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RECOVERY OF HEAVY METAL MINERALS FROM OIL SANDS
AND OIL SAND TAILINGS BY OIL PHASE AGGLOMERATION

BY

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Recovery of Heavy Metal Minerals from Oil Sands
and Oil Sand Tailings by Oil Phase Agglomeration

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ABSTRACT

Heavy metal minerals tend to appear selectively concentrated in specific process streams during the hot water separation of bitumen from oil sands. For instance, minerals of titanium, zirconium, iron, copper, nickel and chromium concentrate in the centrifuge and scroll tailings. As these minerals are preferentially wetted by bitumen, and thus rendered hydrophobic, this property may be used to beneficiate these minerals by using oil phase agglomeration with either syncrude refinery coke or heavy oil as hydrophobic collectors. Materials treated in this manner include Suncor sludge pond tailings, Suncor plant 4 tailings, Syncrude plant 6 tailings and a low grade oil sand. On suitable agitation, the slurry consisting of feedstock, water and collector separated into an aqueous phase and a unitary organic phase consisting of residual organic materials, the collector and heavy metal minerals. The quality of heavy metal concentrate, separated from the organic phase by washing with toluene, depended on the mode and time of agitation, tumbling charge, feed mineral particle size, feed homogeneity and mineral hydrophobicity. Additional parameters investigated include recovery of residual organics in the tailings and the effect of pH of the aqueous phase. After removal of heavy metal minerals and residual organics from the tailings, its settling behavior improved greatly. Similarly the rate of air drying of the resulting sediment improved markedly.

The suitability for subsequent processing of the heavy metal minerals was also investigated, for instance direct chlorination of the minerals for TiO_2 production. The function of reducing agent during chlorination was taken by the adsorbed organic matter on the minerals, rather than the petroleum coke normally used. The recovery of titanium was quantitative, although the product titanium tetrachloride was contaminated with other metal chlorides, their quantities depending on chlorination conditions.

Introduction

The commercial development of the Alberta oil sands based on the hot water separation process developed by Clark and Pasternack (1932), is one of the major advances in the petroleum industry in recent times. Currently, the only products being marketed from the processing of tar sands are synthetic crude oil and sulfur, Walker *et al* (1976). Potential for the recovery of heavy metals, especially titanium, zirconium and vanadium, has only recently been realized.

Oil Sand solids are known to contain small quantities of heavy metal minerals notably those of titanium and zirconium, Kramers and Brown (1976). These minerals occur in low concentrations, but in significant amounts considering the large volumes of material processed (~ two tons of oil sand per barrel of synthetic crude). It has also been observed that these minerals are concentrated along with the bitumen froth in the hot-water separation process, Kramers and Brown (1976), Baillie *et al* (1976). In particular, solids removed from the bitumen froth in the centrifuge stage contain significant amounts of heavy metal minerals of titanium, zirconium and iron with small amounts of vanadium, nickel, copper, chromium and manganese minerals. Typical concentrations of titanium and zirconium in the Scroll centrifuge tailings have been found to be in the range 5-9% and 2-5% by weight of total solids respectively, Trevoy and Maskwa (1980). On the basis of preliminary calculations (Kramers and Brown, 1976), it is said that the tailings stream from an oil sands plant like Syncrude's would provide sufficient feed for a large scale titanium pigment plant, and sufficient zircon feed to satisfy Canadian demand for metallic zirconium.

When the mixture of heavy metal minerals is recovered from the waste stream of the hot-water extraction process, the minerals are selectively wetted and coated with bitumen. We have investigated the feasibility of selective concentration of heavy metals particularly titanium and zirconium from oil sand tailings by the oil phase agglomeration methods making use of their oil wettability Sirianni and Ripmeester (1981), Majid *et al* (1981). We are now extending this work to investigate the effect of variables such as the mode and period of agitation, pH, tumbling charge and the nature of collecting agent on the quality of heavy mineral concentrates obtained from oil phase agglomeration.

The main industrial use of titanium minerals is in the production of titanium dioxide pigments. The titanium pigment industry historically has been based on ilmenite (FeTiO_3), which is dissolved in sulfuric acid, and the titanium precipitated as the dioxide. Another process which is coming into greater use is the chlorination of the titanium mineral followed by vaporization of

titanium tetrachloride followed in turn by hydrolysis to yield the dioxide, Trevoy (1979). The chlorination process is generally based on rutile (TiO_2) and is more acceptable environmentally, as it has fewer by-product disposal problems. This environmental aspect and the fact that reserves of rutile are limited and thus becoming expensive have fostered an active research effort throughout the world to obtain feed material suitable for the chlorination process from other leaner titanium sources. One of the objectives of the present investigation therefore, was to assess the suitability of the heavy metal concentrates obtained from oil sand tailings as feedstock for the chloride process of TiO_2 manufacturing.

Experimental Methods

Samples: Samples studied for the concentration of heavy metal minerals included: Suncor sludge pond tailings, Suncor centrifuge tailings, Syncrude plant 6 tailings and a low grade oil sand sample. Syncrude plant 6 tailings were provided by Dr. A.H. Hardin of Syncrude Canada Ltd. All other samples were obtained from the Alberta Research Council sample bank. Typical compositions of all samples studied are shown in table 1. The mineral portion of the aqueous sludge consisted of $< 38 \mu\text{m}$ size particles while Syncrude plant 6 tailings and Suncor centrifuge tailings solids consisted mainly of coarser material. The oil sand sample studied had about 60% of $< 38 \mu\text{m}$ size particles. The oil content of the samples shown is the toluene extractable portion and does not represent the total organic content of the samples, Majid *et al* (1982). Loss on ignition values shown are for the mineral portion dried at 110°C , Majid and Sparks (1983).

Procedure: Various experiments were conducted by using oil phase agglomeration methods, Sirianni *et al* (1969). Typically, 50-100 g of the tailings were mixed with various amounts of a heavy oil or Syncrude refinery coke. 0.5-1 ml of a 5% sodium silicate solution was then added to this slurry. Some experiments were conducted in the acidic pH range with HCl and HNO_3 . A few experiments were tried in the pH range 8-12 with NaOH . After adjusting the pH of the slurry, it was agitated to allow the hydrophobic carbon to scrub organic material from the effluent. Agitation was continued until the collector and hydrocarbons from the effluent together formed an organic phase in a form allowing ready separation from the remaining tailings. The oil agglomerates/oil phase were then separated from the aqueous phase by screening followed by thorough washing with water to remove mineral matter. Various modes of agitation employed included: 1) A grease kettle, (Sirianni *et al* (1969), 2) A ball mill and, 3) A Waring blender. Oil phase/oil agglomerates were then transferred to a polypropylene centrifuge bottle (Nalgene Lab Ware) with a known volume of toluene to dissolve the bitumen. The contents were then agitated for 30 minutes to facilitate the

dissolution of the bitumen in toluene. The bitumen solution was then separated from the OPS (Oil phase solids), the heavy metal concentrate by centrifuging at ca. 4000 rpm for 2 hours. The bitumen solution was decanted and the contents of the polypropylene flask were washed until the filtrate was colourless, then dried at 110°C to constant weight.

Analysis of Heavy Metal Concentrates (OPS): OPS were ashed at a constant weight to estimate the amount of unextractable organic matter associated with heavy metal minerals, Majid and Sparks (1983). Ashed samples were then employed for the determination of heavy metals. Half of the samples were analyzed in house using quantitative Inductively Coupled Plasma Atomic Emission Spectroscopic methods (ICP-AES) for the estimation of SiO₂, Ti, Zr, V, Ni, Cu, Cr and Mn; the other half were sent to a commercial lab. (Peninsula Chemical Analysis Limited, Niagara Falls) for analyses. Their procedure was as follows:

The samples were initially fused with sodium carbonate to solubilize the sample and destroy the matrix. Sample solutions were then dehydrated twice to remove calcium, and the silica was determined by hydrofluoric acid volatilization. The silica free residues were fused with lithium tetraborate and dissolved in acid for subsequent quantitative analysis. Zirconium was determined by complexometric titration and the balance of the elements were determined by atomic absorption techniques.

Chlorination of OPS: The chlorination was performed in a quartz tube 30 mm in diameter, one end of which was connected to a chlorine gas cylinder and the other end to a glass trap immersed in dry ice-acetone bath. The other end of the trap was connected to a CaCl₂ drying tube. The quartz tube was charged with a) 1 g of OPS, b) 6.4 g of OPS mixed with 15 g of Suncrude refinery coke and c) 1 g of OPS mixed with 0.5 g of Suncor refinery coke contained in a porcelain boat placed in the middle of the quartz tube. The quartz tube was then placed in a tube furnace. The chlorination was effected by the action of 100% chlorine in the 500-900° temperature range. Most of the chlorination products were obtained as a colourless liquid in the trap cooled in a dry ice-acetone bath, however, small amounts condensed as yellowish brown solids on the walls of the cooler parts the reactor tube. The liquid was hydrolyzed with 1N NaOH before analyzing for heavy metals but the solids were submitted for analysis as obtained.

Results and Discussion Concentration of Heavy Metal Minerals

a) From Suncor Aqueous Sludge: Results for the heavy metal concentrates obtained from Suncor sludge pond tailings are listed

in tables 2-4. Two kinds of collecting agents, namely reduced still bottoms and Syncrude refinery coke, were employed using either a grease kettle or a ball mill as agitation devices. In general the quality of heavy metal concentrates obtained using heavy oil in a grease kettle was better than that obtained with a ball mill using coke as a collecting agent. When using heavy oil as a collector the concentration of heavy metals increased 2-20 fold compared with a 2-5 fold increase for coke, except for V and Ni, where the increase was 2-20 times for heavy oil compared with 20-70 times for coke. Higher V and Ni concentrations in the latter case are presumably due to the contributions from coke.

Time of agitation in the grease kettle appears to affect the quality of heavy metal concentrates in terms of titanium and zirconium concentrations. This is shown in figure 1 which shows a plot of titanium and zirconium concentrations versus time. As is apparent from the plot, the concentration of titanium increases while the concentration of zirconium decreases in the heavy metal concentrates, with the increase in the agitation time. This suggests that titanium minerals are more hydrophobic compared with zirconium minerals present in sludge pond tailings.

Since most of the heavy metal minerals present in oil sand tailings are hydrophobic, Trevoy (1979), Sirianni & Ripmeester (1981), Majid *et al* (1981), one would expect the yield of heavy metal minerals to be proportional to the amount of residual organics recovered. Such a correlation is indeed evident from figure 2 which is a plot of the wt.% OPS recovered as a function of residual organics recovery. However, the data for the complete recovery of residual organics does not fit this correlation. The reason for this discrepancy is not completely understood. The coke agglomerates for the complete recovery of residual organics were brittle and weak. It is probable that heavy metal minerals associated with these agglomerates were not strongly held and that some of these were washed away during washing.

There is no correlation between the yield and the quality of heavy metal minerals concentrate recovered from sludge. This suggests that higher recoveries of heavy metal concentrates in some cases is not due to the retention of mineral matter because of incomplete washing.

Tumbling charge appears to affect both the yield and the quality of heavy metal concentrate in terms of Ti and V concentration. In a ball mill without tumbling charge, the amount of heavy metal concentrate obtained was minimum although its quality in terms of Ti and V content was best. However, when a small amount of $\text{Na}_4\text{P}_4\text{O}_7$ was added as a conditioning agent the yield was improved considerably without sacrificing the quality.

Conditioning agent when used in the presence of tumbling media did not have any effect on the quality or quantity of heavy metal minerals. The tumbling medium grinds the heavy minerals, exposing their less hydrophobic surfaces. This explains poor quality and yield of heavy minerals obtained in presence of a tumbling medium.

Results in table 4 demonstrate the effect of pH on the recovery of minerals from Suncor sludge pond tailings. A few experiments were carried out in acidic media using HCl or HNO₃ to determine if metals would be leached into the acids while residual organics agglomerate into coke-oil agglomerates. As is evident from the results in table 4, these experiments were not successful. Only trace quantities of metals dissolved in acids and the recovery of both residual organics and heavy minerals was extremely poor. This is not unexpected, as heavy metal minerals present in oil sand tailings are coated with unextractable organic material that not only renders it hydrophobic but also makes the material inside the coating inaccessible to acids. Since leaching is essentially a surface phenomenon very little if any of the metals should be expected to be leached into acids.

One experiment was carried out at pH 12 using NaOH. The quality of the heavy metal minerals obtained at pH 12 was a little better in terms of titanium, vanadium and nickel content, compared with the one obtained at natural pH (6.7).

Results for the heavy metal concentrates obtained from Syncrude plant 6 tailings are given in table 5. The quality of heavy metal concentrate obtained from Syncrude plant 6 tailings was better than that obtained from sludge pond tailings because of the better quality feed. However, the beneficiation in terms of titanium and copper for Syncrude plant 6 tailings was not as effective as for the sludge pond tailings. Thus the increase in the titanium and copper concentrations was 1-5 fold for Syncrude plant 6 tailings compared with 3-20 fold for sludge pond tailings. Zirconium beneficiation was much better for Syncrude tailings than for the sludge pond tailings, increasing in concentration 3-16 fold in the former case compared to 2-6 in the latter case. This selective beneficiation suggests that Syncrude tailings might contain some titanium minerals that are not associated with organic matter and thus are less hydrophobic. Zirconium minerals on the other hand appear to be more hydrophobic than in the sludge pond tailings. This difference in the hydrophobicity of heavy metal minerals in the Syncrude plant 6 tailings is also supported by the fact that there is no correlation between the amount of residual bitumen recovered and the yield of heavy metal minerals.

The effect of tumbling charge on the quality of heavy metal concentrates in terms of titanium and zirconium is shown in

figure 3. With the increase in tumbling charge the concentration of zirconium initially increases then decreases sharply, and finally decreases slowly. The outside layer of the organic matter associated with the heavy metal minerals is largely oxidized. It is probable that a small tumbling charge grinds only so far as to expose an interior, less oxidized organic layer which will be more hydrophobic. However, with increased tumbling charge the grinding will have an increased abrasive action exposing the mineral surface free of organic matter, and that will have different surface properties from that of minerals coated with organic matter. This will explain the better grade of heavy metal concentrate in terms of zirconium concentration obtained at lower tumbling charge compared with the poor quality at higher tumbling charge. Correlation of the quality of heavy metal concentrate in terms of titanium concentration with tumbling charge is not as good as for zirconium. However, the trend is toward a decrease in concentration of titanium with an increase in tumbling charge. The reason for the poor correlation could be the inhomogeneity of the feed in terms of titanium minerals.

Results for the heavy metal concentrates obtained from Suncor centrifuge scroll tailings are contained in table 6. Suncor centrifuge tailings were similar to the Syncrude plant 6 tailings in that the mineral content of both consisted mainly of coarse sand, and both feeds had high concentrations of titanium and zirconium. The results for the concentration of heavy metals should be similar. Results for the beneficiation of heavy metals from Suncor centrifuge tailings using heavy oil as collector in a grease kettle are indeed comparable with the corresponding results for Syncrude tailings obtained in a ball mill. However, when using a Waring blender as the mode of agitation the quality of heavy metal concentrate obtained was extremely poor. Using a mixture of heavy oil and coke as collector in the Waring blender the quality of heavy metal concentrate was as good as obtained in a grease kettle. Similar effects were also noted in the recovery of organics from Suncor plant 4 tailings, Majid *et al* (1985). The degree of agitation in a blender is too vigorous compared to a ball mill or grease kettle, so that the destructive forces are dominant over the adhesive forces. The oil agglomerates formed in a blender can be expected to be more vulnerable to breakage, resulting in a lower recovery of organic and, consequently, of heavy metal minerals.

The various collectors used for the recovery of heavy metal concentrates included heavy oil, a mixture of heavy oil and coke, petroleum asphaltenes, oleic acid and varsol. As is evident from the results, essentially no beneficiation was noted using petroleum asphaltenes or varsol as collectors. Higher concentration of chromium in the concentrate obtained using

petroleum asphaltenes as collector are mainly due to contributions from chromium contained in the latter. Oleic acid appears to be a better collector when compared with heavy oil. This is because in a blender the recovery of heavy metal concentrate is by froth flotation and not by oil phase agglomeration. Since oleic acid is a better collector in froth flotation compared to heavy oil, the results are not unexpected, Gaudin (1957).

Beneficiation of heavy metal minerals was also attempted with a sample of a low grade oil sand in a grease kettle using heavy oil as collector. The results are given in table 7. The quality of heavy metal concentrate was at least as good as that obtained from sludge pond tailings. This demonstrates that the technique of oil phase agglomeration for the beneficiation of heavy metal minerals is applicable to feeds other than tailings from oil sand plants.

From all the results discussed above it is evident that the grease kettle provides the best mode of agitation for the beneficiation of heavy metals when heavy oil is used as a collector. Some poor grades of heavy metal concentrates obtained with the ball mill were further beneficiated in a grease kettle. The results are shown in table 8. On further beneficiation the loss on ignition which is a measure of the unextractable organic matter associated with heavy metal concentrate, Majid and Sparks (1983) decreases along with SiO_2 content. Decrease in the loss on ignition of heavy metal concentrates is more pronounced in some cases than others. It is probable that some samples have a greater amount of entrapped organic matter which is released on further beneficiation. Beneficiation in terms of titanium and zirconium appears to be related to the decrease in the amount of organic matter associated with heavy metal minerals. When the decrease in the loss on ignition of heavy metal concentrates is more pronounced the concentration of titanium increases but the zirconium content decreases. There is no significant change in titanium content, although zirconium content increases when there is small decrease in the loss on ignition of the heavy metal concentrates. This is consistent with the previously discussed suggestion that zirconium minerals are usually more associated with organic matter than titanium minerals. There was no significant change in the concentrations of vanadium, nickel and manganese. The amounts of copper and chromium in general were also higher after beneficiation.

Chlorination of Heavy Metal Concentrates

Heavy metal minerals obtained from oil sand tailings are said to be better feed-stock for the more popular chlorination process of TiO_2 manufacture compared to the sulfuric acid process

because of the following reasons, Trevoy (1979), a) a low ratio of Fe to Ti is preferable; b) higher levels of impurities such as Cr can be accommodated; c) it is a more acceptable process based upon capital cost of facilities; and d) it is more desirable in view of environmental regulations related to the disposal of plant wastes (chlorine can be recycled). One of the objectives of the present investigation was to test the suitability of heavy metal concentrate obtained from oil sand and oil sand tailings as a feedstock for the chloride process of TiO_2 manufacture. The results are given in table 9. Chlorination of various minerals is usually carried out in the presence of strong reducing agents such as carbon in the form of petroleum coke, Dunn (1960). The chlorination of heavy metal concentrates in the present investigation was carried out in the absence of added coke because of two reasons. Firstly, the heavy metal concentrate contained various amounts of adsorbed organic matter that could act as a reducing agent, and secondly lower quantities of reducing agents suppress the chlorination of silica and alumina fractions, Brin and Eremin (1969) which is desirable in this case. Two products were obtained from the chlorination of heavy metal concentrates: One was a liquid collected in the trap cooled by dry ice and the other a mixture of yellowish brown solids deposited on the walls of the reactor tube. As is evident from the results in table 9, the liquid consisted mostly of titanium tetrachloride with smaller quantities of silicon and iron chloride and trace amounts of vanadium, copper, nickel, manganese and chromium chlorides. It was essentially free of aluminum and zirconium chloride. The major portion of the solid product also was titanium tetrachloride, probably sorbed on other metal chlorides. However, in addition to the impurities associated with the liquid product, the solid product also contained small quantities of aluminum and zirconium chlorides. The amount of silicon, copper, nickel, manganese and chromium present in the solid product was lower than in the liquid product, but its vanadium and iron content was greater compared to that of the liquid product. Elemental composition of the ash from the residue obtained after the chlorination of heavy metal concentrate demonstrates that titanium and chromium were almost completely chlorinated and aluminum, iron, nickel and manganese were partially chlorinated. There was no significant chlorination of the silicon and zirconium minerals. These results clearly demonstrate the suitability of the heavy metal minerals obtained from oil sand and tailings as a feedstock for the chlorination process of TiO_2 manufacture.

At this stage of the work it is premature to comment on the optimum conditions for the chlorination of heavy metal minerals obtained from oil sand and tailings, in order to get relatively pure TiO_2 . Obviously, further work is needed to investigate the effect of such variables as temperature, rate of chlorination, amount of added coke and the conditions for the fractionation of chlorination

products, Bezukladnikov (1961, 1962, 1967), Mehrotra et al (1982).

We have previously demonstrated that hydrophobic materials suggested for the recovery of heavy metal minerals are also good collectors for the recovery of valuable hydrocarbon components (bitumen and naphtha) found in the tailings streams of existing and proposed bitumen separation plants, Sirianni & Ripmeester (1981), Majid et al (1985), Majid and Ripmeester (1983). It was also found that the removal of organic material from the tailings improves its settling behavior and also the rate of water evaporation of the resulting sediment. Water containing less than 0.1% fines can be recovered by decantation, filtration or centrifugation. Over 50% of the water was recovered on free settling of the sediment for a two-week period. The mineral cake obtained by decanting the water after two weeks dried in about 10 days under ambient conditions.

All these results demonstrate that the oil phase agglomeration technique can be useful not only in the recovery of heavy metal minerals and residual hydrocarbons from tailings streams of oil sand plants, but in the elimination of a waste disposal problems as well. The recovery of heavy metal minerals and residual hydrocarbons as valuable byproducts could help defray costs, giving an incentive for cleaning the existing tailing ponds which could be a serious environmental hazard. Figure 4 is a flowsheet that illustrates various steps involved in the suggested scheme for the recovery of heavy metal minerals from oil sand plants tailings streams. It is evident from the flowsheet that the recovery of heavy metal minerals, residual hydrocarbons and water to get clean wastes for disposal should be feasible using existing technology. Although no economic feasibility estimates are available at this stage, it appears that the value of recovered by-products will more than offset the cost of such project.

CONCLUSIONS

1. Beneficiation of heavy metal minerals from oil sand and tailings was achieved employing oil-phase agglomeration techniques with hydrophobic collectors such as refinery coke and heavy oil. The process suggested also recovered residual hydrocarbons from tailings streams. This greatly improves the settling behavior and the rate of water evaporation of the resulting sediment, thus eliminating a waste disposal problem.
2. Simultaneous leaching of heavy metals in acid solutions while agglomerating the residual hydrocarbons was not feasible.
3. Heavy metal mineral concentrate obtained from oil sand and tailings streams was found to be a suitable feedstock for the

chlorination process of TiO_2 manufacture. Adsorbed organic matter associated with heavy metal concentrate could be used in place of all or part of the petroleum coke required as a reducing agent for chlorination.

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Caption for Figures

Figure 1. Effect of the agitation time on the concentration of Ti (—) and Zr (---) in the heavy metal concentrates obtained from Suncor sludge using heavy oil in a grease kettle.

Figure 2. Correlation between the recovery of heavy metal minerals and the recovery of residual organics.

Figure 3. Effect of tumbling charge on the quality of heavy metal concentrates in terms of titanium (—) and zirconium (---).

Figure 4. Flowsheet for the recovery of heavy metal minerals from aqueous effluents.

Table 1: Typical Analyses of Various Samples

| Sample | Composition w/w% | | | Loss on ignition at 400°C (w/w%) ^a |
|----------------------------|------------------|-----|-------|--|
| | Mineral | Oil | Water | |
| Oil Sand | 85 | 12 | 3 | 16 |
| Suncor Aqueous Sludge | 16 | 13 | 71 | 47 |
| Suncor Centrifuge Tailings | 77 | 4 | 19 | 14 |
| Syncrude Plant 6 Tailings | 15 | 9 | 76 | 21 |

a) of the dried solids

Table 2 Chemical Analyses of OPS^a Obtained from
Suncor Aqueous Sludge in a Grease Kettle Using Heavy Oil

| Sample # | Time of Agitation (Hours) | Ash ^b w/w% | Yield ^c | Concentration of Heavy Metals | | | | | | w/w% of Ash | | |
|-------------------|---------------------------|-----------------------|--------------------|-------------------------------|------|------|--------|--------|-------|-------------|--------|--|
| | | | | SiO ₂ | Ti | Zr | V | Cu | Ni | Mn | Cr | |
| Feed | - | 16 | 100 | 53.5 | 1.9 | 0.66 | 0.02 | 0.007 | 0.012 | 0.1 | 0.015 | |
| 1 | 20 | 76.6 | 21.9 | 32.1 | 6.1 | 3.7 | 0.04 | 0.141 | 0.255 | 0.32 | 0.075 | |
| Reject from Above | " | N.D. | 78.1 | 62.1 | 0.3 | 0.3 | 0.015 | 0.005 | 0.009 | 0.03 | 0.008 | |
| 2 | " | 77.6 | 62.0 | 32.1 | 8.1 | 3.4 | 0.04 | 0.046 | 0.077 | 0.251 | 0.077 | |
| Reject from Above | " | 88 | 38 | 79.2 | 0.3 | 0.03 | 0.0075 | 0.0085 | 0.009 | 0.054 | 0.0023 | |
| 3 | 30 | 81.8 | 69 | 44.8 | 14.1 | 1.85 | 0.1 | 0.02 | 0.006 | 0.1 | 0.06 | |
| 4 | " | 78.7 | 29.6 | 33.5 | 14.8 | 1.7 | - | 0.08 | 0.1 | 0.3 | 0.2 | |
| 5 | 45 | 79.7 | N.D. | 33.4 | 18.6 | 1.4 | 0.1 | 0.07 | 0.07 | 0.2 | 0.1 | |

a) Heavy Metal Concentrate, b) Based on the loss on ignition at 500°C, c) wt.% of total solids; N.D. = Not determined.

Table 3 Elemental Analyses and Conditions for the Recovery of OP5a from Suncor Aqueous Sludge*

| Sample # | Conditioning Agent and its conc. ^b | Total Organics Recovered w/w% | Yield of OP5c | Concentration of Heavy Metals w/w% of Solids | | | | | | |
|-------------------|---|-------------------------------|---------------|--|-------|-------|-------|-------|------|------|
| | | | | Ti | Zr | V | Cu | Ni | Mn | Cr |
| Feed | - | - | 100 | 0.9 | 0.029 | 0.024 | 0.02 | 0.006 | 0.2 | 0.06 |
| Coke | - | - | 9.5 | 1.0 | 0.3 | 3.0 | 0.02 | 0.3 | 0.2 | 0.06 |
| 1 | - | 21.8 | 11.4 | 4.0 | 0.12 | 1.2 | 0.1 | 0.42 | 0.3 | 0.1 |
| 2 | Na ₄ P ₄ O ₇ ; 0.15% | 74.6 | 46.2 | 4.0 | 0.12 | 0.96 | 0.1 | 0.3 | 0.3 | 0.1 |
| 3 | - | 79.1 | 46.8 | 2.0 | 0.093 | 0.68 | 0.1 | 0.12 | 0.3 | 0.1 |
| 4 | Na ₄ P ₄ O ₇ ; 0.15% | 100 | 39.6 | 2.3 | 0.12 | 0.78 | 0.1 | 0.14 | 0.3 | 0.1 |
| Reject from Above | " | " | 60.4 | 1.5 | 0.017 | 0.01 | 0.002 | 0.002 | 0.07 | 0.05 |
| 5 | " | 68.6 | 41.0 | 2.7 | 0.11 | 0.92 | 0.1 | 0.39 | 0.3 | 0.2 |
| 6 | Na ₄ P ₄ O ₇ ; 0.5% | 100 | 38.6 | 2.2 | 0.11 | 0.69 | 0.06 | 0.11 | 0.2 | 0.1 |
| 7 | Na ₂ SiO ₃ ; 0.48% | 91.4 | 51.9 | 2.6 | 0.11 | 0.88 | 0.1 | 0.35 | 0.3 | 0.1 |
| 8 | Na ₂ SiO ₃ ; 1.92% | 92.4 | " | 2.2 | 0.1 | 0.92 | 0.1 | 0.38 | 0.3 | 0.1 |

* Mode of Agitation = Ball mill, collector = Syncrude Refinery Coke; Amount of collector = 20-25% of the wt. of tailings; Tumbling charge for experiments 3-8 = 500 gs of 1 cm Al₂O₃ balls.
a) Heavy Metal Concentrate; b) wt.% of the total charge; c) wt/wt% of total solids.

Table 4 Effect of pH on the recovery of Heavy Metals
from Suncor Aqueous Sludge*

| Sample # | Conditioning Agent | pH of the slurry | Total Organics Recovered w/w% | Yield of OPS ^a | Concentration of Heavy Metals w/w% of Solids | | | | | | | |
|---------------------------|--|------------------|-------------------------------|---------------------------|--|--------|-------|------|--------|-------|------|------|
| | | | | | Ti | Zr | V | Cu | Ni | Mn | Cr | |
| Feed | - | 6.7 | - | 100 | 0.91 | 0.029 | 0.024 | 0.02 | 0.006 | 0.2 | 0.06 | |
| Coke | - | - | - | 9.5 | 1.0 | 0.3 | 3.0 | 0.02 | 0.3 | 0.2 | 0.06 | |
| 1 | NaOH | 12 | 73.3 | 36.3 | 2.8 | 0.13 | 1.1 | 0.1 | 0.49 | 0.3 | 0.1 | |
| 2 | HCl; Na ₂ SiO ₃ | 1 | 26.4 | 7.7 | 2.1 | 0.06 | 0.17 | 0.03 | 0.093 | 0.3 | 0.1 | |
| Water Solubles from Above | " | " | " | 24.9 | 0.035 | 0.0035 | 0.085 | 0.2 | 0.036 | 0.6 | 0.03 | |
| 3 | HNO ₃ | " | 4.5 | 1.0 | 1.8 | 0.08 | 0.36 | 0.03 | 0.14 | 0.1 | 0.1 | |
| water Solubles from Above | " | " | " | 17.0 | 0.016 | 0.0037 | 0.18 | 0.01 | 0.067 | 0.6 | 0.1 | |
| 4 | HNO ₃ ; Na ₄ P ₄ O ₇ | " | 9.1 | 7.1 | 1.8 | 0.075 | 0.19 | 0.03 | 0.079 | 0.1 | 0.1 | |
| Water Solubles from Above | " | " | " | 20.3 | 0.047 | 0.0023 | < | < | 0.0001 | 0.033 | 0.2 | 0.03 |

* Mode of Agitation = Ball mill, Speed of Agitation = 100 RPM; Period of agitation = 15 hours;
Collector = Syncrude Refinery Coke; Amount of Collector = 20-25% of the wt. of tailings.
Tumbling charge = 500 gms of 1 cm Al₂O₃ Balls.
a) w/w% of the total solids in tailing.

Table 5 Elemental Composition of OPS^a recovered from
Syncrude plant 6 tailings in a ball mill using heavy oil

| Residual Bitumen Recovered w/w% | Sample # | Tumbling Charge ^b | wt. of heavy oil ^b | Ash ^c w/w% | Yield ^d | Concentration of Heavy Metals w/w% of Ash | | | | | | | | | |
|--|----------------------|---------------------------------|-------------------------------------|--------------------------|--------------------|---|------|------|-------|-------|--------|------|-------|--|--|
| | | | | | | SiO ₂ | Ti | Zr | V | Cu | Ni | Mn | Cr | | |
| 3.1 | Feed | - | - | 16.8 | 100 | 52 | 10.5 | 0.30 | 0.01 | 0.05 | 0.05 | 0.21 | 0.01 | | |
| N.D. | 1 | 45.2 | ? | 78.5 | 49.4 | 22.5 | 30.2 | 1.2 | 0.01 | 0.2 | 0.2 | 0.38 | 0.2 | | |
| 90.3 | 2 | 47.3 | 1.3 | 67.5 | 21.0 | 24.3 | 24.7 | 1.64 | 0.02 | 0.05 | 0.10 | 0.41 | 0.3 | | |
| - | Reject from Above | " | " | N.D | 79.0 | 68.7 | 7.2 | 0.16 | 0.01 | 0.05 | 0.01 | 0.14 | N.D | | |
| 54.8 | 3 | 48.4 | 1.6 | 67.5 | 42.2 | 17.6 | 15.0 | 2.1 | 0.062 | 0.13 | 0.21 | 0.4 | 0.12 | | |
| - | Reject from Above | " | " | N.D | 57.8 | 64.2 | 0.8 | 0.08 | 0.01 | 0.003 | 0.0075 | 0.10 | 0.012 | | |
| 51.6 | 4 | 52.7 | 4.6 | 64.1 | 20.0 | 18.9 | 12.0 | 4.8 | 0.063 | 0.26 | 0.10 | 0.48 | 0.09 | | |
| - | Reject from Above | " | " | N.D | 80.0 | 53.5 | 1.6 | 0.3 | 0.015 | 0.005 | 0.009 | 0.13 | 0.026 | | |
| 61.3 | 5 | 70.0 | 1.6 | 69.4 | 29.9 | 18.1 | 12.1 | 1.3 | 0.1 | 0.1 | 0.06 | N.D | 0.1 | | |
| N.D | 6 | 70.6 | 5.4 | 69.9 | 29.8 | 19.6 | 24.2 | 0.89 | 0.01 | 0.17 | 1.18 | 0.44 | 0.1 | | |
| 83.9 | 7 | 117.5 | 2.35 | 68.8 | 26.8 | 19.0 | 17.7 | 0.18 | 0.01 | 0.05 | 0.05 | 0.5 | 0.2 | | |

a) Heavy Metal Concentrate, b) gms/100 gms of tailings, c) Based on the loss on ignition at 500°C,

d) wt.% of total solids; N.D. = Not determined.

Table 6 Chemical Analyses of OPS^a Obtained from Suncor plant 4 Tailings in a Waring Blender.

| Sample # | Ash w/w% | Yield ^c | Collector | Concentration of Heavy Metals w/w% of Ash | | | | Concentration of Heavy Metals w/w% of Ash | | | |
|---------------------|----------|--------------------|------------|---|------|-------|-------|---|------|------|------|
| | | | | SiO ₂ | Ti | Zr | V | Cu | Ni | Mn | Cr |
| Feed | 70 | 100 | - | 50.0 | 17.6 | 0.69 | <0.02 | 0.05 | 0.04 | 0.13 | 0.03 |
| 1 ^d | 83.8 | 9.5 | H.O | 29.3 | 36.4 | 3.6 | 0.01 | 0.11 | 0.11 | 0.36 | 0.1 |
| Tailings from Above | N.D | 90.5 | " | 88.6 | 3.16 | <0.05 | 0.01 | 0.04 | 0.01 | 0.02 | N.D |
| 2 | 89.7 | 51.4 | H.O | 42.8 | 20 | 0.67 | 0.01 | 0.18 | 0.2 | 0.2 | 0.3 |
| 3 | 78.7 | 21.6 | H.O+C | 20.2 | 30.3 | 4.3 | 0.01 | 0.08 | 0.08 | 0.41 | 0.1 |
| Tailings from Above | N.D | 78.4 | " | 79.6 | 9.45 | 0.18 | 0.01 | 0.05 | 0.03 | 0.07 | N.D |
| 4 | 87.7 | 15.1 | P.A | 49.3 | 17.6 | 1.1 | 0.02 | 0.09 | 0.06 | 0.21 | 0.06 |
| Tailings from Above | N.D | 84.9 | " | 68 | 14 | 1.0 | 0.01 | 0.11 | 0.02 | 0.13 | N.D |
| 5 | 87.2 | 46.1 | oleic acid | 35.5 | 24.4 | 1.35 | 0.01 | 0.05 | 0.04 | 0.23 | 0.1 |
| Tailings from Above | N.D | 53.9 | " | 67.8 | 14.7 | 0.69 | 0.01 | 0.06 | 0.03 | 0.13 | N.D |
| 6 | 98.9 | 37.1 | Varsol | 43.9 | 15.2 | 0.94 | 0.05 | 0.1 | 0.1 | 0.2 | 0.1 |

a) Heavy Metal Concentrate, b) Based on the loss on ignition at 500°C, c) wt.% of total solids; N.D. = Not determined. d) Mode of agitation = grease kettle
H.O = Heavy Oil; H.O+C = heavy oil + coke; P.A = Petroleum Asphaltenes.

Table 7 Elemental Composition of Heavy Metals Concentrate
obtained from low grade oil sands in a ball mill*

| Sample | Ash ^a | Yield ^b | Concentration of Heavy Metals w/w% of Ash | | | | | | | |
|----------------------------|------------------|--------------------|---|-------|-------|-------|------|------|------|------|
| | w/w% | | SiO ₂ | Ti | Zr | V | Cu | Ni | Mn | Cr |
| Feed | 93 | 100 | 74.7 | 1.8 | <0.05 | <0.02 | 0.05 | 0.02 | 0.04 | 0.1 |
| Heavy Metal Concentrate | 82 | 1.6 | 30.3 | 19.73 | 0.05 | N.D | 0.83 | 0.64 | 0.17 | 0.05 |
| Reject from Above | 97.8 | 98.4 | 77.7 | 1.4 | - | N.D | 0.04 | 0.02 | 0.03 | 0.03 |

* Using residual organics from Suncor Sludge Pond Tailings as collectors.

a) Based on the loss on ignition at 500°C.

b) wt.% of total weight of oil sands.

N.D = Not determined.

| Concentration of Heavy Metals w/w% | | | | | | | | | | | | | | | | | | | |
|------------------------------------|--|------------------------|------|------------------|------|------|------|------|------|-------|------|-------|------|-------|------|------|------|-------|-----|
| Sample # | | Ignition at 500°C w/w% | | SiO ₂ | | Ti | | Zr | | V | | Cu | | Ni | | Mn | | Cr | |
| | | B | A | B | A | B | A | B | A | B | A | B | A | B | A | B | A | B | A |
| 1 | | 32.5 | 12.5 | 17.6 | 15.6 | 15 | 25.9 | 2.1 | 1.44 | 0.06 | 0.01 | 0.013 | 0.06 | 0.021 | 0.02 | 0.4 | 0.36 | 0.116 | 0.4 |
| 2 | | 35.9 | 10.0 | 19.3 | 17.0 | 12 | 26.6 | 4.8 | 2.85 | 0.063 | 0.01 | 0.03 | 0.08 | 0.03 | 0.04 | 0.48 | 0.31 | 0.09 | 0.2 |
| 3 | | 32.5 | 15.5 | 29.0 | 24.3 | 15.1 | 24.7 | 2.2 | 1.64 | 0.1 | 0.02 | 0.03 | 0.04 | 0.03 | 0.03 | N.D | 0.41 | 0.1 | 0.3 |
| 4 | | 34.9 | 30.1 | 19.6 | 14.4 | 24.2 | 23.1 | 0.89 | 1.19 | 0.01 | 0.01 | 0.17 | 0.21 | 1.18 | 1.64 | 0.44 | 0.61 | 0.1 | 1.0 |
| 5 | | 10.3 | 9.0 | 42.8 | 39.8 | 20 | 20.1 | 0.67 | 2.6 | 0.01 | 0.01 | 0.18 | 0.06 | 0.2 | 0.05 | 0.2 | 0.23 | 0.3 | 0.3 |

* Heavy Metal Concentrate initially obtained using heavy oil in a ball mill
 A = After refinement, B = Before refinement; N.D = Not determined.

Table 9 Chemical Analyses of the Chlorination Products of OPS*

| Sample | Concentration of Heavy Metals w/w% of Ash | | | | | | | | | |
|---|---|------|------|------|-----|------|------|------|-----|------|
| | SiO ₂ | Fe | Al | Ti | Zr | V | Cu | Ni | Mn | Cr |
| Feed | 33.5 | 14.9 | 3.7 | 14.8 | 1.7 | 0.01 | 0.08 | 0.01 | 0.3 | 0.2 |
| Ash from Residue left after Chlorination | 84.6 | 1.5 | 1.4 | 0.32 | 9.9 | - | 0.1 | 0.06 | 0.3 | 0.03 |
| Sublimed Solids from Chlorination | 1.6 | 5.7 | 3.34 | 10.3 | 2.6 | 0.3 | 0.1 | 0.06 | 0.1 | 0.1 |
| Hydrolyzed Liquid Product from Chlorination | 2.7 | 3.21 | 0.01 | 36.3 | - | 0.1 | 0.2 | 0.2 | 0.3 | 0.6 |

* Heavy Metal Concentrate; Total loss on chlorination = 84.8%







