
IOSI PROJECT FINAL REPORT

Project Number	IOSI 2019-02TA
Project Title	Selective Recovery of Maltenes from TSRU Tailings via Advanced Froth Flotation (proof-of-concept)
Project Budget and Tenure	\$80,000 April 1, 2019 to March 31, 2020
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Date	June 25, 2020

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EXECUTIVE SUMMARY

A one year proof-of-concept project was carried out with an objective to selectively float maltenes from TSRU tailings. Three TSRU tailings samples were provided by Imperial, collected in 2014, April 2019 and October 2019. The study conceptually consisted of two essential steps, the liberation of maltenes from asphaltenes, and the flotation of maltenes and the depression of asphaltenes, although in practice these two steps were likely occurring at the same time.

Pentane and heptane were tested as the liberation solvents to dissolve maltenes away from asphaltene. Twelve other chemicals, lignosulfonate, trichloroisocyanuric acid (TCCA), sodium oleate, dioctyl sulfosuccinate (AOT), tripolyphosphate, lauramide DEA, sodium dodecylbenzenesulfonate (SDBS), hydrogen peroxide, sodium hydroxide, polyethylene oxide (PEO), stearylamine acetate (SAA), turpentine, and tall oil were used as flotation reagents to depress asphaltenes and sands/clays. A total of 47 batch flotation tests were conducted using a Denver D-12 mechanical flotation machine with a 1.5 L stainless steel cell at a pulp temperature of 60°C and natural pH of 7.8. At the end of the project, a satisfactory maltenes product was not produced from the TSRU tailings. But the project led to the following observations and learnings:

- 1) The TSRU tailings samples on average contained 3.3% hydrocarbon in the as-received slurry samples, or 24.2% hydrocarbon on dry solid basis. Maltenes content in the as-received slurry sample averaged 0.6%, or 4.3% on dry solid basis. So maltenes content in the hydrocarbon phase was about 18%.
- 2) The TSRU tailings had a wide particle size distribution up to several hundred μm . The coarse +200 μm fractions were enriched in hydrocarbon and contained about 50% sands/clays and 50% hydrocarbon, while the -200 μm fractions typically only contained 20% hydrocarbon with about 80% sands/clays. Despite the lower hydrocarbon content, the hydrocarbon phase in the fine fractions contained higher concentrations of maltenes, and the maltenes content in the hydrocarbon phase monotonically decreased with increasing particle size.
- 3) In the best test conditions, the maltenes recovery was 75% while asphaltenes recovery was 55%, i.e., a difference of 20 percentage points. Maltene was upgraded from 4.1 wt% (dry solid basis) in the TSRU tailings to 9.7 wt% in the floated concentrate. This was obtained by using 100 g PEO and 6 kg pentane per tonne of as-received TSRU tailings slurry.
- 4) Of the 12 chemicals studied in this project, dioctyl sulfosuccinate (AOT) and polyethylene oxide (PEO) seemed to have demonstrated positive effects of promoting maltenes recovery while depressing asphaltenes and sands/clay recovery.
- 5) The project showed that attempting to use a paraffinic solvent to liberate the maltenes in TSRU tailings from asphaltenes would not work well. Although the solvent could dissolve maltenes, the solvent-maltenes mixture seemed to still adsorb on asphaltenes surface, so that it could not be completely phase separate from the tailings slurry.

Therefore, the focus of any future studies to recover maltenes from TSRU tailings are to continue the work started in this project to find chemicals/process aids that could weaken the attraction between maltenes and asphaltenes, or between paraffinic solvent (with dissolved maltenes) and asphaltene, and could also depress the flotation of asphaltenes. ■

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1 INTRODUCTION

The concept of using froth flotation technique to selectively recover maltenes from TSRU tailings was originated from Imperial. Early 2019, Christopher Lin, Payman Esmaeili, Leyli Mirmontazeri, and Alireza Zehtab Yazdi of Imperial contacted Qi Liu and Xiaoli Tan of the University of Alberta and discussed the possibility, which resulted in the submission of a proof-of-concept proposal on February 8, 2019, “Selective Recovery of Maltenes from TSRU Tailings via Advanced Froth Flotation” (see Appendix I for the proposal). Following the review by the Scientific Advisory Committee (SAC), the proposal was recommended to the Executive Management Committee (EMC) of IOSI for approval as a Technology Accelerator project. EMC carried out an email vote that was concluded on March 2, 2019, and approved the proposal as a one year proof-of-concept technology accelerator project with a budget of \$80,000.

The project was initiated on April 1, 2019 and ended on March 31, 2020, with a total actual expenditure of \$79,270. The objective of the project was to prove or disprove the concept of using froth flotation technique to selectively recover maltenes from TSRU tailings while rejecting asphaltenes and sands/clays. A research associate, Dr. Kaipeng Wang, was appointed from April 1, 2019 to March 31, 2020 to carry out the research.

2 BACKGROUND

2.1 TSRU tailings

The waste stream from a paraffinic froth treatment (PFT) facility goes through a tailings solvent recovery unit (TSRU) where the solvent is recovered and a TSRU tailings stream is discharged that contains water, sands and fine solids, together with asphaltenes, maltenes, and residual solvent. The solvent contents in the PFT waste stream vary between 5 wt% and 10 wt%. After TSRU, the TSRU tailings usually contain 10-15 wt% bitumen, 85-90 wt% water and solids, with traces of solvent (Oil Sands Magazine, 2020).

At Imperial's Kearl operation, the TSRU tailings typically contain 3 wt% bitumen, 90 wt% water and 7 wt% solids. Of the 3 wt% bitumen, about 20 % are maltenes and 80 % are asphaltenes. At the production rate in 2018, Imperial estimated that the losses of bitumen (maltenes) to the TSRU tailings was 6,000 bbl/d. Therefore, there is a strong incentive to recover the maltenes from the TSRU tailings, preferably using a simple froth flotation process that can selectively float maltenes while rejecting asphaltenes as well as sands and clays.

2.2 Froth flotation

Froth flotation is a selective separation process based on differences in the hydrophobicity of the material. It selectively floats and recovers hydrophobic (water-repelling) material while leaving the hydrophilic (water-loving) material behind.

Should the materials to be separated do not conform to the natural hydrophobicity or natural hydrophilicity requirements to achieve a separation, chemical additives, known as flotation reagents, are used to cause the materials to possess desired wettability for separation. These chemicals can selectively render one substance hydrophobic while the others hydrophilic. Therefore, it can be seen that the selection of appropriate flotation reagents is key to the success of froth flotation when the wettability of the materials to be separated needs to be adjusted, which is the case in this project because both maltenes and asphaltenes are inherently hydrophobic. To achieve separation, one of them needs to be made hydrophilic.

Therefore, in the present project, one of the key requirements is to find a chemical additive that can render asphaltenes hydrophilic and non-floatable while the maltenes are floated.

In addition, a pre-requisite for the separation of maltenes from asphaltenes is that the maltenes be "liberated" from the asphaltenes. If the maltenes and asphaltenes are physically attached or associated together, it will not be possible to separate them by froth flotation. It is very likely that the maltenes in TSRU tailings are intimately associated and attached with asphaltenes. Therefore, appropriate measures need to be taken to liberate the maltenes from asphaltenes prior or during flotation.

2.3 Conceptual design of the process

Based on the above analysis, a two-stage liberation-separation process was designed to recover maltenes selectively from the TSRU tailings. Maltenes would be first liberated from asphaltenes,

then they would be floated by air bubbles while appropriate chemicals were used to depress asphaltenes and asphaltenes-coated sands/clays. This conceptual flowsheet is shown in Figure 1.

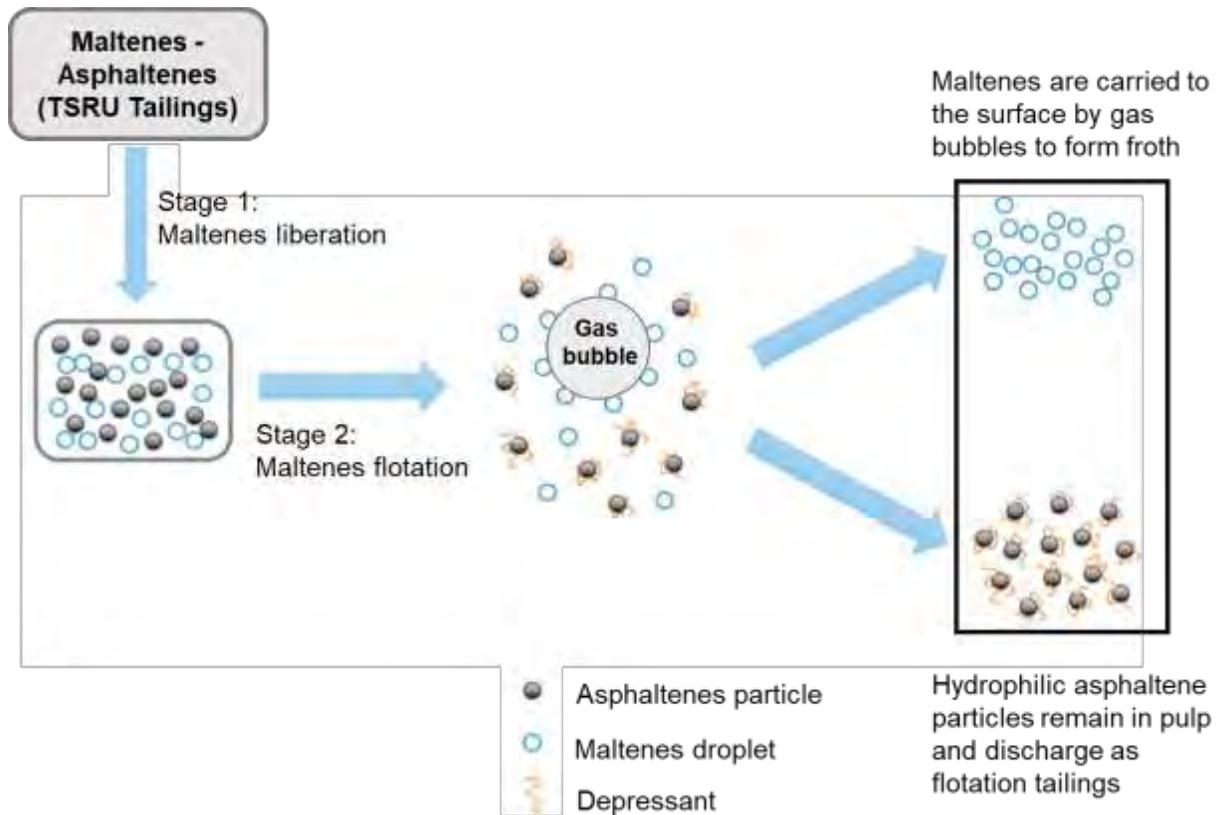


Figure 1 Schematic flowsheet of liberation-separation process for maltenes recovery from TSRU tailings.

Stage 1 – Maltenes liberation

In the TSRU tailings, the maltenes are most likely intimately associated with asphaltenes, that is, they are likely coated on asphaltenes surface due to the nature of the PFT process. The waste stream (PFT tailings) contains residual solvent with dissolved maltenes. When the residual solvent is evaporated (recovered) in TSRU, the maltenes previously dissolved in the solvent are deposited on the surface of asphaltenes and asphaltenes-coated sands/clay surfaces.

Liberation of the maltenes from asphaltenes may be achieved by one of the following methods, or a combination of them:

- (1) The use of a paraffinic solvent, which dissolves maltenes but not asphaltenes. The solvent can then be floated off together with the dissolved maltenes. The use of a flocculant for asphaltenes, such as sulfonated polystyrene (Mazzeo et al, 2018) or poly(maleicanhydride-1-octadecene) (Pillon, 2001) may assist with the phase separation of asphaltene from the solvent.

- (2) The use of a surfactant that can selectively remove maltenes from asphaltenes surface and disperse the maltenes in water, which can then be floated off.
- (3) The use of mechanical attrition to abrade maltenes off the surface of hydrocarbon particles so that maltenes are dispersed in water and then floated off.

Stage 2 – Flotation of maltenes and rejection of asphaltenes

The key challenge in stage 2 is the depression of asphaltenes and asphaltene-coated sands and clays. A search in the literature failed to uncover any schemes or chemicals that can render asphaltenes hydrophilic. In fact, there has been no literature report on any attempt of separating maltenes from asphaltenes by froth flotation.

However, due to the unique bipolar structure of surfactants, we considered that some of the surfactants may possess such an ability so that their hydrocarbon radicals could adsorb on asphaltenes while the polar heads pointing outwards, to render the asphaltenes hydrophilic. The surfactants should preferably contain aromatic groups in the hydrocarbon radicals so that they can impart π - π stacking interaction in addition to hydrophobic association. Humic acid, sodium petroleum sulfonates, sodium lignosulfonates, stearylamine acetate are some of the possible choices.

The other possible method, although a long shot, is to manipulate the surface charges of both asphaltenes and air bubbles to prevent their attachment. Grijalva-Monteverde et al (2005) and Bueno-Tokunaga et al (2015) reported ways to render both asphaltenes surface and air bubble surface positively charged. These could prevent asphaltenes from attaching to air bubbles.

In froth flotation, the entrainment of fine sands and clays is a common phenomenon which lowers the grade of recovered product. Water-soluble polymers, such as polyethylene oxide, polyacrylamide, polyacrylic acid, etc., may be tested to lower the entrainment.

2.4 Research objectives

Recovering maltenes from TSRU tailings by froth flotation was uncharted territory. Therefore the intention of this project was to do a proof-of-concept research to examine the feasibility of some methods that were based on sound scientific reasoning.

The research objective was to investigate chemical additives and physical means to liberate maltenes from asphaltenes in the TSRU tailings, and to carry out batch flotation tests to test the possibility to float the liberated maltenes from the TSRU tailings while attempting to depress asphaltenes and asphaltenes-coated sands and clays.

3 EXPERIMENTAL

3.1 Materials

3.1.1 TSRU tailings samples

Three TSRU tailings samples were provided by Imperial from their Kearl operation and shipped to the University of Alberta. Initially, two plastic pails of a TSRU tailings sample collected in 2014 were received on April 15, 2019. Then, two steel drums of TSRU tailings sample collected in April 2019 were received on September 18, 2019. Lastly, five steel drums of TSRU tailings sample collected in October 2019 were received on October 29, 2019.

The contents of water, sand and total hydrocarbon in the TSRU tailings samples were determined by Dean-Stark procedure. Following Dean-Stark, the C5 maltenes content was determined by dissolving the hydrocarbon obtained from Dean-Stark analysis into pentane for 24 hours, followed by filtration and evaporation of pentane from the filtrate, and weighing the left-over residue. Table 1 shows the composition of the three TSRU samples. As can be seen, the hydrocarbon content in the as-received TSRU tailings ranged from 2.5 wt% to 4.7 wt%, averaging 3.3 wt%. On a dry solid basis, the hydrocarbon content ranged from 22.1 wt% to 28.4 wt%, averaging 24.2 wt%.

Table 1 Composition of the three TSRU tailings samples.

TSRU Tailings Sample	Wet Base (as-received)				Dry Base (water-free)			C5 Maltenes in Hydrocarbon Phase (wt%)
	Solids			Water (wt%)	Sand (wt%)	Hydrocarbon (wt%)		
	Sand (wt%)	Hydrocarbon (wt%)				Maltenes	Others	
		Maltenes	Asphaltenes					
2014	11.7%	0.8%	3.9%	83.6%	71.6%	4.8%	23.6%	16.8%
2019-04	7.7%	0.5%	2.0%	89.8%	77.9%	4.1%	18.0%	18.7%
2019-10	8.8%	0.5%	2.1%	88.6%	77.8%	4.1%	18.1%	18.6%

The C5 maltenes content in the as-received TSRU tailings was between 0.5 wt% and 0.8 wt%, averaging 0.6 wt%. On a dry solid basis, the maltenes content ranged from 4.1 wt% to 4.8 wt%, averaging 4.3 wt%. The maltenes content in the hydrocarbon phase was between 16.8 wt% and 18.6 wt%, averaging 18 wt%.

It is interesting to note that the hydrocarbon content to the TSRU tailings were significantly reduced (from 4.7 wt% to 2.5 wt%) in the last 5 years of operation at Kearl.

3.1.2 Flotation reagents

Reagents used in flotation tests were mostly analytical grade. Lignosulfonate, trichloroisocyanuric acid (TCCA), dioctyl sulfosuccinate (AOT), sodium oleate, tripolyphosphate, lauramide DEA, sodium dodecylbenzenesulfonate (SDBS), and hydrogen peroxide were purchased from Sigma-Aldrich Canada. Pentane, sodium hydroxide and sodium silicate were purchased from Fisher Scientific Canada. Polyethylene oxide (PEO) with a molecular weight of 8M was purchased from Polysciences Inc. Stearylamine acetate (SAA) was purchased from Tokyo Chemical Industry Co. Turpentine and tall oil were industrial grade and obtained from West Fraser Paper Mill, Canada.

3.2 Sieving analysis

Due to the sticky nature of the TSRU tailings, wet sieving was used. Since the hydrocarbon particles in the TSRU tailings were soft and fragile, no beads were used in the wet sieving. A mechanical sieve vibrator together with gentle spray of tap water ensured high sieving efficiency. Seven aperture sizes (500 μm , 300 μm , 200 μm , 150 μm , 75 μm , 38 μm and 20 μm) were used to conduct the wet sieving beginning from the coarser size and moving to the finer size, to obtain 8 size fractions.

3.3 Grinding

A rod mill from Titan Process Equipment Ltd. (Figure 2) was used as one of the methods to liberate maltenes from hydrocarbon granules. The mill was 20 cm in diameter and 30 cm in length, with a volume of approximately 15 L. A total of 25 stainless steel rods with various diameters were used, weighing 15.8 kg (two 3.1 cm diameter, four 2.5 cm, eight 1.8 cm, and eleven 1.2 cm).



Figure 2 Rod mill from Titan Process Equipment Ltd.

3.4 Froth flotation

Batch flotation tests were carried out in a Denver D-12 flotation machine shown in Figure 3, while the typical rougher flotation and rougher-cleaner flotation flowsheet is shown in Figure 4. In brief, 1 L of TSRU tailings sample was used in each rougher flotation test in a 1.5 L stainless steel flotation cell to produce 7 wt% pulp density. Impeller speed of the flotation machine was set at 1200 rpm, while the air flowrate was maintained around 1 L/min during the flotation process. The flotation was carried out at the natural pH of 7.7-7.8 of the slurry at a pulp temperature of 60°C. In

cleaner flotation test, a 1.5 L stainless steel flotation cell was used with 1200 rpm of impeller speed and 1 L/min of air flowrate. Each flotation stage was carried until the froth was barren.



Figure 3 Denver D-12 flotation machine.

In larger batch flotation tests to collect bulk rougher concentrate for subsequent cleaner flotation, 3 L of TSRU tailings sample were used in each rougher flotation with a 3 L stainless steel flotation cell resulting in 10 wt% pulp density. Impeller speed of the flotation machine was set at 1500 rpm and the air flowrate was maintained around 5 L/min during the flotation process.

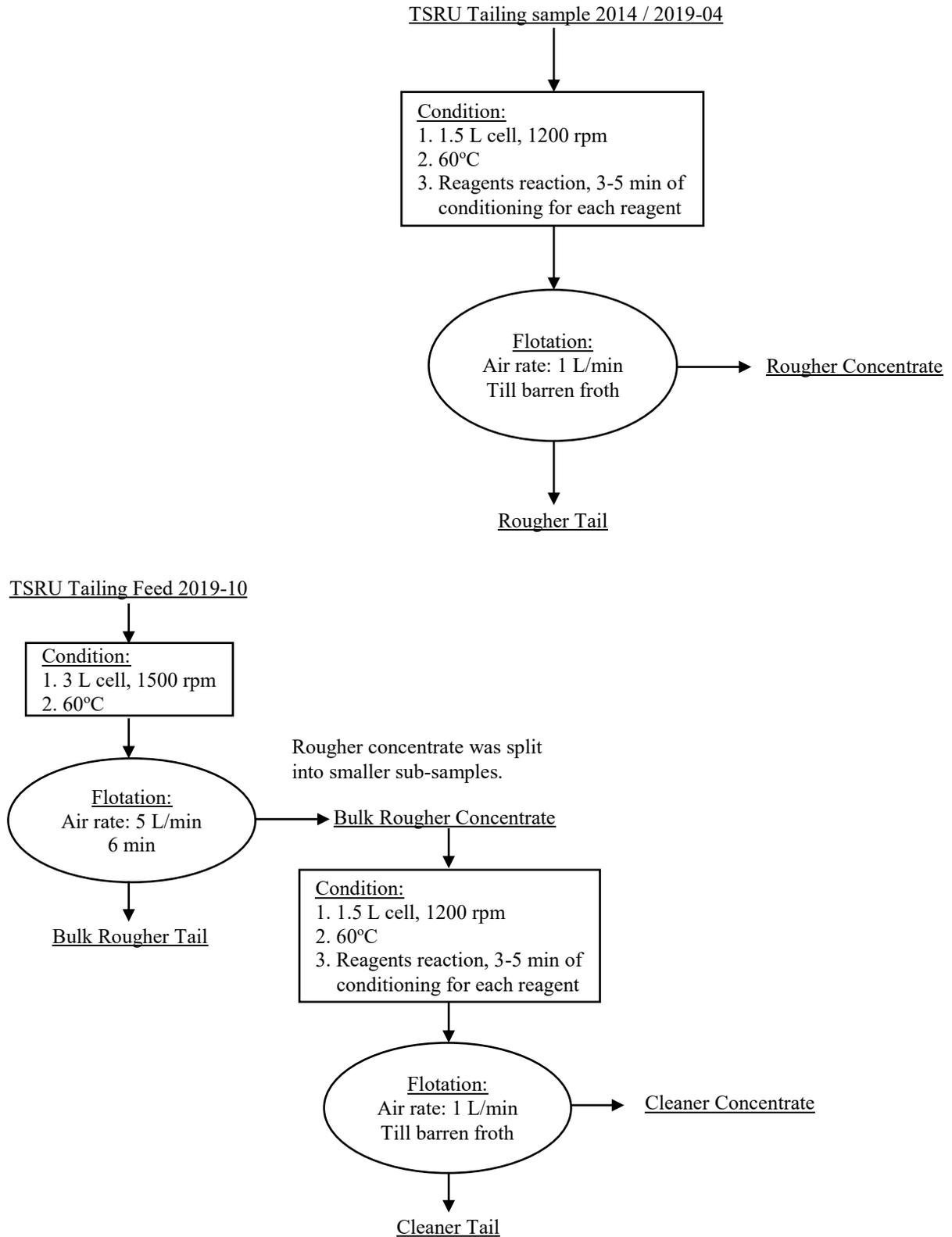


Figure 4 Typical rougher and rougher/cleaner flotation flowsheets.

3.5 Product analysis

The products from sieving and froth flotation were first treated by the Dean-Stark procedure to determine the contents of water, sand and hydrocarbon. The hydrocarbon collected from the Dean-Stark analysis was then dispersed in pentane for 24 hours, followed by filtration to remove the undissolved residue (asphaltenes + small amount of clays) and evaporation of pentane from the filtrate in a rotary evaporator. The residue from the rotary evaporator was weighed and recorded as the weight of C5 maltenes. When C7 maltenes content was desired, the undissolved residue from pentane was taken and dispersed in n-heptane for 24 hours. This was again followed by filtration and evaporation of heptane. The residue after removing n-heptane, plus the C5 maltenes, was considered as the amount of C7 maltenes.

Unless otherwise indicated, the term “maltenes” in this report refers to C5 maltenes.

4 RESULTS AND DISCUSSION

4.1 Size-assay analysis of TSRU tailings

Visual observation during the decantation of TSRU tailings seemed to show that the hydrocarbon distribution varied with particle size. Therefore, a size-assay analysis of TSRU tailings was conducted by wet sieving 1 L of the 2014 TSRU tailings sample into 8 size fractions ranging from 20 μm to 500 μm .

Each size fraction was filtered and dried, then processed through Dean-Stark analysis to obtain the contents of sand and hydrocarbon. The C5 maltenes content was determined by dissolving the hydrocarbon from Dean-Stark analysis into pentane for 24 hours, followed by filtration and evaporation of pentane, and weighing the left-over residue. Subsequently, the residue from pentane dissolution was placed in heptane for 24 hours to dissolve more maltenes. The C7 maltenes content was taken as the sum of the solid residue obtained from heptane solution plus the previously obtained C5 maltenes content. The composition of the different size fractions from the 2014 TSRU tailings sample is shown in Table 2.

Table 2 Composition of different size fractions of the 2014 TSRU tailings (dry solid basis).

Size Fraction (μm)	Mass (g)	Hydrocarbon (g)	Sand (g)	C5 Maltenes (g)	C7 Maltenes, (g)
+500	13.12	6.66	6.46	0.92	1.78
-500+300	14.11	7.20	6.91	0.71	1.56
-300+200	11.06	4.69	6.37	0.74	1.13
-200+150	16.93	3.58	13.35	0.61	0.92
-150+75	25.2	4.47	20.73	1.01	1.37
-75+38	7.17	1.64	5.53	0.40	0.51
-38+20	3.03	0.60	2.43	0.18	0.20
-20	13.61	0.86	13.05	0.44	0.46
Total	104.53	29.70	74.83	5.01	7.93

The data in Table 2 are plotted in several figures to better visualize the trend. The hydrocarbon content in each size fraction is compared in Figure 5. As can be seen, the coarse size fractions were enriched in hydrocarbon, and about 50% of the mass in the +200 μm size fractions was hydrocarbon. In the -200 μm size fractions, the hydrocarbon content was only about 20%, and reduced to less than 10% in the -20 μm fraction. This indicated that the fine size fractions were dominated by sands/clays while the coarse size fractions had equal amount of mineral matter and hydrocarbon.

Figure 6 shows the cumulative distribution of hydrocarbon, C5 maltenes and C7 maltenes versus particle size. It further reveals that the majority of hydrocarbon contained in TSRU tailings was concentrated in the coarse size range, with over 80% of it contained in the +100 μm size. The cumulative distribution of C5 maltenes and C7 maltenes had the similar trend as hydrocarbon distribution.

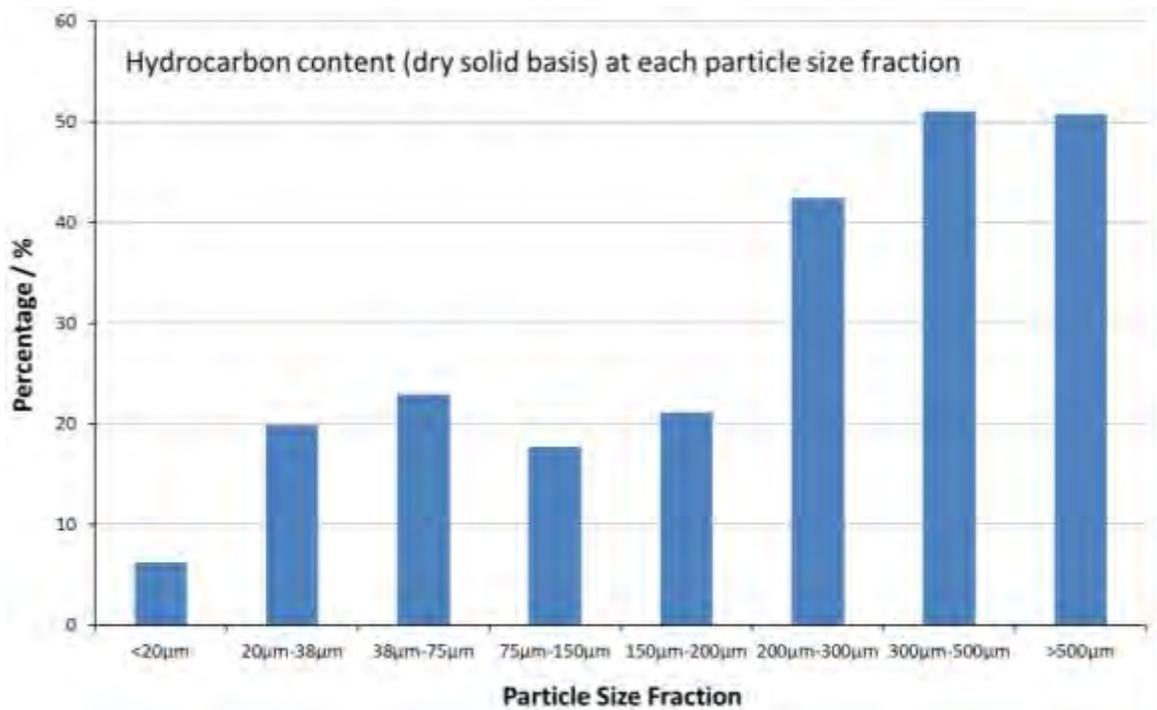


Figure 5 Hydrocarbon content (dry solid basis) in each particle size fraction.

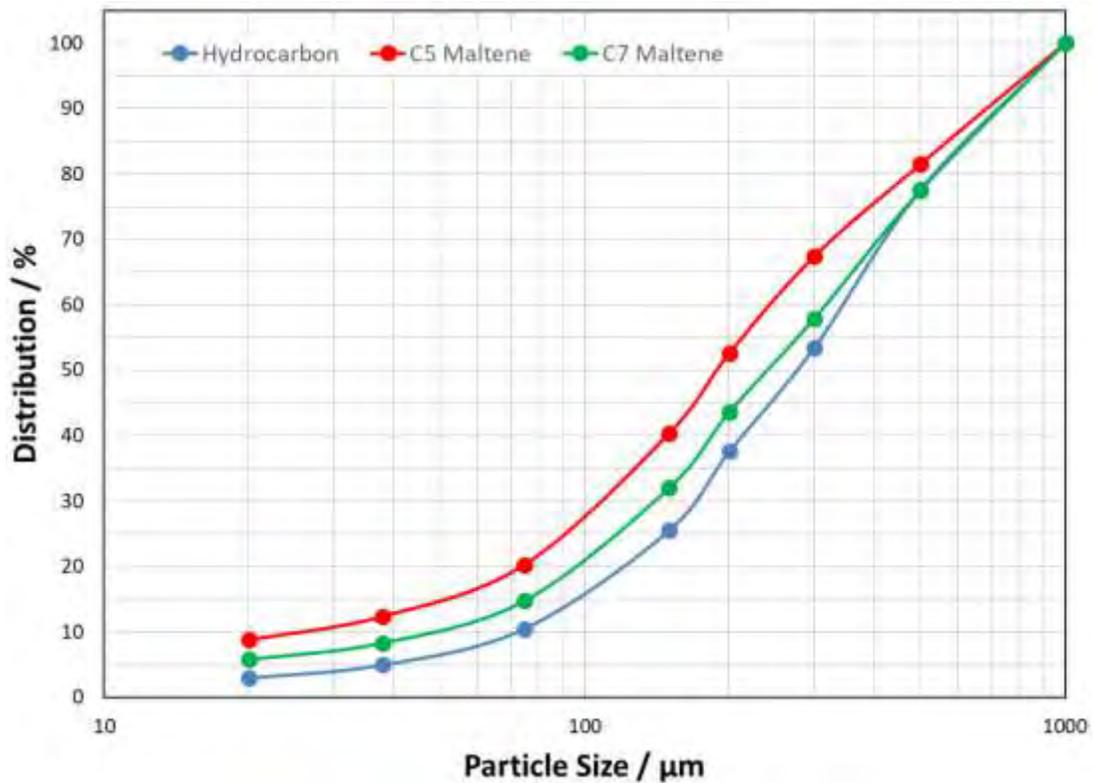


Figure 6 Cumulative distribution of hydrocarbon, C5 maltene and C7 maltene with particle size.

However, despite a lower hydrocarbon content in the fine size fractions, the hydrocarbon in the fine size fraction contained more maltenes. Figure 7 shows the percent maltenes in the hydrocarbon phase as a function of particle size. As can be seen, there is a monotonous decrease in maltenes content in the hydrocarbon phase as particle size increases, despite the higher hydrocarbon content in the coarse size fractions.

Therefore, the fine size fractions were a better feed material for our purpose because of the much higher maltenes content in the hydrocarbon phase than the coarse size fractions, but the fine size fractions contained very little hydrocarbon so that the higher maltenes content did not matter much.

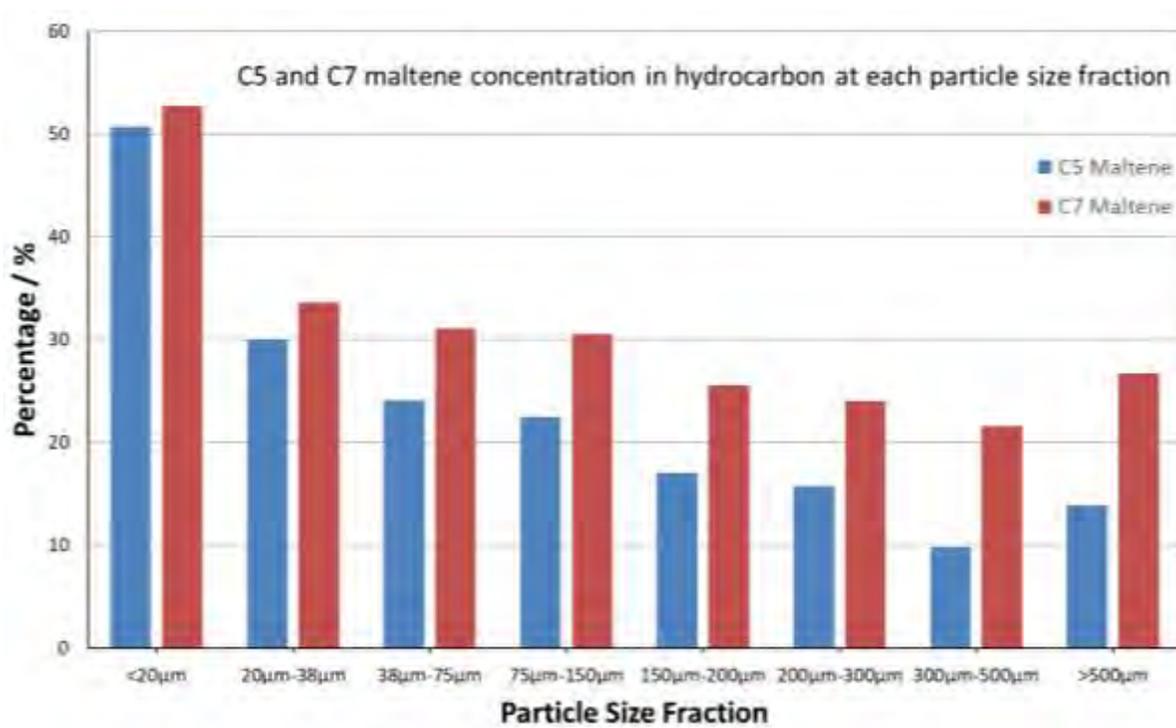


Figure 7 Concentration of C5- and C7 maltenes in hydrocarbon in each particle size fraction.

Nevertheless, the results did seem to confirm one of our hypotheses earlier (Section 2.3 on page 3), that the maltenes were deposited on the surface of asphaltenes or asphaltene-coated sands/clays when the paraffinic solvent was evaporated/recovered in the TSRU. Because small particles have higher specific surface areas, the surface deposition of maltenes would give a higher mass concentrations of maltenes (to hydrocarbon) for the fine size fractions compared with the coarse sizes, assuming the deposit thickness was more or less the same.

4.2 Liberation and flotation

Since there was no effective method to quantify maltenes liberation from asphaltenes without a physical separation step (such as flotation or phase separation), the liberation and flotation of maltenes from asphaltenes in the TSRU tailings are presented and discussed together.

4.2.1 Natural floatability of hydrocarbon in the TSRU tailings

Flotation tests were conducted at a pulp temperature of 60°C with no additives to investigate the natural floatability of hydrocarbon phase and the frothing property of the TSRU tailings samples. Surprisingly, significant differences in froth layer appearance and hydrocarbon recovery were observed for the three batches of TSRU tailings samples under identical flotation conditions. The froth appearances are shown in Figure 8, the recoveries are compared in Figure 9, and the test procedures and results are summarized in Table 3 for the three TSRU tailings samples.



Figure 8 Froth appearance of different TSRU tailings samples during flotation under identical conditions: natural pH of 7.8, pulp temperature 60°C, 1.5 L cell, 1200 rpm, 1 L/min air.

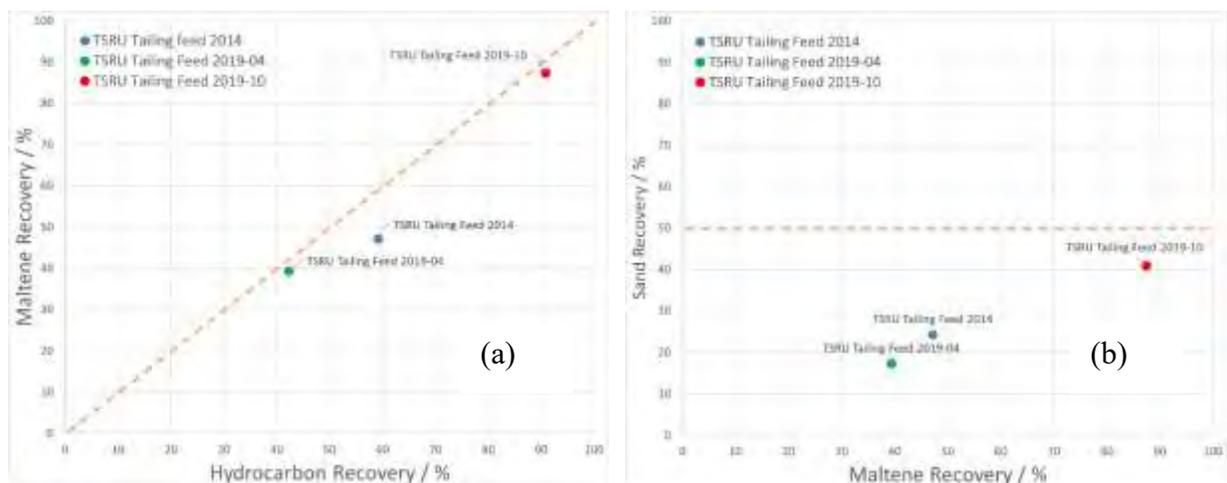


Figure 9 Hydrocarbon recovery and sand rejection, (a). maltenes recovery versus hydrocarbon recovery; (b). sand recovery versus maltenes recovery.

Table 3 Results of the natural floatability of hydrocarbon in TSRU tailings samples.

TSRU Tailings Sample	Temp. (°C)	pH	Reagents	Results	Comments
2014	60	7.8	N/A	Recovery: 47.2% Maltenes 59.2% Hydrocarbon 24.3% Sand	
2019-04	60	7.7	N/A	Recovery: 39.3% Maltenes 42.2% Hydrocarbon 17.3% Sand	
2019-10	60	7.8	N/A	Recovery: 87.3% Maltenes 90.8% Hydrocarbon 40.9% Sand	High maltenes recovery

Figure 8 shows that the natural frothing ability of the 2014 and the 2019-10 TSRU tailings samples were fairly good, but the 2019-04 TSRU tailings sample was weaker, which likely partly contributed to its poor natural floatability. While the two “older” samples floated poorly, the newest sample, collected in October 2019 was found to be much more floatable. During aeration of this sample, much denser and finer bubbles were observed which formed a thicker froth layer. The recovery of both hydrocarbon and maltene reached 90% when the sample was heated to 60°C with no other additives, and sand recovery was 40%. The grade of maltenes (on the dry solid base) was increased to 7.2% in the rougher concentrate, compared with 4.1% in the original TSRU tailings feed.

However, for all three TSRU tailings samples, the recoveries of maltenes was either the same as hydrocarbon recovery (2019-04 and 2019-10 TSRU tailings), or about 10% lower than hydrocarbon recovery (the 2014 TSRU tailings sample). No selective separation was observed based on natural floatability (Figure 9 and Table 3).

4.2.2 Screening of chemicals for selective recovery of maltenes

At the start of the project, the thinking was to use a paraffinic solvent such as pentane to treat the TSRU tailings, so that maltenes in the TSRU tailings could be dissolved in pentane which was then floated by injected air bubbles. However, during discussion with the industry stewards, it became clear that it was not desirable to add any solvent to the TSRU tailings.

At the same time, the size-assay tests of the TSRU tailings were just completed (Section 4.1), and the results indicated that the maltenes were most likely deposited on the surfaces of asphaltenes and asphaltenes-coated sands. Therefore, various surfactants were tested aiming at “stripping” off the maltenes from these surfaces. In the meantime, testwork was also conducted using pentane as a maltenes liberation aid in order to recover it. The hope was that a potential maltenes recovery facility, such as a flotation column, may be installed ahead of TSRU unit in the plant. Since the waste stream from paraffinic froth treatment process contained 5-10 wt% paraffinic solvent, the dissolved maltenes in paraffinic solvent could be recovered.

Therefore, the initial series of flotation tests were set up as simple rougher flotation, including heating the pulp to 60°C, then adding a chemical, mostly alone but may also be in combination, then carrying out the flotation for several minutes until the froth was barren. The tests were first carried out on the 2014 TSRU tailings sample, and when the sample ran out, a new batch that was collected in April 2019 was used to continue the flotation testwork.

Different reagents in various categories were tested including conventional surfactants, solvents, oxidation reagents, inorganic salts and polymers. Since it was anticipated that maltenes separation would be difficult, the strategy was to use the reagents under extreme conditions, i.e., at high dosages and at different combinations that might work. It was reasoned that once it was found to work, the dosages could be cut back and the reagent combinations may be simplified. Note that the dosages of reagents were against dry solids weight of the TSRU tailings in the report.

The test conditions and results are summarized in Tables 4 and 5, for the 2014 TSRU tailings sample and the 2019-04 TSRU tailings sample, respectively.

Table 4 Rougher flotation tests for reagent screening using 2014 TSRU tailings sample. Pulp temperature 60°C. Natural pH of 7.8. 1.5 L cell, 1200 rpm, 1 L/min air.

Test#*	Reagent (g/t dry solids)	Results	Comments
TSRU05	Not used	Recovery: 47.2% Maltenes 59.2% Hydrocarbon 24.3% Sand	This served as a baseline test at 60°C.
TSRU06	1,000 g/t PEO	Recovery: 51.8% Maltenes 55.0% Hydrocarbon 17.9% Sand	PEO had demulsification function, and could also flocculate and depress fine sands
TSRU07	1,000 g/t PEO 54,672 g/t Pentane (10 mL)	Recovery: 74.7% Maltenes 58.0% Hydrocarbon 23.0% Sand	Pentane concentration was 5.4 wt% of dry TSRU tailings, and about 0.6 wt% in as-received TSRU tailings
TSRU11	1,000 g/t PEO 20,000 g/t H ₂ O ₂	Recovery: 55.4% Maltenes 61.6% Hydrocarbon 25.0% Sand	Tried oxidation reagent to render asphaltene hydrophilic and non-floatable
TSRU12	1,000 g/t PEO 6,000 g/t NaOH	Recovery: 41.2% Maltenes 36.7% Hydrocarbon 22.3% Sand	Used caustic soda to help liberation
TSRU13	1,000 g/t PEO 1,000 g/t Tall oil	Recovery: 47.7% Maltenes 51.0% Hydrocarbon 29.7% Sand	Tall oil is a waste by-product from pulp and paper mills
TSRU14	1,000 g/t PEO 1,000 g/t Sodium oleate	Recovery: 53.4% Maltenes 59.4% Hydrocarbon 61.5% Sand	Sodium oleate is similar to Tall oil but has a higher purity
TSRU15	1,000 g/t PEO 1,000 g/t SAA	Recovery: 28.0% Maltenes 30.5% Hydrocarbon 14.2% Sand	Stearylamine acetate was able to depress sands, but also affected maltene recovery
TSRU16	1,000 g/t PEO 1,000 g/t Lignosulfonate	Recovery: 25.9% Maltenes 32.3% Hydrocarbon 12.2% Sand	Lignosulfonate was known to interact with asphaltene from our other work
TSRU17	1,000 g/t PEO 1,000 g/t SDBS	Recovery: 57.4% Maltenes 60.1% Hydrocarbon 32.3% Sand	Hoped that SDBS could liberate maltene
TSRU18	1,000 g/t PEO 6,000 g/t TCCA 6,000 g/t NaOH	Recovery: 47.9% Maltenes 54.2% Hydrocarbon 21.5% Sand	

* Tests that are missing from the numbering sequence were not subjected to product analysis based on visual observation which indicated poor separation.

Table 5 Rougher flotation tests for reagent screening using 2019-04 TSRU tailings sample. Pulp temperature 60°C. Natural pH of 7.8. 1.5 L cell, 1200 rpm, 1 L/min air.

Test#	Reagent (g/t dry solids)	Results	Comments
TSRU05 Repeat	Not used.	Recovery: 39.3% Maltenes 42.2% Hydrocarbon 17.3% Sand	Poor floatability compared to TSRU05. Poor natural floatability of this sample.
TSRU21	100 g/t PEO 6,000 g/t NaOH	Recovery: 90.0% Maltenes 91.4% Hydrocarbon 64.8% Sand	Better floatability than TSRU12. Effect of NaOH was more obvious on this sample than the previous.
TSRU22	2,000 g/t PEO 6,000 g/t NaOH	Recovery: 83.4% Maltenes 86.2% Hydrocarbon 48.2% Sand	Higher dosage of PEO depressed sands more
TSRU23	2,000 g/t PEO 6,000 g/t NaOH 2,000 g/t SAA	Recovery: 75.0% Maltenes 79.6% Hydrocarbon 40.1% Sand	
TSRU24	2,000 g/t PEO 6,000 g/t NaOH 2,000 g/t Lignosulfonate	Recovery: 85.7% Maltenes 85.8% Hydrocarbon 42.9% Sand	
TSRU26	1,000 g/t PEO 5,000 g/t Turpentine	Recovery: 78.1% Maltenes 82.5% Hydrocarbon 42.4% Sand	Turpentine is a waste by-product from pulp and paper mills. It functions as a frother mostly.
TSRU27	1,000 g/t PEO 500 g/t AOT	Recovery: 87.1% Maltenes 80.1% Hydrocarbon 42.7% Sand	
TSRU28	1,000 g/t PEO 1,000 g/t Lauramide DEA	Recovery: 62.6% Maltenes 67.7% Hydrocarbon 36.2% Sand	
TSRU29	1,000 g/t PEO 5,000 g/t Triphosphosphate	Recovery: 21.6% Maltenes 17.6% Hydrocarbon 10.1% Sand	Phosphate is a good dispersant

As can be seen from Tables 4 and 5, there were no significant separation between maltenes and asphaltenes. The recoveries of the hydrocarbon phase and maltenes fluctuated but they seemed to move together. The sand recovery was generally lower than hydrocarbon recovery.

To better visualize the trend, the test results in Tables 4 and 5 are plotted in Figures 10 and 11. In Figure 10, the maltenes recovery is plotted as a function of overall hydrocarbon recovery. For a perfect separation with 100% maltenes recovery and zero asphaltenes recovery, the plot should follow the solid green line, i.e., 18% hydrocarbon recovery corresponded to 100% maltenes recovery because the maltenes content in the hydrocarbon phase was about 18%. The red dashed diagonal line shows where maltenes recovery is equal to hydrocarbon recovery, i.e., there is no selective separation if test data fall on this line. As can be seen, most of the test points fell along the dashed diagonal line, indicating no separation between maltenes and asphaltenes. The only test that stands out slightly was test TSRU 07, in which the maltenes recovery was about 16 percentage higher than hydrocarbon recovery (Table 4 and Figure 10). In this test, the maltene recovery was about 75%, and asphaltene recovery was about 55% (for a total hydrocarbon recovery of about 58%), so that maltenes recovery was 20 percentage points higher. This was the test in which pentane was added, so clearly it did help with maltenes liberation and separation from asphaltenes. Figure 11 shows the sand recovery as a function of maltenes recovery. Again, test TSRU 07 stands out at high maltenes recovery and low sand recovery.

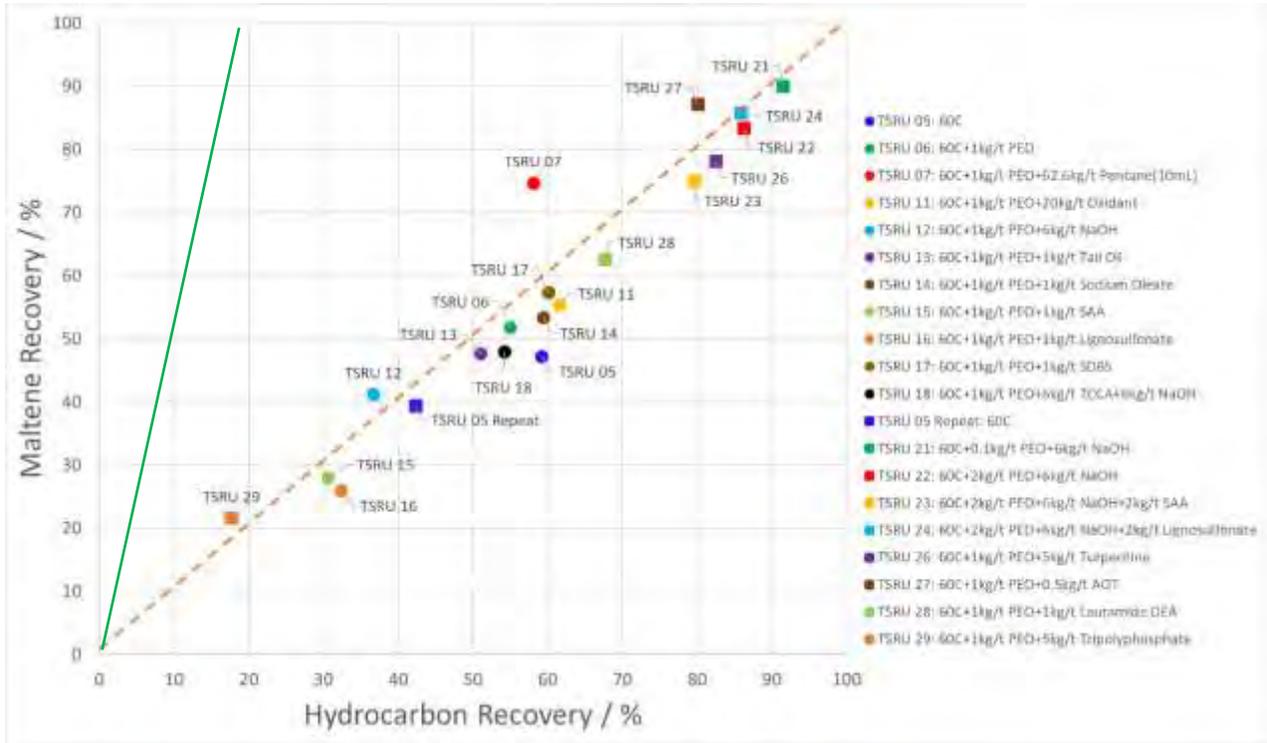


Figure 10 Separation of maltenes in rougher flotation (maltenes recovery versus hydrocarbon recovery).

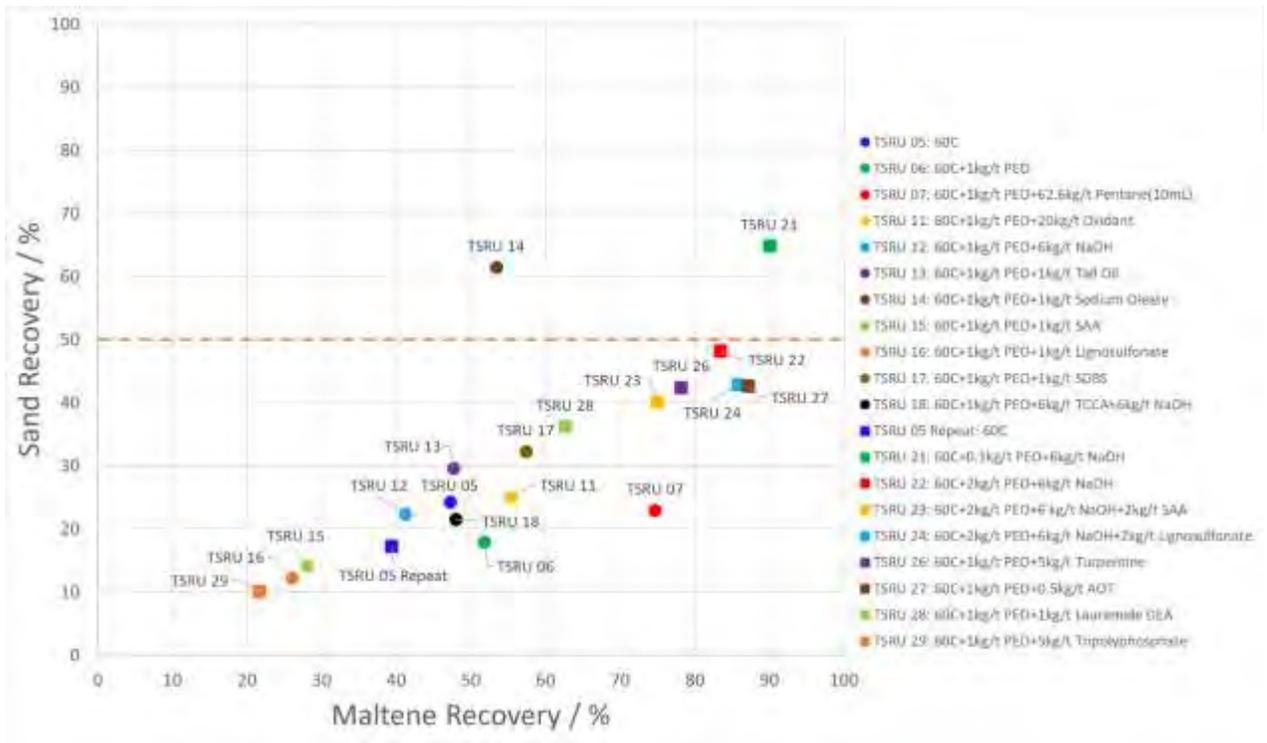


Figure 11 Rejection of sand in rougher flotation (sand recovery versus maltenes recovery).

As the floatability of TSRU tailings samples collected in 2014 and 2019-04 were different under the same flotation conditions, the results of rougher flotation tests conducted on the two samples were not directly comparable. However, the following common reagent effect and trend can be summarized:

- 1) Polyethylene oxide (PEO) showed depressing ability to sand with no adverse effect on maltenes flotation. Comparing TSRU 05 and 06, it can be seen that after adding 1,000 g/t PEO, the sand recovery dropped by 7 percentage points and the maltenes recovery increased by 4 percentage points. Comparing TSRU 21 and 22, an increase in PEO dosage from 100 g/t to 2,000 g/t caused a sharp drop of sand recovery by 17 percentage points, but the maltenes recovery only dropped by 6 percentage points.
- 2) Pentane showed the ability to liberate and recover maltenes from asphaltenes while only slightly affecting the recovery of hydrocarbon and the rejection of sand. Comparing TSRU 06 and 07, the use of 54 kg/t pentane raised maltenes recovery by 23 percentage points but with only 3 percentage point increase of hydrocarbon recovery and 5 percentage point increase of sand recovery. The grade of maltenes (dry base) was increased to about 10% in the rougher concentrate, compared with 4.8% in the TSRU tailings feed. The dosage of added pentane was equivalent to about 5.4% of dry TSRU tailings, or about 0.6% of as-received TSRU tailings sample.
- 3) Stearylamine acetate (SAA) depressed hydrocarbon and sand proportionally, but did not help maltenes liberation. Comparing TSRU 22 and 23, it can be seen that the addition of 2,000 g/t SAA lowered the recoveries of hydrocarbon and sand by 7-8 percentage points, but with similar drop in maltenes recovery.
- 4) Lignosulfonate showed depressing ability to sand rather than to hydrocarbon, but did not help maltene liberation or selective recovery. Comparing TSRU 22 and 24, it can be seen that the addition of 2,000 g/t lignosulfonate lowered sand recovery by 5 percentage points, but both the recoveries of maltenes and hydrocarbon were un-affected.
- 5) Dioctyl sulfosuccinate (AOT) seemed to have the ability to liberate maltenes from asphaltene. It helped the recoveries of hydrocarbon and maltenes, more so for maltenes, but did not float much sand. In TSRU 27 where 500 g/t AOT was used, 87.1% of maltenes was recovered, which was higher than hydrocarbon recovery by 7 percentage points. Meanwhile, nearly 60% of sand was rejected as well.
- 6) NaOH promoted the recoveries of hydrocarbon and sand, but did not help maltene liberation.
- 7) Other tested reagents did not show much effect in either maltenes recovery or sand rejection.

4.2.3 Cleaner flotation for selective maltene recovery

After the completion of the simple rougher flotation tests, it became clear that the current PFT plant layout at Kearn would not be able to accommodate a flotation facility prior to TSRU.

Consequently the use of paraffinic solvent to assist maltenes recovery from TSRU tailings was not desirable, despite the observed encouraging results from the least section (test TSRU 07).

At the same time, the TSRU tailings sample collected in October 2019 was found to be much more naturally floatable: with no additives, simply heating the pulp to 60°C allowed more than 90% of the hydrocarbon and maltenes to be floated while rejecting 60% of sand. Therefore, it was decided to collect a rougher concentrate from the TSRU tailings sample by a simple flotation at pulp temperature of 60°C with no additives, then the rougher concentrate would be cleaned to selectively float maltenes.

This flowsheet arrangement was logical in that the high maltenes recovery in rougher flotation ensured minimum loss of maltenes, while in the cleaner flotation of the rougher concentrate, a paraffinic solvent may be used to help liberation and recovery of the maltenes from asphaltenes.

The previous scoping tests showed that pentane and dioctyl sulfosuccinate (AOT) were able to selectively liberate maltenes from asphaltenes; polyethylene oxide (PEO) and lignosulfonate acted as depressants to sand; stearylamine acetate (SAA) exhibited the depressing ability to both sand and hydrocarbon. Therefore, several cleaner flotation tests were carried out by using different combinations of these reagents. Test procedures and results are summarized in Table 6. The performance of maltenes separation and sand rejection are plotted Figure 12 and Figure 13.

Table 6 Cleaner flotation tests for maltenes recovery. Pulp temperature 60°C. 1.5 L cell, 1200 rpm, 1 L/min air.

Sample	Test#	Reagent (g/t dry solids)	Results	Comments
Rougher Concentrate from 2019-10 TSRU Tailings sample. Maltene recovery was 90% in the rougher float.	TSRU32	1,000 g/t PEO 5,000 g/t Tripolyphosphate 1,500 g/t AOT 1,500 g/t Lignosulfonate	Recovery: 90.6% Maltenes 89.8% Hydrocarbon 73.4% Sand	
	TSRU32 kinetics 2 min	1,000 g/t PEO 5,000 g/t Tripolyphosphate 1,500 g/t AOT 1,500 g/t Lignosulfonate	Recovery: 21.5% Maltenes 17.0% Hydrocarbon 13.0% Sand	
	TSRU33	1,000 g/t PEO 5,000 g/t Tripolyphosphate 45,000 g/t Pentane 1,500 g/t Lignosulfonate 1,500 g/t SAA	Recovery: 58.0% Maltenes 49.6% Hydrocarbon 31.7% Sand	
	TSRU34	1,000 g/t PEO 5,000 g/t Tripolyphosphate 2,000 g/t NaOH 1,500 g/t Lignosulfonate 1,500 g/t SAA	Recovery: 93.4% Maltenes 91.2% Hydrocarbon 67.9% Sand	
	TSRU35	1,000 g/t PEO 5,000 g/t Tripolyphosphate 45,000 g/t Pentane 1,500 g/t Lignosulfonate	Recovery: 80.8% Maltenes 77.5% Hydrocarbon 55.2% Sand	No SAA compared to TSRU33
	TSRU36	1,000 g/t PEO 5,000 g/t Tripolyphosphate 1,500 g/t Lignosulfonate 1,500 g/t SAA 45,000 g/t Pentane	Recovery: 62.8% Maltenes 52.5% Hydrocarbon 32.0% Sand	Switched sequence of reagent compared to TSRU33

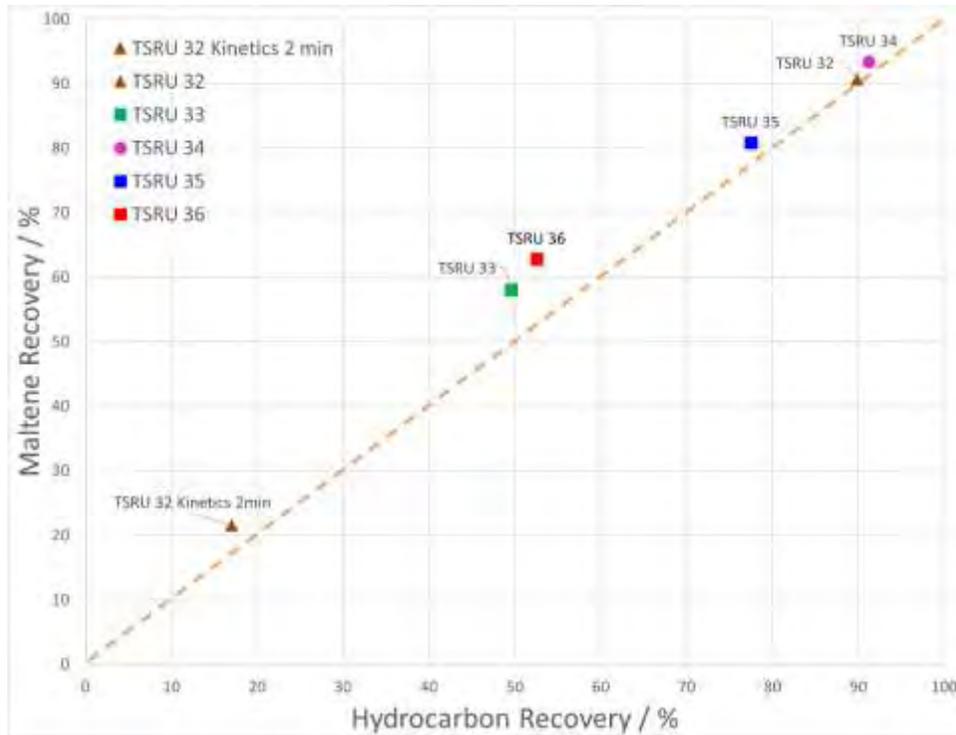


Figure 12 Separation of maltenes in cleaner flotation (maltenes recovery versus hydrocarbon recovery).

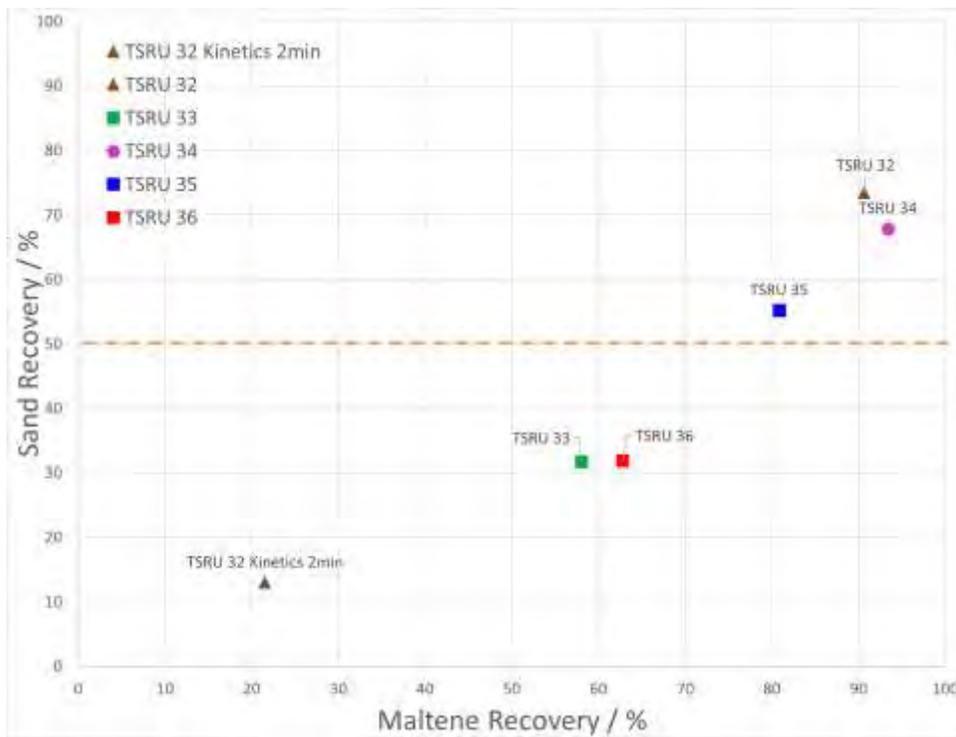


Figure 13 Rejection of sand in cleaner flotation (sand recovery versus maltenes recovery).

As can be seen from Figure 12, while the test conditions allowed the data points to all shift to above the dashed diagonal line, they are not far off from the diagonal line suggesting the separation was not effective. The main observations from these 5 tests are:

- 1) Dioctyl sulfosuccinate (AOT) showed the ability to liberate maltenes from asphaltenes during the first 2 minutes of cleaning flotation, and it depressed asphaltenes to some extent as well (TSRU 32 Kinetics 2 min). However, at moderate dosage it promoted the overall floatability of hydrocarbon and maltenes (90% of final recoveries for both maltenes and hydrocarbon). Dose control is important and needs to be optimized.
- 2) In test TSRU 34, NaOH promoted the flotation of both hydrocarbon and maltenes at over 90% recoveries but no separation of the two. Moreover, an undesirable high sand recovery (70%) was observed.
- 3) Comparing TSRU 33 and 35, it can be seen that stearylamine acetate (SAA) showed stronger selective depression to asphaltenes and sand than lignosulfonate but less adverse effect on maltenes flotation.
- 4) Pentane helped maltene liberation and separation from asphaltene, similar to what was observed in the rougher flotation tests.
- 5) In general, more than 30% of sand were rejected at the depressants combination of polyethylene oxide (PEO), lignosulfonate and stearylamine acetate (SAA).

4.2.4 Effect of physical liberation on selective maltenes recovery

Grinding was used as an alternative to liberate maltenes from hydrocarbon. Four cleaner flotation tests were carried out with two minutes grinding of rougher concentrate samples prior to cleaner flotation. Lower pulp temperature of 35°C used in tests TSRU 38 and 40 was for better retention of pentane in pulp. Test procedures and results are summarized in Table 7, and Figures 14 and 15.

Table 7 Cleaner flotation tests for maltenes recovery with pre-grinding

Sample	Test#	Temp. (°C)	Reagent (g/t dry solids)	Results	Comments
Ground Rougher Concentrate from 2019-10 TSRU Tailings sample. Maltene recovery was 90% into the rougher float.	TSRU37	60	1,000 g/t PEO 5,000 g/t Tripolyphosphate 45,000 g/t Pentane	Recovery: 61.2% Maltenes 60.4% Hydrocarbon 35.8% Sand	No depressants
	TSRU38	35	1,000 g/t PEO 5,000 g/t Tripolyphosphate 45,000 g/t Pentane	Recovery: 29.2% Maltenes 28.2% Hydrocarbon 19.1% Sand	Low temp. compared to TSRU37
	TSRU39	60	1,000 g/t PEO 5,000 g/t Tripolyphosphate 1,500 g/t Lignosulfonate 1,500 g/t SAA 45,000 g/t Pentane	Recovery: 46.2% Maltenes 41.3% Hydrocarbon 22.2% Sand	Ground sample compared to TSRU 36
	TSRU40	35	1,000 g/t PEO 5,000 g/t Tripolyphosphate 1,500 g/t Lignosulfonate 1,500 g/t SAA 45,000 g/t Pentane	Recovery: 18.3% Maltenes 16.1% Hydrocarbon 11.9% Sand	Low temp. compared to TSRU39

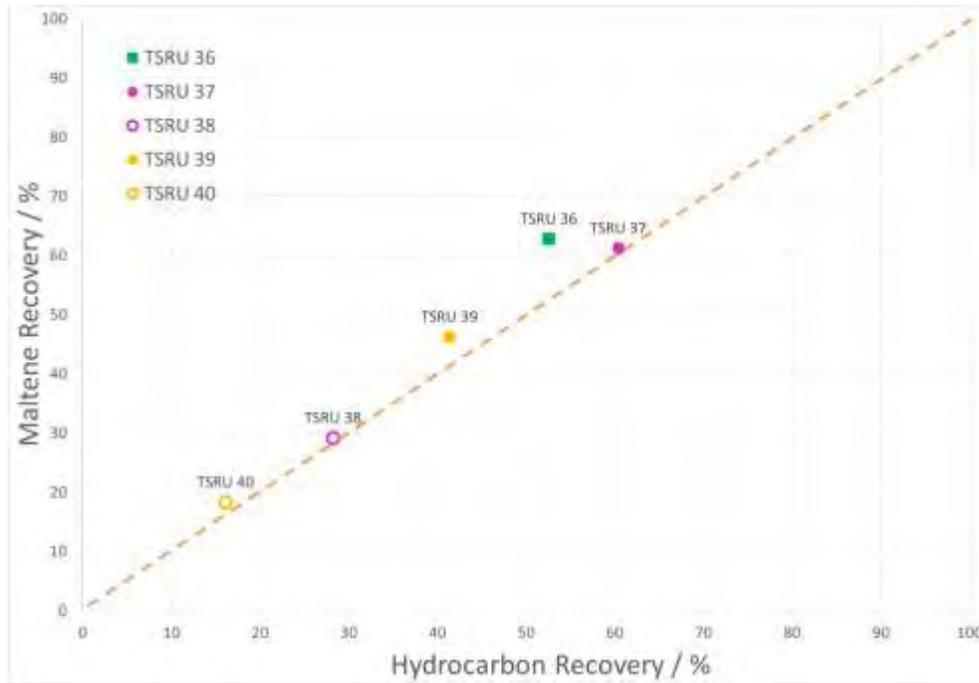


Figure 14 Separation of maltenes in cleaner flotation with pre-grinding (maltenes recovery versus hydrocarbon recovery).

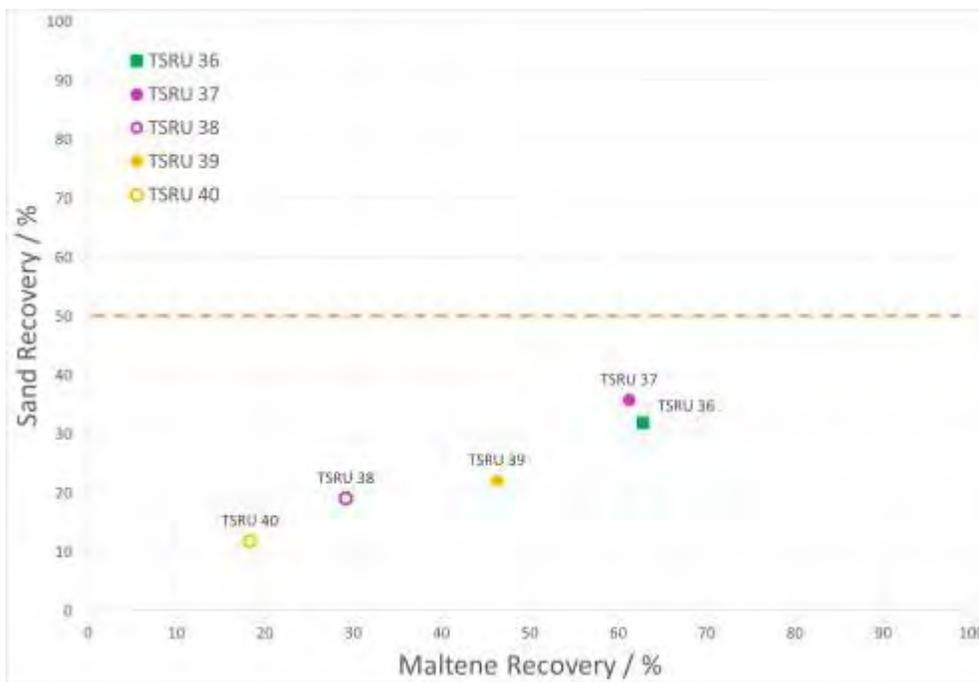


Figure 15 Rejection of sand in cleaner flotation with pre-grinding (sand recovery versus maltenes recovery).

It was clear that grinding did not help liberate and separate maltenes from asphaltenes, as can be seen by comparing the results of tests TSRU 36 and TSRU 39. On the other hand, a low temperature flotation resulted in a significantly low maltenes recovery (61.2 % at 60°C vs 29.2% at 35°C) indicating the important role of high temperature on maltenes recovery.

4.2.5 Maltenes recovery using n-heptane as a liberation solvent

At this point of the project, we suspected that the maltenes in the TSRU tailings sample was not liberated to any meaningful extent to achieve maltenes/asphaltenes separation. The addition of pentane helped the liberation and separation the most, but its dosage was not optimized, and its low boiling point made its residence time in the 60°C pulp questionably short.

To rectify this, we tested a heavier paraffinic solvent, n-heptane, so that its residence time would be longer in flotation. The details of these tests are shown in Table 8, and Figures 16 and 17.

Table 8 Cleaner flotation tests for maltenes recovery by using n-heptane as solvent. Pulp temperature 60°C.

Sample	Test#	Reagent (g/t dry solids)	Results	Comments
Rougher Concentrate from 2019-10 TSRU Tailings sample.	TSRU44	1,000 g/t PEO 5,000 g/t Tripolyphosphate 1,500 g/t Lignosulfonate 1,500 g/t SAA 98,000 g/t n-Heptane	Recovery: 68.5% Maltenes 66.0% Hydrocarbon 47.7% Sand	Similar condition as test TSRU 39 but used n-heptane at twice the dosage as pentane
	TSRU45	1,000 g/t PEO 5,000 g/t Tripolyphosphate 98,000 g/t n-Heptane 1,500 g/t Lignosulfonate 1,500 g/t SAA	Recovery: 68.4% Maltenes 54.7% Hydrocarbon 38.2% Sand	Add heptane prior to depressants. Compare with TSRU44
Maltene recovery in the rougher float was 90%.	TSRU46	147,000 g/t n-Heptane 1,000 g/t PEO 5,000 g/t Tripolyphosphate 1,500 g/t Lignosulfonate 1,500 g/t SAA	Recovery: 43.5% Maltenes 46.0% Hydrocarbon 41.8% Sand	Add n-heptane in the very beginning with longer soaking time of 3 h
	TSRU47	196,000 g/t n-Heptane	Recovery: 66.8% Maltenes 66.6% Hydrocarbon 56.4% Sand	n-Heptane only, and soaked with TRU tailings for 3 h. Compare with TSRU46

Test TSRU 44 was conducted at similar conditions as test TSRU 39, except that pentane was replaced by n-heptane, and the n-heptane dosage was twice of pentane. When compared with test TSRU 39, the recovery of hydrocarbon, maltenes and sand all increased in test TSRU 44 but almost in parallel and did not show any preferential separation among the three components. In test TSRU 45 n-heptane was added prior to the depressants resulting in a better rejection of sand but a lower hydrocarbon recovery than TSRU 44. In test TSRU 46, the heptane was “soaked” with the TSRU tailings sample for 3 hours prior to the addition of other reagents, and test TSRU 47 was similar to test TSRU 46 except that the heptane dosage was higher and no other reagent was used. As can be seen from Table 8 and Figure 16, only test TSRU 45 showed some separation of maltenes from hydrocarbon, again by a difference of about 15 percentage points, similar to TSRU 07 (Table 4) where a much simpler scheme was used (i.e., 1 kg/t PEO and 54 kg/t pentane).

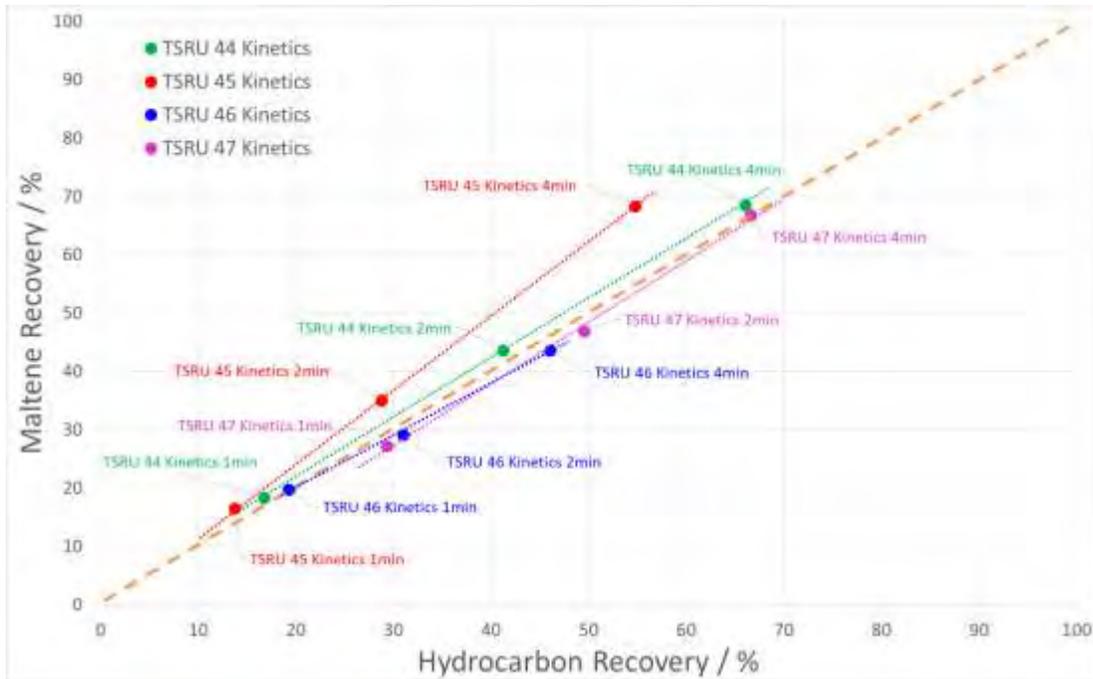


Figure 16 Separation of maltenes in cleaner flotation by using heptane with different reagents conditioning (maltenes recovery versus hydrocarbon recovery).

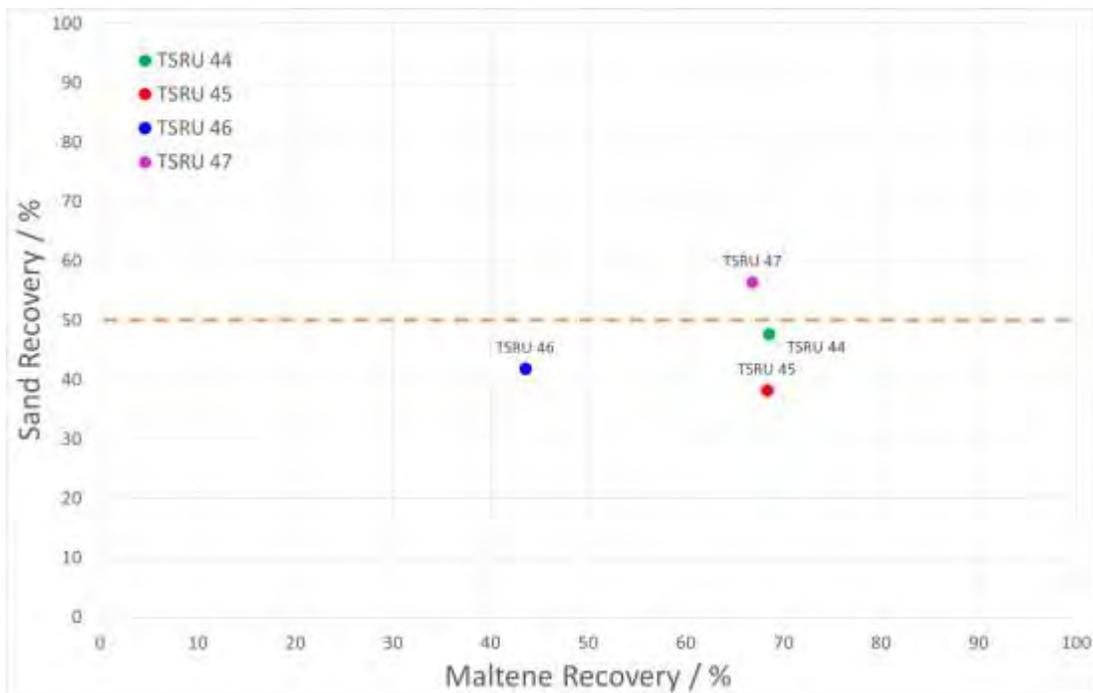


Figure 17 Rejection of sand in cleaner flotation by using heptane with different reagents conditioning (sand recovery versus maltenes recovery).

We attempted to treat the TSRU tailings in n-heptane for a longer period of time (3 hours) so that the maltenes could be completely extracted by n-heptane. After phase separation, it was observed that the top layer of the n-heptane phase separated from the pulp was less than the added quantity of n-heptane. Depending on the treatment time, the phase-separated n-heptane quantity varied between 1/3 to 1/2 of the originally added quantity (the longer the treatment time, the less was recovered). After determining the maltenes concentration in the recovered n-heptane phase, it was clear that, had the added n-heptane been able to be fully recovered, the maltenes recovery would be 100%. In other words, the maltenes could completely dissolve in n-heptane, but the n-heptane-maltenes mixture could not be completely recovered by either phase separation, or froth flotation. One of the reasons is the formation of rag layer containing significant amount of n-heptane with dissolved maltenes depending on the agitation condition. However, the amount of n-heptane in the top layer was still less than added n-heptane, even when a rag layer was not observed. It is possible that some of the added n-heptane could adsorb on asphaltenes surface and accumulate in the pores of asphaltenes particles in an aqueous medium.

At the start of this project, the initial thinking was that by using a paraffinic solvent to dissolve the maltenes, the solvent-maltenes mixture may then be recovered by froth flotation. But the observations described above using n-heptane showed that the recovery of the solvent-maltenes mixture would not be complete due to the loss of the solvent in a rag layer or on asphaltenes particle surfaces. A demulsifier is likely required to break the rag layer for solvent recovery, but the solvent that is adsorbed on the surface of asphaltenes is more challenge to be liberated and recovered. Therefore, it seems that using a paraffinic solvent to “liberate” maltenes from asphaltenes would not be a straightforward approach. The only way to liberate maltenes is to find a suitable chemical that can “desorb” maltenes from asphaltenes surface, or “desorb” paraffinic solvent with dissolved maltenes. After this proof-of-concept project study, we are still far from identifying a suitable chemical. Some of our tested surfactants, such as AOT and PEO, have shown beneficial effects. If any future project is to be funded to tackle this challenging problem, it should focus on the actual physical state and distribution of maltenes in TSRU tailings as a starting point. Especially noteworthy is to examine how the resins component in maltenes is attracted to asphaltenes and how this attraction may be weakened.

5 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

A one year proof-of-concept project was carried out with an objective to selectively float maltenes from TSRU tailings. This was the first of such an attempt as no information could be found from the literature. The recovery of maltenes from TSRU tailings entailed the liberation of maltenes from asphaltenes, the major hydrocarbon matter in the TSRU tailings, and then the flotation of maltenes while the asphaltenes were depressed.

Three TSRU tailings samples were provided by Imperial, and they were collected in 2014, April 2019 and October 2019, respectively. While the newest sample (October 2019) had excellent natural floatability, with the hydrocarbon and maltenes recovery of over 90% simply by heating the pulp to 60°C followed by aeration, the older samples only had a natural floatability of less or around 50%, a result likely caused by aging.

The study was conceptually divided into two essential steps, the first was the liberation of the maltenes from asphaltenes, and the second was the flotation of maltenes and the depression of asphaltenes, although in practice these two steps may be occurring concomitantly. At present there is no method to study one step independent of the other.

Pentane and n-heptane were tested as the solvent that could dissolve maltenes but not asphaltenes, therefore could act as the liberation agent. Twelve other chemicals, lignosulfonate, trichloroisocyanuric acid (TCCA), dioctyl sulfosuccinate (AOT), sodium oleate, tripolyphosphate, lauramide DEA, sodium dodecylbenzenesulfonate (SDBS), hydrogen peroxide, sodium hydroxide, polyethylene oxide (PEO), stearylamine acetate (SAA), turpentine, and tall oil were used as flotation reagents to depress asphaltenes and/or asphaltene-coated sands/clays. A total of 47 batch flotation tests were conducted using a Denver D-12 mechanical flotation machine with a 1.5 L stainless steel cell, at a pulp temperature of 60°C and natural pH of 7.8.

At the end of the project, a satisfactory maltenes product was not produced from the TSRU tailings. But the project led to the following learnings and observations:

- 1) The TSRU tailings samples on average contained 3.3% hydrocarbon in the as-received slurry samples, or 24.2% hydrocarbon on dry solid basis. Maltenes content in the as-received slurry sample averaged 0.6%, or 4.3% on dry solid basis. Therefore, maltenes content in the hydrocarbon phase was about 18%.
- 2) The TSRU tailings had a wide particle size distribution, up to several hundred μm . The coarse +200 μm fractions were enriched in hydrocarbon and contained about 50% sands/clays and 50% hydrocarbon, while the -200 μm fractions typically only contained about 20% hydrocarbon with about 80% sands/clays.
- 3) Despite the lower hydrocarbon content, the hydrocarbon phase in the fine fractions contained higher concentrations of maltenes. In fact, the maltenes content in the hydrocarbon phase monotonically decreased with increasing particle size. This was believed to be caused by the deposition of maltenes on asphaltenes surface when the paraffinic solvent was evaporated (recovered) in the TSRU process. Finer asphaltenes particles had a higher specific surface area,

thus giving a higher surface deposited maltenes per unit mass, assuming the deposited maltenes layer thickness was the same for coarse and fine fractions.

- 4) The best results observed in this study was when 1 kg/t polyethylene oxide (PEO) and 54 kg/t pentane were used to treat the TSRU tailings, followed by flotation. Under this condition, maltenes recovery was 75%, while asphaltene recovery was 55%, and sand recovery was 23%, i.e., the maltenes recovery was 20 percentage points higher than asphaltenes, and the maltenes grade was increased from 4.1 wt% in the feed (on dry solid basis) to 9.7 wt% in the floated concentrate. The dosage may appear to be high, but they were against dry solids weight of the TSRU tailings. Since the TSRU tailings contained about 11% solids, the dosages translated to 100 g/t PEO and 6 kg/t pentane for as-received TSRU tailings. It was also important to note that 6 kg/t pentane was equivalent to 0.6 wt% pentane in the TSRU slurry.
- 5) Of the 12 chemicals studied in this project (besides the two solvents), dioctyl sulfosuccinate (AOT) and polyethylene oxide (PEO) seemed to have demonstrated positive effects of promoting maltenes recovery while depressing asphaltenes and sands/clay recovery.
- 6) The project showed that attempting to use a paraffinic solvent to liberate the maltenes in TSRU tailings from asphaltenes would not work well. Although the solvent could dissolve maltenes, the solvent-maltenes mixture seemed to still adsorb on asphaltenes surface, so that it could not be completely phase separate from the tailings slurry or floated off. Depending on agitation, sometimes a rag layer could form, further trapping the solvent-maltenes mixture.
- 7) Therefore, the key technical challenges to recover maltenes from TSRU tailings are first to find chemicals/process aids that could weaken the attraction between maltenes and asphaltenes, or between paraffinic solvent (with dissolved maltenes) and asphaltene, then find chemicals that could depress the flotation of asphaltenes.

5.2 Recommendations for possible future work

The research team conducted a comprehensive literature survey during this proof-of-concept project about the chemistry and properties of the different bitumen components in the Alberta oil sands, which revealed that separating maltenes from asphaltenes is a challenging topic. Since one of the components in maltenes, resins, is in many ways very similar to asphaltenes, it can be considered as a “light” fraction of asphaltenes. The resins content in maltenes vary depending on the sources of bitumen, but since the maltenes in TSRU tailings have gone through paraffinic froth treatment, it may have been enriched in resins content. Therefore, any future work on this topic should focus on resins/asphaltenes interactions, and any means to weaken such interactions, i.e., to continue the work started in this project to identify chemicals/process aids that can weaken the attraction between maltenes and asphaltenes, or between paraffinic solvent and asphaltenes, and depress the flotation of asphaltenes.

6 ACKNOWLEDGEMENTS

Financial support is provided by the Institute for Oil Sands Innovation. We also appreciate the technical insight and input from Payman Esmaili, Leyli Mirnontazeri, and Alireza Zehtab Yazdi from Imperial, who provided invaluable advice and guidance to this project.

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APPENDIX: PROPOSAL AS APPROVED

Selective Recovery of Maltenes from TSRU Tailings using Froth Flotation

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Feb 8, 2019

Background and Hypotheses

- Composition of TSRU tailings: bitumen (including precipitated asphaltene) 10 wt%, water 30 wt%, and solids 60 wt%
 - ✓ Hydrocarbons: asphaltene (80 wt%) & maltenes (20 wt%)
- Simple air flotation
 - ✓ Bitumen is floated with air bubbles → no selectivity → undesirable
 - ✓ Precipitated asphaltenes may also float with air bubbles due to the hydrophobic nature of asphaltenes → no selectivity → worse scenario
- A two-stage process is proposed to recover maltenes selectively
 - Stage 1: Maltenes liberation from tailings pulp, esp. from asphaltene
 - Stage 2: Selective maltenes flotation for recovery

Stage 1. Maltenes liberation (i.e. phase separation of maltenes and asphaltenes)

Proposed approaches

- Addition of small dosage of collector to induce separation of maltenes and asphaltenes. The collector could be organic solvent with b.p. range 100-200°C and solubility parameters between 14.0–16.0 MPa^{1/2} such as n-octane, n-nonane, n-dodecane, kerosene, etc.
- CO₂ injection to induce phase separation of maltenes and asphaltenes¹.
- Asphaltene flocculants addition such as sulfonated polystyrene² and poly(maleicanhydride-1-octadecene)³ to promote phase separation of maltenes and asphaltenes .
- A combination of above approaches.

¹ Qi Liu, Xiaoli Tan. IOSI 2017-15: CO₂ assisted paraffinic froth treatment.

² Mazzeo et al. Energy & Fuels 2018 32 (2), 1087-1095.

³ Pillon Petroleum Science and Technology, 2001, 19: 7-8, 863-873.

Stage 2. Selective maltenes flotation

Proposed approaches

- Alter asphaltenes' wettability by depressant addition.
 - ✓ Proposed depressants interact with asphaltene particles through multiple interactions such as π - π , hydrophobic, and hydrogen bonding interactions to alter the wettability of asphaltene from hydrophobic to hydrophilic.
 - ✓ Commercially available water-soluble surfactants with suitable functional groups such as humic acids, sodium petroleum sulfonates, sodium lignosulfonates, etc. as depressants to interact with asphaltenes.

Stage 2. Selective maltenes flotation

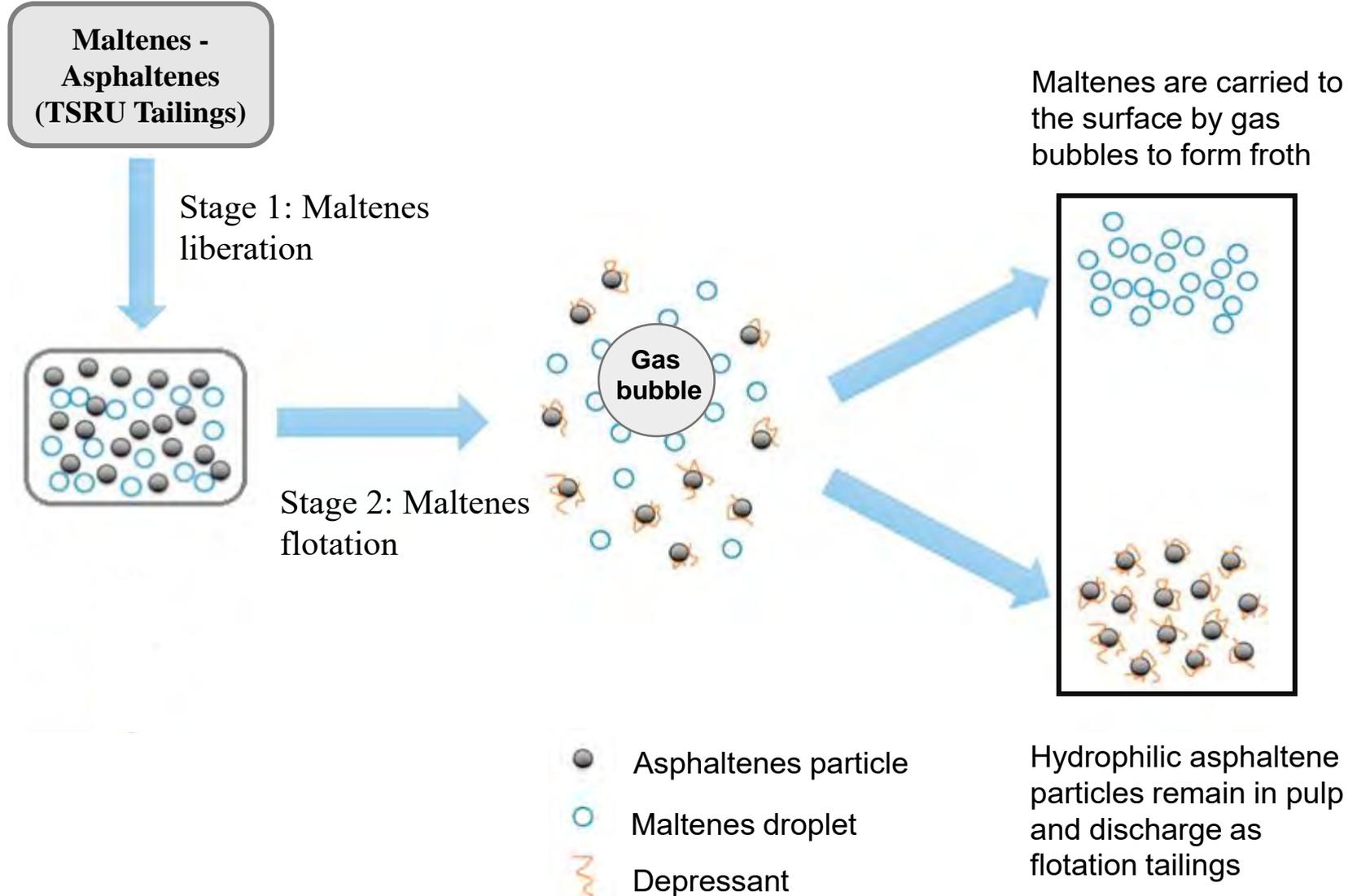
Proposed approaches (cont.)

- Alter surface charge of gas bubbles, asphaltenes and maltenes by manipulating water chemistry, so that gas bubbles have the same type of charge to asphaltenes particles and opposite type of charge to maltenes drops.
 - ✓ Variation of pH of tailings water¹ in a practical range to avoid any detrimental effect of recycle water on bitumen recovery.
 - ✓ Chelation agent in combination with multivalent metal ions such as EDTA + CuSO₄¹ to alter the charges of asphaltenes selectively from negative to positive.
 - ✓ Reagents to tune charge of gas bubbles such as dodecylamine² to alter the charges of air bubbles from negative to positive.

1. Grijalva-Monteverde et al. Energy & Fuels 2005, 19, 2416-2422.

2. Bueno-Tokunaga et al. International Journal of Mineral Processing 140 (2015) 50–57.

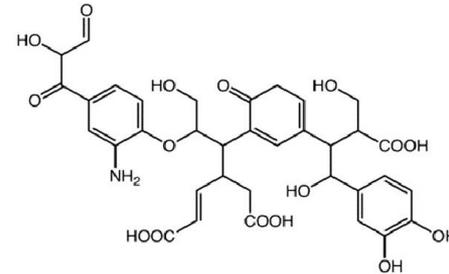
Illustration of example approach for maltenes recovery



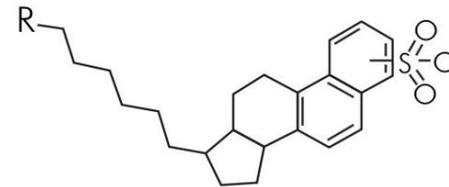
* Tailing solids and water are not shown in the illustration for simplicity

Example Depressants

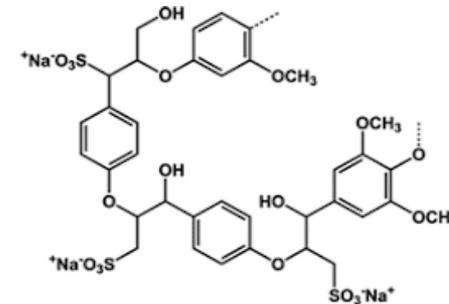
- Humic acids



- Sodium petroleum sulfonates

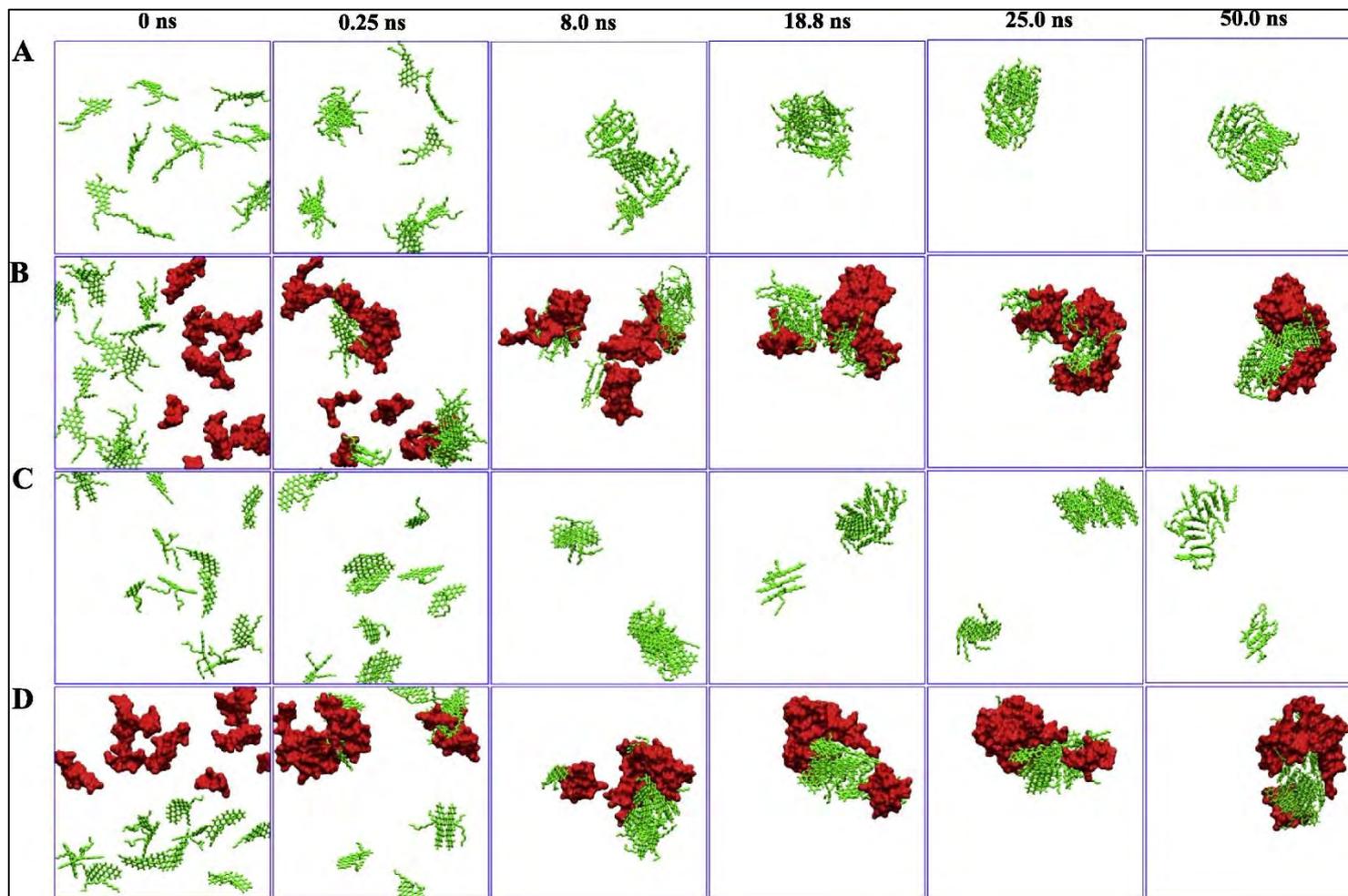


- Sodium lignosulfonates



- The proposed depressants with different chemical functional groups have been reported to have strong interactions with asphaltene components in the literature

Co-aggregation of humic acid and asphaltene in water environment, where humic acid aggregates covers asphaltene aggregates



Molecular dynamic simulation of co-aggregation process of asphaltene (green) with humic acid (red) in bulk water systems. Water molecules are not shown to highlight the aggregate structure.

Proposed Experiments

- Apparatus: Denver flotation cell & Hybrid batch flotation column
- Materials:
 - ✓ TSRU tailings
 - ✓ Maltenes in simulated tailings
 - ✓ Maltenes + precipitated asphaltene in simulated tailings
- Parameters to be investigated
 - ✓ Type and dosage of collector, flocculant and depressant
 - ✓ Type of gas for flotation (such as air, N₂, O₂, and CO₂)
 - ✓ pH
 - ✓ Temperature
 - ✓ Flotation time and aeration rate
 - ✓ Mixing energy
 - ✓ Froth quality
 - ✓ Flotation efficiency

Hybrid batch flotation column

Camera, laser and LED light system to monitor separation process



Column with adjustable height

Bottom-driven mechanical stirrer + gas supply line

Motor control unit

Business Justification

- The recovery of maltenes from TSRU tailings has two benefits:
 - Significant economic benefit from the valuable maltenes, in which a few percentage increase to the overall bitumen recovery rate has great incentive to oil sands industry. In September 2018, the bitumen production from Imperial Kearn Mine is 220 kbbl/day with an average bitumen recovery of 89.1%. Given a 2 percentage points increase in bitumen recovery, additional 4.4 kbbl/day bitumen could be produced that equals to US\$110,000/day @ US\$25/bbl bitumen.
 - Environmental benefit is significant. With less bitumen being rejected to tailings, the GHG emissions from tailings ponds could be reduced.
- The froth flotation is a mature technique used in water-based bitumen extraction, thus there is no technical challenge or risk to scale up so long as the chemistry works.

Timeline & Budget

- One year from the project starts
- Researcher: one postdoctoral fellow (PDF)
- Budget: \$80,000/year (PDF salary and benefit: \$55,000, supplies and misc: \$25,000)

Selective Recovery of Maltenes from TSRU Tailings *via* Advanced Flotation

Objective: Recover maltenes from a mixture of maltenes/asphaltenes via selective flotation of TSRU tailings

Background

- Bitumen losses in TSRU tailings is estimated 6 kbd (YTD 2018)
- Composition of TSRU tailings: bitumen 3 wt% (20% maltenes + 80% asphaltenes), water 90 wt%, and solids 7 wt%
- Simple air flotation → asphaltenes and maltenes will float with air bubbles due to hydrophobic nature → no selectivity

Deliverables

Conducting theoretical and experimental (using flotation column) studies to develop a two-stage process for selective separation of maltenes:

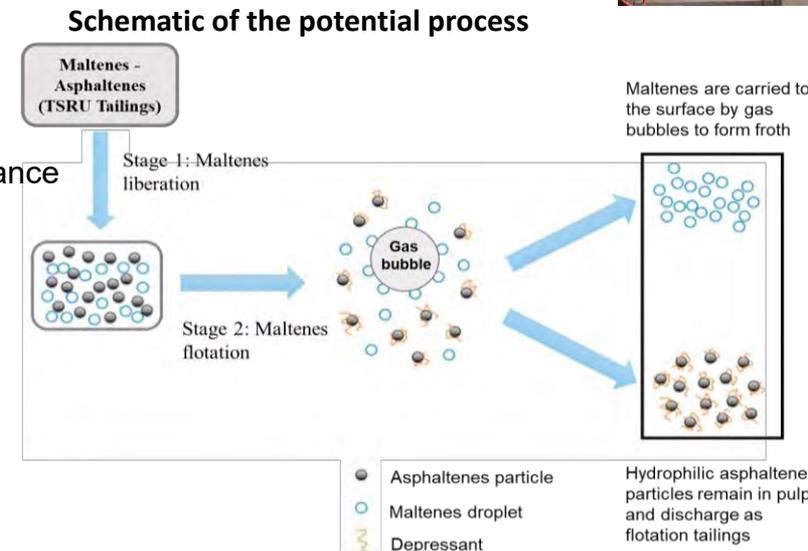
- Stage 1: Maltenes liberation from asphaltenes in the TSRU tailings using collectors (e.g. kerosene), CO₂ injection and asphaltene flocculants (e.g. sulfonated polystyrene)
- Stage 2: Selective flotation of maltenes from asphaltenes using depressants (e.g. humic acids) and pH variation (e.g. multivalent metal ions)

Business Value

- Potential opportunity to recover ~ 3 - 6 kbd maltenes
- Reduce bitumen loss to tailings ponds and improve environmental performance

Timeline/Budget

- One year
- Personnel: one postdoctoral fellow (PDF)
- Budget: \$80,000/year (salary/supplies)



Gantt Chart of the Maltene/Asphaltene project:

