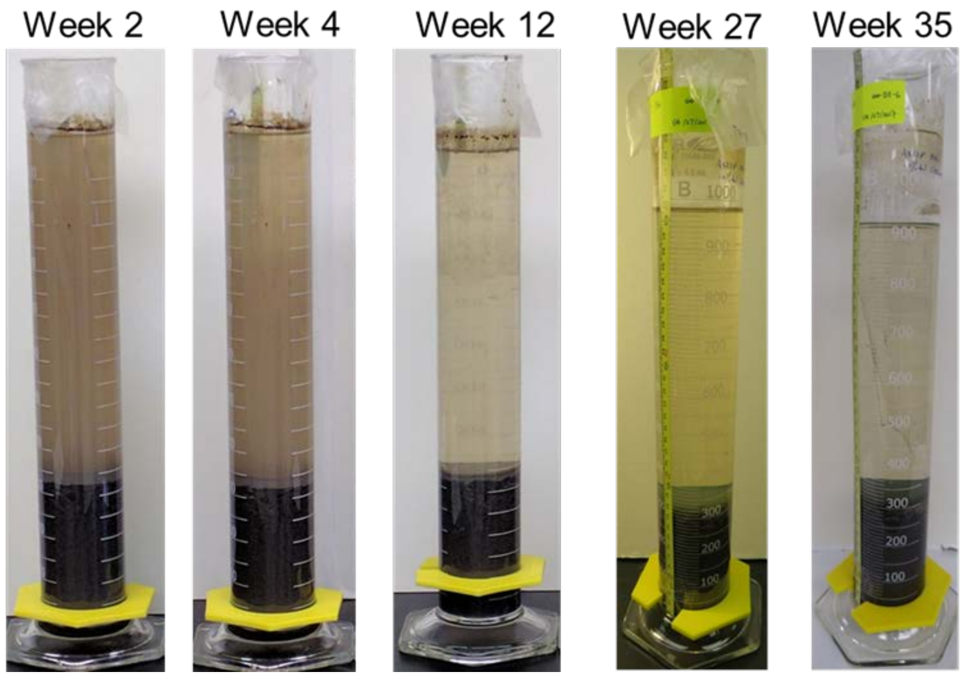


Figure 25. The photos of settling tests of flocculated diluted FFT-1 (10 wt%).

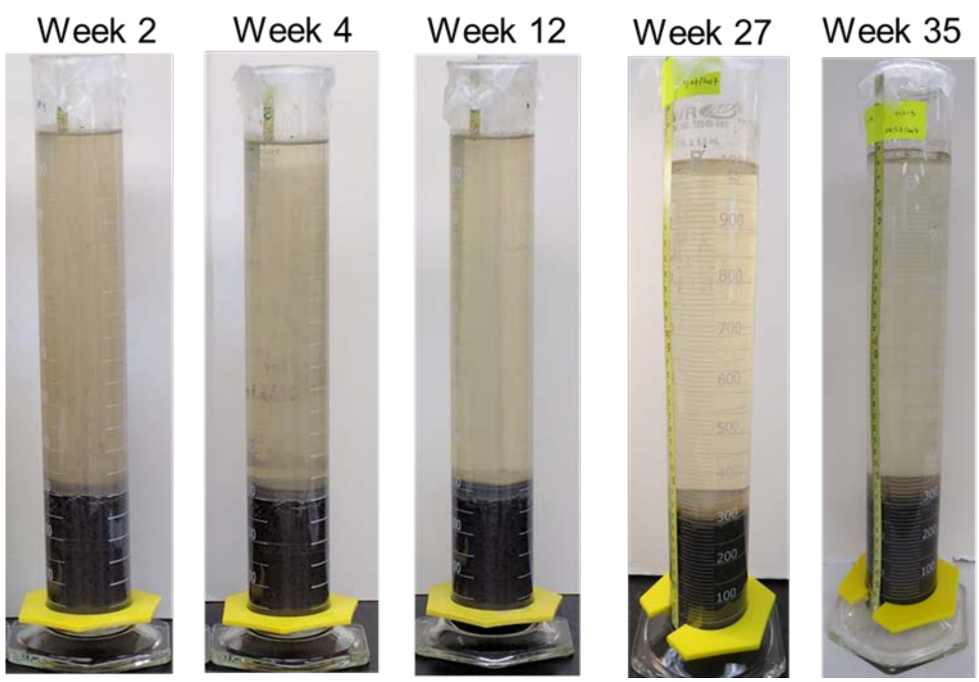


Figure 26. The photos of settling tests of flocculated diluted cleaned FFT-1 (10 wt%).

The flocculated diluted uncleaned FFT-1 settled faster at the free settling zone (0-30 seconds) as shown in Table 8. Throughout the whole settling process (35 weeks) the flocculated diluted uncleaned FFT-1 produced a lower mudline height than the flocculated diluted cleaned FFT-1 (Figure 27). It was observed that the volume of flocculated diluted cleaned FFT-1 expanded slightly after 21 weeks of settling possibly due to microbial activity. The p-value of the T-Test on the final normalized mudline heights of both samples was 0.08 larger than 0.05. So the final normalized mudline heights obtained by flocculated diluted cleaned FFT-1 were not statistically significantly different from that obtained by flocculated diluted uncleaned FFT-1.

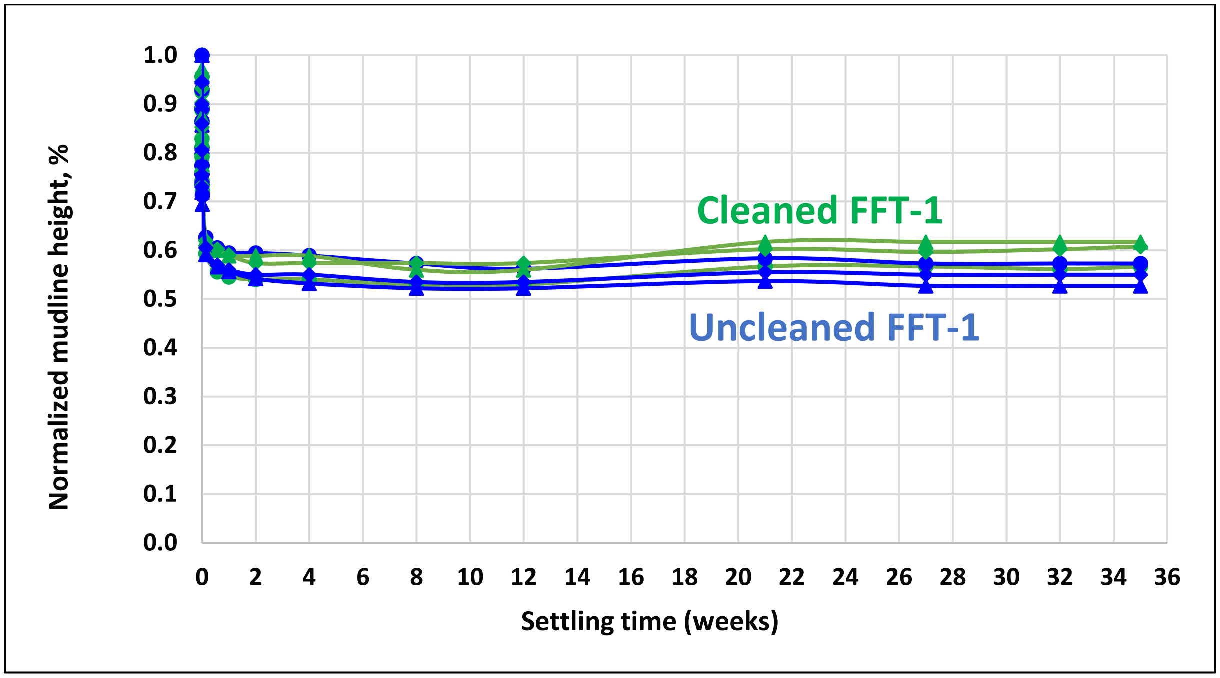


Figure 27. Settling curves of flocculated diluted FFT-1 and flocculated cleaned diluted FFT-1 with 1-stage washing.

Table 8. The settlement rate of flocculated diluted cleaned and flocculated uncleaned FFT-1 at the free settling zone.

Sample	Settlement rate (m/h)			
	Test #1	Test #2	Test #3	Average
Flocculated diluted uncleaned FFT-1	1.56	1.08	1.32	1.32
Flocculated diluted cleaned FFT-1	0.96	0.60	0.96	0.84

3.2.3.6 Column dismantling results of diluted raw and cleaned FFT-1 with one-stage washing

The settling columns were dismantled after 35 weeks of settling. A subsample of the release water from each column was dried to determine the total solids content of the water. The sediment from each column was divided into three layers: top layer, middle layer and bottom layer. Each layer of the sediment was tested on the static yield stress using a Brookfield DVIII HB rheometer. A subsample of each layer was dried to determine the total solids plus bitumen content of the sediment.

In contrast to the undiluted FFT, the flocculated tailings had a higher total solid content in the release water than the unflocculated tailings (Figure 28). The cleaned tailings produced more consistent result than the uncleaned tailings.

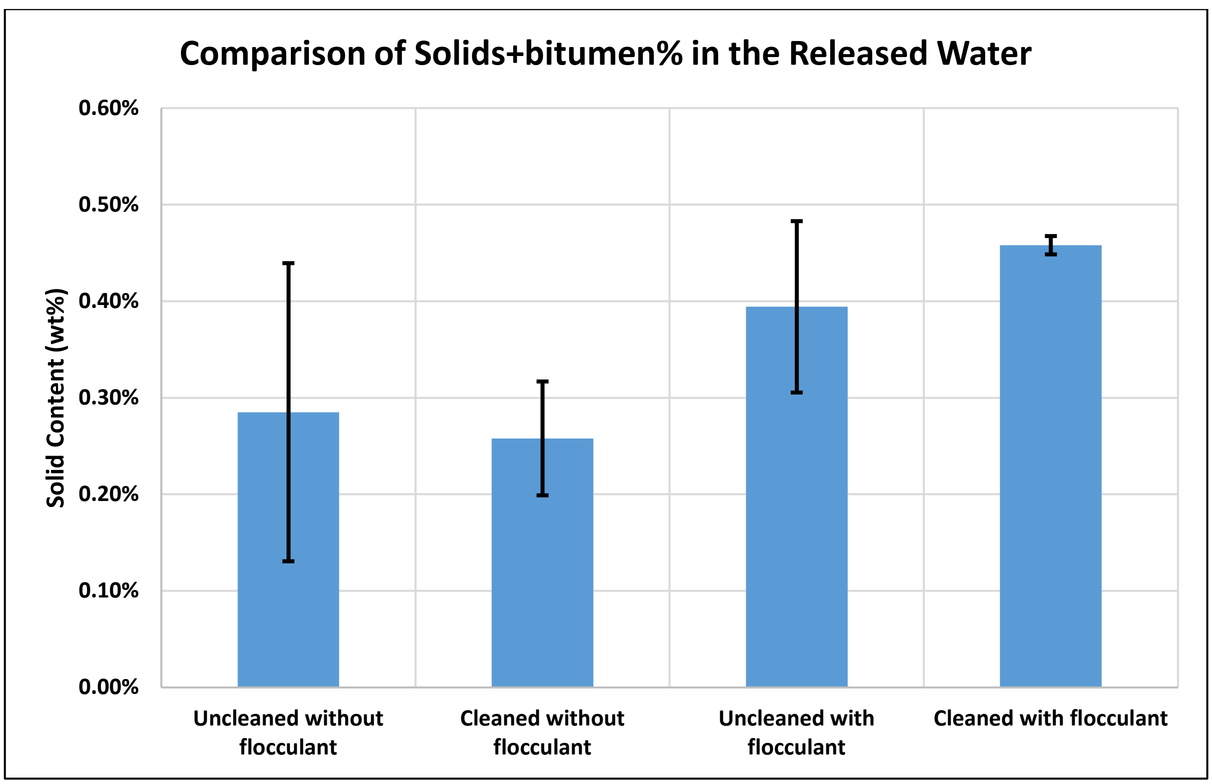


Figure 28. The solids and bitumen content in the released water of diluted FFT-1 after 35 weeks settling (error bar: standard deviation).

The total solids plus bitumen content in each sediment layer was measured and shown in Figure 29. The flocculated diluted FFT-1 produced higher total solids plus bitumen content than unflocculated diluted FFT-1. The bitumen content in the uncleaned and cleaned FFT-1 were determined by D&S and it was assumed that all the bitumen were homogeneously distributed in the sediment after settling tests. The solids content in the each layer sediment was calculated by subtracting the bitumen content from the total solids plus bitumen content and the values are shown in Figure 30. The cleaned diluted FFT-1 produced a similar solids content in the sediment as the uncleaned diluted FFT-1. The flocculated samples produced higher average solids% than the unflocculated samples in the sediment. The T-test analysis showed that in the bottom and middle layer the solids% in the sediment produced by the flocculated diluted cleaned FFT-1 was not significantly different from that produced by the flocculated diluted uncleaned FFT-1. But in the bottom layer the solids% in the sediment produced by the flocculated diluted cleaned FFT-1 was significantly higher than that produced by the flocculated diluted uncleaned FFT-1.

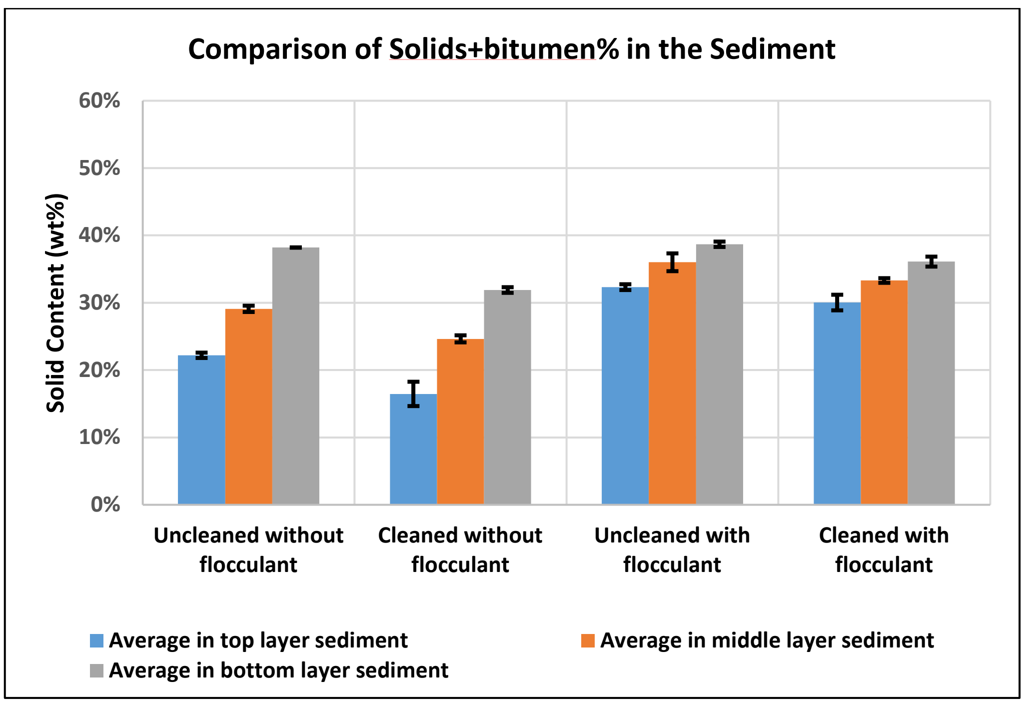


Figure 29. The solids and bitumen content in the sediment of diluted FFT-1 after 35 weeks settling (error bar: standard deviation).

The static yield stress of flocculated diluted FFT-1 is shown in Figure 31. The static yield stress of unflocculated diluted samples were under-range of the Brookfield DVIII HB rheometer. The static yield stress of the top and middle layers for both raw and cleaned diluted FFT-1 were comparable, but the bottom layer of flocculated diluted cleaned FFT-1 showed lower static yield stress than that of uncleaned FFT-1. Compared to the flocculated undiluted FFT-1 samples, the flocculated diluted FFT-1 samples had lower yield stress due to the lower solids content of the diluted samples.

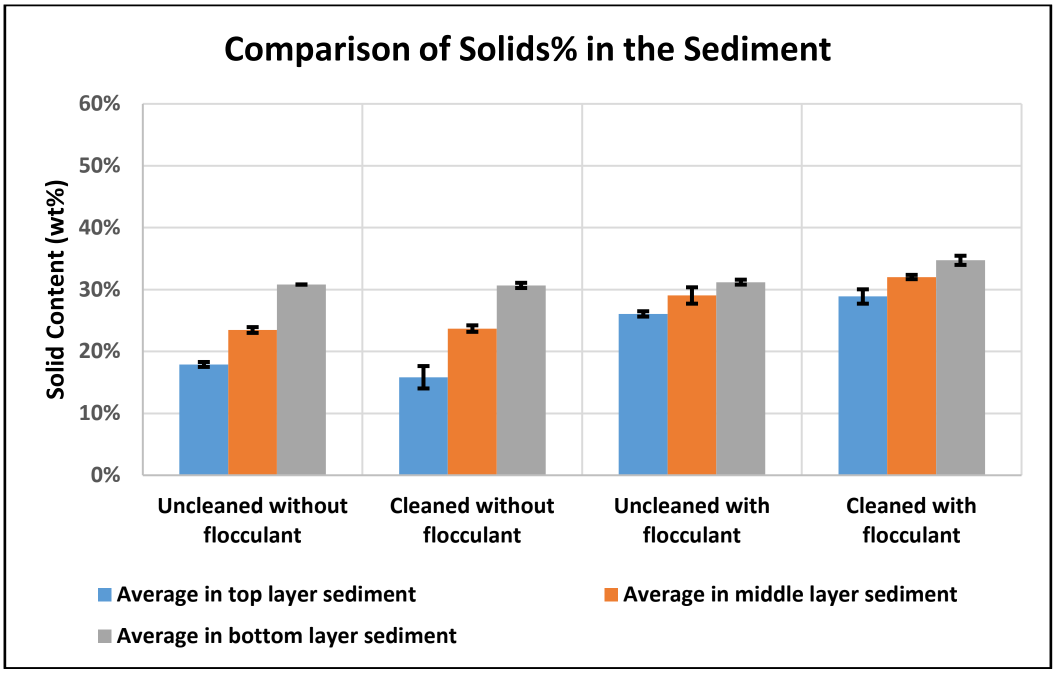


Figure 30. The solids content in the sediment of diluted FFT-1 after 35 weeks settling (error bar: standard deviation).

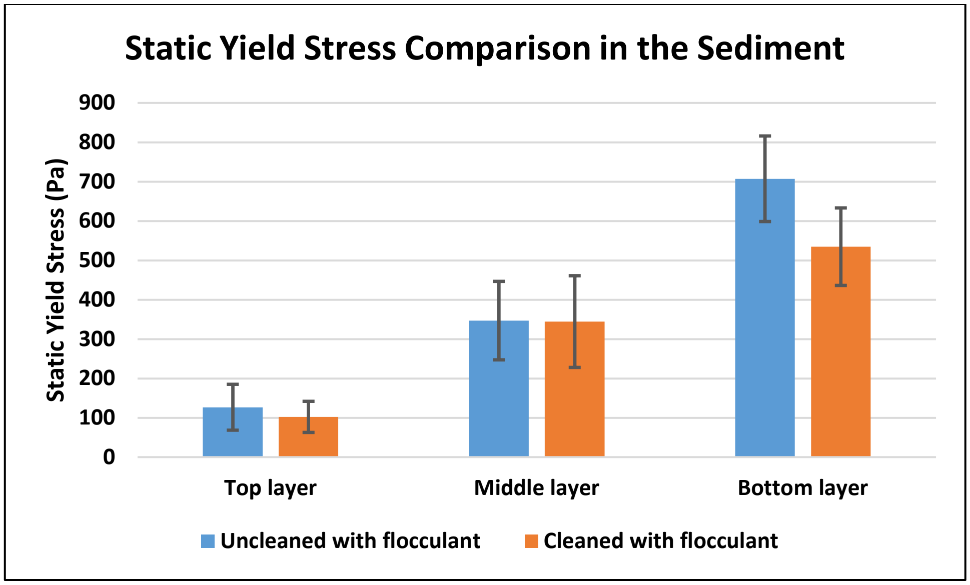


Figure 31. The static yield stress in the sediment of flocculated diluted FFT-1 after 35 weeks settling (error bar: standard deviation).

3.3 Further Optimization of Bitumen Extraction Conditions and Evaluation of Cleaned FFT

3.3.1 Further optimization of bitumen extraction conditions – two-stage washing

When analyzing the initial flocculation and settling results, no significant benefit was seen from bitumen removal and in fact showed a potential adverse effect in the form of significant microbial activity. In reviewing the data it was determined that the residual bitumen of FFT-1 was lower than before but that the cleaning only brought the bitumen content to within the low-normal range for FFT-1 (1.46%) (Table 9).

Table 9. 10th, 50th and 90th percentile of bitumen, mineral and B/S ratio for historical pond data (fines >50%) (Taken from Kaminsky & Omotoso, 2016).

	Bitumen	Mineral	B/S ratio
D10	0.9	20.7	0.03
D50	2.9	36.2	0.08
D90	5.5	58.3	0.15

It was hypothesized that additional cleaning may have additional benefit. Hence a two-stage washing was adopted as shown in Figure 32. The D&S of the cleaned FFT-1 with two-stage washing (Table 10) showed the B/S decreased to 0.03 which brought the FFT-1 to the very low end (D10) of typical FFT (Kaminsky & Omotoso, 2016). In addition, a low-bitumen FFT (FFT-2) was added to the study to see how the process worked on an FFT with an already low bitumen content. Another reason to introduce the FFT-2 into this study was HSE concerns of FFT-1 (odorous).

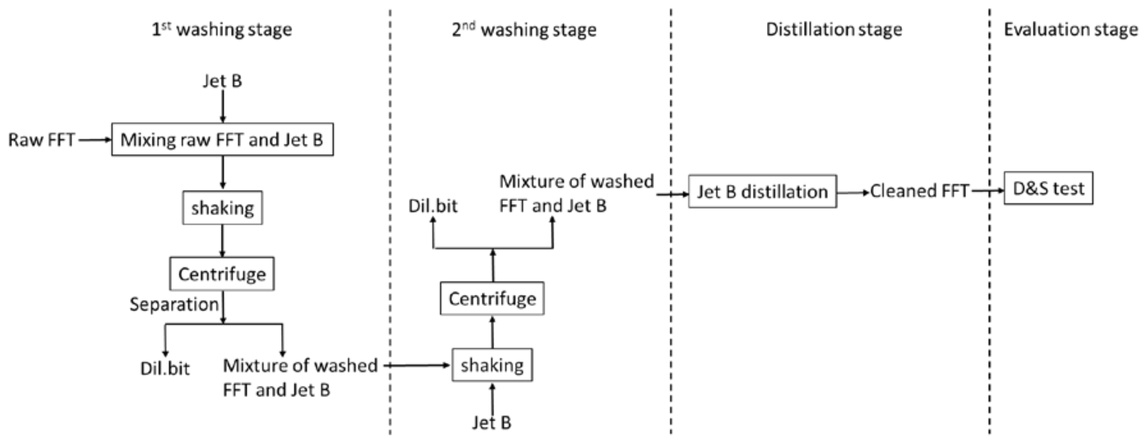


Figure 32. Bitumen extraction process with a two-stage washing using Jet B solvent.

Table 10. Characterization of cleaned FFT-1 using Jet B solvent.

	Raw FFT-1	Cleaned FFT-1 with single washing stage	Cleaned FFT-1 with two washing stages
Bitumen content (wt%)	7.81	1.46	0.84
Solids content (wt%)	32.09	36.28	32.35
Water content (wt%)	60.04	61.91	66.07
Jet B content (wt%)	--	0.35	0.73
Bitumen to solids ratio (B/S)	0.24	0.04	0.03
MBI of solids (meq/100 g)	10.6	10.6	9.5

The B/S of the raw FFT-2 was 0.05 and decreased to 0.02 after a two-stage washing process using Jet B (Table 11). The residual Jet B content was calculated by subtracting the total contents of bitumen, solids and water obtained by D&S from 100%. The result showed that there was residual Jet B (1.23 wt%) in the cleaned FFT-2 sample after distillation. An assessment of the residual Jet B in the FFT-2 sample after washing and after cleaning was conducted at MAXXAM and the results are shown in Table 12. The Jet B content obtained by MAXXAM analysis was much lower than the values obtained by COSS. This is because the COSS method was a rough approximation which assumed all the closure errors in the Dean stark were due to Jet B.

Table 11. Characterization of cleaned FFT-2 using Jet B solvent.

	Raw FFT-2	Washed FFT-2 with two washing stages	Cleaned FFT-2
Bitumen content (wt%)	1.23	0.43	0.41
Solids content (wt%)	24.68	22.79	26.54
Water content (wt%)	73.64	70.21	71.82
Jet B content (wt%)	--	6.57	1.23
Bitumen to solids ratio (B/S)	0.05	0.02	0.02
MBI of solids (meq/100g)	14.1	--	13.8

Table 12. The residual Jet B content in washed and cleaned FFT-2 samples by MAXXAM.

Sample	Test #1 (wt%)	Test #2 (wt%)	Test #3 (wt%)	Average Jet B content (wt%)
Washed FFT-2 before distillation	0.29	0.23	0.23	0.25
Cleaned FFT-2 after distillation	<0.08	<0.08	<0.08	<0.08

3.3.2 Effect of bitumen removal on flocculation on both raw and cleaned FFT with two-stage washing

The two types of raw and cleaned FFT samples were evaluated by the preliminary flocculation test. Both cleaned FFT samples were produced by the two-stage washing procedure with a single round of distillation. The tailings samples were flocculated using polymer A3338 with a concentration of 0.45 wt% prepared with process effluent water (PEW) using a titration flocculation method. The titration flocculation method is able to provide an indicator of flocculation performance to some extent, but the full flocculation performance requires the dosage curve testing using a one-dose flocculation method. The full flocculation performance was not performed in this stage due to the budget and timeline. For the titration flocculation test, the flocs which appeared to the operator to produce the largest amount of release water was considered the optimal flocs. The total solids plus bitumen content of the optimal flocs were measured after 24 hours. It was assumed that all the bitumen in FFT was trapped in the flocs after flocculation. The solids content was then calculated by subtracting the bitumen content from the total solids plus bitumen content. The flocculant dosages to obtain optimal flocs were reduced by 42-48% after cleaning as shown in Figure 33. The solids% and clay to water ratio (CWR) in the flocs obtained by the titration flocculation method reflect the performance of the type of FFT (Figure 34 and Figure 35). The FFT-1 with higher solids% and bitumen% showed better performance after cleaning, but the FFT-2 with lower solids% and bitumen% showed a slight reduction in the performance of flocculation.

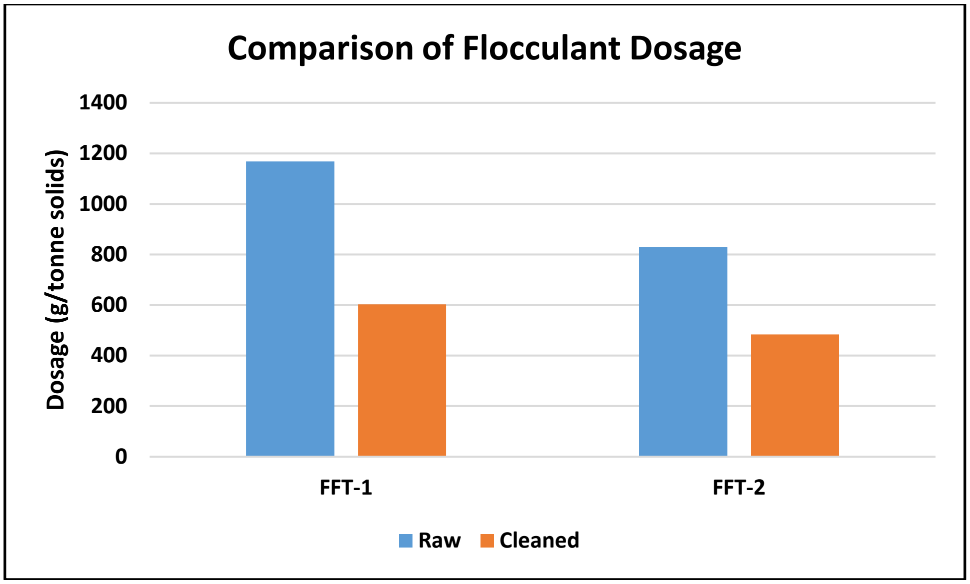


Figure 33. Flocculant dosage comparison of raw and cleaned FFT samples.

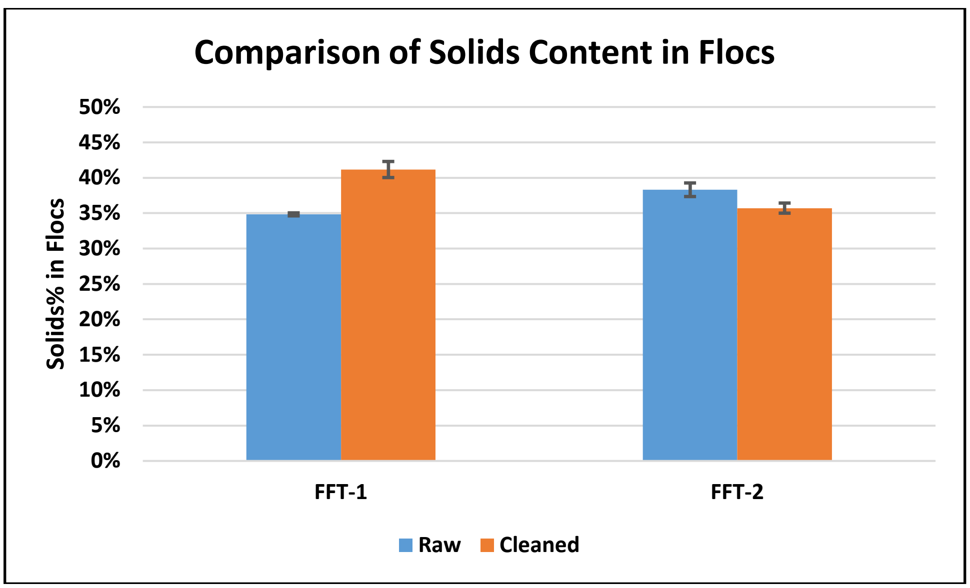


Figure 34. The comparison of solids content in the flocs after 24 hours water release for raw and cleaned FFT samples.

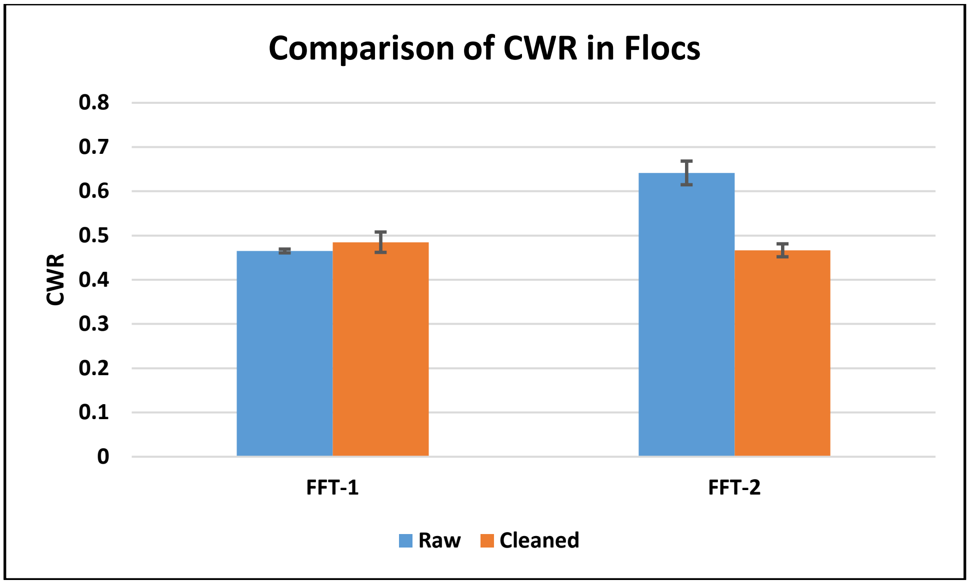


Figure 35. The comparison of clay to water ratio (CWR) in the flocs after 24 hours water release for raw and cleaned FFT samples.

A T-Test with two samples assuming unequal variances were used to analyze the whether raw and cleaned FFT samples were statistically significantly different between the means of solids%. The alpha value was set at 0.05 for the T-Test, so if the p-value was less than 0.05, there was a statistically significant difference. Table 13 shows the solids% in the flocs obtained by cleaned FFT were statistically significantly different from those obtained by raw FFT for both types of FFT. But overall the solids% in the flocs of cleaned FFT (FFT-1 and FFT-2 combined) were insignificantly different from those of raw FFT (FFT-1 and FFT-2 combined). The results of solids% and CWR in the flocs may not reflect the true performance since the titration flocculation method is not able to produce optimal flocs compared with the one-dose flocculation method.

Table 13. P-value obtained from T-Test with two samples assuming equal variance between the solids% in the flocs of raw and cleaned FFT. P-value<0.05 means statistically significant difference.

	P-value		
Sample	**Cleaned FFT-1**	**Cleaned FFT-2**	**Combined cleaned FFT**
Raw FFT-1	0.01		
Raw FFT-2		0.02	
Combined raw FFT			0.25

3.3.3 Effect of bitumen removal on drying test on both raw and cleaned FFT with two-stage washing

The flocs of two types of raw and cleaned FFT samples were collected and filled in the drying vessels (Sieve #18) for the drying test. The vessels were not covered and the loss of water to drainage and evaporation was measured every 24 hours until no weight change was observed for three consecutive days. The static yield stress was also measured each day until the samples reached the limit of the instrument range at 40 kPa. Two pans of water were setup next to the samples to aid in the determination of the weight% solids gain at 100% of potential evaporation and to compare actual evaporation (AE) to potential evaporation (PE).

Figure 36 shows that polymer treated FFT-2 samples dried at a higher rate than the polymer treated FFT-1 samples. But when the drying rate was corrected by the evaporation rate of a pan of water placed in the same location (PE) as shown in Figure 37, the differences of drying rate were determined to be due to position within the room.

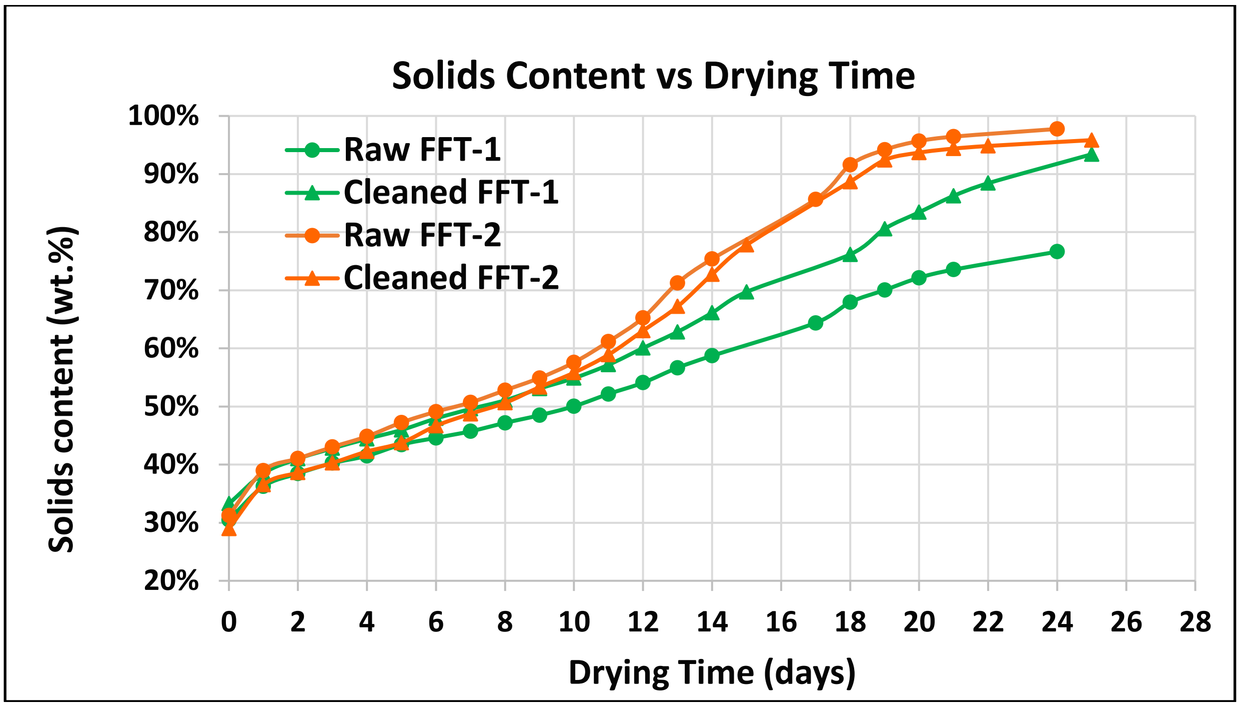


Figure 36. Drying curves of raw and cleaned FFT samples treated with flocculant.

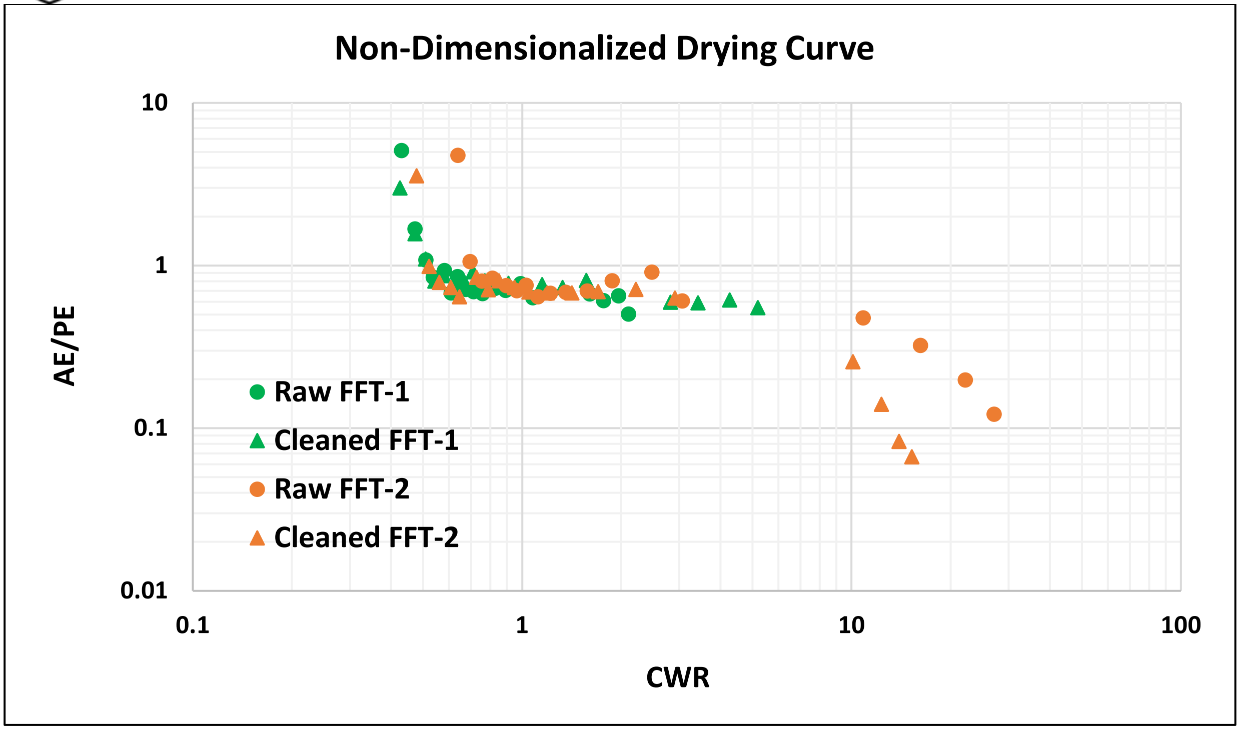


Figure 37. Comparison of the non-dimensionalized drying curves of all the FFT samples treated with polymer.

The strength gain of flocculated FFT samples with drying time increased faster after cleaning (Figure 38). So the bitumen removal helps improve the strength gain faster with time. The strength gain of flocculated cleaned FFT-1 was comparable with the flocculated raw FFT-1 with the increase of solids content (Figure 39). The strength gain of flocculated cleaned FFT-2 was faster than the flocculated raw FFT-2 with the increase of solids content.

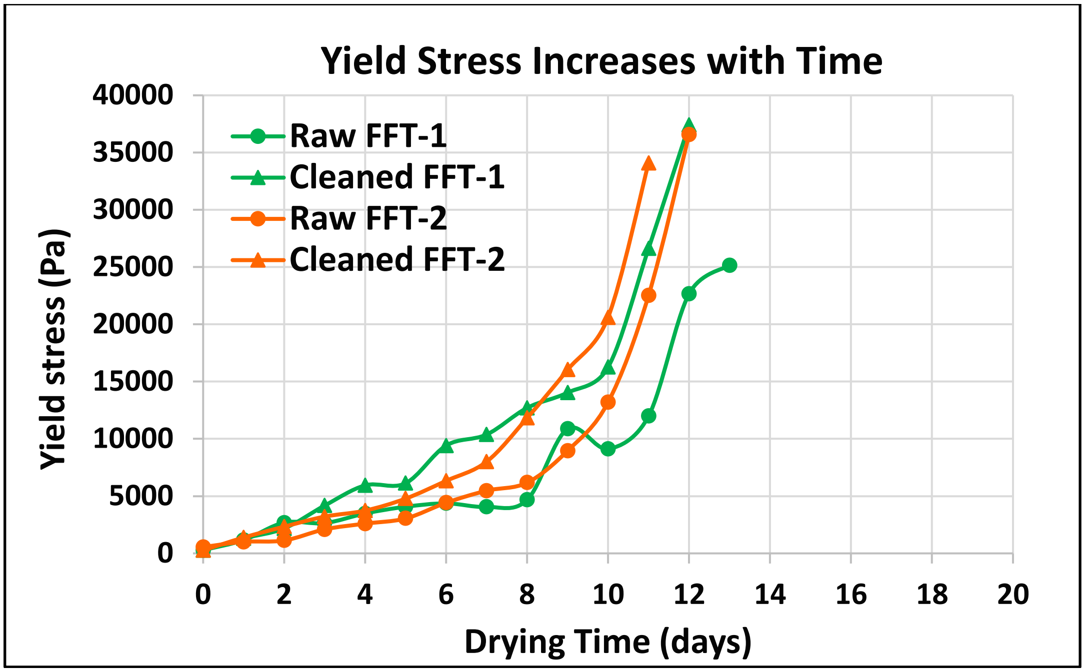


Figure 38. Strength development of the polymer treated FFT samples based on the drying time.

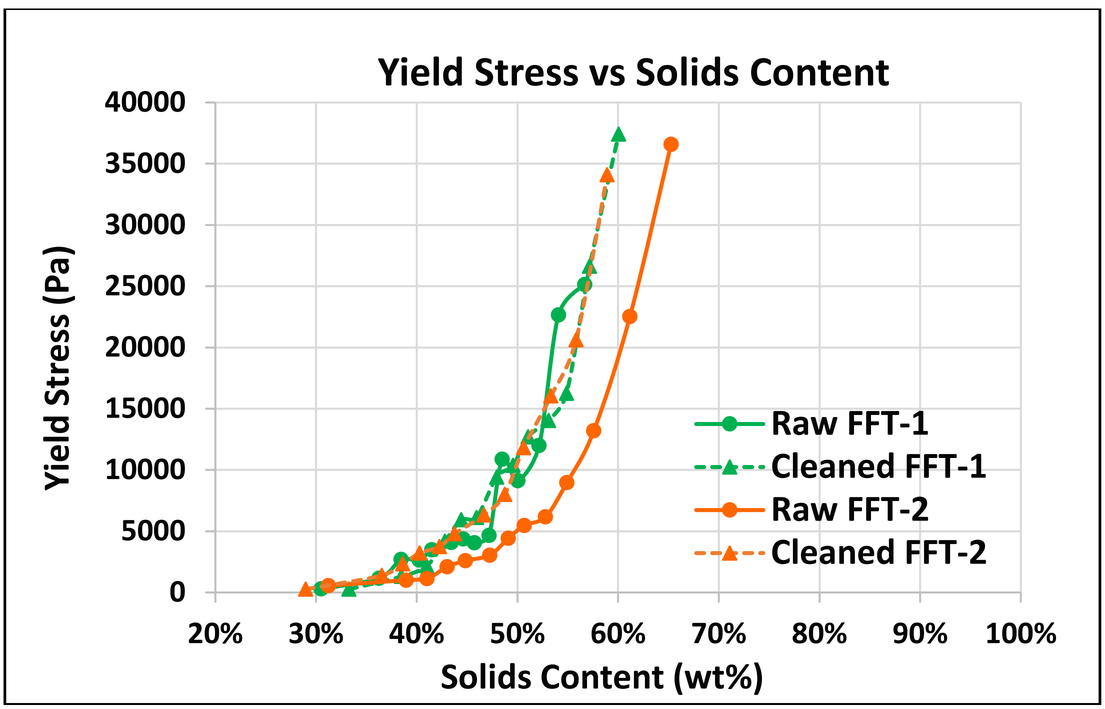


Figure 39. Strength development of the polymer treated FFT samples based on the solids content.

3.4 Further Optimization of Distillation Conditions and Evaluation of Cleaned FFT

3.4.1 Further optimization of distillation conditions

Because the settling tests of cleaned FFT-1 showed microbial activity, it was considered likely that there was residual Jet B in the cleaned FFT-1 due to the incomplete distillation. Furthermore in the drying test a slight residual odor of Jet B was noted in the cleaned samples. This was in spite of the fact that the Jet B in the sample was not detectable in the MAXXAM tests.

In order to remove as much residual Jet B as possible from the cleaned FFT, the distillation was performed for multiple rounds with ~1.5 hours each round. Water was added between each distillation round to maintain water content. The water was added to avoid drying out the clays which could potentially change the clay's properties and increase losses by having stuff stick to the bottom of the distillation kettle. Since the mixture in the distillation bottle contained two immiscible liquids (water and Jet B), a steam distillation was actually employed resulting in a lower boiling point than Jet B itself.

TGA analysis was used to determine whether the difference in Jet B content could be measured between distillation rounds. TGA is a method of thermal analysis in which the mass of a sample is measured over time as the temperature changes. In this study TGA was conducted to identify water and Jet B loss in the samples as the temperature gradually raised from room temperature to 200°C. The TGA curves of Figure 40 and the differential thermal analysis (DTG) curves of Figure 41 showed that the majority of the mass loss for cleaned FFT-2 samples occurred in the 95-110°C temperature range. The loss peaks represent the mixture of the two boils – water and Jet B. Jet B is a mixture of hydrocarbons with a boiling point range between 50 and 270°C according to the safety data sheet. As more rounds of distillation were conducted the mass loss was observed to decrease and shift to a lower temperature range due to the steam distillation. This change in mass loss was attributed to a change in Jet B content of the sample. Given the difference in the TGA data and the change in noticeable odor three rounds of distillation was selected for the future samples.

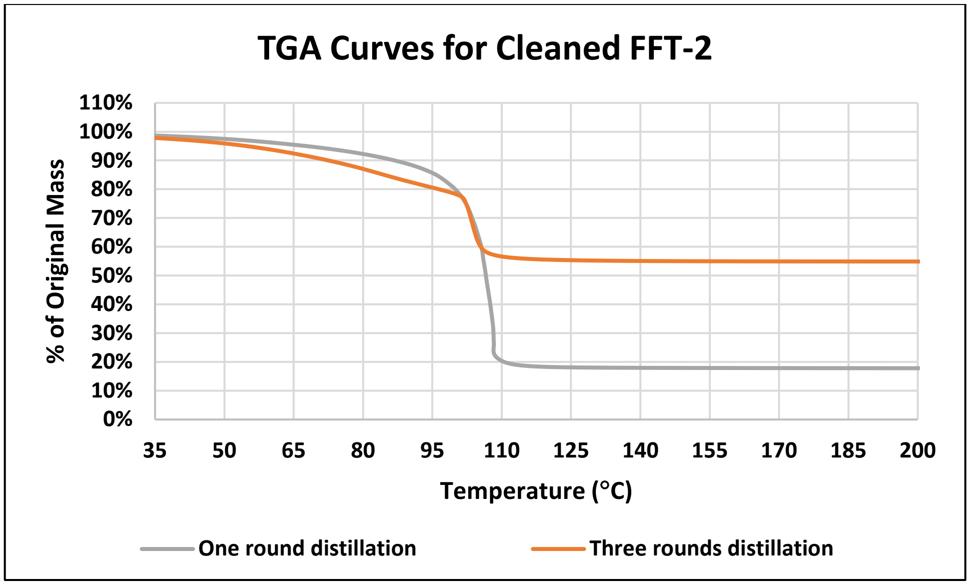


Figure 40. TGA results for cleaned FFT-2 with one, vs three rounds of distillation.

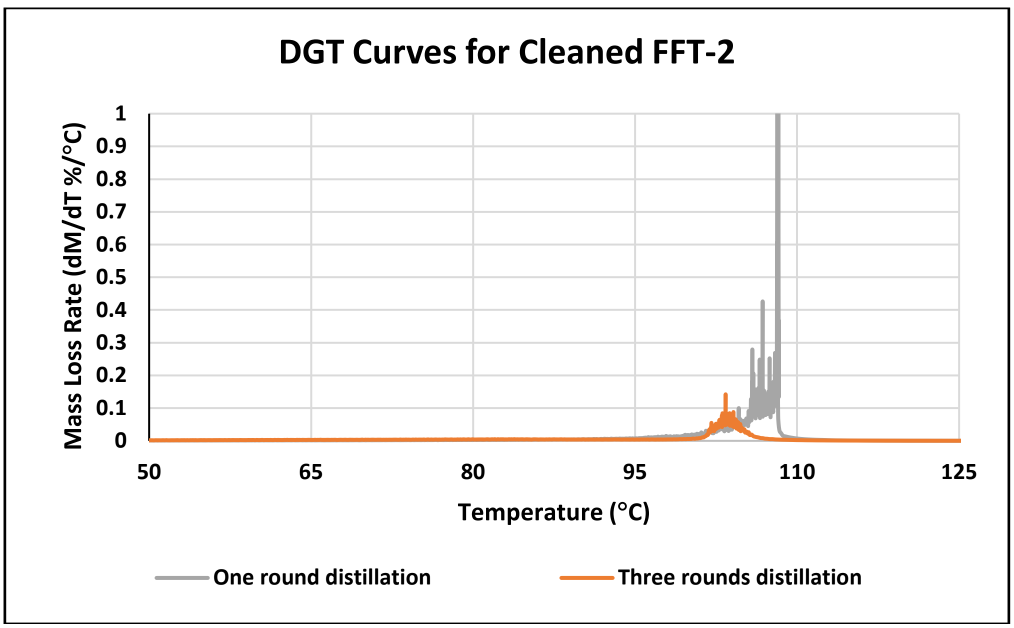


Figure 41. DTG curves for cleaned FFT-2 with one vs three rounds of distillation.

To confirm that the TGA was able to detect the JET B, washed and distilled samples were compared (Figure 42). As shown in Figure 43 the mass loss in the 90-110°C range was significantly higher in the washed samples than in the cleaned sample. The results indicated that most of the Jet B solvent was distilled out of the cleaned FFT samples but there was still

Jet B residual in the cleaned FFT samples even after 3 rounds of distillation, however the residual was fairly small and the odor had almost entirely disappeared from the sample.

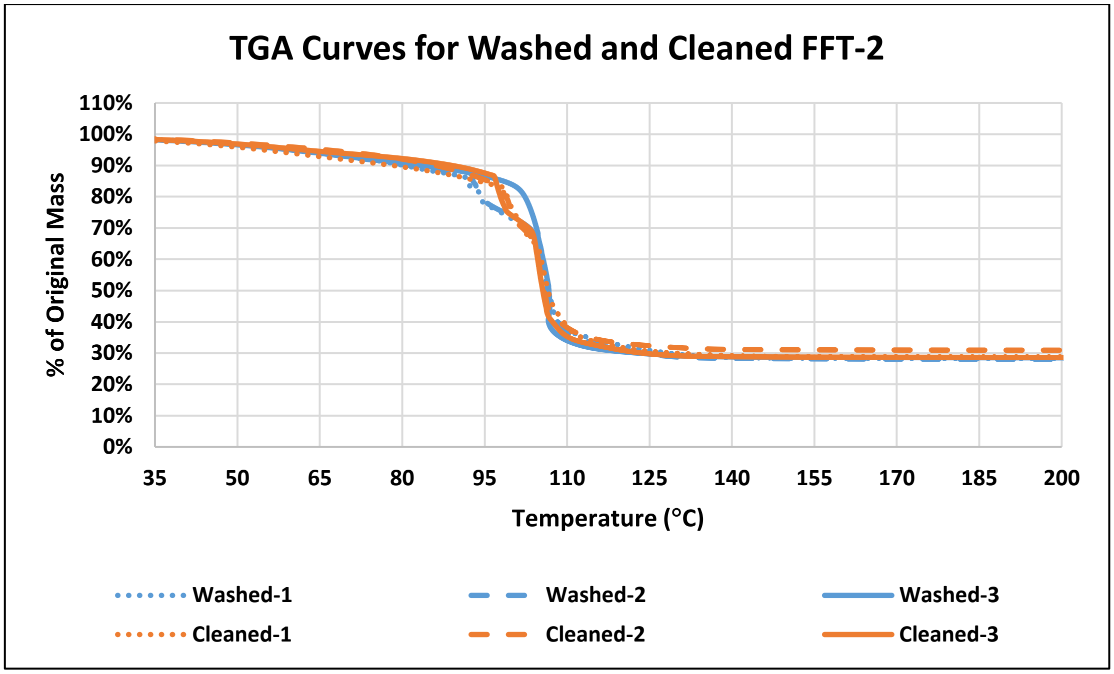


Figure 42. TGA results for washed (before distillation) and cleaned FFT-2 (after distillation) samples performed in triplicate.

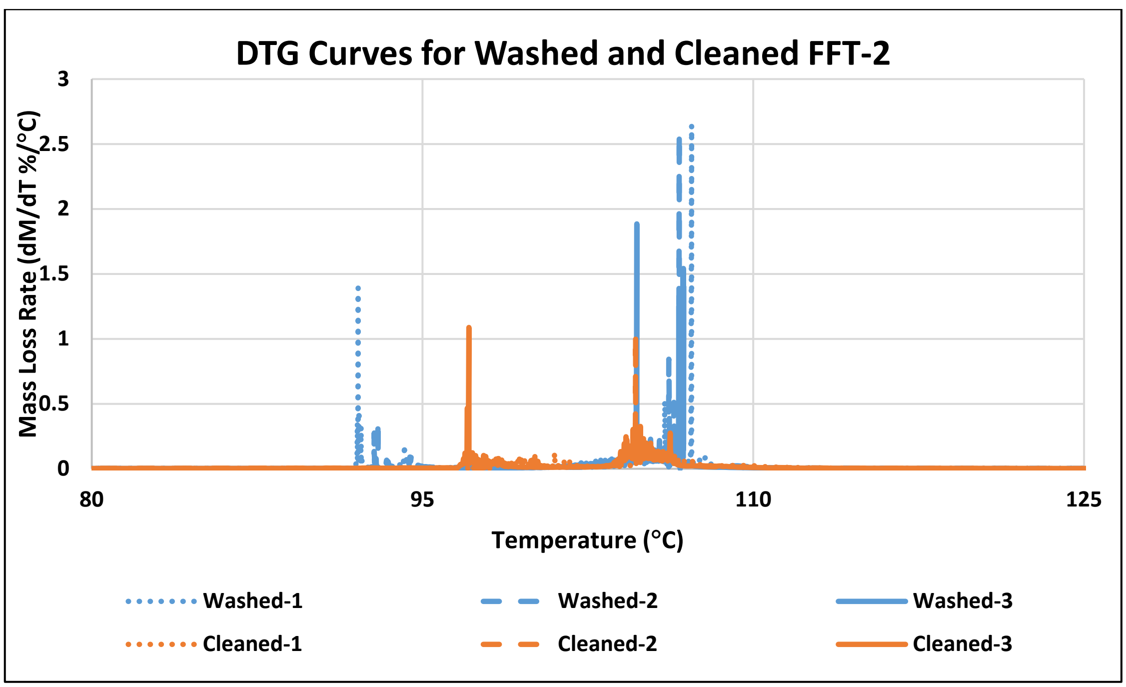


Figure 43. DTG curves for washed and cleaned FFT-2 samples performed in triplicates.

The distillation setup used at COSS was a similar to the Dean & Stark setup which was not ideal for steam distillation and thus not efficient as the pilot equipment previously used by Titanium corporation. The operating procedure of the steam distillation was not optimized due to the facility limit. It is likely that the difficulty in removing the Jet B experienced by COSS is due to these limitations.

Overall, the optimal FFT cleaning process using Titanium's technology is summarized as follows. This process is named "optimal FFT cleaning process".

- Solvent (Jet B) to feed (FFT) ratio in each washing stage – 0.5:1
- Shaking time of the mixture of FFT and Jet B in each washing stage – 30 minutes
- Centrifuge time to separate the solvent phase and sediment phase in each washing stage – 45 minutes
- Two-stage washing
- Three-round distillation on washed FFT with 1.5 hours distillation in each round

3.4.2 HSE Challenges of FFT-1

The disadvantage of FFT-1 was the irritating odor which led to a worker developing a persistent headache and therefore was unsafe to the lab operators and required high air circulation. Although volatile organic compound (VOC) testing showed the levels were acceptable, the decision was made to switch to FFT-2 to avoid any adverse HSE impacts when being sent for geotechnical testing. For this reason FFT-2 was selected for the consolidation testing.

3.4.3 Effect of Optimal Cleaning of FFT-2 on Consolidation

The Cleaned FFT-2 sample using the optimal cleaning process along with the raw FFT-2 sample as a control were sent to Thurber for the consolidation test. The testing at Thurber comprises: 1) material characterization testing and 2) compressibility and hydraulic conductivity testing using several different methods.

3.4.3.1 Materials Characterization Testing

The two samples were characterized by Thurber (Table 14) and the results with the typical FFT properties (FTFC, 1995) (Kaminsky & Omotoso, 2016) are shown in Table 15. As shown, the FFT selected was on the high end for clay content and activity but was within the typical range.

Table 14. Material characterization testing methods and references by Thurber.

Test method	Standards/Reference
Water content / solids content	ASTM D2216-10
Methylene blue index	AST Methylene Blue Procedure, 2004
Particle size distribution by sieve-hydrometer	AASHTO T 88-10; ASTM D7928-17
Atterberg limits (liquid, and plastic)	ASTM D4318-17
Specific gravity	ASTM D 854-14

The Unified Soil Classification System (USCS) is a soil classification system used in engineering and geology to describe the texture and grain size of a soil (ASTM D-2487). Both cleaned and raw FFT-2 samples are in the group of clay of high plasticity (CH) or organic clay (OH) which represents liquid limit 50 or more (Figure 44).

Figure 45 shows the Unified Oil Sands Tailings Classification System (UOSTCS). Both cleaned and raw FFT-2 samples in the fine tailings zone 1 (F-1) which had a sand to fines ratio (SFR) 1 or less and fines to water ratio (FWR) less than the static segregation boundary.

Table 15. Cleaned and uncleaned FFT-2 samples characterization provided by Thurber compared with regular FFT range.

Testing item		**Cleaned FFT-2**	**Uncleaned FFT-2**	**Regular FFT**
USCS		CH or OH	CH or OH	CH or OH
UOSTCS		F-1	F-1	F-1
Initial solids content (wt%)		26.9	25.4	38±14
Specific gravity (kg/m^3)		2.44	2.43	2.2-2.58
Particle size distribution (PSD) test	**Fines content (%)**	99.4	99.9	85±35
	Clay size content (%)	47.8	46.5	18-52
	SFR	0.01	0.00	≤1
Atterberg limits	**wL (%)**	73	64	40-75
	wP (%)	31	26	10-20
	PI (%)	42	38	23-37
	Activity	0.88	0.82	0.44-2.06
MBI (meq/100 g)		13.8	13.3	7.5±(5-14)
Clay content from MBI (%)		99	95	51±(40-100)

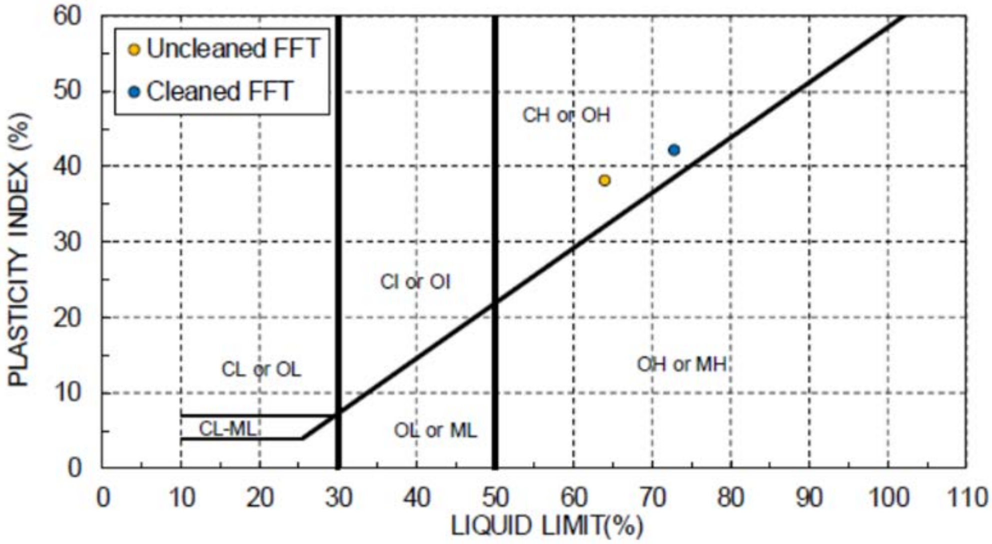
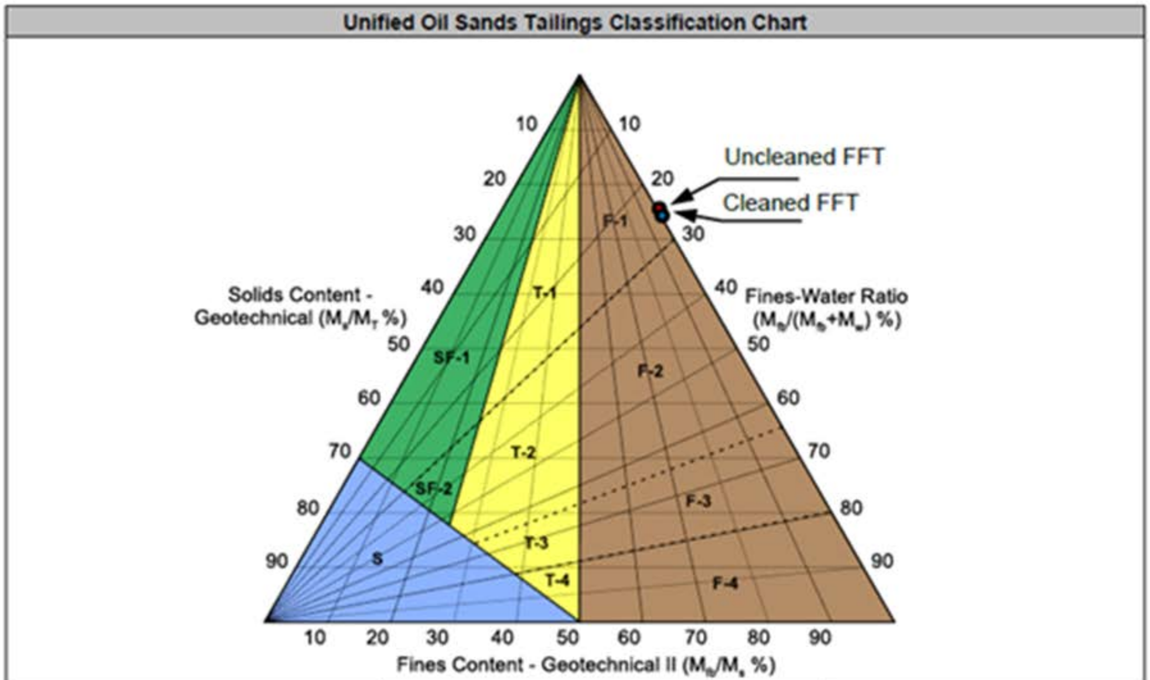


Figure 44. Plastic Chart of cleaned and raw FFT-2 samples. CL: clay of low plasticity; OL: organic clay and organic silt of low plasticity; ML: silt of low plasticity; CH: clay of high plasticity; MH: silt of high plasticity; OH: organic clay and organic silt of high plasticity.

The initial solids contents (total solids plus bitumen contents), specific gravity, and PSD results (Figure 46) were comparable for both cleaned and raw FFT-2 samples and in the range of typical FFT.



Primary division		Secondary division	Symbols	Name
Sand Tailings Sand void ratio ≤ 1.1		None	S	Sand
Fines Dominated Tailings Sand void ratio > 1.1	Sandy-Fine Tailings SFR ≥ 3 (fines content geotechnical II ≤ 25%)	FWR < static segregation boundary	SF-1	Sandy Fine Tailings - Zone 1
		Liquid limit > FWR ≥ static segregation boundary	SF-2	Sandy Fine Tailings - Zone 2
	Transition Tailings 3 > SFR > 1 (25% < fines content geotechnical II < 50%)	FWR < static segregation boundary	T-1	Transition Tailings - Zone 1
		Liquid limit > FWR ≥ static segregation boundary	T-2	Transition Tailings - Zone 2
		Plastic limit > FWR ≥ liquid limit	T-3	Transition Tailings - Zone 3
		FWR ≥ plastic limit	T-4	Transition Tailings - Zone 4
	Fine Tailings SFR ≤ 1 (fines content geotechnical II≥ 50%)	FWR < static segregation boundary	F-1	Fine Tailings - Zone 1
		Liquid limit > FWR ≥ static segregation boundary	F-2	Fine Tailings - Zone 2
		Plastic limit > FWR ≥ liquid limit	F-3	Fine Tailings - Zone 3
		FWR ≥ plastic limit	F-4	Fine Tailings - Zone 4

Figure 45. Unified Oil Sands Tailings Classification System.

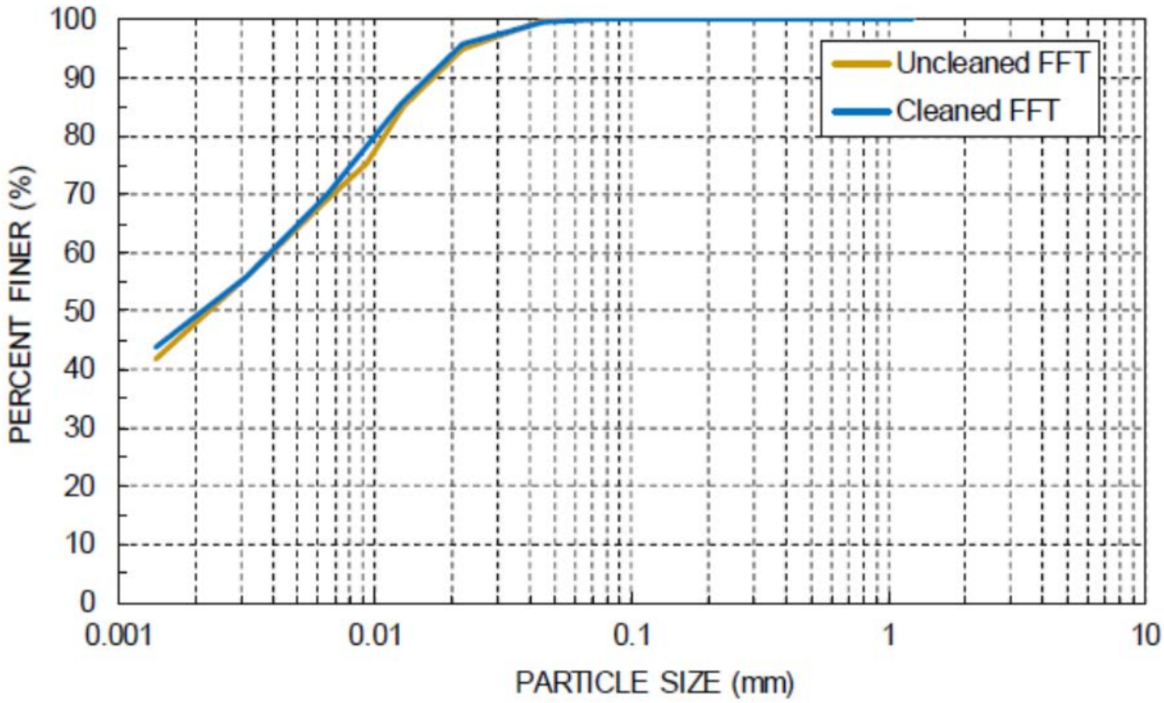


Figure 46. The particle size distribution of cleaned and raw FFT-2 samples.

The Atterberg limits (ASTM D4318-17) are a basic measure of the critical water contents of a fine grained soil: liquid limit (wL) and plastic limit (wP). The liquid limit (wL) is conceptually defined as the water content in percentage of a soil at the arbitrarily defined boundary between the semi-liquid and plastic states. The plastic limit (wP) is the water content in percent of a soil at the boundary between the plastic and semi-solid states. The plastic index (PI) is the range of water content over which a soil behaves plasticity. It is calculated as the difference between the liquid limit and the plastic limit. The activity is the ratio of the plasticity index of a soil to the percent by mass of particles having an equivalent diameter smaller than 2 µm. The cleaned FFT-2 using the optimal cleaning process showed slightly difference from the raw FFT-2 samples in the Atterberg limits testing, but difference was small and the Atterberg limits properties of both FFT-2 samples were in the typical FFT range.

The methylene blue index (MBI) and resulting calculated clay content were comparable for both cleaned and raw FFT-2, but they were high compared with typical FFT. The results of the index testing shows that any difference in behavior in consolidation can best be attributed to the change in bitumen content as the other indicators were virtually identical between the samples.

3.4.3.2 Compressibility and hydraulic conductivity tests

Compressibility indicates the response of soil particles to the applied pressure and leads to a better estimation of settlement (Jeeravipoolvarn, 2010). Hydraulic conductivity describes the ease with which a fluid can move through pore spaces or fractures. Compressibility and hydraulic conductivity testing were conducted by Thurber (Table 16). The compressibility test included the combined step loading large strain consolidation (LSC) and seepage induced consolidation (SIC) tests, rapid centrifuge consolidation (RCC) test, and compressibility standpipe (CS) test. The hydraulic conductivity test included the constant flow rate test (parts of LSC test), hindered sedimentation (HS) test, and rapid centrifuge consolidation (RCC) test.

Table 16. The methods of compressibility and hydraulic conductivity testing at Thurber.

Testing group	Test method	Standards/references
Compressibility	Combined step loading large strain consolidation (LSC) and seepage induced consolidation (SIC) tests.	Thurber LSC test memorandum; (Monte & Krizek, 1976); (Imai, 1979); (Huerta, et al., 1988); (Gjerapic, et al., 2017)
	Rapid centrifuge consolidation (RCC) test	(Mikasa & Takada, 1984); (Eckert, et al., 1996); (McDermott & King, 1998)
	Compressibility standpipe (CS) test	(Scott, et al., 2008)
Hydraulic conductivity	Constant flow rate test (parts of LSC test)	ASTM D5856-15
	Hindered sedimentation (HS) test	(Tan, et al., 1990); (Pane & Schiffman, 1997); (Scott, et al., 2008)
	Rapid centrifuge consolidation (RCC) test	(Mikasa & Takada, 1984); (Eckert, et al., 1996); (McDermott & King, 1998)

A brief description of the testing methods used in the compressibility and hydraulic conductivity tests (Jeeravipoolvarn, 2010) is summarized in Table 17. The large strain consolidation (LSC) test used load increments to increase the effective stress. At the end of each loading step, void ratio and effective stress were obtained and a hydraulic conductivity test was performed. The advantage of the LSC test is that it is a direct measurement and it does not include any complicated data interpretation. The disadvantage is that it takes a long time to complete especially when a low hydraulic conductivity sample is tested starting at a low initial solids content.

The seepage induced consolidation (SIC) test is used to study the consolidation by applying pressure on a soil sample through water flow. At the end of each applied hydraulic pressure, water content and pore pressure with depth was determine to calculate the compressibility. The flow rate measurement is used to calculate the hydraulic conductivity.

A compressibility standpipe (CS) test is to determine the compressibility through evaluating effective stress and void ratio via pore pressure measurement and density measurements. A hindered sedimentation test is used to measure the settling velocity of the interface between slurry and supernatant water. It is used to obtain the material's hydraulic conductivity at higher void ratios.

Table 17. The description of testing method used in the compressibility and hydraulic conductivity tests.

Test method	Description
Step loading large strain consolidation (LSC) test	Use load increments to increase the effective stress. At the end of each loading step, void ratio and effective stress are obtained and a hydraulic conductivity test is performed.
Seepage induced consolidation (SIC) test	Study consolidation by applying pressure on a soil sample through water flow. At the end of each applied hydraulic pressure, water content and pore pressure with depth was determine to calculate the compressibility. The flow rate measurement is used to calculate the hydraulic conductivity.
Compressibility standpipe test	Determine the compressibility through evaluating effective stress and void ratio via pore pressure measurement and density measurements
Hindered sedimentation (HS) test	Measure the settling velocity of the interface between slurry and supernatant water to obtain the material's hydraulic conductivity at higher void ratios

All the samples were homogenized using a hand drill inside a 20 L bucket for 5 minutes or until a homogenous mixture was obtained before testing. Once the sample was homogenized it was immediately subsampled using a beaker to obtain representative specimens for testing.

The compressibility for cleaned and uncleaned FFT-2 were similar (Figure 47). The hydraulic conductivity for cleaned FFT was slightly higher than the uncleaned FFT at the initial void ratio of ~5 (Figure 48). Their hydraulic conductivities were similar at lower void ratios (or higher effective stress). This indicates that in the initial stages of consolidation there may be a slight advantage of bitumen removal, however, when compared to the range of hydraulic conductivity for FFT at this void ratio this advantage is insignificant. Moreover, other treatment techniques such as flocculation show a larger benefit in this range (Znidarcic, et al., 2016). At the higher stresses no difference in conductivity were noted showing no advantage or disadvantage to consolidation. Additional details of the data can be found in the report by Thurber attached as Appendix B.

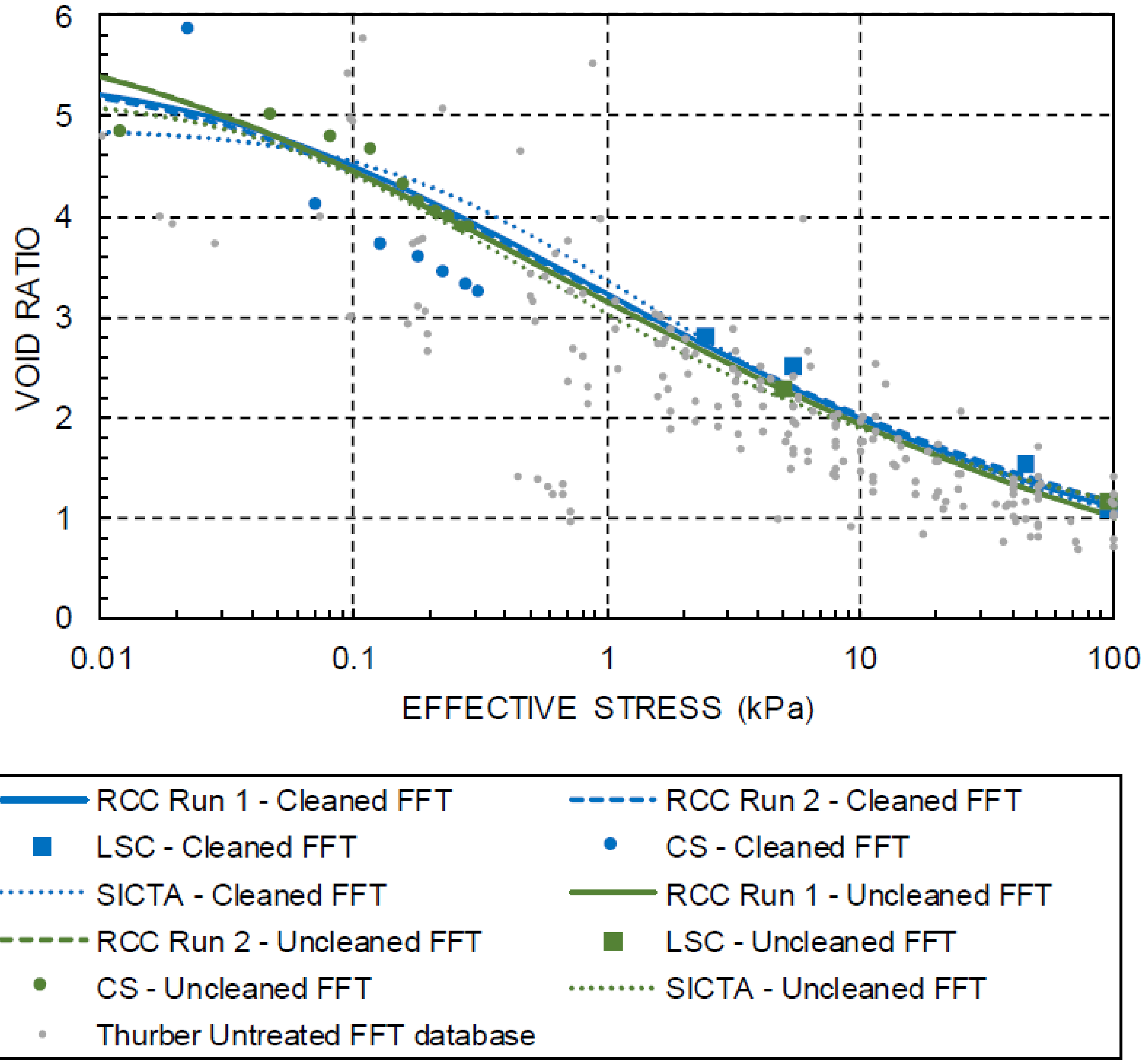


Figure 47. Compressibility comparison between cleaned and uncleaned FFT-2.

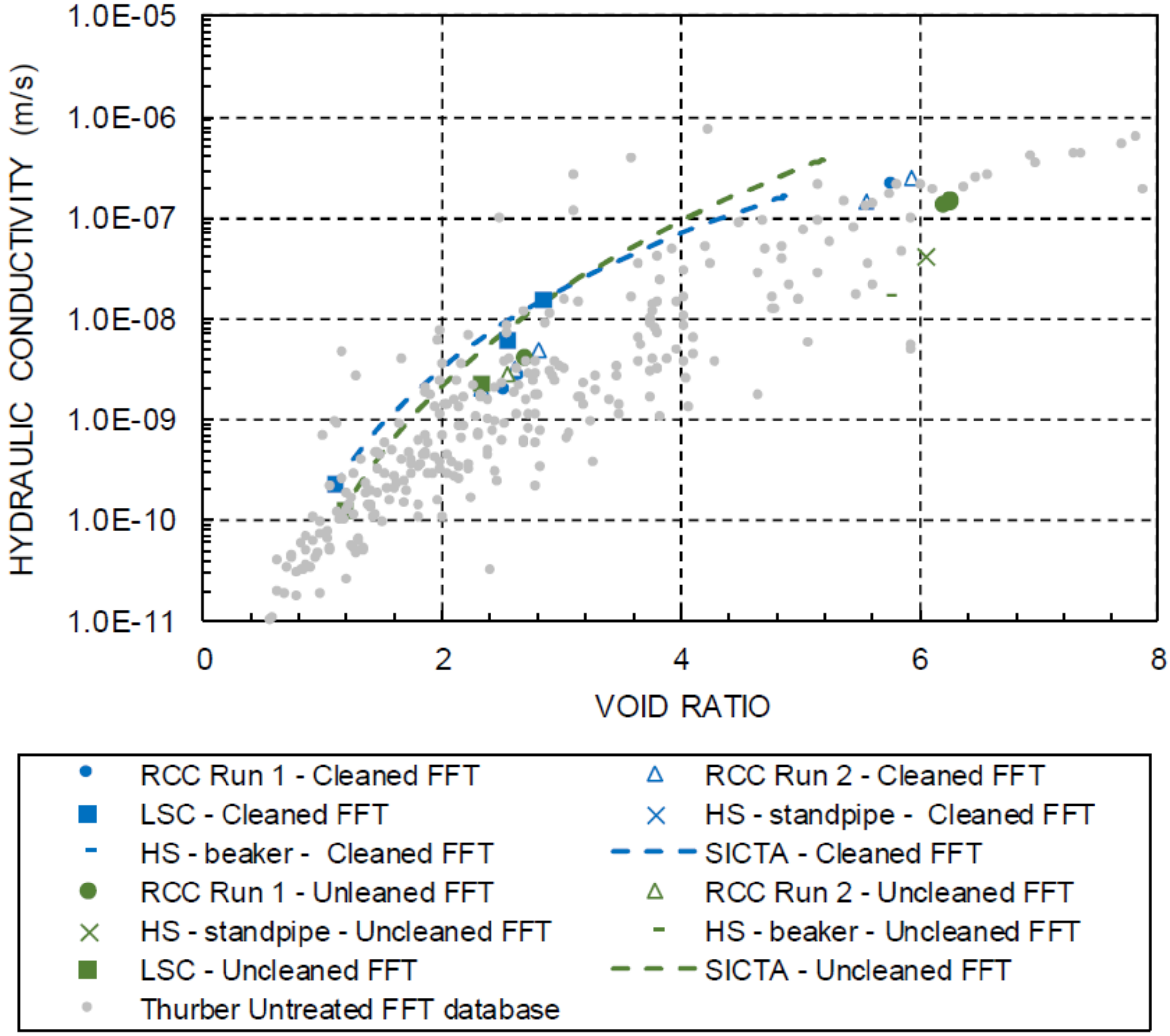


Figure 48. Hydraulic conductivity comparison between cleaned and uncleaned FFT-2.

3.4.3.3 The observation of consolidation test

During the seepage induced consolidation (SIC) test under the externally applied stress condition, the supernatant water color became black for the cleaned FFT-2. It remained clear for the uncleaned FFT-2. The photographs for both samples were provided by Thurber in Figure 49. The black supernatant water was not investigated or tested by Thurber. During the compressibility standpipe (CS) test under the self-weight stress condition, the supernatant water of the cleaned FFT-2 was not transparent but was not black (Figure 50). The supernatant water of uncleaned FFT-2 was transparent. It would not be unreasonable to hypothesize that the formation of the black supernatant water was related to the hydraulic gradient and externally applied pressure moving black material from the tailings into the supernatant water.

COSS believed that the bitumen in the cleaned FFT-2 was affected by the solvent during the extraction process resulting in low viscosity. The bitumen with low viscosity had higher mobility than that in the uncleaned FFT-2. Therefore, the bitumen in the cleaned FFT-2 was able to more easily to migrate from the solid phase to the top. The black substance was collected during the dismantling of the test and will be investigated in future work, which is beyond the scope of this report.

During the formation of the black supernatant water in the cleaned FFT-2, gas was generated during the SIC test. It was unclear if the compressibility and hydraulic conductivity of the cleaned FFT-2 obtained from SIC and LSC tests were altered due to these processes, however it was observed that consolidation progress in the cleaned samples was halted completely in the final stage of loading for a period of time until the test was partially dismantled to allow the gas to escape.

a) Cleaned FFT-2 b) Uncleaned FFT-2

Figure 49. The photographs during SIC test on a) cleaned FFT-2 and b) uncleaned FFT-2.

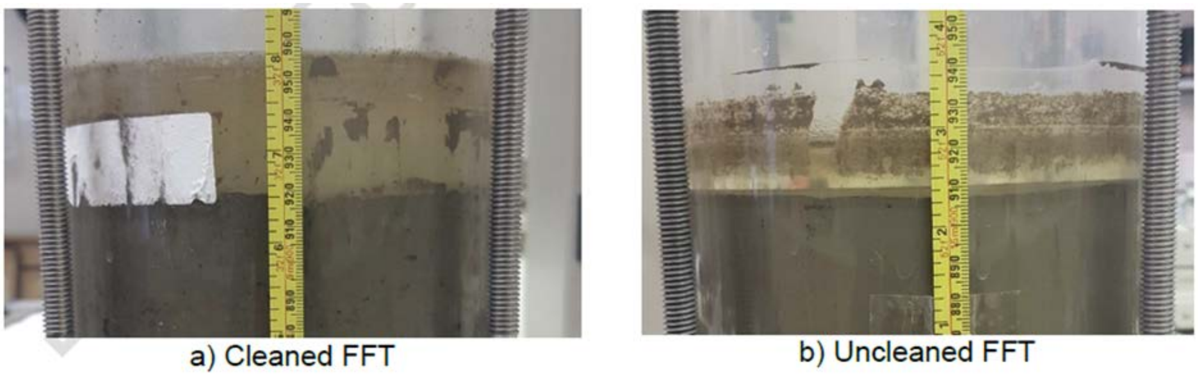


Figure 50. The photographs during the standpipe test on a) cleaned FFT-2 and b) uncleaned FFT-2.

The settling mudline height results during the standpipe test are shown in Figure 51. Cleaned FFT-2 had a higher initial settling rate than uncleaned FFT-2. But after 33 days of settling, uncleaned FFT-2 had a lower mudline height than the cleaned material. With time during the compressibility standpipe and large strain consolidation tests, macro features including surficial cracks, internal cracks and gas bubbles were observed in the cleaned FFT-2. For the compressibility standpipe test on the cleaned FFT-2, cracks occurred, which caused the interface settlement (which had already stopped moving earlier) to move again (at ~70 days settling in Figure 51). This phenomenon was not observed in the uncleaned FFT-2. A photograph of these features during the compressibility standpipe test was provided by Thurber in Figure 52.

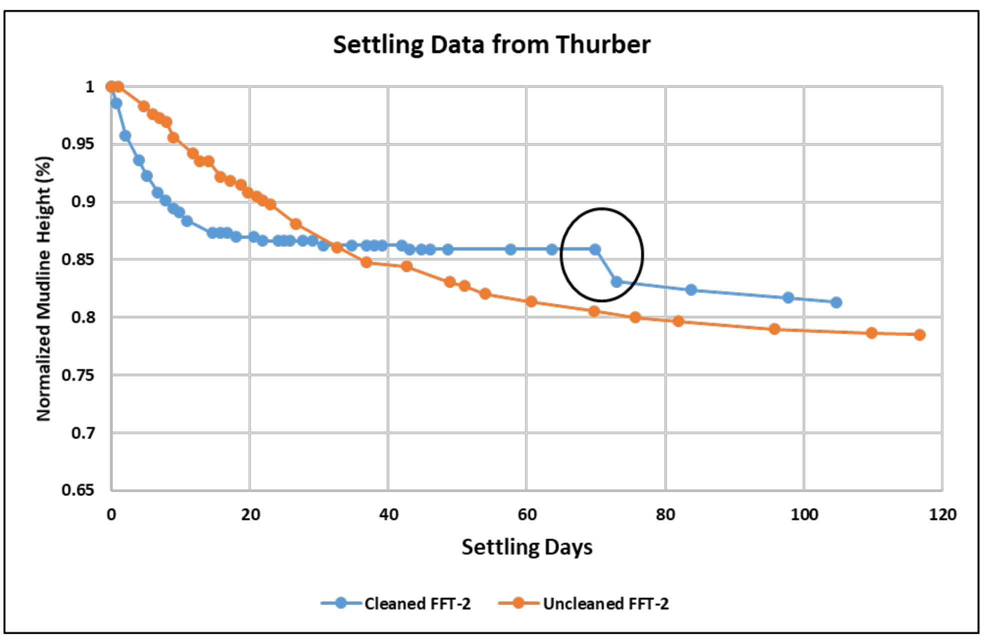


Figure 51. Settling curves of cleaned and uncleaned FFT-2 during the standpipe tests.

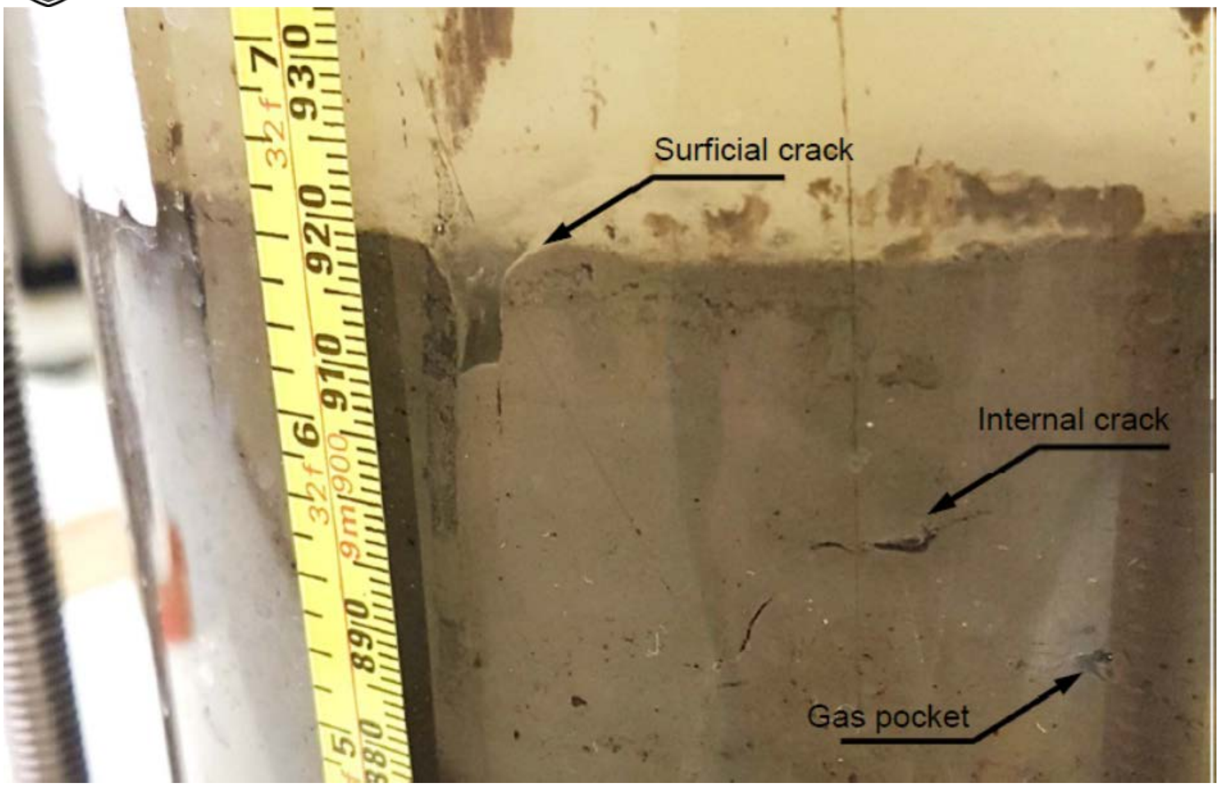


Figure 52. Surficial crack occurred in the cleaned FFT.

The FFT-2 columns after consolidation were subsampled for further characterization. The cleaned FFT-2 sample stalled in the final consolidation load due to the gas generation which produced counter-force to the consolidation force and the buildup of the black particles in the filter for the dissipating water. This combination required Thurber to stop the final load and partially dismantle the column to clean the filter and release the gas. The dirty water was collected at this time. The column was then reassembled and the load applied. Final consolidation was reached within 4 days of the load being reapplied. The cake after consolidation clearly showed bubbles in the cross section (Figure 53) and the cake was very smelly, indicating methanogenesis was occurring in the sample.

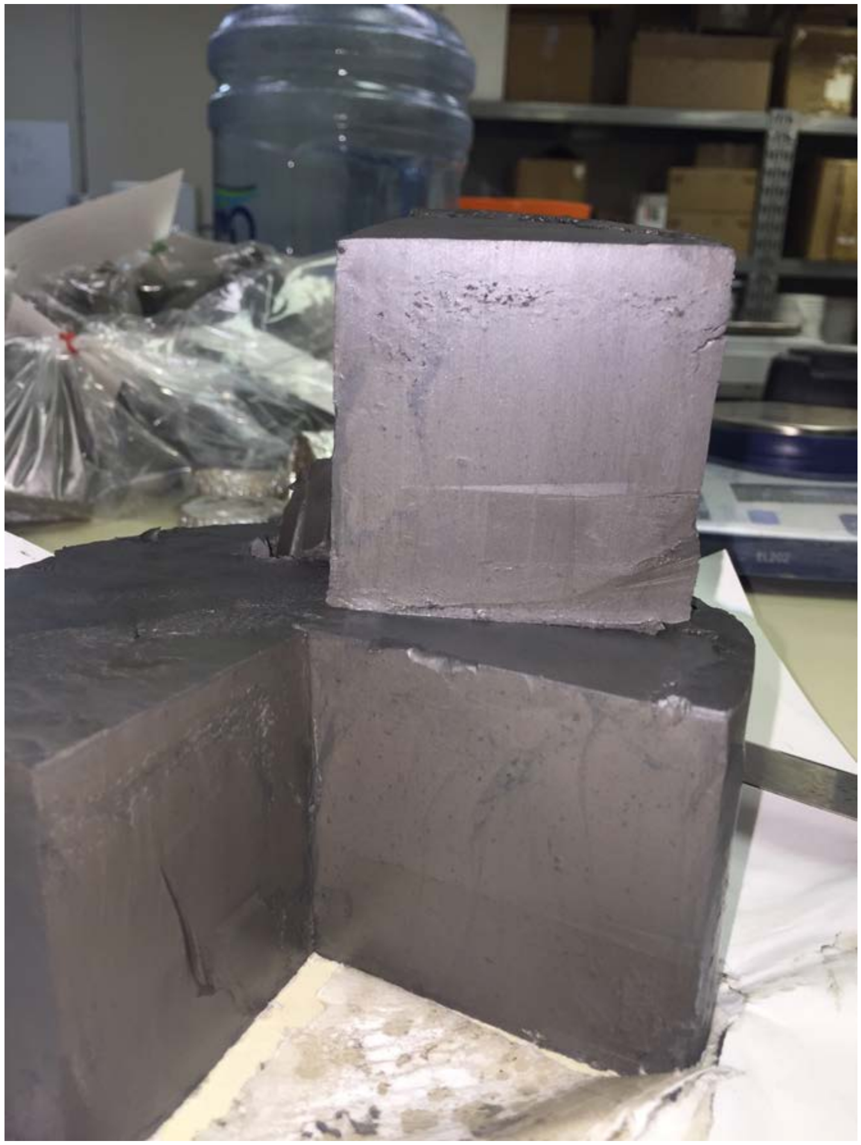


Figure 53. The cross section of the cake of cleaned FFT-2 after consolidation, showing bubbles in the top section of the cake

3.5 Phase 2 – Investigation of Different Solvent to Feed Ratio (S/F) of the Optimal FFT Cleaning

With the funding from NSERC ARDII program, the bitumen extraction using different solvent to feed ratios (S/F) in each washing stage and the effect on the flocculation test were fully investigated. This was considered Phase 2 of the test program. In this phase, FFT-2 was cleaned using two-stage washing and three-round distillation with 1.5 hours each round. In each washing stage, three solvent to feed ratios – 0.5, 0.25, and 0.1 – were used to clean FFT-2. Finally the cleaned FFT-2 was flocculated to assess the impact of the different S/F ratios on flocculation performance.

3.5.1 Characterization of cleaned FFT-2 with different S/F

The cleaned FFT-2 samples with different S/F were characterized by D&S as shown in Table 18. With the decrease of the S/F, the bitumen to solids ratio (B/S) of the cleaned FFT-2 maintained the same value (0.02). Therefore, in the S/F range that was tested, the amount of Jet B used in the washing stage did not affect the efficiency of bitumen extraction for the low bitumen content type of FFT used.

Table 18. The D&S results of cleaned FFT-2 with different S/F washing, bitumen spiked FFT-2, and raw FFT-2.

Sample	S/F in each washing stage	Bitumen (wt%)	Solids (wt%)	Water (wt%)	B/S	MBI (meq/100 g)
Cleaned FFT-2	0.5	0.50	27.02	71.38	0.02	15.7
	0.25	0.54	26.24	73.53	0.02	15.7
	0.1	0.44	22.87	76.99	0.02	15.3
Bitumen spiked FFT-2	-	1.61	28.11	69.11	0.06	16.0
Raw FFT-2	-	1.23	24.68	73.64	0.05	14.1

The viscosity of the Diluted Bitumen obtained from the 0.25 and 0.5 of S/F in each washing stage were measured using a Brookfield DVIII LV Rheometer in order to see the correlation between the viscosity property and solids content of the diluted bitumen. A reasonable Power Law mathematical model (Equation 3) fit (Figure 54) was obtained after removing the static yield stress data for all samples. The yield stress calculated from the Herschel-Bulkley model is shown in Table 19. The viscosity properties of the Diluted Bitumen tested were very similar between the two S/F values tested.

Equation 3. Power Law Model

$$\tau = kD^n$$

Where τ is shear stress (Pa); τ^0 is yield stress (Pa); k is consistency index (Pa·s); D is shear rate (sec^{-1}); n is flow index.

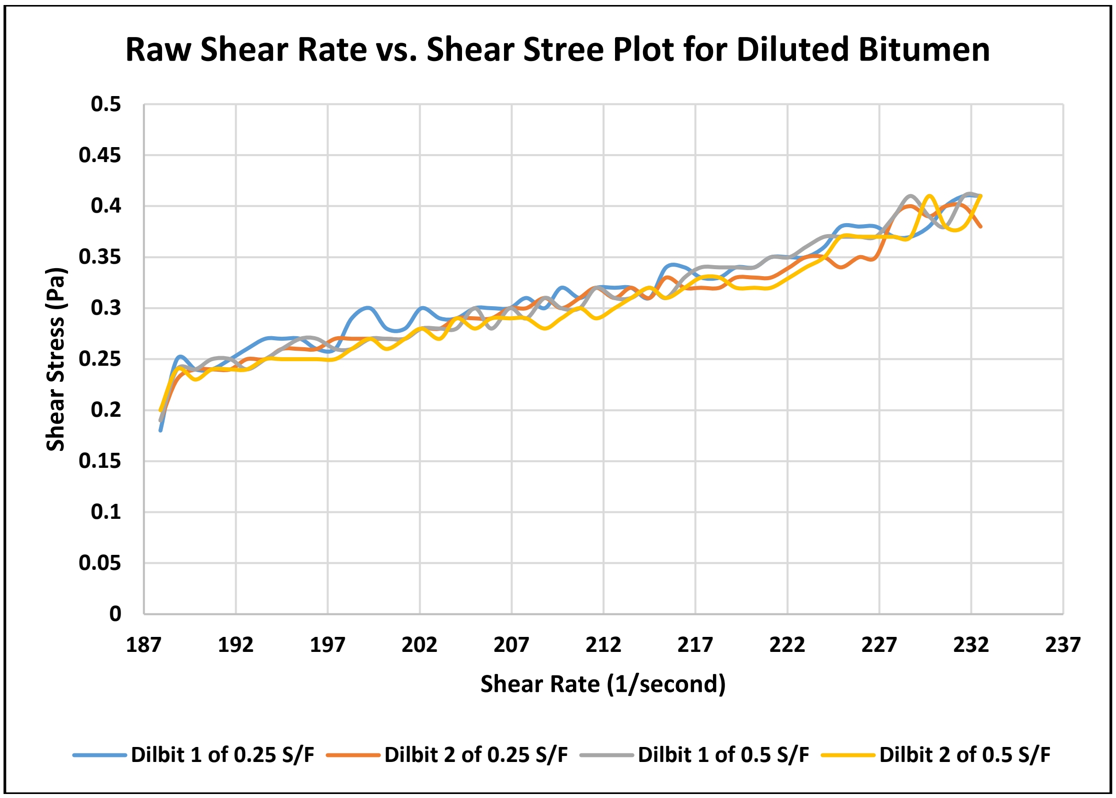


Figure 54. Room temperature raw shear rate vs. shear stress plots after removing the static yield stress data for the Diluted Bitumen produced from the washing stage. Diluted Bitumen 1: the Diluted Bitumen from the first washing stage; Diluted Bitumen 2: the Diluted Bitumen from the second washing stage.

Table 19. Yield stress of diluted bitumen calculated from Herschel-Bulkley model.

Sample	S/F	Washing stage taken from	Consistency Index (Pa·s)	Flow Index
Diluted bitumen	0.25	1	6E-07	2.47
		2	5E-07	2.49
	0.5	1	2E-07	2.66
		2	3E-07	2.57

3.5.2 Effect of different S/F on flocculation on FFT-2 before and after optimal cleaning

The impact of cleaned FFT-2 with different S/F on the flocculation was investigated by dosage curve testing using a one-dose flocculation method. Dosage curve testing is able to provide an insight to the full dosage range and one-dose flocculation method can provide more accurate prediction of the flocculation performance than titration method used in Phase 1 study. The results of the dosage curve test are the optimal dosage of flocculant (polymer A3338 in this study) and the solids% in the flocs. The optimal polymer dosage is the dosage that produces the highest solids% in the flocs.

The cleaned FFT-2 obtained by 0.5 of S/F showed a wide range of dosage window and comparable solids% in the flocs with the raw FFT-2 (Figure 55). The cleaned FFT-2 obtained by 0.25 of S/F required 25% lower polymer dosage and produced 12% higher solids% in the flocs than raw FFT-2. The cleaned FFT-2 by 0.1 of S/F required 60% lower polymer dosage and produced 5% higher solids% in flocs. Low polymer dosage required is favorable due to the low cost.

Bitumen spiked FFT-2 was obtained by spiking uncleaned FFT-2 with the bitumen extracted from the 0.1 of S/F bitumen extraction process. The D&S result of the bitumen spiked FFT-2 showed the B/S was 0.06 higher than raw FFT-2 (0.05) (Table 18).

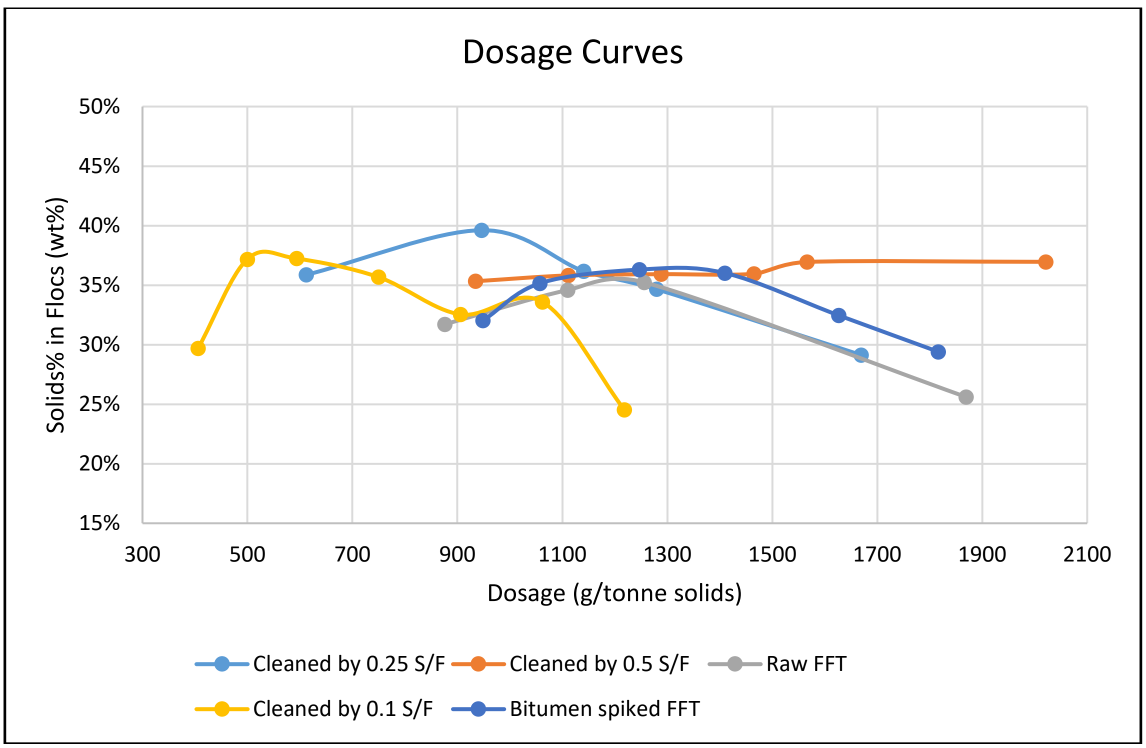


Figure 55. The dosage curves of flocculated cleaned, raw, and bitumen spiked FFT-2.

The required optimal dosage of different cleaned FFT-2 and raw FFT-2 were compared in Figure 56 and the corresponding solids% of the flocs obtained at the optimal dosage were shown in Figure 57. The cleaned FFT-2 required lower optimal polymer dosage than the uncleaned FFT-2 due to the impact of the bitumen in the sample. Bitumen spiked FFT-2 was tested on flocculation in order to confirm the bitumen impact on the flocculation. The bitumen spiked FFT-2 required higher optimal polymer dosage than raw and cleaned FFT-2 (Figure 56).

The solids plus bitumen content in flocs was measured by oven heating after 24 hours water release of the flocculated FFT. The solids% in flocs were calculated by subtracting the bitumen% from the solids plus bitumen content assuming all the bitumen left in the flocs. The highest solids% in flocs was obtained by the cleaned FFT-2 with 0.25 of S/F (Figure 57). The assumption was that the clays cleaned by the 0.25 S/F were of the most homogeneous active surfaces leading to the best flocculation performance. The bitumen spiked FFT-2 produced comparable solids% in flocs with uncleaned FFT-2 and cleaned FFT-2 with 0.5 of S/F.

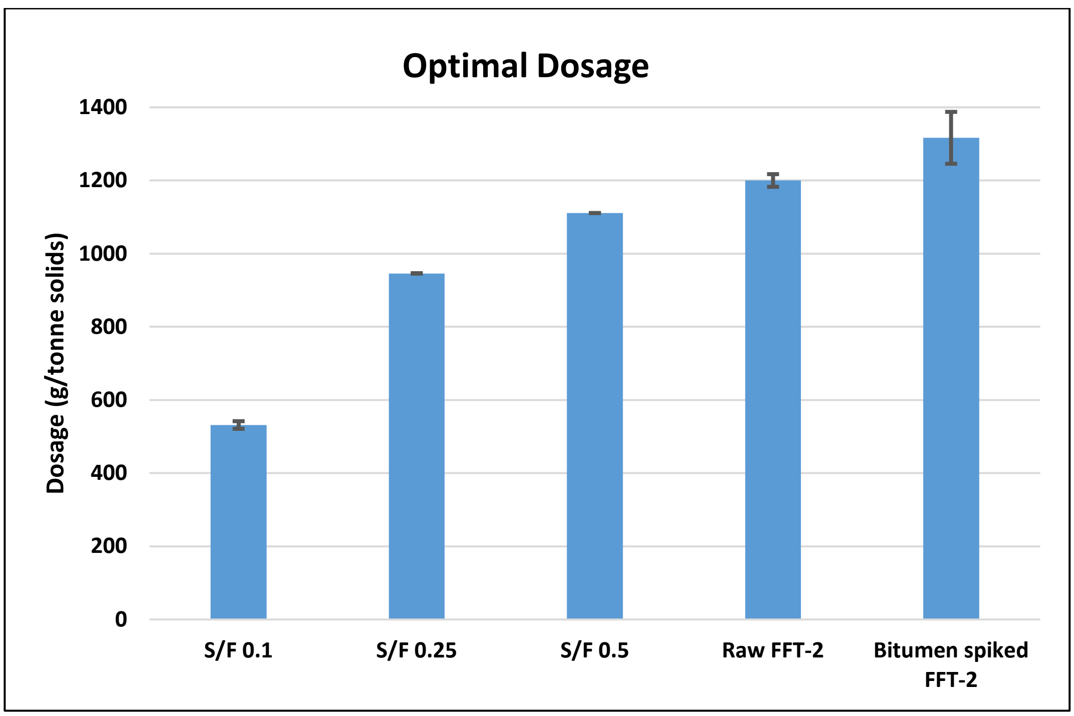


Figure 56. Comparison of the optimal polymer dosage required to flocculate cleaned FFT-2 with different S/F in each washing stage, raw FFT-2, and bitumen spiked FFT-2.

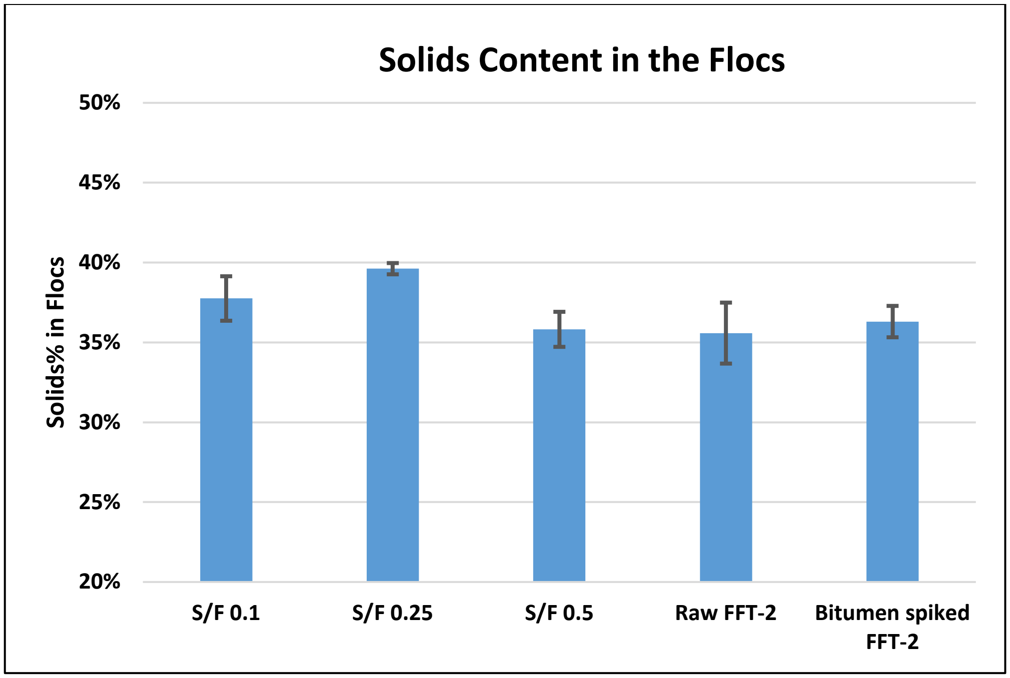


Figure 57. Comparison of solids content in flocs of cleaned FFT-2 with different S/F in each washing stage, raw FFT-2, and bitumen spiked FFT-2.

3.6 Summary of Cleaned FFT Generation

As summarized in Table 20, a total 71.7 kg of FFT-1 and 51.2 kg of FFT-2 were treated with the lab based version of Titanium's cleaning process. In FFT-1 39.7 kg of FFT-1 were washed and cleaned. There were 21.2 kg of FFT-1 washed but not cleaned awaiting further instructions at the end of this project. The calculation diagram of the overall mass balance is shown in Figure 59. The calculated overall mass balance is shown Table 21, solids mass balance, bitumen mass balance, and Jet B mass balance were calculated as shown in Table 22.

Table 20. Summary of raw FFT cleaned with Titanium's technology.

Phase	Sample	S/F at each washing stage	# of washing stage	# of distillation round	B/S of cleaned FFT	Mass of raw FFT (kg)	Total mass of raw FFT (kg)
Phase I	**FFT-1**	0.5	1	1	0.04	67.8	71.7
		0.5	2	1	0.03	3.9	
	FFT-2	0.5	2	1	0.02	8.1	51.2
		0.5	2	3	0.02	13.3	
Phase II	**FFT-2**	0.5	2	3	0.02	11.4	
		0.25	2	3	0.02	9.4	
		0.1	2	3	0.02	9.0	

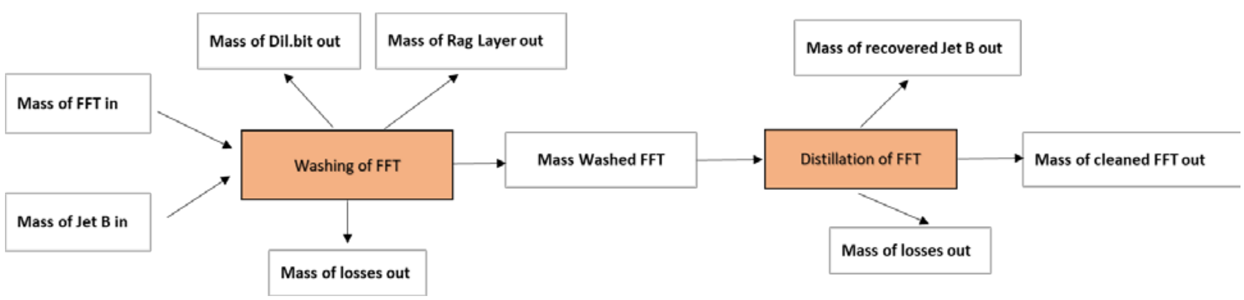


Figure 58. Diagram of overall mass balance of bitumen extraction on FFT using Jet B.

Table 21. The overall mass balance (kg) of bitumen extraction process on two types of FFT.

Sample	Total FFT in (kg)	Total Jet B in (kg)	S/F in each washing stage	# of washing stage	# of distillation round	Washing stage				Distillation stage			
						Diluted Bitumen out (kg)	Rag layer out (kg)	Losses (kg)	Washed FFT out (kg)	Washed FFT in (kg)*	Recovered Jet B (kg)	Cleaned FFT out (kg)	Losses (kg)
FFT-1	71.7	37.95	0.5	1 & 2	1	39.73	4.16	1.69	64.09	42.77	1.13	39.70	1.94
FFT-2	32.9	33.0	0.5	2	1 & 3	32.7	-	3.2	29.9	29.9	0.9	25.0	4.1
FFT-2	9.4	4.8	0.25	2	3	5.6	-	0.0	8.5	8.5	0.1	7.6	0.8
FFT-2	9.0	1.8	0.1	2	3	2.0	-	0.0	8.8	8.8	0.1	7.2	1.5

*21.2 kg of FFT-1 were washed but uncleaned.

Table 22. The components mass balance (wt%) of bitumen extraction process on two types of FFT.

Sample	Component	Total in (wt%)	Washing stage				Left as washed but not distilled (wt%)	Distillation stage			
			Out in Diluted Bitumen (wt%)	Out in rag layer (wt%)	Losses & taken out (wt%)*	Out in Washed FFT (wt%)		Washed FFT in (wt%)	Out in Recovered Jet B (wt%)	Out in cleaned FFT (wt%)	Losses & taken out (wt%)*
FFT-1	**Solids**	100	0.3	0.3	3.4	96.0	31.2	64.8	0.0	60.4	4.4
	Bitumen	100	77.5	1.9	4.6	15.9	5.5	10.4	0.0	7.9	2.5
	Jet B	100	92.9	0.5	-	7.1	2.4	4.7	3.0	1.0	0.7
FFT-2	**Solids**	100	0.3	-	18.7	81.0	0	81.0	0.0	80.9	0.1
	Bitumen	100	67.2	-	0.6	32.2	0	32.2	0.0	27.7	4.5
	Jet B	100	94.5	-	0.1	5.4	0	5.4	3.5	1.0	0.9

*Samples were taken out for characterization.

In all 60.4 wt% of the solids entering the process were recovered in the cleaned product for FFT-1, the majority of the remaining solids were washed but not distilled. 77.5 wt% of the bitumen entering the process from FFT-1 was collected after cleaning with 15.9% remaining with the solids as residual. 92.9 wt% of Jet B were collected with diluted bitumen with an additional 3% recovered during distillation approximately 1.0 wt% of Jet B were left in the cleaned FFT-1 as residual.

For FFT-2, 80.9 wt% of the solids entering the process were recovered in the cleaned product. 67.2 wt% of the bitumen entering the process from FFT-2 was collected after cleaning with 27.7% remaining with the solids as residual. 94.5 wt% of Jet B were collected with diluted bitumen with an additional 3.5% recovered during distillation. Approximately 1.0 wt% of Jet B were left in the cleaned FFT-2 as residual.

4. Conclusion and Recommendations

In this project, COSS in collaboration with Titanium, has investigated the bitumen extraction conditions by using Jet B solvent to clean FFT using a lab scale version of Titanium's process to validate the effect of bitumen removal on the FFT consolidation and final remediation. Two types of cleaned FFT, FFT-1 with high bitumen to solids ratio (B/S) and FFT-2 with low bitumen to solids ratio, were generated and evaluated by lab scale settling tests, flocculation tests, drying tests, and consolidation tests. The conclusions are as follows:

1) Titanium's solvent extraction technology can effectively remove bitumen from the FFT. Approximately 70% of the bitumen present in the FFT was recovered into a diluted bitumen stream and the bitumen to solids ratio of FFT was reduced to ~0.03.
2) The optimal bitumen extraction conditions were determined to be 30 minutes of shaking of the mixture of FFT and Jet B, 45 minutes of centrifugation to separate the solvent phase and sediment phase, 2 stages of washing, and 3 rounds of distillation (1.5 hours per distillation).
3) A solvent (Jet B) to feed (FFT) ratio (S/F) of 0.5 is optimal for FFT with a high bitumen to solids ratio, but S/F of 0.25 is optimal for the FFT with a low bitumen to solids ratio.
4) The cleaned FFT samples (diluted and undiluted) showed expanded volume and higher mudline height during the 1 L settling test than the uncleaned FFT samples due to gas generation.
5) Cleaned, undiluted FFT produced more condensed sediment than uncleaned FFT at the end of 35-week settling.
6) The bitumen removal by Titanium's process did not impact the drying rate of the flocculated FFT studied.
7) The cleaned FFT improves the flocculation performance by reducing the flocculant dosage required and increasing the final sediment density.
8) The cleaning process had no significant impact on the consolidation rate of the FFT.
9) Cleaned FFT generated a turbid, black, release water during consolidation.

Based on the results, COSS' recommendations are as follows:

1) The study provides a directional indication that removing bitumen using Titanium's process can reduce flocculant dosage and potentially improve flocculation performance particularly for flocculation treatment targeting a dry landscape.
2) An improved steam distillation setup which can simulate the pilot equipment is highly recommended for any future bench scale testing.

3) It appears that Titanium’s treatment of FFT increases the mobility of residual bitumen and organic matter. It is not recommended for Titanium to treat FFT that will be placed in an aquatic environment.

4) It appears that Titanium’s treatment of FFT increases microbial activity in the cleaned FFT. It is recommended that further evaluation of this impact be conducted prior to implementation of Titanium’s technology to treat FFT. It is expected that this impact may be largely due to the inefficiency of solvent removal at the lab scale, but this should be confirmed with samples from pilot or commercial scale.

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List of Acronyms

AE	Actual evaporation
ASTM	American Society for Testing and Materials
B/S	Bitumen to solids ratio
CH	Clay of High Plasticity
CL	Clay of low plasticity
COSS	Centre for Oil Sands Sustainability
CS	Compressibility standpipe
CWR	Clay to water ratio
D&S	Dean and Stark
FFT	Fluid fine tailings
FWR	Fines to water ratio
HS	Hindered sedimentation
HSE	Health, safety, and environment
KPI	Key performance indicator
LSC	Large strain consolidation
MBI	Methylene blue index
MH	Silt of high plasticity
ML	Silt of low plasticity
OH	Organic clay and organic silt of high plasticity
OL	Organic clay and organic silt of low plasticity
PE	Potential evaporation
PEW	Processed effluent water
PI	Plastic index
PSD	Particle size distribution
RCC	Rapid centrifuge consolidation
S/F	Solvent to feed ratio
SIC	Seepage induced consolidation
SOP	Standard Operating Procedure
SFR	Sand to fines ratio
TGA	Thermal gravimetric analysis
UOSTCS	Unified Oil Sands Tailings Classification System
USCS	Unified Soil Classification System
wL	Liquid limit
wP	Plastic limit