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Settling behaviour of syncrude sludge pond tailings after treatment by oil phase agglomeration. Part II : effect of conditioning agents and pH modification

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REPORT-RAPPORT

DATE: AUGUST 1991

No. EC-1221-91S

SUBJECT — SUJET

SETTLING BEHAVIOUR OF SYNCRUDE SLUDGE POND
TAILINGS AFTER TREATMENT BY OIL PHASE AGGLOMERATION
PART II: EFFECT OF CONDITIONING AGENTS AND PH
MODIFICATION

(Report#5)

FOR — POUR

SLUDGE FUNDAMENTALS CONSORTIUM c/o AOSTRA

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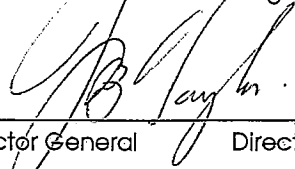
KEY WORDS : AGGLOMERATION, SLUDGE, SETTLING, FRACTIONATION, CONDITIONING,
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EXECUTIVE SUMMARYOBJECTIVES.

- Selective removal of bitumen and hydrophobic solids from sludge in order to understand the role of these components in sludge stability.
- To study the settling behaviour of cleaned sludge in order to understand why sludge is slow to consolidate.
- To study the effect of various conditioning agents and pH modifiers on the removal of bitumen and hydrophobic solids and subsequent settling behaviour of cleaned sludge, in order to investigate the possibility of modification of the properties of sludge components.

Highlights

- Sludge has been treated by oil phase agglomeration to remove selectively bitumen, as well as fine and coarse hydrophobic solids.
- Tests have been carried out without prior conditioning (blank), as well as after conditioning with sodium silicate, sodium hydroxide, potassium hydroxide, sulphuric acid, sodium pyrophosphate, a mixture of sodium pyrophosphate and sodium hydroxide, and disodium salt of 4,5-dihydroxy-1,3-benzene-disulphonic acid (tiron).
- The effect of pH modification has also been studied.

- Sedimentation of the clean sludge after the removal of bitumen and hydrophobic solids has been studied by gravity settling as a function of time.
- Conditioning of sludge with sodium silicate, adjusted to pH 10, followed by oil phase agglomeration treatment, resulted in sludge differentiation into four layers: clear water, a colloidal suspension, a thin, dark brown interface layer and a clean well compacted sediment.
- Oil phase agglomeration treatment alone , or in combination with reagents other than sodium silicate , resulted in sludge fractionation into three layers only. In these cases no interface layer was observed.
- The best settling performance was obtained with sodium silicate conditioning at pH 10.
- In tests where sodium silicate was added, about 80 ± 5 w/w % of total sludge solids separated into dense layers, compared with only 38 ± 12 w/w % or less of total solids in other tests.
- Sodium silicate acts as a pH modifier, as a conditioning agent for hydrophobic solids and as a dispersant for clay particles (viscosity modifier).
- For sodium silicate treated sludge, the removal of oil phase solids had a more pronounced effect on sediment compaction than did bitumen removal.
- The appearance and downward movement of a brown interface layer, containing coarser surface active, hydrophobic solids, is associated with the best overall settling performance.

- The residual colloidal suspension after settling the bulk of the solids was apparently amorphous in nature, perhaps through surface alteration.
- Preferential dispersion of finer clay particles is important for the breakup of sludge structure.
- The mode and degree of agitation as well as the concentration of sodium silicate play an important role in sludge conditioning.

Interpretation

Ultra-fine and coarse hydrophobic particles (oil phase solids, OPS) associated with the bitumen phase, and hydrophillic colloidal clay particles, are all actively involved in sludge structure. Similar observations have been made by Kessick. Conditioning with sodium silicate may dissolve and thus remove finely divided Al and Fe compounds. Also, hydrophobic particles may be altered by displacement of organic coatings or by direct adsorption to form a hydrophillic film. Thus conditioning can eliminate the particle bonding mechanisms, resulting in a breakup of sludge structure. Under these conditions coarse particles settle rapidly while finer colloidal, clay particles are dispersed to form a sol rather than a gel type structure.

OBJECTIVES

- 1). Selective removal of residual bitumen and hydrophobic solids by oil phase agglomeration without dilution or contamination with chemicals. The subsequent study of the settling behaviour of the treated sludge should help elucidate the role of these components in sludge stability.
- 2). Fractionation of clean sludge into coarse solids and finer non-settling solids fractions. Characterization of these fractions in order to understand why sludge is slow to consolidate.
- 3). Effect of conditioning agents and pH modification on the removal of bitumen and hydrophobic solids and study of the settling behaviour of the cleaned sludge.

This study is directed towards gaining insight into the following questions:

- i). Is it possible to control the properties of sludge components e.g. by surface modification using conditioning agents?
- ii). What properties of sludge components are significant in its consolidation behaviour.

INTRODUCTION

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 [1]. This increase is largely the result of water hold-up in the fines fraction from the tailings, arising primarily from the 'middlings' treatment circuit. Long term economical and environmentally acceptable operation of this process ideally depends on being able to reduce the tailings volume. Therefore, economical reduction of the water content of tailings fines is of critical interest.

In our previous work, we have developed a novel technique for the recovery of residual organics as well as oil wettable solids from the aqueous tailings streams of bitumen separation plants. 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 [2-5]. The removal of organic fractions from tailings has been found to alter its settling behaviour. Recently, we investigated the settling behaviour of cleaned sludge after the removal of bitumen and hydrophobic organic coated solids at pH 10, using sodium silicate as a pH modifier [6]. In this investigation we have carried out a number of experiments to study the effect of pH modification and various conditioning agents.

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 ± 0.03
Conductivity (ms/cm)	1.6 ± 0.01
Total Solids [Gravity] ,wt. %	26.6 ± 0.1
Bitumen [OWS] ,wt. %	0.9 ± 0.05 (1.1 ± 0.2)
Solids [OWS] ,wt. %	25.6 ± 0.1 (26.5 ± 0.9)
Density (calculated) ,g/ml	1.19
Solids ,< 44μ (%)	99.2 ± 1.0
Solids ,< 22μ (%)	94.9 ± 1.9
Solids ,< 11μ (%)	83.7 ± 2.1

Values in parenthesis were determined at NRC.

Recovery of Bitumen and Oil Phase Solids (OPS). A stirring device with two sets of contra-rotating blades (grease kettle) was used to separate free and emulsified bitumen from the sludge [5]. 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. 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 collector oil was separated from the remaining suspension. For experiments using sodium silicate the oil phase and associated solids, obtained after sludge treatment, was washed several times with 0.01 % sodium silicate solution to remove any occluded, 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 predetermined amount of bitumen present in the original sludge sample. After solvent removal, a hydrophobic, dark powder remained; this material has been described previously as oil phase solids (OPS), [9].

Gravity Sedimentation Measurements. Cleaned aqueous sludge samples were transferred to 500 ml graduated glass cylinders. The suspensions obtained by washing the oil phase after sludge

treatment were centrifuged and the settled solids added to the sludge in the cylinders. As some losses due to evaporation occurred during agitation in the grease kettle, the supernatant obtained from the centrifugation of washings was used to restore the volume of sludge in the cylinders to 500 ml (the original volume of the untreated sludge). Hence, there was no net dilution in the volume of the sludge. The cylinders were sealed with parafilm in order to prevent losses due to evaporation during the prolonged settling tests.

The cylinder contents were allowed to gravity settle for specified periods. The sludge was found to fractionate into various layers. The heights of the interfaces for these layers (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. The organic carbon content of the solids fractions obtained from the settled sludge was determined using a Leco CR12 carbon analyzer, 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 semi-quantitatively by comparing their X-ray diffraction (XRD) peak intensities with those of standards. XRD patterns were recorded using a SCINTAG PAD V automated power

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 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 total % of crystalline components.

RESULTS

A number of experiments, under different conditions, were carried out in a grease kettle to remove bitumen and OPS from Syncrude sludge pond samples. Table 2 lists the test conditions for these experiments. The main variables investigated included: pH, conditioning agents, amount of collector oil and the agitation time.

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 used was sodium silicate or a mixture of sodium pyrophosphate and sodium hydroxide, the clean sludge separated into four layers: relatively clean water on top followed consecutively by a suspension of colloidal solids, a thin brown layer and a clean compacted solids layers. The formation of these four layers is illustrated in Figure 1a. For the all other experiments not involving these reagents the thin brown layer was not observed and only three layers were obtained. The volume percent distribution of these layers for various experiments are listed in Table 3. Tables 4 and 5 list the distribution of solids among the layers.

Clean solids, from the various fractions, obtained after gravity settling, were analyzed for C, S, Na, Al and Fe. These results are shown in Tables 6 and 7.

DISCUSSION

Gravity Settling Tests. In previously reported work it was noted that treatment of tailings pond sludge to remove residual bitumen and oil wettable solids (OPS) altered the settling behaviour of the sludge [4,6]. It appeared that the removal of bitumen and the associated OPS destroyed the gel-like structure of the sludge, allowing more rapid settling of the coarser ($>2\mu\text{m}$) solids. The earlier work used sodium silicate as the pH modifier. Those results clearly demonstrated that sodium silicate can play a significant role in the breakage of sludge structure. In this investigation we have studied the role of other conditioning agents, together with the effect of pH modification, on the settling behaviour of sludge.

After agglomeration treatment the samples treated with sodium silicate rapidly separated into the four distinct regions described earlier in this report. The formation of an interface layer was only observed when the sludge was treated with sodium silicate or a mixture of sodium hydroxide and sodium pyrophosphate. None of the other conditioning agents tested resulted in the formation of this layer. The formation of the interface layer was also pH dependent and no such layer was observed below pH 10. It is not completely understood why this interface layer, with its high carbon content is not formed after treatment with other conditioning agents.

Sodium silicate being, a good dispersant, probably acts to coat the surface of the colloidal clay particles believed to be, at least partly, responsible for the sludge stability. Dispersion of the ultra-fines leads to the collapse of 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 will initially rise to the top of the suspension. As increasing amounts of solids settle, the suspension density decreases relative to these solids which will then move down in the cylinder as a discrete band eventually settling on top of the coarse, clean sediment.

Figure 1 illustrates the results of settling tests for a number of experiments, including blanks. The photograph (Figure 1b) shows the differentiation into layers for a sludge treated with sodium silicate after 90 days settling. It is obvious from the plots in Figure 1, that despite good bitumen and OPS recoveries, 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. However, the consolidation behaviour of the unmodified (unconditioned) sludge improved slightly after the removal of bitumen and OPS. However, the result was still not as good as in the sodium silicate treated blank tests. Sludge treated with sodium silicate showed the

best consolidation behaviour at pH 10 after removal of both bitumen and OPS. For tests 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 increased 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 poor consolidation was observed, compared to results obtained at higher pH.

It now appears that the initial mixing conditions used during the addition of sodium silicate for pH adjustment is also significant, in terms of sludge fractionation into layers. This conclusion is based on the observation that in a few tests the interface layer was not formed although the tests had been apparently carried out under optimum conditions in all other respects. Intense agitation during pH adjustment may be a requirement for complete disruption of sludge structure to occur. Further work will be necessary to confirm this point.

Table 3 lists the volume percent distribution of the fractions obtained in the various settling tests. As discussed above the highest consolidation levels were only obtained when sodium silicate was used. The results of various tests, carried out under similar experimental conditions are shown graphically in Figures 2-4. Figure 2 is a plot of volume percent sediment against wt.

percent bitumen recovered. Although there is some scatter in the data points, There appears to be a linear correlation between the amount of bitumen collected from the sludge and the volume of the sediment obtained; similar correlations appear to exist for OPS and IOC recovery (Figures 3,4). However, the correlation between the IOC and sediment volume appears to be much better than that for the corresponding case for OPS. This suggests that the surface active hydrophobic solids fraction, containing strongly adsorbed humic matter [9-12], plays an important role in the stability of the sludge.

A relatively clear water layer formed slowly in all cases. However, the amount of water separated could not be measured accurately because of the indistinct interface and the consequent difficulty in achieving a clean separation of the layer for solid determination. Hence, the results listed in Table 2 should only be considered approximate.

Solids Content of Sediment Fractions Table 4 lists the solids content of the various fractions separated after treatment and settling for different periods of time. Solids content of the water layer varied considerably. However, the water recovered from experiments carried out in the presence of sodium silicate had the highest solids content. This is consistent with sodium silicate being a good dispersant for clay minerals. Also, the greatest separation of clear water appears to be associated with low solids

content. For sodium silicate conditioned sludge the solids content of the interface and sediment layers was 30 ± 15 % and 60 ± 3 w/w % respectively. For conditioners other than sodium silicate, the solids content of the sediments ranged from a low of 28 % to a high of 60 % with an average value of 44 ± 9 w/w %. These results clearly demonstrate that of all the conditioning agents tested, sodium silicate is the best. This reagent appears to be essential for sludge destabilization under natural gravity conditions.

The data plotted in Figure 5 demonstrates the effect of bitumen and OPS (IOC) removal on the amount of solids settled. For bitumen and OPS there appears to be a linear correlation between the recovery of these components and the degree of sediment compaction. The data for IOC is best represented by a higher order plot. However, these results clearly demonstrate that the removal of even a small proportion of bitumen and OPS (IOC) had a major effect on separability of the coarse solids fraction.

The suspension fraction contained slow settling ultra-fine particles and occupied the bulk of the graduated cylinder. The amount of solids in this fraction varied considerably. The least amount of solids (8 ± 2 w/w %) was obtained for tests carried out with sodium silicate at pH 10. All other tests gave much higher solids content, ranging from 15-31 w/w %. These results are consistent with the characteristics of the interface and sediment layers, indicating that a significant sludge structure breakdown

occurs with sodium silicate conditioning.

Distribution of Solids between Sedimented Fractions The solids distributions between the various fractions are listed in Table 5. These results should be considered together with the data for volume % distribution of the various layers and the solids content of these fractions in order to draw meaningful conclusions. The water recovered was much cleaner, containing less than 1 % of the total solids for unmodified sludge and for tests carried out with either low sodium silicate concentrations ($\text{pH} < 10$) or with other conditioning agents. When sodium silicate was used as a conditioning agent at $\text{pH} 10$, or greater, about 80 ± 5 w/w % of the total solids settled rapidly into the sediment and interface layers, compared with 38 ± 12 w/w % in other tests. The corresponding values for the solids remaining in suspension were 20 ± 5 w/w % for sodium silicate treated samples and 68 ± 15 w/w % for the remaining tests.

The Effect of pH and Conditioning Agent on Sediment Characteristics. Data plotted in Figure 6 demonstrates the effect of pH and conditioning agents on Sediment characteristics such as: volume percent distribution, cake density, and total solids. It is obvious from this Figure that the best results were obtained for tests carried out using sodium silicate at $\text{pH} 10$, where the highest proportion of total solids settled to a sediment layer having the highest cake density. Increasing sodium silicate concentration also

affected sediment characteristics, with improvements in volume, cake percent solids and total solids being observed. However, at pH greater than 11.5, sodium silicate treated samples suffered a slight decrease in settling performance.

The tests with sodium pyrophosphate, a mixture of sodium pyrophosphate and sodium hydroxide, tiron and sodium hydroxide alone show similar results for distribution of total solids in the sediment layer. On the other hand potassium hydroxide appears to be the least effective of all the conditioning agents tried. Tiron is known to dissolve amorphous alumino-silicates and hydrous oxides of Si and Al, which are suspected of being responsible for the stability of sludge [13-15]. However, it appears that the dissolution of this material alone is not enough for structure breakdown. The role of sodium pyrophosphate with sodium hydroxide could be to release strongly adsorbed humic acids from mineral surfaces. It is known that sodium pyrophosphate will complex with Ca, Al and Fe, thus converting complex organic salts of these metals to soluble sodium salts [12]. If the medium is sufficiently alkaline, then sodium humate will dissolve. This explains why a mixture of sodium pyrophosphate and sodium hydroxide is more effective than sodium pyrophosphate alone.

Effect of Agitation Time on Sediment Characteristics The effect on sediment characteristics of contact time with the oil collector is shown in Figure 7. Longer agitation times result in a slight decrease in the settling performance. This behaviour could be

related to the selectivity of the oil towards particles with different hydrophobic characteristics; initially, the collecting oil is relatively non-selective towards such particles but over time, as it becomes more saturated, those particles with less affinity to the oil will be rejected. It is possible that these particles, with intermediate hydrophobicity are important contributors to sludge structure and the fact that they are not removed has an adverse effect on sludge separation.

The cake density of the sediment obtained after settling an untreated (blank) sample was comparable to those from the samples subjected to oil contact. This arises because those solids with the least water retention capability settle in this test. The amount of sediment, however, was very low in this case.

Effect of Settling Time on Sediment Characteristics The data in Figure 8 demonstrates the effect of settling times on sediment characteristics. In general, settling, in terms of sediment volume and compaction, improves with time. However, the results for one and ten days of settling appear to be anomalous. The cake density of the sediment obtained after one day's settling was the highest observed owing to the fact that, initially, the coarsest solids settle. These solids will have the least water retention capability and therefore the highest cake percent solids. The sediment obtained after 10 days had the highest volume and total solids but lowest cake density. The higher volume of sediment at this time

suggests that settling is almost complete and that compaction becomes the dominant factor for longer settling times.

X-Ray Diffraction Analysis of Settled Fractions Semi-quantitative X-ray diffraction analysis results for solids from different layers were similar to the ones reported previously [6]. These results showed that the sediment solids consisted largely of crystalline forms of mica, kaolinite and quartz. The other fractions showed these minerals in significantly lesser amounts and x-ray amorphous material was found to predominate over crystalline species.

Elemental Analysis of Settled Fractions. Table 6 summarises the carbon and sulphur analyses of fractions separated during the various tests. In general, the sediment fractions had the lowest carbon and sulphur contents, this corresponds 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 layers had a significantly higher carbon and sulphur content than other fractions. This fraction is believed to play an important role in the formation of sludge [6].

Table 7 lists Na, Al and Fe analyses of various fractions. For tests 5-7 and 9 (unmodified sludge) the concentration of both Al and Fe appear to be low for the sediment solids compared with

suspension solids. Concentrations of Al and Fe appear to be highest in the water phase as indicated from the analysis of the sample from test # 9 (the only water result available for unmodified sludge). The results of test # 8, which was carried out under similar conditions to 5-7 and 9, appear to be anomalous. For test # 8 there is a uniform distribution of Al and Fe in both the sediment and suspensions. However, for test # 8 the settling time was 90 days compared with 40 days for the other tests. These results suggest that a significant amount of Al and Fe remain suspended in the water phase as finely divided colloidal particles which settle very, very slowly. For the remaining tests there is no significant difference in the concentration of these elements for the suspension and sediment fractions. However, the interface fraction has higher concentrations of both Al and Fe. Tests other than 5-10 were carried out at alkaline pHs higher than that for unmodified sludge. It is possible that at these pHs most of the finely divided Al and Fe dissolve thereby accounting for the observed uniform distribution of these elements in the suspension and sediment. Higher concentrations of Al and Fe in the interface layer results from the enrichment of this hydrophobic fraction [16] with these elements.

CONCLUSIONS

Conditioning of sludge with sodium silicate, followed by oil phase agglomeration treatment to remove bitumen and oil phase solids (OPS), results in destabilization of the sludge. About 80 ± 5 w/w % of the solids settle rapidly within hours to a compact layer containing 60 ± 3 w/w % of solids. The removal of bitumen and OPS without prior chemical conditioning or the use of other conditioning agents such as: sulphuric acid, sodium hydroxide, potassium hydroxide, sodium pyrophosphate, mixture of sodium pyrophosphate and sodium hydroxide and tiron was not as effective in the breakdown of sludge structure. The role of sodium silicate appears to be three fold: firstly, it acts as a pH modifier, possibly dissolving amorphous oxides of Al and Fe, present as an outer coating on sludge particles and acting as a binder for various sludge components, secondly, it may modify the surface of hydrophobic solids by direct adsorption or by displacing the organic coating, thirdly it acts as a viscosity modifier by dispersing clay particles involved in the water-in-bitumen emulsions involved in the bitumen based 'Kessick type' structure.

For sodium silicate treated sludge, the removal of surface active, hydrophobic particles (OPS) had a more pronounced effect on sediment compaction than bitumen removal alone. Initially, the rate of sediment compaction increases with increase in OPS removal until an optimum value is reached, beyond which there is no further

improvement. Also, the appearance and downward movement of an interface layer, containing surface active hydrophobic solids, is associated with the best settling performance. This clearly demonstrates that surface active hydrophobic solids containing adsorbed humic matter, play an active role in sludge stability.

The mode and degree of initial agitation, as well as the concentration of the conditioning agent, play an important role in sludge conditioning, removal of OPS /bitumen and subsequent settling behaviour of the cleaned sludge.

RECOMMENDATIONS

- Determine the effect of initial mixing during the conditioning step.
- Evaluate the effect of sodium silicate concentration rather than pH.
- Use more efficient means of removing bitumen and OPS from sludge (e.g. Coke/Coal oil agglomeration).
- Use other agitation modes e.g. Blendor.
- Test the role of bitumen, emulsifier and OPS by reintroducing them separately to clean sludge.
- Compare OPS with interface solids (wettability, adsorbed organic matter, particle size distribution and characterization of mineral portion)
- Study the role of iron and aluminium, by carrying out tests on unmodified sludge and analyzing the solids in various phases (water phase in particular) after different settling periods.

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Table 2. Test Conditions & Recovery Data for Bitumen & OPS Removal from Syncrude Sludge*

1 Test #	2 Ref. #	3 Conditioning Agent	4 pH	5 Collector Oil (g/100g sludge)	Recovery		Notes
					6 Bitumen (w/w% of total)	7 OPS (w/w% of solids)	
1 (Blank)	4197-89	-	7.5	-	-	-	f,g
2 (Blank)	4278-08	-	7.5	-	5	0.02	f,i
3 (Blank)	4197-84	Na-silicate	10	-	-	-	f,g
4 (Blank)	4278-10	Na-silicate	10	-	4	0.02	f,i
5	4278-32	-	7.5	1	21	1.7	e,i
6	4278-34	-	7.5	2	28	2.3	e,i
7	4278-38	-	7.5	3	31	0.7	e,i
8	4278-12	-	7.5	3	41	1.8	f,i
9	4278-36	-†	7.5	4	62	2.5	e,i
10	4197-104	H ₂ SO ₄	2.0	4	-58 ₊	0.6	f,i
11	4278-60	NaOH	8.0	4	14	0.6	f,i
12	4278-58	NaOH	9.0	4	17	0.4	f,i
13	4278-56	NaOH	10.0	4	24	0.3	f,i
14	4278-76	KOH	10.0	4	73	1.8	f,i
15	4278-80	Na ₄ P ₂ O ₇	9.0	4	52	2.0	f,i
16	4278-82	NaOH+Na ₄ P ₂ O ₇	10.0	4	76	2.2	f,i

Table 2. Test Conditions & Recovery Data for Bitumen & OPS Removal from Syncrude Sludge*

1 Test #	2 Ref. #	3 Conditioning Agent	4 pH	5 Collector Oil (g/100g sludge)	Recovery		N otes
					6 Bitumen (w/w% of total)	7 OPS (w/w% of solids)	
17	4278-84	Tiron	10	4	45	1.5	F, i
18	4278-66	Na-sillicate	8.0	4.5	39	0.8	F, i
19	4278-62	Na-sillicate	9.0	4	46	0.8	F, i
20	4197-102	Na-sillicate	10.0	4	75	2.2	F, i
21	4278-68	Na-sillicate	11.5	4	19	0.5	F, i
22	4197-97	Na-sillicate	10	1	24	0.4	F, i
23	4197-88	Na-sillicate	10	3	58	1.4	F, i
24	4278-72	Na-sillicate	10	5	65	2.2	F, i
25	4278-70	Na-sillicate	10	8	119	7.6	F, i
26	4278-50	Na-sillicate	10	4	65	0.8	a, i
27	4278-48	Na-sillicate	10	4	65	1.5	b, i
28	4278-16	Na-sillicate	10	3.5	31	1.3	f, h
29	4278-52	Na-sillicate	10	4	93	1.3	c, j
30	4278-54	Na-sillicate	10	4	94	1.1	c, k
31	4278-44	Na-sillicate	10	4.5	77	2.6	d, i
32	4278-40	Na-sillicate	10	1	24	0.6	d, i

Table 2. Test Conditions & Recovery Data for Bitumen & OPS Removal from Syncrude Sludge*

1 Test #	2 Ref. #	3 Conditioning Agent	4 pH	5 Collector Oil (g/100g sludge)	Recovery		Notes
					6 Bitumen (w/w% of total)	7 OPS (w/w% of solids)	
33	4278-14	Na-sillicate	10	4	99	4.2	d, j
34	4278-28	Na-sillicate	10	1	24	0.5	c, j
35	4278-26	Na-sillicate	10	2	39	0.6	c, j
36	4278-30	Na-sillicate	10	2	32	0.8	c, j
37	4278-64	Na-sillicate	10	4	92	1.3	f, j
38**	4197-94	Na-sillicate	10	3	49	1.1	f, j

* Mode of agitation : Grease Kettle; Sample undiluted unless stated otherwise

** Dilution 3.5 times ; † Sulphuric acid has been widely used to separate asphaltic substances from crude oil but large quantities of oil can be lost as sludge [17].

Settling Times : a) 1 day ; b) 10 days ; c) 15 days ; d) 20 days ; e) 40 days ; f) 90 days
Agitation Times : g) 0 ; h) 6 hours ; i) 24 hours ; j) 7 days ; k) 14 days

Table 3. Volume & Distribution of Sludge Fractions Obtained From Gravity Settling Tests

Test #*	Volume & Distribution			
	Water	Suspension	Interface	Sediment
1 (Blank)	-	68	-	32
2 (Blank)	16	15	-	69
3 (Blank) **	59	37	-	4
4 (Blank)	7	23	-	70
5	5	92	-	3
6	3	93	-	4
7	5	92	-	3
8	17	8	-	75
9	4	93	-	3
10	20	80	-	-
11	8	68	-	24
12	8	68	-	24
13	9	71	-	20
14	8	72	-	20
15	7	73	-	20
16	8	74	8	10
17	23	70	-	7
18	7	80	-	13

Table 3. Volume & Distribution of Sludge Fractions Obtained From Gravity Settling Tests

Test #*	Volume & Distribution			
	Water	Suspension	Interface	Sediment
19	4	76	-	20
20	5	69	3	22
21	6	64	2	28
22	3	70	3	22
23	7	68	6	19
25	11	62	2	25
27	-	62	4	34
28	15	63	4	18
29	12	44	26	18
30	14	50	16	20
31	3	77	1	19
32	3	77	2	18
33	20	52	3	25
34	5	73	3	19
35	3	82	1	14
36	5	75	4	16
37	7	63	3	27
38	29	53	5	13

* Experimental conditions listed in Table 2.** Sludge diluted with distilled water by 3.5 times the original volume. Actual water recovery -40 %.

Table 4. Solids Content of Sludge Fractions Obtained From Gravity Settling Tests

Test #*	Solids Content W/W %			
	Water	Suspension	Interface	Sediment
1 (Blank)	-	31	-	34
2 (Blank)	0.1	28	-	31
3 (Blank)	-	16	-	58
4 (Blank)	1.7	15	-	26
5	1.7	23	-	44
6	2.2	21	-	43
7	5.7	22	-	48
8	0.2	19	-	28
9	4.5	20	-	48
10	0	34	-	-
11	0	26	-	43
12	0	26	-	43
13	1.3	25	-	45
14	0.3	29	-	32
15	0.5	19	-	60
16	0.4	1) 8 ; 2) 22	17	60
17	0	20	-	61
18	0.5	27	-	39

Table 4. Solids Content of Sludge Fractions Obtained From Gravity Settling Tests

Test #*	Solids Content W/W %			
	Water	Suspension	Interface	Sediment
19	0	16	-	46
20	4	6.5	41	61
21	5.8	8.3	46	61
22	5	7.9	43	61
23	4	10	31	61
25	2.4	8.8	32	63
27	-	8.0	35	54
28	4.2	6.7	37	59
29	7.8	11	31	57
30	6.9	10	39	58
31	6.0	7.6	43	61
32	5.9	8.7	39	60
33	3.3	6.2	33	56
34	4.4	8.0	35	60
35	2.1	6.6	44	61
36	1.3	7.3	37	61
37	1.5	8.4	33	58
38	1.3	3.1	21	57

* Experimental conditions are given in Table 2. Numbers greater than 10 have been rounded to the nearest whole number.

Table 5. Distribution of Total Solids of Sludge Fractions Obtained From Gravity Settling Tests

Test #*	Solids Content (W/W % of total solids)			
	Water	Suspension	Interface	Sediment
1 (Blank)	-	65	-	35
2 (Blank)	0	17	-	83
3 (Blank)	-	58	-	42
4 (Blank)	>1	15	-	84
5	0	92	-	8
6	0	90	-	10
7	1	88	-	11
8	0	7	-	93
9	>1	86	-	13
10	0	100	-	-
11	0	59	-	41
12	0	59	-	41
13	0	62	-	38
14	0	76	-	24
15	0	61	-	39
16	0	58	5	37
17	0	58	-	42
18	0	79	-	21

Table 5. Distribution of Total Solids of Sludge Fractions Obtained From Gravity Settling Tests

Test #*	Solids Content (W/W % of total solids)			
	Water	Suspension	Interface	Sediment
19	0	61	-	39
20	>1	17	4	78
21	1	17	4	78
22	1	12	8	79
23	1	33	9	57
25	1	15	1	83
27	-	15	5	80
28	3	19	8	70
29	3	16	30	51
30	3	17	23	57
31	>1	26	5	68
32	>1	28	3	68
33	3	13	5	79
34	>1	24	5	70
35	0	25	8	67
36	0	20	8	72
37	1	18	4	77
38	5	20	11	64

* Experimental conditions listed in Table 2. All numbers rounded to the nearest whole number.

Table 6. Carbon & Sulfur Content of Solids obtained from gravity
Setting Tests

Test #*	C w/w %				S w/w %			
	Water	Susp.	Inter- face	Sed.	Water	Susp.	Inter- face	Sed.
1	-	6.2	-	6.4	-	ND	-	ND
2	ND	5.7	-	5.3	ND	0.4	-	0.2
3	ND	7.6	-	4.1	ND	ND	-	ND
4	12.5	18.5	-	3.8	0.9	0.9	-	0.2
5	ND	5.3	-	1.2	ND	0.3	-	0.1
6	6.2	4.3	-	1.9	ND	0.2	-	0.1
7	ND	5.4	-	2.0	ND	0.3	-	0.2
8	7.3	5.7	-	5.4	ND	0.3	-	0.4
9	6.5	3.1	-	0.9	ND	0.2	-	0.1
10	ND	12.3	-	-	ND	ND	-	-
11	ND	4.7	-	4.7	ND	0.3	-	0.3
12	ND	4.8	-	4.8	ND	0.3	-	0.3
13	5.5	4.8	-	4.6	ND	0.3	-	0.3
14	9.8	6.5	-	6	ND	0.2	-	0.2
15	4.5	13.4	-	2.9	ND	0.8	-	0.1
16	6.0	7.6	20.3	1.3	0.9	2.0	1.0	0.1
17	12.2	7.6	-	4.9	7.3	0.4	-	0.3
18	5.4	5.0	-	4.3	ND	0.3	-	0.3
19	-	6.3	-	1.5	-	0.5	-	0.5
20	20.8	6.7	12.0	1.7	ND	ND	ND	ND
21	7.6	8.1	15.8	1.6	0.5	0.2	0.7	0.1