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# Waste Processing and Recycling in Mining and Metallurgical Industries

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## Treatment of oily sludge from Athabasca tailings pond by oil phase agglomeration\*

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### ABSTRACT

The hot water process used by Suncor and Syncrude to extract bitumen from the Athabasca oil sands produces tailings with about 35% more volume than that occupied by the bituminous sands before mining. This increase is largely the result of water hold-up in the fines fraction from the tailings, arising primarily from the 'middlings' treatment circuit. In our previous work, we have demonstrated that when sludge is treated by oil phase agglomeration to separate free hydrocarbons and hydrophobic solids, its structure can be broken and its settling characteristics markedly altered. The treatment involves the use of a mixer with contra-rotating blades coated with vacuum still bottoms as the collector phase. Conditioning agents may be used to enhance the separation process. After treatment the bulk of the solids then settle out as a dense sediment, leaving a dilute suspension of ultra-fine particles comprising about 20% of the original sludge solids.

\* "This work was performed under the Sludge Fundamentals Consortium Agreement"- Participants: Alberta Energy, Alberta Oil Sands Technology and Research Authority, Alberta Research Council, Environment Canada, Energy Mines and Resources (CANMET), the National Research Council, Suncor Inc., and Syncrude Canada Ltd. Issued as NRCC No. 32963

## INTRODUCTION

The two commercial oil sands surface mining plants in Alberta use the Hot Water process for bitumen extraction and as a result generate large quantities of fine tails, (1-3). The fine-grained, sludge component of this waste is the most troublesome because of its stability and poor compaction potential. These sludges have a gel-like consistency and contain about 75 w/w% water. At the present time the sludges are impounded behind sand dykes. Long term economical and environmentally acceptable operation of the Hot Water Process ideally depends on being able to reduce the tailings volume. Therefore, the reduction of the water content of fine tails is of critical interest.

In our previous work, we have demonstrated that techniques such as liquid-phase agglomeration (oil phase agglomeration) can be used to remove selectively a hydrophobic component from a generally water wet system, (4-6). The approach involves the application of oil phase agglomeration (liquid-liquid transfer), using a mixer with contra-rotating blades and with vacuum still bottoms as the collector phase. Treatment of the sludge to separate free hydrocarbons and hydrophobic solids, resulted in markedly different settling behaviour. In this investigation a number of experiments were carried out to study the settling behaviour of sludge after various levels of treatment. X-ray diffraction, carbon, aluminium and iron analyses were carried out on the different solid fractions separated from the treated sludge.

## EXPERIMENTAL METHODS

**Sample description.** Aqueous sludge from the 17m level of the Syncrude tailings pond was pumped into 200 L plastic drums, (7). Each drum was inverted five times (with a barrel tipper) before being divided among a number of 5 L plastic jugs, which were then stored in a cooler at  $\approx 10^{\circ}\text{C}$ . The results presented in this report were obtained on these sub-samples, provided courtesy of R. Schutte of Syncrude Canada Ltd. Before further sub-sampling, each jug was shaken vigorously by hand to ensure thorough mixing. The physicochemical properties of sludge, provided by Syncrude are presented in Table 1, (8).

Table 1. Physicochemical properties of Syncrude Sludge

Property	Value
pH at $17.8 \pm 0.5^{\circ}\text{C}$	$7.83 \pm 0.03$
Conductivity (ms/cm)	$1.6 \pm 0.01$
Total Solids [Gravity], wt. %	$26.6 \pm 0.1$
Bitumen [OWS], wt. %	$0.9 \pm 0.05$ ( $1.1 \pm 0.2$ )
Solids [OWS], wt. %	$25.6 \pm 0.1$ ( $26.5 \pm 0.9$ )
Density (calculated), g/ml	1.19
Solids, $< 44\mu$ (%)	$99.2 \pm 1.0$
Solids, $< 22\mu$ (%)	$94.9 \pm 1.9$
Solids, $< 11\mu$ (%)	$83.7 \pm 2.1$

Values in parenthesis were determined at NRC.

**Recovery of Bitumen and Oil Phase Solids (OPS).** A stirring device, with a set of contra-rotating blades (grease kettle), was used to separate free and emulsified bitumen from the sludge, (3). A known amount of reduced still bottoms (obtained from Esso Research Ltd.) diluted with 5 parts Stoddard solvent was applied to the stirring vanes of the mixer to act as the collector phase for the hydrophobic solids and bitumen. The following reagents were used to adjust sludge pH in different tests: Sodium silicate, sodium hydroxide, potassium hydroxide, sulphuric acid, sodium pyrophosphate, a mixture of sodium hydroxide and sodium pyrophosphate and the disodium salt of 4,5-dihydroxy-1,3-benzene-disulphonic acid (tiron).

At the end of the mixing period the collector oil, and associated solids, were separated from the remaining suspension. For experiments using sodium silicate the oil phase, obtained after sludge treatment, was washed several times with 0.01 % sodium silicate solution to remove occluded, normally water dispersible solids. After washing, the collector oil was removed from the grease kettle by dissolving it in toluene. This solution was then transferred to a soxhlet extractor to separate the collected solids from

the oil phase. Toluene was evaporated from the collector oil by means of a Brinkman Rotovaporator at 80°C under reduced pressure. The recovery of bitumen was estimated from the difference between the original and final weights of the collector oil and the estimated amount of bitumen present in the original sludge sample. After bitumen and toluene removal, a hydrophobic, dark powder remained; this material has been described previously as oil phase solids (OPS), (8).

**Gravity Sedimentation Measurements.** Cleaned aqueous sludge samples were transferred to 500 ml graduated glass cylinders. The suspensions obtained during washing of the oil phase after sludge treatment were centrifuged and the settled solids added back to the sludge in the cylinders. Evaporation losses, occurring during agitation in the grease kettle, were replaced with the supernatant obtained from centrifugation of the wash liquor. Hence, sludge dilution or concentration effects were avoided. The cylinders were sealed with parafilm in order to prevent losses due to evaporation during the prolonged settling tests.

Gravity settling was followed for periods up to 90 days. The treated sludges separated into layers; the height of the each interface (in ml) was recorded along with the elapsed time. At the end of each test the layers were carefully separated, weighed and then dried at  $100 \pm 10^\circ\text{C}$  in order to determine their solid contents.

**Elemental Analyses.** A Leco CR12 carbon analyzer was used to determine the organic carbon content of the solids fractions, obtained from the settled sludge, after decomposing carbonate carbon using dilute HCl. Sulphur was analyzed as total sulphur using X-ray fluorescence spectroscopy. Metals were determined by a quantitative, Inductively Coupled Plasma Atomic Emission Spectroscopic method (ICP-AES).

**Mineral Composition.** Mineral (crystalline) composition of the samples was determined semiquantitatively by comparing their X-ray diffraction (XRD) peak intensities with those of standards. XRD patterns were recorded using a SCINTAG PAD V automated powder diffractometer equipped with a graphite monochromator using  $\text{CoK}\alpha$  radiation ( $\lambda = 1.7902\text{\AA}$ ). The amount of each of the minerals in the samples was estimated by multiplying the peak intensity of the characteristic reflection for the respective mineral by the intensity factor for that mineral as determined from XRD data for a set of standard mixtures. The standards were measured under identical experimental conditions, including sample preparation, radiation source and diffraction geometry. The amount of poorly crystalline components (X-ray amorphous) was expressed by the difference of 100 and the percentage of crystalline components. Results from this technique become unreliable for finer particles owing to peak broadening.

## RESULTS AND DISCUSSION

A number of experiments were carried out under different conditions to test the efficiency of bitumen and OPS removal from Syncrude sludge pond samples. The main variables investigated included: pH, conditioning agents, amount of collector oil and the agitation time.

The effect of the amount of collector oil on the recovery of bitumen and OPS is demonstrated on Figure 1. In these tests the pH and agitation times were kept constant. There is a good first order correlation between the amount of collector oil used and the recovery of bitumen; the correlation coefficient for the least squares fit was found to be 0.98. The data for OPS is best represented by a third order fit. Figure 2, plots bitumen recovery against the amount of IOC (Insoluble Organic Carbon) collected, using a second order fit. IOC is a more realistic measure of the recovery of OPS in view of the fact that some solids with little or no associated organic material might be collected along with the OPS fraction. The amount of OPS collected with the greatest amount of collector oil used (7.7 g/ 100 g of sludge) was taken as the value for the total amount of OPS present in sludge. The results suggest that the two components (bitumen and OPS) are not separated at the same efficiency over the entire range of conditions, most likely owing to the fact that the OPS are a mixture of solids with different degrees of hydrophobicity.

**OPS/Bitumen Ratio.** This ratio is a measure of the selectivity of the collector oil towards the OPS and bitumen components. The OPS/Bitumen ratio has been plotted in Figure 3. The data is best represented by

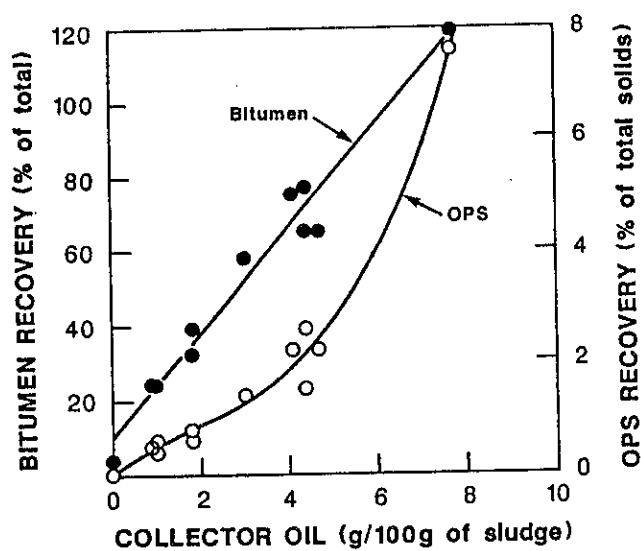


Fig.1 Effect of the amount of collector oil on the recovery of bitumen and OPS at pH 10 adjusted with sodium silicate

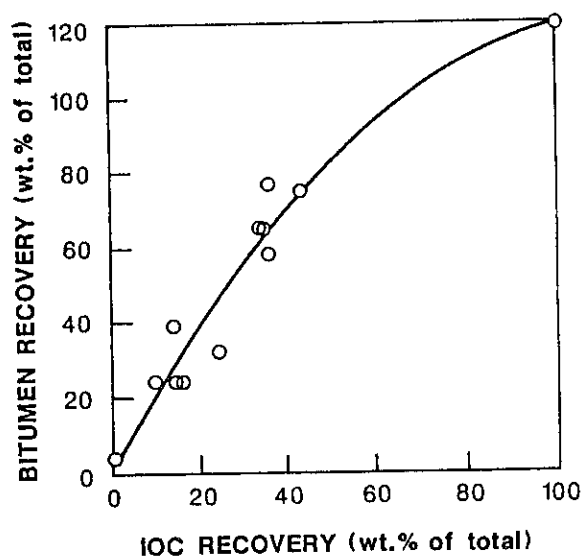


Fig. 2 Correlation between the recovery of bitumen and IOC (OPS)

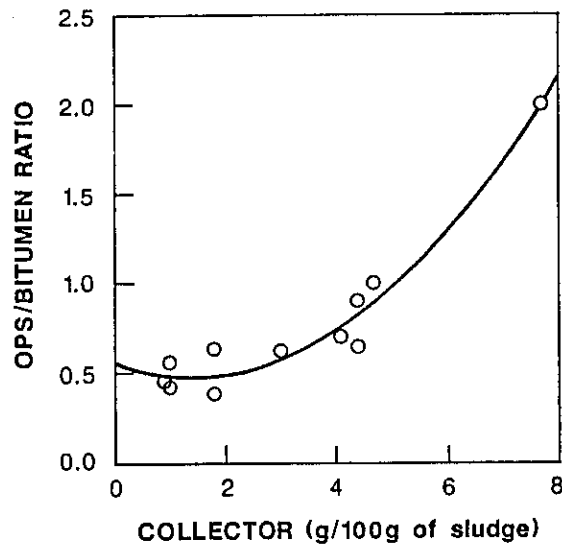


Fig.3 Effect of the Amount of Collector on the ratio of OPS/Bitumen

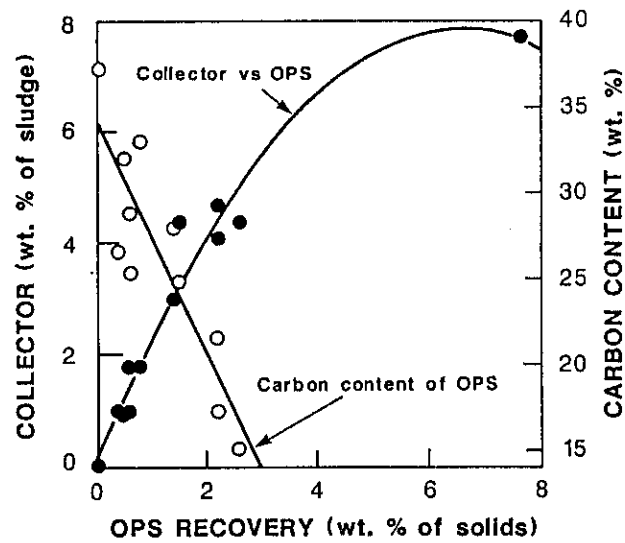


Fig. 4 Effect of the amount of collector oil on the recovery and grade of OPS



a second order fit. An initial low ratio suggests that with small amounts of collector oil bitumen is selectively collected in preference to OPS. However, the ratio increases significantly at higher collector oil levels. This behaviour can be explained on the basis of the difference in the degree of hydrophobicity of bitumen and OPS. Bitumen, being more hydrophobic than OPS, will be collected first, followed by increasing amounts of the less hydrophobic OPS, as available adsorption sites increase with amount of oil. It is also possible that with increasing amounts of collector oil the proportion of weakly hydrophobic material associated with the OPS also increases. This is supported by the fact that the hydrophobic character of OPS, as expressed by its carbon content, varies considerably. In general the carbon content of the OPS obtained using lower amounts of collector oil is much higher (25-40%) than the carbon content (14-25%) of the OPS obtained with larger amounts of collector oil. This is demonstrated in Figure 4, which is a plot of the carbon content of the OPS against the amount of OPS as a function of the amount of collector oil. These results suggest that an excess of oil is less selective for OPS, (10) owing to less competition for adsorption sites. In most instances the collector oil reaches its approximate steady-state solids content before the same conditions are established for selectivity. It therefore seems apparent that competition for oil entrainment then occurs among the particles; those with more hydrophobic surfaces may well be able to displace from the oil those with less oil wettable surfaces.

In view of the nature of the collector oil/solids aggregate, mechanical energy will have a considerable influence on the migration of internally entrapped particles to the oil/water interface. In the event that these particles are not appropriately wetted by the oil, their rejection into the aqueous phase will then follow, resulting in an upgrading of the hydrophobic nature, as indicated by the higher carbon content, of the solids remaining in the oil phase.

**Gravity Settling Tests.** Gravity settling of the clean sludge, after removing bitumen and OPS, was carried out in graduated glass cylinders for different periods of time. When the conditioning agent was sodium silicate or a mixture of sodium pyrophosphate and sodium hydroxide, the clean sludge separated into four layers, namely: relatively clean water on top, followed consecutively by; a suspension of colloidal solids, a thin brown interface layer and a clean compacted solids layers. The formation of these four layers is illustrated in Figure 5. For all other experiments, not involving these reagents as conditioning agents, the thin brown layer was not observed and only three layers were obtained. The formation of the interface layer was also pH dependent and no such layer was observed below pH 10.

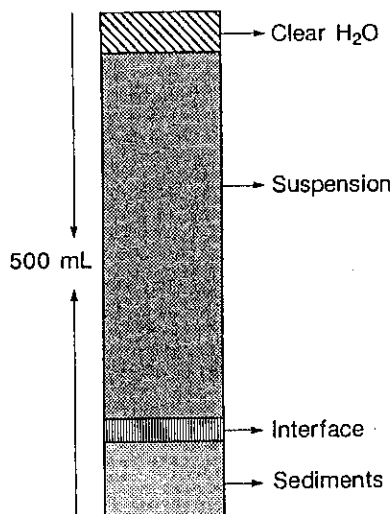


Fig. 5 Four layers obtained from settling



Sodium silicate acts to disperse the aggregated colloidal clay particles; this leads to the collapse of the sludge structure, freeing the entrapped coarser mineral particles and allowing them to settle rapidly (within about 24 hours). The high carbon content of the brown interface particles results in a relatively low density for this fraction. Consequently, these particles initially rose to the top of the higher density suspension. As increasing amounts of other solids settled, the suspension density decreased, resulting in a migration of the interface solids down the cylinder as a discrete band, eventually coming to rest on top of the coarser, densely packed clean sediment.

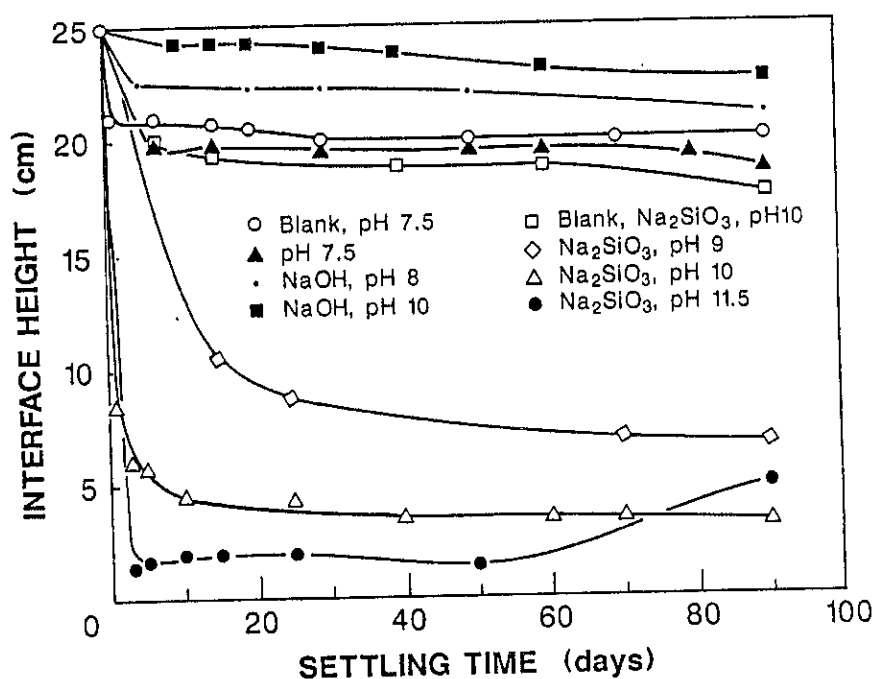


Fig. 6 Settling Curves for Treated and Untreated Syncrude Sludge

Figure 6 illustrates the results of settling tests for a number of experiments including blanks. The interface height (in cms) of the suspension and sediment layers measured as a function of time has been plotted in these graphs. The higher values correspond to the poor compaction of the sediment layer. It is obvious from the plots, that despite good bitumen and OPS recoveries in most cases, significant consolidation of the bottom layer was only achieved when the sludge had been treated with sodium silicate. For example, consolidation of the bottom layer for the sodium hydroxide treated sludge was worse than that obtained in the blank tests. The consolidation behaviour of the unconditioned sludge improved slightly after the removal of some bitumen and OPS but the result was still not as good as in the sodium silicate treated blank tests. Sludge showed the best consolidation behaviour after treatment with sodium silicate at pH 10 and removal of both bitumen and OPS. For tests carried out at pH 10 rapid settling occurred within hours and consolidation approached an equilibrium value in about 10 days, after which change was extremely slow. At pH 11.5 the sediment volume initially decreased rapidly but then essentially remained unchanged for 50 days. After this time the sediment volume started to increase

again. At pH 8.0 very little settling occurred at all, whereas at pH 9.0 slow settling and only poor consolidation was observed.

**Separation Index.** Although good sediment compaction was obtained in a number of tests this indicator is not a good measure of the separation efficiency of the solids from sludge because it does not take into account the amount of solids remaining in the suspension. Therefore, the results have been expressed in terms of a separation index in order to make a more meaningful comparison of the results. A separation index (SI) was calculated as follows:

$$SI = (W_T \times W_F) + W_M, \text{ where}$$

$W_T$  = Total solids fraction in the sediment layer,

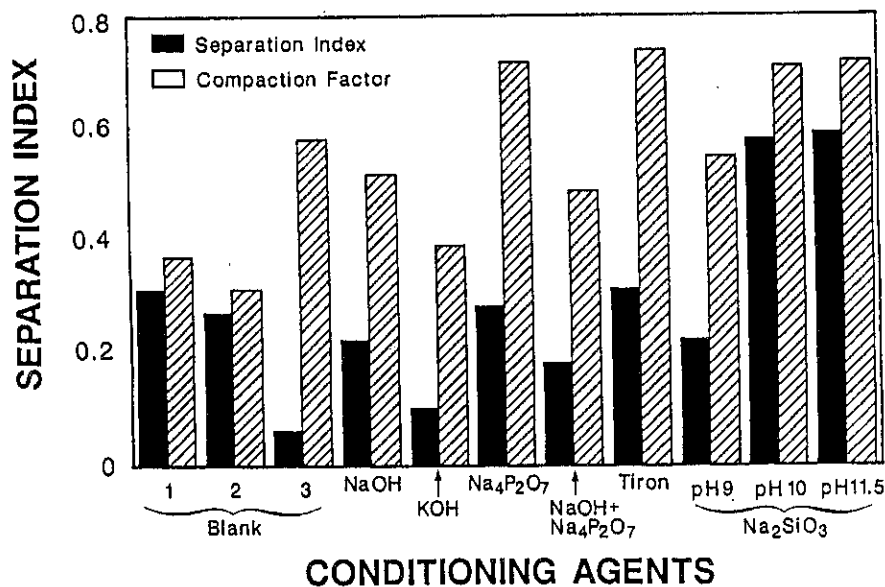
$W_F$  = Solids content of the sediment,

$W_M$  = Maximum solids fraction obtainable under natural gravity settling conditions for clay particles of uniform size. A value of 0.83 was calculated as follows:

$$W_M = S_f + (W_f + S_f), \text{ where}$$

$S_f$  = Voidage for clay solids  $(0.655) \times \text{Density of solids } (2.6) = 1.703$

$W_f$  = Voidage for water  $(0.345) \times \text{density of water } (1) = 0.345$



1, untreated, 2, Conditioned with sodium silicate pH 10, no collector; 3, untreated with collector

Fig. 7 The Effect of Various Conditioning Agents on the Separation Index and compaction of the sediment

Figure 7 illustrates the results for both the SI and the compaction factor, calculated by dividing the solids fraction ( $W_F$ ) of the sediment by  $W_M$ . It is obvious from an examination of this data that use of a separation index allows better discrimination between the results of settling tests compared to the

compaction factor alone. Whereas the tests carried out using tiron and sodium pyrophosphate gave the best compaction the comparison of separation index results indicate that these tests were in fact similar to the blank tests. This arises because the actual amount of dense sediment obtained was very low. Based on these results it is obvious that the sedimentation behaviour of the samples conditioned with sodium hydroxide, potassium hydroxide and a combination of sodium hydroxide/sodium pyrophosphate was in fact worse than the blank tests. The blank test carried out with collector oil alone showed the worst behaviour. The best settling performance was obtained with sodium silicate conditioning, at pH 10. In this case the highest proportion of solids settled to a sediment layer having the highest density.

The role of sodium silicate appears to be three fold: firstly, it acts as a pH modifier, possibly resulting in the dissolution of amorphous oxide coatings on sludge components, secondly, it may modify the surface of hydrophobic solids by direct adsorption or by displacement of organic coatings, thirdly it acts as a viscosity modifier by dispersing aggregated clay particles. Thus, conditioning with sodium silicate eliminates particle bonding mechanisms, causing a breakup of sludge structure. Under these conditions coarse particles will settle rapidly while finer colloidal, clay particles will remain dispersed to form a sol rather than a gel type structure.

Semi-quantitative X-ray diffraction analysis on solids taken from different layers showed that the sedimented solids consisted largely of crystalline forms of mica, kaolinite and quartz while the other fractions showed these minerals in significantly lesser amounts with x-ray amorphous material predominating.

**Elemental Analysis of Settled Fractions.** The solids obtained from the various fractions separated during these tests were also analyzed for carbon and sulphur. In general, the coarse sediment fractions had the lowest carbon and sulphur contents, corresponding to the visual impression that these were clean, relatively uncontaminated solids. The suspension solids had almost the same composition as the solids in the 'clear' water phase indicating that the latter are probably a finer subfraction of the suspension solids. The interface layer fraction had significantly higher carbon and sulphur contents than other solids; this fraction is believed to play an important role in the formation of sludge, (11). Al and Fe elemental results indicated that the interface layer had the highest concentration of these elements, probably because of enrichment of these elements in the humic matter associated with this fraction, (12). Solids from the sediment fraction usually had a lower concentration of these elements compared to the suspension fraction.

## CONCLUSIONS

Conditioning of fine tails with sodium silicate, followed by oil phase agglomeration treatment, to remove bitumen and oil phase solids (OPS), results in destabilization of the sludge. The removal of bitumen and OPS without prior chemical conditioning or the use of other conditioning agents was not as effective in the breakdown of the tailings structure. The role of sodium silicate appears to be three fold: firstly, it acts as a pH modifier, possibly resulting in the dissolution of highly active amorphous oxide coatings on sludge particles secondly, it may modify the surface of hydrophobic solids by direct adsorption or by displacement of organic coatings, thirdly it acts as a viscosity modifier by dispersing aggregated; colloidal clay particles.

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