Methods to Reduce Production of Oil Sands Mature Fine Tailings



B. Ozum

Apex Engineering Inc., Edmonton, Alberta, Canada J.D. Scott University of Alberta, Edmonton, Alberta, Canada

ABSTRACT

The Clark Hot Water Bitumen Extraction process uses *NaOH* or sodium salts of weak acids as extraction process aids. These additives increase extraction efficiency; however they cause production of tailings with poor settling and consolidation properties which result in the formation of mature fine tailings and increase the salinity, specifically the Na^{+} concentration, of the recycled release water. We are investigating the performance of alternative extraction additives; *CaO* for adjusting *pH*, *O*₃ as an oxidant to produce surfactants from bitumen asphaltenes and biodiesel such as fatty acids methyl esters as surfactant additives. These additives improve the efficiency of extraction process, produce tailings with friendly geotechnical properties and eliminate accumulation of *Na+* concentrations in the recycled release water. Also, we have investigated production of nonsegregating tailings from the blend of cyclone underflow and thickener underflow using *CaO*, or *CaO* and *CO*₂ as additives. Implementation of both of these extraction and nonsegregating tailings production processes could reduce the environmental impacts of oil sands plants.

RÉSUMÉ

Le Clark Eau Chaude Extraction du Bitume processus utilise *NaOH* ou sels de sodium d'acides faibles comme le sida processus d'extraction. Ces additifs efficacité d'extraction augmentation, mais ils provoquent la production de résidus de régler pauvres et propriétés de consolidation, qui entraînent la formation de résidus fins mûrs et d'augmenter la salinité, en particulier concentration de Na^+ , de l'eau recyclée communiqué. Nous étudions les performances d'extraction des additifs de substitution; *CaO* pour ajuster le *pH*, *O*₃ comme oxydant pour produire des tensioactifs à partir des asphaltènes du bitume et du biodiesel, comme les acides gras des esters méthyliques comme additifs tensioactifs. Ces additifs améliorent l'efficacité du processus d'extraction, produisent des résidus avec amicale propriétés géotechniques et d'éliminer l'accumulation de concentrations de *Na*⁺ dans l'eau de sortie recyclés. En outre, nous avons étudié la production de résidus non ségrégatifs du mélange de sousverse cyclone et underflow épaississant en utilisant le CaO, *CaO* ou *CO*₂ et comme additifs. La mise en œuvre de ces deux procédés d'extraction et non ségrégatifs résidus de production permettrait de réduire les impacts environnementaux des plantes des sables bitumineux.

1 INTRODUCTION

1.1 Conventional Bitumen Extraction and Tailings Disposal Practices

In northern Alberta bitumen is produced from surface mineable oil sands by using some version of the Clark Hot Water Extraction (CHWE) process; a simplified schematic of which is depicted in Figure 1. In this process, oil sands ore-water slurry is conditioned using caustic *NaOH* or sodium salts of weak acids as extraction process aids, which maintains the *pH* of the ore-water slurry at around 10.5-11.0. At elevated *pH* the asphaltic acids, which are of partly aromatic, containing oxygen functional groups such as phenolic, carboxylic and sulphonic types, become water soluble and act as surfactants reducing the surface and interfacial tensions and promotes the efficiency of bitumen extraction (Moschopedis et al, 1977 and 1980).

The CHWE process was discovered by Dr. Karl A. Clark and his coworkers at the Alberta Research Council during the 1930s; some versions of which are being implemented commercially in almost all oil sands plants (Clark and Pasternack, 1932; Clark 1939). The use of chemical additives in the extraction process provides the most optimum conditions to maintain high bitumen extraction efficiency; however it produces tailings with poor settling and consolidation properties and increases the salinity, specifically the Na^{+} concentration, of the release water (MacKinnon and Sethi, 1993).

Oil sands plants produce large volumes of tailings; about 1.5 m³ of tailings per barrel of bitumen which is composed of sand, clay, water and residual bitumen. Conventionally, oil sands tailings is discharged into tailings ponds without any treatment to alter its geotechnical properties. The tailings discharged from the CHWE extraction process has very poor settling and consolidation properties because of clay dispersion caused by the use of the NaOH additive. Tailings discharged from the extraction plant is a segregating type because of its low solids contents. When deposited in a tailings pond, the sand settles out rapidly to form dykes and beaches while, depending on the makeup of the tailings stream and the method of deposition, only onethird to one-half of the fine (<45 µm size) material is captured or retained in the tailings sand deposits. The majority of the fines separate or segregate during tailings sand deposition and flow into the pond in suspension to form fluid fine tailings. The fine tailings settle in about two years to form mature fine tailings, a fluid tailings about 33% solids content which is almost all fines (Scott and Ozum, 2010). Over a two year period the fine particles settle and form Mature Fine Tailings (MFT), which is a stable suspension of fluid fine tailings that has undergone settlement and compression to about 33% solids content by mass. Further densification of the MFT is a very slow process; as a result of which all tailings produced and discharged into tailings ponds without any treatment contribute to the accumulation of MFT. Accumulation of MFT is considered as an environmental liability; both oil sands industry and government regulatory agencies have committed to reduce the production of MFT as outlined in the ERCB Directive 074, February 3, 2009.

The oil sands industry has developed a non-caustic, Low Temperature (or low energy) Extraction (LTE) process replacing the CHWE process to improve the thermal efficiency and to reduce the environmental impact of oil sands plants (Burns et al, 1998; Jawrazi 1990). The LTE process was implemented at two commercial plants which produced tailings with improved settling characteristics; however it attained lower than expected extraction efficiency. To boost the extraction efficiency the LTE process has been modified to some version of the CHWE process by increasing both temperature and pH.

The oil sands industry has also investigated solutions for the MFT production problem. As a result, production of Composite (or Consolidated) Tailings (CT), as depicted in Figure 2, was developed at the University of Alberta and implemented commercially at two commercial oil sands plants (Caughill et al. 1993). Production of CT requires sufficiently high solids contents, which is accomplished by the use of cyclones separating the whole tailings into Cyclone Underflow composed of high solids contents and low fines content (>55% solids and <7% fines) and Cyclone Overflow composed of low solids content tailings with a high fines content (<30% solids and >50% fines). A nonsegregating CT mixture is produced by blending Cyclone Underflow and existing MFT, usually at a sand-fines ratios (SFR) of 4 to 5, with the addition of gypsum (CaSO₄) as a coagulant additive to prevent segregation.

Although CT production technology can accelerate tailings densification and reclamation, the continuous accumulation of Ca^{2+} and SO_4^{2-} ions in the recycle water detrimentally affects bitumen extraction efficiency. The chemistry of process affected water after implementation of CT production technology is being monitored (Allan 2008a, 2008b; MacKinnon, 2001). The overall tailings balance shows that implementation of the CT production process doesn't significantly reduce the MFT inventory since additional MFT is produced from the Cyclone Overflow effluent. Also, the CT process doesn't improve the thermal energy efficiency of the oil sands plants because of the discharge of warm Cyclone Overflow into the tailings pond. Furthermore, CT production may cause H_2S emissions from the tailings ponds by anaerobic reduction of SO_4^{2-} by the residual bitumen in the tailings (Redfield et al, 2003; Salloum et al, 2002).

The conclusion of the above review is that neither the LTE nor the CT production processes are the solutions for

the release water salinity and the accumulation of the MFT problems. Development of novel bitumen extraction and tailings disposal processes are needed to address these problems.

2 ALTERNATIVE BITUMEN EXTRACTION AND TAILINGS DISPOSAL PROCESSES

Bitumen extraction involves disintegration of the oil sands ore matrix into an ore-water slurry followed by the liberation/mobilization and aeration of bitumen. This process results in the recovery of bitumen in the form of a froth composed of about 60% bitumen, 30% water and 10% solids by mass. Ore characteristics, extraction temperature, hydrodynamics and process water chemistry are the major factors affecting the performance of the extraction process (Masliyah et al. 2004; Kasperski, 2001). Reduction of the surface and bitumen-water interfacial tensions increases the bitumen recovery efficiency by promoting disintegration of the oil sands ore structure, detachment of bitumen from the sand and attachment of bitumen to air bubbles.

Process water chemistry is controlled by the ore characteristics as well as by the additives used in the extraction and tailings disposal processes. Process water chemistry plays the key role in altering surface and interfacial tensions; therefore, process water chemistry controls efficiency of bitumen extraction and the geotechnical characteristics of the tailings. Therefore, existing water salinity and MFT production problems could be ameliorated by controlling the release water chemistry while modifying the extraction and tailings disposal processes.

2.1 Bitumen Extraction Using *CaO* and *O*₃

Existing MFT production and water salinity problems predominately evolve from the use of *NaOH* as an additive in the extraction process; the resolution of which would be possible if novel extraction process additives could be found to replace *NaOH*.

The purpose of the present research study was to investigate alternative chemicals to adjust the pH of the ore-water slurry, produce additional surfactants from bitumen asphaltenes in oil sands ore-water slurry and use surfactants from external sources. Constraints for our research to find these alternatives are that the process has to be simple, cost effective and environmentally friendly. All extraction experiments were performed using the Denver D-12 Flotation Cell apparatus. The bitumen, water, and solids contents of all samples were determined using the Dean-Stark extraction process.

Based on the results of laboratory scale bitumen extraction tests we are proposing alternatives to the CHWE process by adjusting the *pH* of the ore-water slurry with *CaO* (lime) replacing *NaOH*. Then treating the orewater slurry with O_3 (ozone) to produce additional surfactants by in-situ oxidation of bitumen asphaltenes or by addition of biodiesel (*BD*), such as fatty acids methyl esters, as a surfactant from external sources (Babadagli et al, 2008; Ozum and Scott, 2009; Babadagli and Ozum, 2010). When *CaO* is added into an ore-water slurry it forms $Ca(OH)_2$, which increases the *pH* of the ore-water slurry and participates in the following major reactions:

$$Ca, Mg(HCO_3)_2 + Ca(OH)_2 \leftrightarrow 2Ca, MgCO_3 + 2H_20$$
[1]

$$2Clay - Na + Ca(OH)_2 \leftrightarrow (Clay)_2 Ca + 2NaOH$$
[2]

which reduce Ca^{2+} concentration in the release water and produces tailings with flocculated clay particles. The ion exchange reaction between the clay and Ca^{2+} as described in Equation [2] results in the reduction of Ca^{2+} in the slurry and produces tailings with limited clay dispersion, therefore, with improved settling and consolidation properties.

Long term effects of the use of CaO as an extraction process aid was tested by recycling the release water five times (described by LC#1 to LC#5) and adding CaO at a dosage of 150 mg-CaO/kg-ore in each cycle. Extraction tests were performed in each cycle at 50 °C temperature. In these tests, after each extraction test cycle was completed, about 1.2 L of release water was diverted to our laboratory; 300 mL of which was used for the water chemistry analysis and the remaining 900 mL was used for three additional extraction tests; one test without any additive and two tests using additional CaO at a dosage of 60 mg-CaO/kg-ore. Oil sands ore used in these tests was a normal grade ore with 9.8% bitumen, 4.6% water, 85.1% solids (14.2% which was fines, $<45 \mu m$). Extraction test results and corresponding water chemistry data are presented in Tables 1 and 2.

Data presented in Tables 1 and 2 suggest that addition of *CaO* as a *pH* adjusting chemical in the extraction process doesn't increase the Ca^{2+} concentration in the release water. Therefore, it doesn't produce release water which could harm the extraction process efficiency. The ion exchange reaction expressed in Equation 2 causes flocculation of clay size particles. The tailings produced with *CaO* addition as an extraction process aid, therefore, would have improved settling and consolidation properties which would reduce the production of MFT.

Bitumen asphaltenes could be oxidized to surfactants using suitable oxidants (Moschopedis and Speight, 1975). Oxidation of bitumen asphaltenes promotes the hydrophilic characteristic of bitumen by newly formed - C=O (ketone) and -COOH (carboxyl) functional groups; which results in the reduction of the bitumen-water interfacial tension. Therefore, it should be expected that controlled oxidation of bitumen asphaltenes would promote bitumen extraction efficiency.

We have investigated the effect of oxidation of bitumen asphaltenes with O_3 on bitumen extraction efficiency and release water chemistry. Oxidation reactions of O_3 in aqueous environments are carried out by direct oxidation with relatively slow reaction kinetics as well as by the formation of highly reactive OH^* and HO_2^* radicals with relatively fast chemical kinetics (Hoigne, 1988). The *pH* of the aqueous environment, as expected, also influences the reactivity of these radicals; an increase in *pH* results in an increase of radical reactions. Therefore, the use of O_3 as an oxidant to produce surfactants from bitumen asphaltenes would work better if the ore-water slurry is firstly treated with *CaO*.

The effects of O_3 on bitumen extraction efficiency and release water chemistry are presented in Tables 3 and 4. In these tests low grade ore with 7.7 % bitumen, 9.7 % moisture, 82.4 % solids and 27.7 % fines (<45 µm fraction of the solids) contents and an ore considered as normal to low grade with 8.1 % bitumen, 6.6 % moisture, 84.8 % solids and 17.3 % fines (all by mass) contents are used. The low grade ore used in these tests had a high fines content, which therefore could be considered as a problematic type ore. The data presented in Tables 3 and 4 suggest that the use of O_3 as an extraction process aid at less than 100 mg/kg-ore dosages, after conditioning the ore-water slurry with *CaO*, could promote bitumen extraction efficiency without harming release water chemistry.

The effect of the use of O_3 in the extraction process on the fuel quality of bitumen was also tested by measuring the TAN (total acid number, mg KOH/g-bitumen) of different bitumen samples which are presented in Table 5. Data presented in Table 5 suggest that alkalinity provided by the use of *CaO* reduces the TAN of the produced bitumen.

The solubility of *CaO* and *O*₃ in water increases as the temperature decreases; therefore, most of our laboratory scale extraction tests using *CaO* and *O*₃ as extraction process additives were performed at 40 °C slurry temperature and at about 5 °C *O*₃ temperature (i.e. air containing <0.3 % by mass *O*₃ was injecting into the orewater slurry). These solubility properties of *CaO* and *O*₃ as a function of temperature could result in the reduction of extraction temperatures to 35 to 40 °C.

2.2 Bitumen Extraction Using CaO and BD (Biodiesel)

Performance of BD (biodiesel) as a surfactant additive in ore-water slurry based extraction systems was also tested. Most of these tests were performed using BD derived from canola oil and tall oil fatty acids; i.e. canola and tall oil fatty acids methyl esters; the chemical formula of which are C_nH_m -COOCH₃ (m<2n+1). Tall oil is a byproduct of the pulp & paper mills using the bleached Kraft As seen from the chemical formula, BD has process. both hydrophobic hydrocarbon $C_n H_m$ and hydrophilic ester -COOCH₃ functional groups which promote the attachment of BD to both bitumen and water. Wetting properties of the process water and BD on bitumen and spread of BD and tall oil fatty acids in water are depicted in Figure 3 and Figure 4. Photographic images show that BD-bitumen interfacial tension is smaller than waterbitumen interfacial tension ($\gamma_{BD/B} < \gamma_{W/B}$) and BD-water interfacial tension is smaller than tall oil fatty acid (TOFA)water interfacial tension ($\gamma_{BDW} < \gamma_{TOFAW}$). Because of these surface tension properties, the use of BD as a surfactant additive in steam assisted thermal in-situ bitumen recovery processes was also investigated (Babadagli and Ozum, 2010).

Experimental data on the performance of *BD* as a surfactant additive and on the release water chemistry are presented in Table 6 and Table 7 respectively. Data presented in Table 6 are typical for the performance of

surfactants. As seen in Table 6, addition of *BD* beyond a critical dosage doesn't increase bitumen extraction efficiency. Data presented in Table 7 show that the use of *BD* as a surfactant additive in ore-water slurry based extraction systems doesn't have any significant impact on the release water chemistry. Visual inspection of the tailings produced from the extraction tests using BD as a surfactant additive suggests that the tailings would have acceptable settling and consolidation properties which would result in reduction of MFT production.

3 PRODUCTION OF NONSEGREGATING TAILINGS

For the disposal of oil sands tailings we have investigated production of NST (nonsegregating tailings) from the blend of course cyclone underflow, fine thickener underflow (i.e. thickened cyclone overflow) and optionally fine MFT; which could be an alternative to the conventional CT process. We recommend using *CaO* or *CaO* and *CO*₂ as additives to prevent segregation, instead of *CaSO*₄, which also improves the release water chemistry simultaneously (Ozum and Scott, 2009).

The geotechnical properties of oil sands tailings are controlled by the ore characteristics as well as by the additives used in the extraction process. Conditions favouring dispersion of clay in the extraction process promotes bitumen extraction efficiency; however, it produces tailings with poor settling and consolidation properties. Hydrometer-Sieve tests were performed on middling tailings using two different methods: (i) following ASTM Designation: D422-63 (Reapproved 1998) and Designation: D4221-99 by using sodium ASTM hexametaphosphate ((NaPO₃)₆) as dispersant; and, (ii) without using any dispersant. . Hydrometer-Sieve Test results using these two methods were almost similar for the middling tailings produced with the CHWE process; which indicates that the extent of clay dispersion caused by the process is considerably high. Hydrometer-Sieve test results on a typical middling tailings, produced at a commercial plant operating with a non-additive extraction process, are presented in Figure 5 which shows that the non-additive extraction process produces middling tailings with less clay dispersion. Hydrometer-Sieve test data support the relations between the extent of clay dispersion and extraction efficiency as well as with the poor settling and consolidation characteristics of the tailings.

As previously discussed, the modification of the bitumen extraction process to reduce clay dispersion would result in a major reduction in the production of MFT compared to the existing MFT output. Regardless of the extraction process being used, oil sands tailings must have acceptable settling, consolidation and nonsegregating properties for their safe disposal. Generally, oil sands tailings has to be cycloned or centrifuged with a chemical additive to improve its geotechnical properties without harming the release water chemistry and environment.

We have tested the performance of *CaO* (lime) as an additive to prevent segregation, i.e. to produce a nonsegregating tailings product (Scott et al, 2007). A segregation boundary line for a *CaO* additive was established and plotted along the segregation lines for

other additives as depicted in Figure 6. As can be deduced from Figure 6, there are three options to produce a nonsegregating tailings if the whole tailings stream composition is not suitable to produce a nonsegregating tailings stream:

(i) increase the solids content, preferably using cyclones and thickening the cyclone overflow to above 40% solids content using high performance thickeners, as depicted in Figure 6.

(ii) increase the fines content; which is not practical beyond a critical fines content due to the reduction in permeability and water dewatering rate; and,

(iii) use additives such as *CaO* to prevent segregation.

Laboratory scale tests showed that *CaO* addition as low as 0.6 kg-*CaO*/m³-NST would be sufficient to prevent segregation; however, higher dosages around 0.8 kg-*CaO*/m³-NST could be needed for high fines NST mixtures. Excess amounts of *CaO* would not cause any harm; it could be utilized to reduce bicarbonate hardness of the make-up water with the chemical reaction expressed in Equation [1]. Also, atmospheric *CO*₂ would consume excess *Ca(OH)*₂ which would precipitate in the form of *CaCO*₃ by the following reaction:

$$Ca(OH)_2 + CO_2 \leftrightarrow CaCO_3 + H_2O$$
[3]

The use of *CaO* as an additive to produce NST; therefore, reduces Ca^{2+} and Mg^{2+} concentrations in the release water to be recycled to the extraction process. The reduction in Mg^{2+} concentration is due to the coprecipitation with calcium carbonate minerals and at a higher pH (pH>10.5) by the precipitation of Brucite ($Mg(OH)_2$) (Donahue at al, 2008).

Similar to CT production, a NST mix could be prepared from the blend of cyclone underflow, thickener underflow and existing MFT, as depicted in Figure 7. Addition of MFT into NST mix would be optional depending on the desired sand to fines ratio (SFR). The advantage of using CaO or CaO & CO₂ as additives is that settling, consolidation and nonsegregating properties of the NST mix are improved and the salinity of the release water in terms of Ca^{2+} , Mg^{2+} and Na^{+} concentrations are reduced simultaneously. The simultaneous use of CaO as an additive for both the bitumen extraction and NST production processes would provide an additional advantage since the tailings to be handled would have different characteristics. Our visual observations suggest that the settling, consolidation and nonsegregating properties of the tailings would be improved by using CaO and O₃, or CaO and BD as extraction process additives.

4 CONCLUSIONS

Bitumen extraction efficiency, geotechnical properties of the oil sands tailings and salinity of the release water are appreciably influenced by the extraction process aids. The use of caustic *NaOH* as an additive in the CHWE process promotes bitumen extraction efficiency; however, it is the source of existing MFT production and water salinity problems at the oil sands plants. As alternatives to *NaOH* additive in the CHWE process, we have investigated potential use of *CaO* and *O*₃, or *CaO* and *BD* as additives to maintain high bitumen extraction efficiency, reduce or eliminate production of MFT and decrease the release water salinity simultaneously. It is proposed that production of mature fine tailings would be reduced or eliminated by the post processing of the tailings discharged from the extraction process using *CaO* or *CaO* and *CO*₂ as additives as well as implementing novel extraction processes using *CaO* and O₃, or *CaO* and BD. Use of *CaO* as additives in both extraction and NST production of NST from the tailings produced by using *CaO*, *O*₃ and *BD* as extraction process additives has to be studied at a larger scale.

ACKNOWLEDGEMENTS

Funding provided by the Alberta Energy Research Institute and the Industrial Research Assistance Program-National Research Council are appreciated. NST production work was partially sponsored by Shell Energy Canada and Canadian Natural Resources Limited.

REFERENCES

- Allan, E.W. 2008a. Process water treatment in Canada's oil sands industry: Part I. Target pollutants and treatment objectives, J. Environ. Eng. Sci. 7, 123-138.
- Allan, E.W. 2008b. Process water treatment in Canada's oil sands industry: Part II. A review of emerging technologies, *J. Environ. Eng. Sci. 7, 499-524.*
- Babadagli, T., Burkus, T., Moschopedis, S.E. and B. Ozum. 2008. Bitumen Extraction from Oil Sands Ore-Water Slurry Using CaO (Lime) and/or Ozone, SPE 117677, SPE/PS/CHOA International Thermal Operations and Heavy Oil Symposium, October 20-23, Calgary, Alberta, Canada.
- Babadagli, T. and Ozum, B. 2010. Biodiesel as Surfactant Additive in Steam Assisted Recovery of Heavy-Oil and Bitumen, *SPE 133376, SPE Western Regional Meeting*, May 27-29, Anaheim, California, USA.
- Burns, R., Tipman, R., Firmin, K. Mikula, R.J., Munoz, V.A., Kasperski, K.L. and Omotoso, O.E. 1998. Bitumen Release Mechanisms and New Process Development, Seventh UNITAR International Conference on Heavy Crude and Tar Sands, Paper No. 1998.226, October 27-30, 1998, Beijing, China.
- Caughill, D.L., Morgenstern, N.R., and Scott, J.D. 1993. Geotechnics of Nonsegregating Oil Sand Tailings, *Canadian Geotechnical Journal, 30: 801-811.*
- Clark, K.A. 1939. The Hot Water Method for Recovering Bitumen from Bituminous Sand, *Report on Sullivan Concentrator, Alberta Research Council*, Alberta Canada.
- Clark, K.A. and Pasternack, D.S. 1932. Hot Water Separation of Bituminous Sand, *Ind. Eng. Chem. 24,* 1410.
- Donahue, R. Jeeravipoolvarn, S., Scott, J.D. and Ozum, B. 2008. Properties of Nonsegregating Tailings Produced from the Aurora Oil Sands Mine Tailings", *Proceedings, First International Oil Sands Tailings*

Conference, pp. 143-152, December 7-10, Edmonton, Alberta, Canada.

- Hoigne, J. 1988. The Chemistry of Ozone in Water,
- Process Technologies for Water Treatment, Edited by S. Stucki, Plenum Publication Corporation.
- Jawrazi, W. 1990. Dredging and Cold Water Extraction Process for Oil Sands, *Proceedings of AOSTRA Oil Sands 2000 Conference, March 26-28, 1990, Section 2, Paper No. 4*, Edmonton, Alberta, Canada.
- Kasperski, K.L. 2001. Review of Research on Aqueous Extraction of Bitumen from Mined Oil Sands, *Natural Resources Canada, Western Research Centre, Division Report May 2001, CWRC 01-17.*
- MacKinnon, M. and Sethi, A. 1993. A comparison of the physical and chemical properties of the Tailings ponds at the Syncrude and Suncor oil sands plants, *Proceedings of Fine Tailings Symposium, Oil Sands-Our Petroleum Future Conference,* April 4-7, Edmonton, Alberta, Canada.
- MacKinnon, M. 2001. Process Affected Waters: Impact of Operating Factors On Recycle Water Quality, *CONRAD Extraction Fundamentals and Process Water Workshop*, May 7-8, Fort McMurray, Alberta, Canada.
- Masliyah, J., Zhou, Z., Xu, Z, Czarnecki, J. and Hamza, H. 2004. Understanding Water-Based Bitumen Extraction from Athabasca Oil Sands, *Can. J. Chem. Eng.*, *82*, 628-654.
- Moschopedis, S.E. and Speight, J.G. 1975. Oxidation of a bitumen, *Fuel*, *54*(*3*), *210-212*.
- Moschopedis, S.E., Schulz, K.F., Speight, J.G. and Morrison, D.N. 1980. Surface-Active Materials from Athabasca Oil Sands, *Fuel Processing Technology, 3:* 55-61.
- Moschopedis, S.E., Fryer, J.F. and Speight, J.G. 1977. Water-soluble constituents of Athabasca bitumen, *Fuel, 56: 109-110.*
- Ozum, B. and Scott, J.D. 2009. Reduction of Oil Sands Fine Tailings, *Tailings and Mine Waste 2009 Conference*, November 1-4, Banff, Alberta, Canada.
- Redfield, E., Croser, C, Zwiazek, J.J., MacKinnon, M.D. and Qualizza, C. 2003. Responses of Red-Osier Dogwood to Oil Sands Tailings Treated with Gypsum and Alum, *J. Environ. Qual. 32:1008-1014.*
- Salloum, M.J., Dudas, M.J. and Fedorak, P.M. 2002. Microbial reduction of amended sulfate in anaerobic mature fine tailings from oil sand, *Waste Management* & Research, 20(2), 162-171
- Scott, J.D., Donahue, R., Blum, J.G. Paradis, T. G., Komishke, B. and Ozum, B. 2007. Production of Nonsegregating Tailings with CaO or CaO and CO₂ for Improved Recycle Water Quality, *CONRAD's Water Usage Workshop*, November 21 & 22, Calgary, Alberta, Canada.
- Scott, J.D. and Ozum, B. 2010. Oil Sands Tailings: What Needs to be Done. *Mining.com Magazine*, *September*.

	Froth	Bitumen	Bitumen	Bitumen	Water	Solids
CaO	Yield	Yield	Recovery	in Froth	in Froth	in Froth
(mg/kg-ore)	(g)	(g)	(%)	(%)	(%)	(%)
LC#1						
0	125.4	27.1	92.3	21.6	34.1	45.4
60	128.7	27.8	94.8	21.6	34.9	42.7
60	131.5	28.3	96.4	21.5	35.0	41.7
LC #2						
0	128.6	27.7	94.6	21.6	31.7	45.5
60	138.6	28.1	95.7	20.2	33.6	44.7
60	136.5	28.2	96.2	20.7	33.5	44.5
LC#2-A						
0	142.8	26.6	92.7	18.6	30.3	46.5
60	138.5	28.3	96.7	20.5	33.9	44.3
60	149.7	27.8	95.2	18.6	34.7	45.6
LC#3						
0	139.0	28.3	96.5	20.3	33.5	45.1
60	143.0	27.3	93.1	19.1	34.5	44.9
60	151.1	29.2	99.7	19.3	32.9	46.4
LC#4						
0	143.2	27.1	92.9	18.9	35.7	45.2
60	135.1	28.2	96.2	20.9	34.0	44.0
60	128.1	27.3	93.3	21.3	35.9	41.0
LC#5						
0	138.2	27.8	94.8	20.1	34.4	43.6
60	143.1	28.1	95.9	19.7	31.7	47.5
60	144.3	27.8	95.0	19.3	33.7	45.9

 Table 1. Long term affect of CaO addition on bitumen recovery efficiency.

 Table 2. Long term effect of CaO addition on release water chemistry.

CaO		Conduc.	Alkalinity (mg CaCO3/L)				Cations	Anions		
mg/kg Ore	pН	(mS)	Total	CO3 ⁼	HCO3	Na+	Mg2+	Ca2+	CI-	SO₄ ⁼
LC#1	8.2	1.492	307	0	307	441	8	8	171	158
Blank	8.3	1.372	230	0	230	340	9	8	165	174
60	8.5	1.412	233	6	227	338	10	10	174	184
60	8.5	1.44	247	6	241	338	10	10	176	185
LC#2	8.1	1.462	225	0	225	373	9	10	177	220
Blank	7.7	1.319	156	0	156	308	10	9	164	218
60	7.8	1.393	169	0	169	322	12	13	174	231
60	7.9	1.388	170	0	170	326	12	13	172	229
LC#2-A	7.9	1.527	230	0	230	401	9	10	174	213
Blank	7.8	1.406	152	0	152	300	12	11	175	243
60	7.9	1.479	171	0	171	335	13	13	176	250
60	7.9	1.474	171	0	171	312	13	13	181	252
LC#3	7.7	1.479	176	0	176	354	9	12	180	254
Blank	7.8	1.404	115	0	115	297	13	12	176	275
60	8.1	1.484	133	0	133	310	14	15	184	290
60	8	1.487	136	0	136	314	14	15	184	289
LC#4	7.4	1.516	155	0	155	352	12	15	187	277
Blank	7.9	1.516	103	0	103	313	16	15	192	321
60	8.1	1.523	118	0	118	334	16	14	184	311
60	8.1	1.525	119	0	119	309	17	17	191	320
LC#5	7.5	1.53	137	0	137	358	13	15	187	293
Blank	7.8	1.533	93	0	93	316	18	15	196	343
60	7.8	1.544	109	0	109	303	19	18	195	339
60	7.8	1.529	111	0	111	330	18	18	187	324

Table 3. Extraction data using CaO and O₃ at 40 $^{\circ}$ C.

			Froth	Bitumen	Bitumen	Bitumen	Solids
Ore	CaO	03	Yield	Yield	Recovery	in Froth	in froth %
Туре	(mg/kg ore)	(mg/kg ore)	(g)	(g)	(%)	(%)	(%)
Low	150	-	102.6	12.4	53.6	12	43.1
Low	150	-	107.6	13.1	56.7	12.1	40.5
Low	150	38.4	109.2	14.6	63.5	13.4	39.3
Low	150	37.6	111.4	14.3	61.9	12.8	39.4
Normal/Low	150	40.8	125.6	13.5	55.3	10.8	52.1
Normal/Low	150	41.6	123.8	13.8	56.4	11.1	52.2
Normal/Low	150	-	120.7	13.0	53.1	10.7	53.3
Normal/Low	150	-	122.2	13.3	54.3	10.9	52.6
Normal/Low	-	-	117.8	12.8	52.2	10.8	50.3
Normal/Low	-	-	123.3	12.6	51.5	10.2	53.1

Table 4. Water chemistry corresponding to Table 3

Ore-Water	CaO	03		Conduc.	Alkalir	Alkalinity (mg CaCO3/L) Cations (mg/L)					Anions (mg/L)		
Туре	(mg/kgOre)	(mg/kg ore)	рH	(mS)	Total	HCO3	Na	K	Mg	Ca	CI	S04	
RPW(*)			8.5	1.555	412	400	361	18	8	7	168	88	
Low	150		8.5	1.482	297	287	356	21	11	13	165	173	
Low	150		8.6	1.500	301	291	353	22	12	14	170	176	
Low	150	38.4	8.5	1.520	266	260	361	21	11	13	168	186	
Low	150	37.6	8.5	1.509	274	268	361	22	11	13	168	176	
Normal/Low	150	40.8	8.1	1.651	218	218	354	27	22	26	170	335	
Normal/Low	150	41.6	8.1	1.653	226	226	355	27	21	25	173	324	
Normal/Low	150		7.7	1.649	262	262	359	27	21	25	173	304	
Normal/Low	150		8.1	1.668	257	257	362	27	22	26	174	317	
Normal/Low	-		8.0	1.651	250	250	362	27	21	24	174	313	
Normal/Low	-		8.0	1.622	250	250	354	27	20	23	172	299	

(*) Row Process Water

Table 5. Bitumen TAN by using CaO and O_3 additives.

Sample	Sample	Average TAN				
ID	Treatment	mg KOH/g Bitumen				
ARC1107-Ore-2	Bitumen from Ore	3.52				
ARC1107-25	80 ppm CaO+O ₃	3.03				
ARC1107-27	80 ppm CaO	3.15				
ARC1107-29	03	2.96				
ARC1107-31	Blank (No Additive)	3.13				

ppm: mg additive/kg-ore

	Bitumen	Bitumen
BD	Recovery	Recovery (*)
(mg/kg ore)	(%)	(%)
-	72.5	72.5
-	74.6	74.6
433	81.7	81.4
433	81.9	81.2
867	83.6	82.5
867	81.8	80.8
1667	80.7	78.7
1667	84.3	82.3
3333	84.4	80.3
3333	83.1	79.0

Table 6. Bitumen extraction using BD as a surfactant additive.

(*) Corrections are made for the amount of used BD

Table 7. Water chemistry corresponding to Table 6.

		Conduc.	Alkalinity (mg CaCO3/L)			Cat	ions (mg	Anions (mg/L)			
Treatment	pН	(mS)	Total	CO3	HCO3	Na	K	Mg	Ca	Cl	SOx
APW (*)	8.6	1.327	392	16	376	269	23	11	12	187	24
-	8.6	1.342	278	10	268	369	22	11	17	170	120
-	8.6	1.373	283	10	273	356	23	11	17	180	125
433	8.5	1.397	295	8	298	363	24	11	19	182	123
433	8.6	1.405	290	8	282	336	26	11	20	189	128
867	8.5	1.374	291	8	283	353	23	11	19	176	123
867	8.5	1.417	298	8	290	367	25	12	17	183	126
1667	8.6	1.345	270	10	260	353	22	11	17	171	132
1667	8.6	1.385	277	10	267	335	24	11	16	185	132
3333	8.5	1.356	291	8	283	338	22	12	20	174	121
3333	8.5	1.401	298	8	290	354	23	11	18	183	126

(*) Artificial Proces Water



Figure 2. Production of Composite Tailings (CT).



water on bitumen

BD on bitumen

Figure 3. Wetting of water and BD on bitumen.





$\gamma_{BD} \pi < \gamma_{TOF4} \pi$

Figure 4. Spread of BD and tall oil fatty acids in water.



Figure 1. CHWE process schematics.



Figure 5. Dispersed and nondispersed PSD.



Figure 6. Segregation boundary diagram.



Figure 7. Production of nonsegregating tailings (NST).