Residual bitumen recovery from oil sand tailings with lime

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ABSTRACT

All oil sands plants operating in Alberta, Canada use the Clark Hot Water Extraction process. This process causes production of mature fines tailings (MFT) at 30-35% solids content which remains in a fluid state for decades because of its very slow consolidation rate. Existing mature fines tailings inventory is approaching 10^9 m^3, remediation of which by thin layer deposition and centrifuging are being tested by oil industry. Residual bitumen in mature fine tailings can complicate remediation, as it can interfere with the performance of coagulants and polymers which hinders the dewatering process. To support oil industries mature fine tailings remediation effort, we have investigated a method that reduces residual bitumen content, facilitates dewatering of the mature fine tailings and improves process water chemistry, simultaneously, by using lime as a process aid between 750 to 1500 mg-*CaO*/kg-MFT dosages. Experimental observations suggest that the residual bitumen of the mature fine tailings could be recovered by flotation process with about 5-10 minutes retention time. This investigation shows that use of lime could enhance the performance of mature fine tailings remediation processes.

1 BACKGROUND

Development in refining technology since 1940's had a great impact on the utilization of heavy oil and bitumen to refinery feedstock all over the world. This scenario positioned Alberta's Athabasca oil sands bitumen of 7-10 API gravity and Peace River and Cold Lake heavy oil of 8-19 API gravity deposits as one of the largest hydrocarbon reserves in the world. Athabasca oil sand deposits lie under 141,000 square kilometres (54,000 square mile), contain about 270×10^9 m^3 or 1.7 trillion barrels of bitumen in-place. Oil sands consist of 0 to 19 % (averaging 12 %) bitumen, 84 to 86 % mineral matter predominantly quartz, silts and clay and 3-6 % water. Clays are present in the forms of discontinuous beds or bands varying from 1 cm to 15 cm in thickness, which are composed of mainly kaolinite and a lesser amount of illite (Kaminsky, 2008; Carrigy, 1966).

Sand particles in Athabasca deposits are water-wet; for a typical sand grain of about 100 μm diameter, the water film thickness is of about 2 μm. Because of this structure, about 15% of the Athabasca oil sands deposits are suitable for bitumen production by surface mining followed by ore-water slurry based extraction processes. In Alberta, bitumen is commercially produced since 1967; daily production of which reached at 1.3×10^6 barrels in 2014. Clark Hot Water Extraction (CHWE) process developed at the Alberta Research Council during 1930s, or its slight modified versions, are used at all commercial plants (Clark, 1939; Clark and Pasternack, 1932).

CHWE process uses caustic *NaOH* as an extraction process additive, which provides acceptable bitumen extraction efficiency; however, it accumulates *Na*$^+$ ions in process water, disperses silt-clay size particles and produces toxic mature fine tailings (MFT), a tailings effluent of about 32% solids content, 98% of fines (-325 mesh, <45 μm diameter). Oil sands plants are

discharging about 3.3 m³ of tailings, 1.5 m³ of which becomes mature fine tailings (MFT), to produce one barrel of bitumen. Existing MFT inventory is about 10^9 m³, which is growing in accelerated manner because of the commissioning of new plants and capacity increase in existing plants. Increasing MFT inventory is a serious liability for the oil sands operations.

Oil sands industry and government regulating agencies acknowledge the severity of the MFT problem; both industry and all levels of government have devoted sincere effort to solve or to reduce the magnitude of the MFT problem. Remarkable results of these efforts were the low temperature non-additive bitumen extraction process and development of the Composite Tailings (CT) process.

Non-additive extraction process could reduce thermal energy demand and eliminate Na^+ accumulation in process water. It could also reduce MFT production since dispersion of silt-clay size particles were suppressed by elimination of the $NaOH$ addition into extraction process slurry. Unfortunately, non-additive extraction processes provided lower than expected bitumen recovery efficiency and extraction plants at Albian Sands' Muskeg River Mine and Syncrude Canada Ltd.'s Aurora Mine were modified to versions of the CHWE process.

The CT process was based on the cycloning of the whole tailings followed by treating the blend of Cyclone Underflow effluent (about 63% solids; <10% of which are fines, < 45 μm size particles) and existing MFT (about 33% solids; >98% of which are fines) with gypsum ($CaSO_4$). The blending must produce a CT that behaves as a nonsegregating tailings material; however, the CT must also have an acceptable hydraulic conductivity, which limits the sands-to fines (S/F) ratio of the CT to be in the range of 4 to 5 (Matthews et al, 2002; Morgenstern and Scott, 1997; Caughill et al, 1993). The concerns over the use *of $CaSO_4$* as an additive to prevent segregation are that it increases process water Ca^{2+} concentration and emits hazardous H_2S by anaerobic bacterial reduction of SO_4^{2-} species with residual hydrocarbon in the tailings. Suncor Energy Inc. has decided to discontinue CT production while Syncrude Canada Ltd. and Shell Canada Ltd. are continuing to use some form of CT. Other plant operators are prepared to implement CT in the near future.

The CT process was a great invention for the future development of oil sands tailings disposal practices; however, commercial implementation didn't result in a substantial change in the existing MFT inventory, since Cyclone Overflow (>10% solids, >55% fines) produced during the CT process results in fine tails that will become new MFT. A modified version of the CT, the nonsegregating tailings (NST) production process was developed at our laboratory (Ozum et al, 2014). In NST production process the whole tailings is cycloned, the Cyclone Overflow effluent is thickened using high performance thickeners, then the blend of Cyclone Underflow and Thickener Underflow is treated with lime (CaO, or $Ca(OH)_2$ in aqueous environments) or CaO and CO_2. If CaO is also used as an extraction process additive, a small amount of existing MFT could also be added into the NST material.

For the last decade, oil sands operators have tested Tailings Reduction Operation (Suncor Energy Inc.), In-Line Thickening (Syncrude Canada Ltd.), Atmospheric Drying (Shell Canada Ltd.) and Centrifuge Technology (Syncrude Canada Ltd. and Shell Canada Ltd.) for further consolidation of the existing MFT into a smaller volume to comply with the directives of the Alberta Energy Regulator (COSIA, 2014; ERCB, 2009). In all of these processes polymeric additives are used to flocculate MFT as an initial step for its further processing. Residual bitumen trapped in MFT interacts with the polymeric additives; removal of which from MFT could improve the performance of the polymeric additives.

In the present study, based on our previous experience using of lime (CaO) as additive for bitumen extraction and NST production processes, the performance of CaO is investigated for the removal of residual bitumen from MFT with an emphasis on understanding how CaO alters clay characteristics and process water chemistry.

2 RESIDUAL BITUMEN RECOVERY IN MFT

2.1 Bitumen production by ore-water slurry based extraction processes

Bitumen production using ore-water slurry based extraction processes involves three fundamental processes by which a bitumen rich froth, composed of about 60% bitumen, 30% water and 10% solids, is formed. Bitumen is recovered from the extraction process froth by naphthenic or paraffinic treatment processes. Bitumen produced by naphthenic treatment process contains about 18% asphaltenes; therefore, it is converted to synthetic crude oil (SCO) and shipped refineries by coking followed by hydrotreating processes (Gray, 2015). Bitumen produced by naphthenic treatment process contains about 8% asphaltenes, therefore, it can be accepted as a feedstock by the refineries equipped with a hydrocracker unit. At oil sands plants tailings effluents from the extraction and froth treatment plants are combined into the whole tailings stream. As a result, unrecovered bitumen in the extraction plant tailings and unrecovered bitumen and solvent in the froth treatment plant tailings are blended into the whole tailings. When the whole tailing is discharged into the tailings ponds, some hydrocarbons will separate and float on the surface of tailings ponds; however, a fraction of the hydrocarbons will be trapped in the MFT.

The amount of residual bitumen or residual hydrocarbons trapped in in MFT depends on the oil sands characteristics (sand and fines-clay composition, connate water salinity, bitumen characteristics) as well as the nature of extraction process (temperature, hydrodynamics and additives). It is speculated that regardless of the differences in bitumen extraction plants, the mechanism of residual bitumen or hydrocarbons captured in MFT have similarities. Understanding these mechanisms would help to develop processes for the recovery of residual bitumen from any tailings effluent including the MFT.

During the last seven decades a large number of publications have been generated on bitumen production using oil sands ore-water slurry based extraction processes (Liu et al, 2005; Masliyah et al, 2004; Kasperski, 2001). Existing knowledge proposes that bitumen extraction in ore-water slurry based systems involves three fundamental steps: liberation of bitumen from oil sands matrix, followed by coalescence of bitumen droplets and aeration of bitumen droplets to form a bitumen rich froth (Masliyah et al, 2011). Alkaline reagent, such as *NaOH*, conditioning of ore-water slurry to liberate bitumen was developed in 1930s, which became a standard process used at all commercial plants. Alkaline conditioning increases *pH* of the extraction process slurry and produces surfactant species with carboxylic and sulfonic acids functional groups from bitumen asphaltenes naturally contained in bitumen. These surfactant species reduce water surface and bitumen-water interfacial tensions, promote silt-clay size particle dispersion and liberation of bitumen from sand grains by increasing disjoining pressure in the water film between sand grains and bitumen. Existing literature and commercial experience teaches us that overall performance of the extraction process is controlled by the interaction of the alkaline additive with process water and silt-clay size particles, as well as by the temperature, hydrodynamics and retention time of the process vessels.

2.2 Interactions between bitumen-clay and process water

Oil sands ore-water slurries are different than many mining industry slurries, because of the clay component of the oil sands ore. Clay minerals are fine grained (<2 μm size) hydrous silicates, commonly of aluminum and magnesium. Clays are made of layers built from components with tetrahedrally and octahedrally coordinated cations. The most common characteristics of the clay minerals are that, they form varying degree of plasticity when mixed with water, lose adsorbed and constitutional water when heated and yield refractory materials at high temperature. Because of these characteristics clays minerals are used in many industries; however, they are also the source of many industrial challenges.

Surface of clay minerals have active functional groups of a few nanometers scale, which are of negatively charged isomorphic substitution sites (Si^{4+} by Al^{3+} and Al^{3+} by Fe^{2+}), neutral siloxane surfaces, hydroxyl surfaces and broken edge sites. In the case of oil sands slurries, all of these active sites involve interactions between bitumen, clay and process water, as well as particle-particle interactions (Solc et al, 2011; Johnston, 2010 and 2008). Bi-wetting characteristic of kaolinite could stabilize oil-in-water and water-in-oil emulsions by Pickering effects (Jiang et al, 2011; Kpogbemaboua et al, 2014). Process water *pH* and ion concentration are also important parameters influencing bitumen extraction and tailings settling and consolidation characteristics, because of their effect on clay surface chemistry in relations to particle-bitumen, particle-water (swelling, viscosity, yield stress) and particle-particle (flocculation) interactions (Wang et al, 2014; Zbik et al, 2008).

In summary, clay minerals are the source of many challenges that are been experienced with bitumen extraction and tailings disposal processes. The present study, recovery of residual bitumen from MFT, or more generally reducing the amount of unrecovered bitumen in the extraction process slurry, also faces the similar challenges.

2.3   Residual bitumen in oil sands tailings

Bitumen trapped in oil sands tailings may be result of: (i) incomplete bitumen recovery in extraction process slurry because of the formation of stable bitumen-in-water emulsions; (ii) rejection of asphaltenes in the froth treatment plant by the use of paraffinic or naphthenic treatments; and (iii) incomplete separation of bitumen froth because of the formation of stable rag layer in froth treatment process. Both sources of unrecovered bitumen in oil sands tailings, as well as dewatering characteristics of oil sands tailings and MFT, are related to the bitumen-water interfacial tension and interactions of clay particles with themselves and with bitumen and process water. All of these interactions are influenced by process water chemistry; therefore, chemical additives that can alter and control process water chemistry can be used to promote residual bitumen recovery and tailings dewatering characteristics.

Incomplete bitumen recovery in the extraction of process slurry is a consequence of the reduced bitumen-water interfacial tension and Pickering effect of bi-wetting clay particles, mostly kaolinite clays, attached to bitumen-water interface. Reduction of bitumen-water interfacial tension promotes bitumen liberation from sand particles and promotes attraction of bitumen to water; however, it obstructs coalescence of bitumen droplets and attachment of air bubbles to bitumen droplets in extraction process slurry (Pan et al, 2012; Pan and Yoon, 2010). Large retention times are required in alkaline based extraction processes to overcome the reduced speeds of coalescence and aeration kinetics. Pickering effect of clay particles in extraction process slurry could happen by attachment of bitumen to clay particles, especially to kaolinite clay since it has bi-wetting characteristic. Also, excess divalent cations such as Ca^{2+} and Mg^{2+} could act as a binder between negatively charged clay and bitumen droplet surfaces (Konan et al, 2007). Differences in the effect of additives on slurry *pH* (i.e. *CaO* increase *pH* while *CaSO₄* doesn't) is another factor to be focused on.

3   EXPERIMENTAL

In the present study performance of two calcium based additives, lime (*CaO*) and gypsum (*CaSO₄*), were tested on the recovery of residual bitumen from MFT. These additives were selected because of a long history of the use of *CaSO₄* to produce CT and recent increase in interest in nominating *CaO* as additives for tailings disposal and bitumen extraction processes (Chalaturnyk et al, 2002; Scott et al, 2007).

Two different MFT samples were used in the present study, their compositions based on Dean-Stark extraction were 27.4% solids, >99% fines, 1.65% bitumen, 1.17 g/cm^3 bulk density and 32.5% solids, >99% fines, 2.9% bitumen, 1.23 g/cm^3 bulk density.

3.1   Column settling experiments

In these tests 1 kg MFT (27.4% solids content) was mixed with *CaO* and *CaSO₄·2H₂O*, that were both either slaked or dissolved in approximately 10 mL distilled water, with a paddle mixer at 200 rpm for 5 minutes. *CaO* and *CaSO₄* were added at different dosages to evaluate effects of two calcium based additives on dewatering characteristics of MFT. Slurry was then placed in a 2 L beaker. Immediately after *CaO* addition, bitumen was observed to release from the MFT and float to the surface.

Column settling tests were performed by treating MFT (27.4% solids content) with *CaO* and *CaSO₄* at different dosages to evaluate effects of two calcium based additives on dewatering characteristics of MFT. In these tests it was also observed that *CaO* and *CaSO₄* performed differently on the release of residual bitumen recovery from MFT.

3.2   Jar test for water chemistry and viscosity

Jar experiments were performed to investigate effect of additive and its dosage on the *pH* of the MFT slurry and release water chemistry.

Approximately 140 g of homogenized MFT were mixed in a 120 mL jar with *CaO* and *CaSO₄·2H₂O* additives, that were both either slaked or dissolved in approximately 5 mL distilled water, and shaken for 15 minutes using a wrist action shaker. Additives were used between 250 to 3000 ppm dosages on an MFT mass basis. The treated MFT samples were first visually assessed for bitumen release. The treated MFT was then analyzed for viscosity at 200 rpm using a vane spindle (V-73) on a Brookfield rheometer (RV-DVT).

Finally, water was recovered from the treated MFT by centrifuged at 13,000 x g for 2 hours. The released water recovered by centrifuging was filtered to remove >0.22 μm particles and submitted to University of Alberta for water chemistry analysis; ICP-AES (cations), ion-exchange (anions) and titration (alkalinity).

3.3   MFT Flotation

Released residual bitumen from MFT was recovered by air flotation using a 1 L glass flotation apparatus. The MFT sample in the flotation apparatus was mixed by a magnetic stirbar. Flotation experiment was performed by placing approximately 500 g of MFT into the apparatus, adding *CaO* or *CaSO₄·2H₂O*, both either slaked or dissolved in approximately 5 mL distilled water, followed by mixing with the stirbar and air injection at approximately 100 mL/min for 5 minutes. The resulting froth was removed and analysis by Dean-Stark extraction.

4   RESULTS AND DISCUSSIONS

In the present study the role of Ca^{2+} to release residual bitumen trapped in MFT was investigated. For this purpose *CaO* and *CaSO₄* additives were selected as the source of Ca^{2+}; the major difference is that *CaO* addition increases *pH* of MFT while *CaSO₄* doesn't. Because of this difference, it is hoped that the role of slurry *pH* on the interactions of Ca^{2+} with the clay-bitumen-water system, as discussed in Sections 2.1 and 2.2, would be better understood.

4.1   Bitumen liberation during settling experiments

The ability for *CaO* to release residual bitumen from MFT was observed while evaluating performance of *CaO* as an additive for dewatering MFT. In these tests immediately after *CaO* addition bitumen was observed to be released from the MFT. Unlike *CaO*, *CaSO₄* appeared to actually promote the trapping of residual bitumen in the MFT better than the control. The differences between *CaO* and *CaSO₄* addition is that *CaO* affects the *pH* of the slurry and alters

interactions between the clay-bitumen-water species. Furthermore, the ionic composition of the process water may affect the stability of clay-bitumen interactions. A better understanding of both *pH* and chemical composition of the water could provide insight into the mechanism of residual bitumen liberation and help to develop a MFT de-oiling process.

4.2 Effect of CaO and CaSO₄ additives on water chemistry and viscosity

The effect of *CaO* and *CaSO₄* on *pH* and process water chemistry was investigated by performing jar tests. Similar to the settling experiment, bitumen was liberated during the mixing process. The extent of bitumen liberation was visual assessed and is presented in Table 1 and Figure 1. The visual observations of the flotation test made for a low dose *CaO* addition, 13 mmol/kg-MFT or 750 ppm *CaO*, are shown in Figure 2. The best bitumen liberation was observed using about 30 mmol of *CaO* per kg of MFT (about 1500 ppm). It appears that overdosing *CaO* may decrease bitumen liberation, which is speculated to result from an increase in slurry viscosity. When *CaSO₄* is used as an additive, it immediately yielded a viscous slurry, did not produce any froth and furthermore splattered the thickened slurry throughout the flask.

Table 1. Visual assessment of bitumen liberation from MFT

CaO		CaSO₄·H₂O	
Dose mmol/kg*	Bitumen Release	Dose mmol/kg*	Bitumen Release
0	-	0	-
4	-	3	-
9	+	6	-
13	++	9	-
18	++		
27	+++		
36	+++		
53	++		

* MFT mass basis; bitumen recovery: - no, + some, ++ lots, +++ covers surface

No Additive (*) *CaO CaSO₄ CaO CaSO₄*
27 mmol 27 mmol 53 mmol 53 mmol

Figure 1. Bitumen released from MFT by *CaO* and *CaSO₄*; (*) dosages are in mmol/kg-MFT.

The viscosity of the slurries was determined at 50 rpm as shown in Figure 3. Unlike CaSO₄, *CaO* initially decreases the viscosity of the slurry up to doses of about 35 mmol/kg (2000 ppm); however, over this dose a significant increase is observed in the viscosity. On the other hand all doses of CaSO₄ result in a high viscosity that is independent of additive dose. The slight decrease in viscosity might help to explain why bitumen is able to liberate from the MFT and should aid in recovery by flotation.

After measuring viscosity, the water was removed from the slurry by centrifuge and analyzed for *pH* and water chemistry, results of which are presented in Table 2. The trends for *pH* and ionic concentrations with increasing additive dose are plotted in Figures 4 and 5.

CaO has a significant effect on the bicarbonate concentration in the MFT, where the bicarbonate decreases with *CaO* addition, likely consumed and converted to *CaCO₃* according to Equation 1. The *pH* slowly increases, as the system remains buffered by bicarbonate at *pH* 8 and Ca^{2+} is depleted from the system, likely lowering the viscosity; however, after a *CaO* dose of

approximately 20 mmol/kg (1000 ppm) the *pH* rises rapidly approaching 12. At this high *pH* all of the bicarbonate is consumed, which corresponds with the increase in viscosity, as all Ca^{2+} can now start to flocculate clays according to Equation 2.
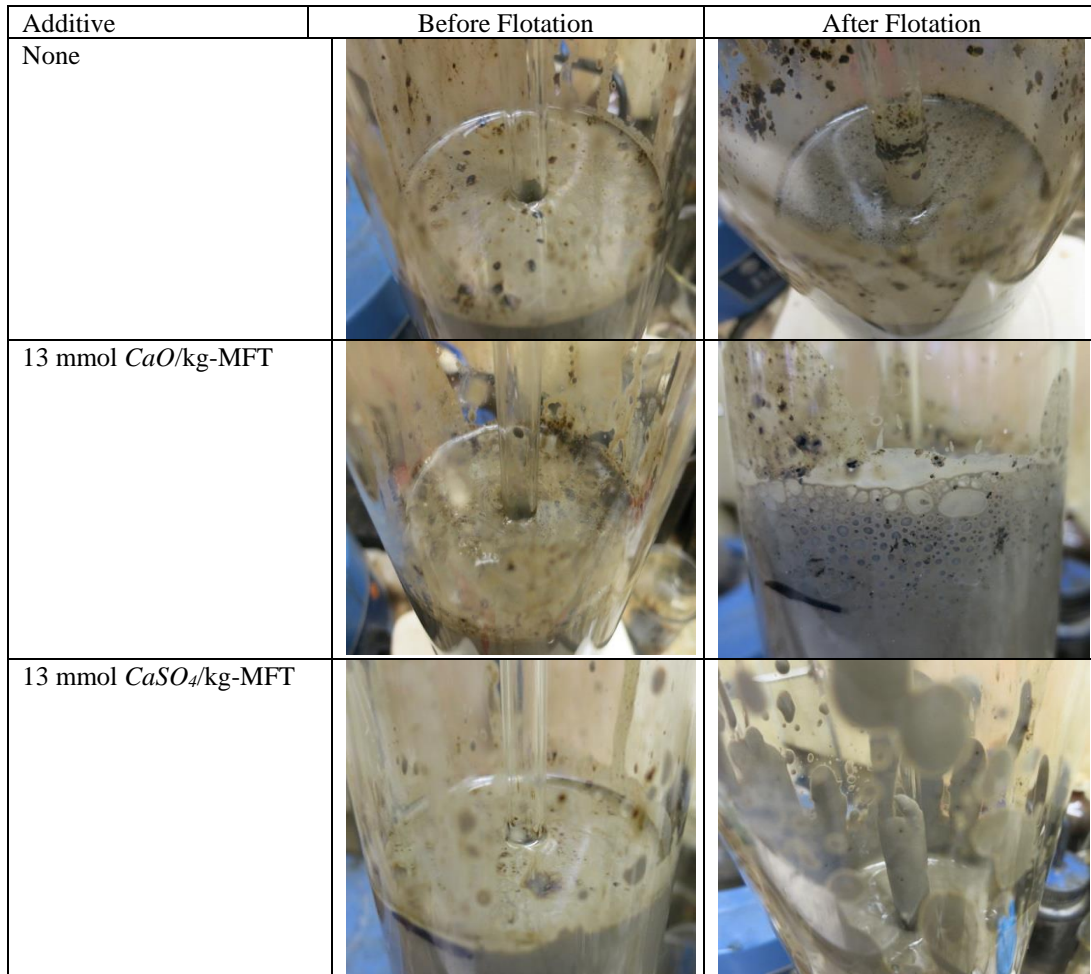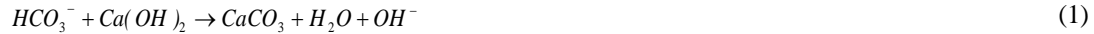
$$HCO_3^- + Ca(OH)_2 \rightarrow CaCO_3 + H_2O + OH^- \tag{1}$$

$$2Clay^- + Ca^{2+} \leftrightarrow Clay - Ca - Clay \tag{2}$$

Additive	Before Flotation	After Flotation
None		
13 mmol *CaO*/kg-MFT		
13 mmol *CaSO₄*/kg-MFT		

Figure 2. Observations of flotation experiment performed on MFT.

CaSO₄ addition does not significantly affect the *pH*, precipitate as much *CaCO₃*; or reduce solution bicarbonate concentration at the same level as *Ca*O. Calcium (Ca^{2+}), magnesium (Mg^{2+}) and sodium (Na^+) concentrations increased with increasing *CaSO₄* dose. While *CaSO₄* appears to promote an initial increase in viscosity, likely through reaction in Equation 2, it appears that beyond a small initial amount the excess Ca^{2+} ions stay dissolved in the water and do not contribute to additional clay flocculation. The combination of the viscosity and water chemistry results suggest that at low doses, 750 to1500 ppm, *CaO* can be used to increase *pH* and lower viscosity to promote residual bitumen recovery by flotation.
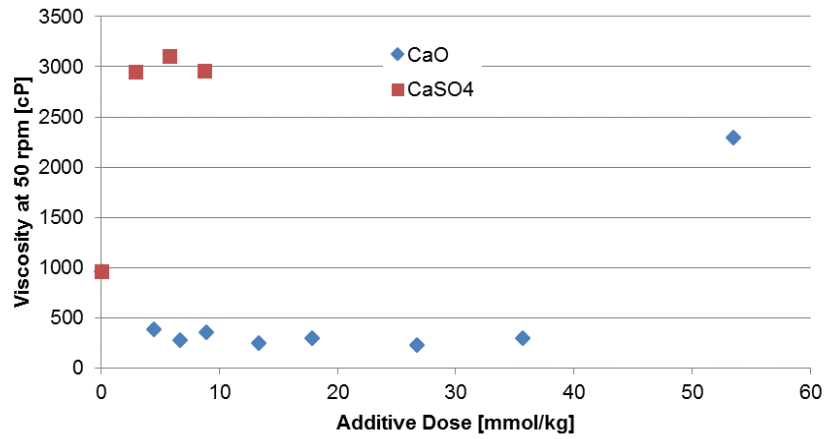
Figure 3. Effect of *CaO* and *CaSO₄* on MFT viscosity.

Table 2. Effect of *CaO* and *CaSO₄* on MFT pH and water chemistry

| Additive Type	Additive Dose *			HCO_3^-	CO_3^{2-}	OH^-	Mg^{2+}	Na^+	Ca^{2+}	K^+	Cl^-	SO_4^{2-}
	ppm	mmol/kg	*pH*	mM	mM	mM	mM	mM	mM	mM	mM	mM
Control	0	0	8.3	9.8	0.1	0.0	0.3	9.9	0.5	0.4	5.1	0
CaO	250	4.5	8.7	8.3	0.2	0.0	0.2	12.7	0.3	0.3	5.3	0.2
CaO	375	6.7	8.7	6.8	0.2	0.0	0.2	11.2	0.2	0.3	5.4	0.2
CaO	500	8.9	8.7	7.8	0.2	0.0	0.3	15.3	0.4	0.4	5.4	0.3
CaO	750	13.4	8.6	4.7	0.1	0.0	0.1	12.8	0.2	0.3	5.4	0.3
CaO	1,000	17.8	8.6	3.5	0.1	0.0	0	11.2	0.2	0.3	5.5	0.4
CaO	1,500	26.7	9.5	3.1	0.3	0.0	0	12.0	0.2	0.3	5.5	0.7
CaO	2,000	35.7	9.8	4.0	0.7	0.1	0	11.6	0.1	0.3	5.3	0.4
CaO	3,000	53.5	11.6	7.4	1.8	3.6	0	15.1	0.6	0.5	5.4	0.6
CaSO₄.2H₂O	500	2.9	8.9	12.6	0.4	0.0	1.2	20.4	0.8	0.8	5.1	0.6
CaSO₄.2H₂O	1,000	5.8	8.4	9.0	0.1	0.0	2.4	23.1	2.4	1.0	5.0	2.2
CaSO₄.2H₂O	1,500	8.7	8.6	7.3	0.1	0.0	3.3	21.1	4.6	1.2	4.9	3.8

* MFT mass basis
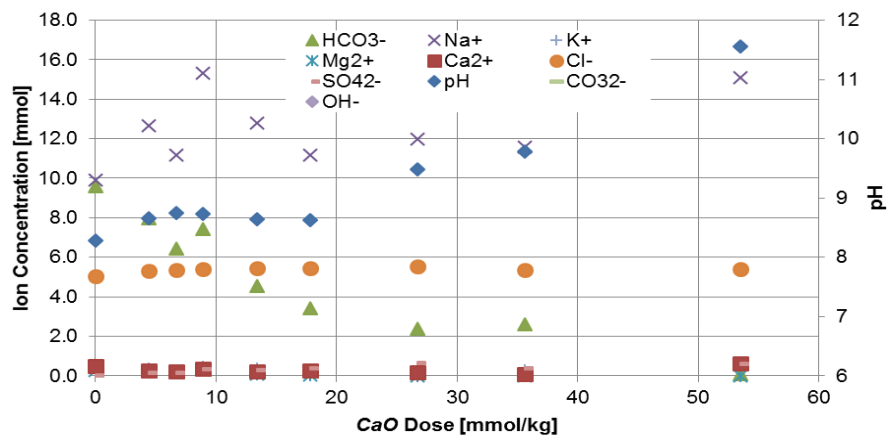
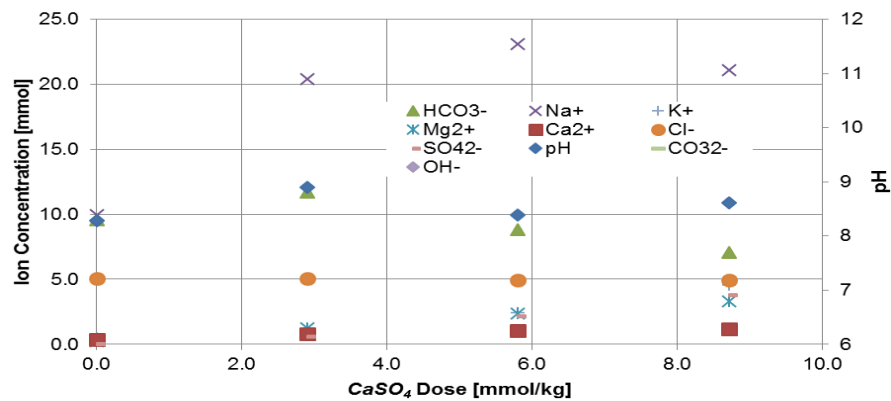Figure 4. Effect of *CaO* on MFT *pH* and water chemistry.

Figure 5. Effect of $CaSO_4$ on MFT *pH* and water chemistry.

5 CONCLUSIONS AND FUTURE WORK

Investigations into *CaO* for dewatering of MFT additionally demonstrated that *CaO* appears to be an effective additive to recover the residual bitumen from MFT. Further investigation demonstrated that *CaO*'s ability to increase *pH* and decrease bicarbonate concentration likely play critical roles to destabilize the interaction between bitumen and clays in the MFT matrix. The altered water chemistry allows for *CaO* to decrease the viscosity of MFT which would aid recovery of the residual bitumen by flotation processes. Initial investigation into a model flotation indicates that *CaO* enhances flotation; however, additional research is required to optimize the experiment. Lime was clearly more effective than *CaSO₄* in recovering residual bitumen from MFT. Successful recovery of the residual bitumen from MFT by *CaO* should improve the effectiveness of further MFT processing techniques, such as the production of NST or dewatering of MFT by centrifugation.

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