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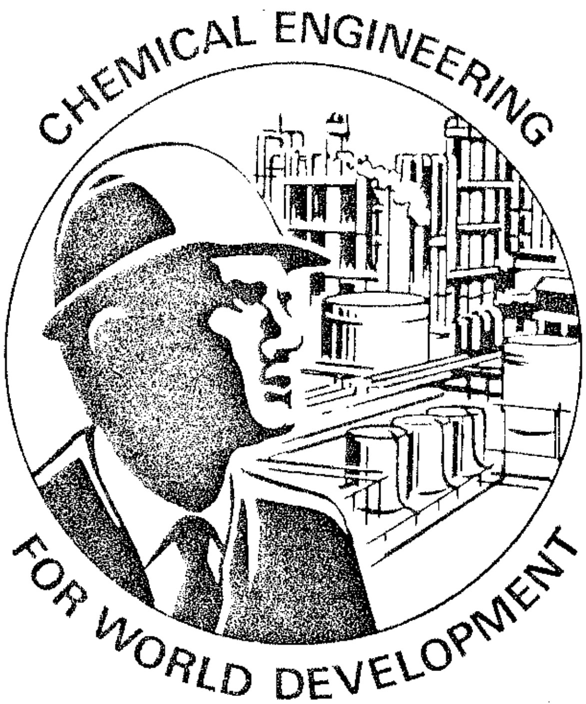

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Recovery of Heavy Minerals from Oil Sand Tailings

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Introduction

The commercial development of the Alberta Oil sands based on the hot water separation process developed by Clark[1] 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[2]. Potential for the recovery of heavy metals especially titanium, zirconium and vanadium has only recently been realized[2-3].

It has been reported that tar sands solids contain about 0.05 wt.% elemental zirconium and 0.21 wt.% elemc tal titanium. However, only recently it has been found that zirconium as zircon and titanium as rutile are surprisingly highly concentrated in the sand separated from diluted bitumen in the centrifuging step of the hot water process.[3,5] Data from Syncrude Canada Ltd.[6] indicate titanium and zirconium concentrations of 8 per cent and 4% respectively in the centrifuge tailings. On the basis of preliminary calculations[3] 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 minerals is recovered from the waste stream of the hot water extraction process, the minerals are selectively wetted and coated with bitumen.[5] Because of this (Oil Wettability) property of the heavy minerals it should be possible to concentrate these metals using the oil phase agglomeration method.[7] The purpose of this study, therefore, was to study the feasibility of the selective concentration of heavy metals particularly titanium and zirconium from various tailings using oil phase agglomeration methods.

Experimental

Experiments were conducted as outlined in figure 1, using oil phase agglomeration methods.[9] Reduced still bottoms were used as a collecting agent in most experiments. Oil agglomerates were separated from the sand and clay tailings using 30 mesh size screen and washed several times with water to remove clay. Bitumen was then recovered by Soxhlet extraction using toluene. The solids were first dried at 110°C, then ashed to constant weight at 400°C. Semi-quantitative analysis for heavy metals was performed on the ashed samples using a DC-Arc Emission spectrographic method.

Results and Discussion

Typical compositions of the three tailings studied, i.e. Suncor aqueous sludge and plant 4 centrifuge tailings and Syncrude plant 6 centrifuge tailings, are shown in table 1 together with the analysis for an oil sand sample. The mineral portion of the aqueous sludge and Syncrude plant 6 tailings consisted of >38 μm size particles while Suncor centrifuge tailings consisted mainly of coarser material. The oil sand sample studied had about 60% of >38 μm 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.[8] Loss on ignition values shown are for the mineral portion dried at 110°C.

Figure 1 is a generalized scheme for the concentration of heavy elements using oil phase agglomeration methods. Not only are the heavy elements concentrated using this method, but also the oil present in the tailings or the tar sands is recovered almost quantitatively. The solids associated with the recovered oil are brownish black in colour and contain about 10-30% of adsorbed organic matter which could not be extracted using any of the solvents (benzene, toluene, chloroform, methylene chloride, methanol, acetonitrile, pyridine, DMSO, benzene-methanol (4:1)) tried. Low temperature ashing was used to remove the organic matter from these solids.

TABLE 1. TYPICAL ANALYSES OF VARIOUS TAILINGS

SAMPLE	Composition wt.% Mineral	Oil	Water	wt.% Loss on ignition at 400°C[a]
Tar Sand	85	12	3	16
Suncor aqueous sludge	16	13	71	47
Suncor Plant 4 Tailings	77	4	19	14
Syncrude Plant 6 Tailings	15	9	76	21

a) of the dried tailings

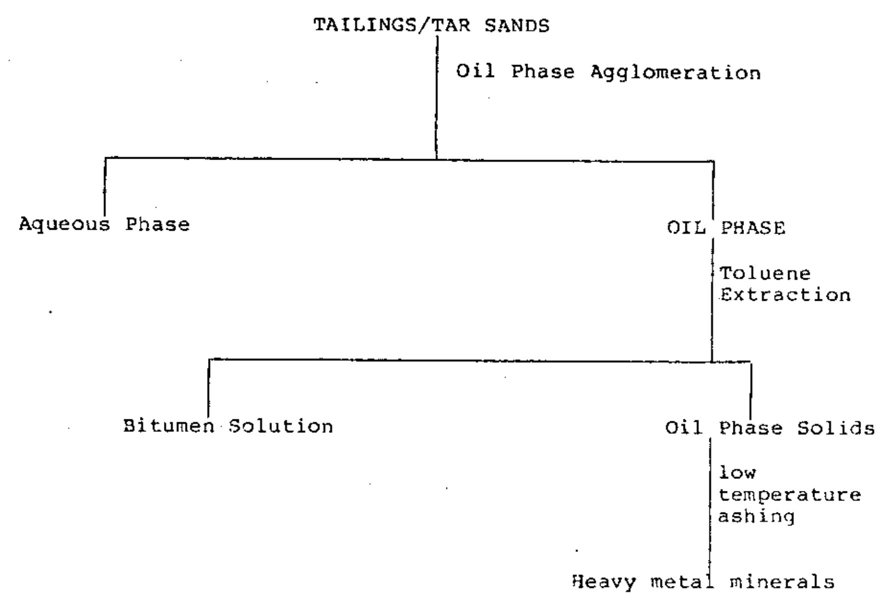

FIGURE 1 - Flow sheet for the concentration of heavy elements.

A semi-quantitative heavy metal analysis of various feeds is shown in table 2. The concentration of all heavy elements analyzed is many folds higher in the tailings than in the tar sands. Coke and fly ash seem to have even higher concentrations of titanium and vanadium than the solids from tailings. However, the oil phase agglomeration treatment of the tailings is quite attractive because bitumen as well as heavy metals are recovered, yielding both cleaner tailings and useful products.

TABLE 2. TYPICAL HEAVY METAL ANALYSES[a]

	BITUMEN	COKE	FLY[b] ASH	TAR SAND	SUNCOR SLUDGE	SUNCOR PLANT 4 TAILINGS	SYNCRUDE PLANT 6 TAILINGS
Ti	6	>30	2.5	0.3	6	3	20
Zr	0.03	1	-	0.03	2	0.1	1
V	10	0.6	4	-	0.2	0.1	0.3
Cr	0.1	0.3	-	-	0.03	0.03	0.1
Cu	0.03	0.03	-	0.003	0.03	0.03	0.03
Ni	3	0.1	1	0.01	0.03	0.03	0.06
Mn	0.3	0.2	-	0.03	0.2	0.2	0.3
Fe	6	3	6	0.2	3	3	10
Ash	1	8	70	82.0	12	70	13

a) Semi-quantitative analyses as wt.% of the ash.
b) Ref. 2.

Table 3 lists the concentrations of the heavy elements in the concentrates obtained from oil phase agglomeration. A comparison of the concentrations and concentrates and feeds for a tar sand sample and one of the tailings samples is shown in table 4. It is obvious from the numbers that all the metals except iron can be concentrated using this technique. The concentration of zirconium is almost increased ten fold, whereas the highest increase is for Cr, Ni and Cu (15-100 times).

Since the metals are already in high concentration in the tailings the yield of metal concentrates is about 15 times higher from the tailings as compared to the tar sands. The quantity of adsorbed organic matter on the metal concentrates as determined from the loss on ignition at 400°C is higher for the concentrates obtained from aqueous sludge than for the ones obtained from tar sands or other tailings.

The results shown in tables 3 and 4 are for some of the better grade concentrates obtained during this study. Usually the grades of concentrate vary from batch to batch particularly because the feed is not homogeneous. However, it is possible to upgrade a low grade concentrate. This was done by taking the low grade concentrate as a feed. The results are shown in table 5. About 20% clay and silica of the feed was rejected during refining, along with 2/3 of the iron. All other metals had higher concentrations. The most notable increase was observed for Cr (30 times). Copper, nickel and vanadium concentrations each increased by a factor of 3, while the increase in the concentrations of Zn and Mn was twofold.

Of the factors affecting the grades and yields of the metal concentrates, the three most significant were (i) pH, (ii) feed particle size and (iii) the device used for oil phase agglomeration. The affect of pH on the grade of metal concentrate is shown in table 6. In general, a slightly acidic medium generates the highest quality concentrate, and a slightly alkaline medium is better than a neutral solution. Whereas silica is depressed at both acidic and alkaline pH, the iron and titanium concentrations seem to be independent of pH contrary to the other metals, chromium seems to be preferentially concentrated at higher pH. Although

TABLE 3. HEAVY ELEMENT CONCENTRATES

	TAR SANDS	FLY[a] ASH	SUNCOR SLUDGE	SUNCOR PLANT 4 TAILINGS	SYNCRUDE PLANT 6 TAILINGS
YIELD (wt.% of Solids)	1.6	70	25	35	35
Loss on Ignition	18	30	27	9	14
Ti	30(0.3)	2.5	>30(0.6)	>30(6.0)	>30(3.0)
Zr	1.4(0.03)	-	10(0.03)	10(0.1)	10(0.3)
V	0.3	4	0.3	0.6	1
Cr	0.2	-	0.3	0.6	3
Ni	3	1	1	0.3	3
Cu	1	-	0.3	0.3	1
Mn	0.1	-	0.6	0.6	0.6
Fe	10	6	10	10	10

(a) Ref. 2.

TABLE 4. COMPARISON OF THE HEAVY METAL CONTENT OF CONCENTRATES AND FEEDS

Metals	Concentrations wt.% of Ash			
	Tar Sand		Syncrude Plant 6 Tailings	
	Feed	Concentrate	Feed	Concentrate
Ti	1.0	30(0.3)	20	>30(3.0)
Zr	0.03	1.4(0.03)	1	10(0.3)
V	-	0.3	0.3	1
Cr	-	0.2	0.1	3
Ni	0.003	3	0.03	3
Cu	0.01	1	0.06	1
Mn	0.03	0.1	0.3	0.6
Fe	0.2	10	10	10

Values in parentheses are the concentration of titanium and zirconium in the tailings.

TABLE 5. REFINING

	Analyses (wt.%) Before	After
Loss on Ignition	27	10
Fe	10	3
Cu	0.3	1
Ni	1	3
V	0.3	1
Zr	3(0.6)	6(3.0)
Ti	30(3.0)	>30(20.0)
Mn	0.3	0.6
Cr	0.1	3.1

Values in parentheses are the concentrations of titanium and zirconium in tailings.

TABLE 6. pH EFFECT

Metals	Concentrations (wt.%)		
	pH 5-7	pH 7.0	pH 7.0-9.0
Si	20	>30	20
Fe	10	10	10
Ti	>30(1.0)	>30(3.0)	>30(3.0)
Zr	10(0.3)	3(0.6)	6(0.3)
V	0.6	0.1	0.3
Cr	0.3	0.3	1
Cu	0.3	0.3	0.1
Ni	0.3	0.1	0.1
Mn	0.6	0.6	0.3

Values in parentheses are the concentrations of titanium and zirconium in the tailings.

the heavy metals recovery is better from a slightly acidic medium, the recovery of oil is very poor at that pH; so that best results are obtained by first working in the alkaline region and then refining the concentrates at a lower pH.

The grade and yield of heavy metal concentrates, and the recovery of oil from oil sands and tailings by the agglomeration methods discussed here also depend on the nature of the mineral matter contained in the feed. Usually better recoveries were obtained from the feeds containing higher % of fines. The recovery efficiency of oil as well as heavy metals was also dependent on the particular device used in the oil phase agglomeration method. The three devices used were Waring blender, ball mill and a grease kettle. Best grades and lowest yields were obtained using a grease kettle. The Waring blender gave poorest grades and highest yields of heavy metal concentrates. Results from the ball mill were in between. Oil recoveries followed the same trends, i.e. best recoveries were obtained using a grease kettle whereas poorest recoveries resulted using a Waring blender.

Separation of the heavy elements was tried using a density differentiation method. The results are shown in table 7. As is apparent from this table, the heavier fraction certainly has greater concentrations of zirconium, iron, manganese, chromium, copper and tin. There is a little less silica in the heavier fraction but the concentrations of vanadium, titanium and nickel seem to be unaffected.

TABLE 7. REFINEMENT OF HEAVY ELEMENT USING DENSITY DIFFERENTIATION METHOD

Metals	Concentration (wt.%)	
	Light fraction	Heavy fraction
Si	>30.0	30
Ti	>30.0	>30.0
Zr	6.0	10.0
V	1.0	1.0
Fe	6	10
Mn	0.2	0.6
Ni	0.1	0.1
Cr	0.3	0.C
Cu	0.06	0.3
Sn	-	0.1

TABLE 8. MAGNETIC SEPARATION

Metals	Concentration (wt.%)	
	Magnetic	Non-magnetic
Si	20	30
Ti	>30.0	>30.0
Zr	10	10
V	1	1
Fe	10	6
Ni	0.3	0.3
Cu	0.2	0.1
Cr	0.3	0.1
Mn	0.3	0.3
Sn	0.03	-

Magnetic separations were also attempted. Although the study is only of preliminary nature at this stage, a few interesting observations were noted. Heavy metal concentrates were found to be non-magnetic before ashing but became magnetic after ashing. In most cases the ashed samples were so magnetic that the separations into magnetic and non-magnetic fractions were poor. The results of the analyses of the magnetic and non-magnetic fractions so separated are shown in table 8. In general the magnetic fractions were low in silica and had slightly higher concentrations of iron, copper, chromium and tin.

Conclusion

In summary the situation is as outlined in point form below:

1. There is a large reservoir of titanium and zirconium in the tailings from oil sand hot water plants. The quantities could be enough to provide sufficient feed for a large scale titanium pigment plant and sufficient zircon feed to satisfy Canadian demand for metallic zirconium.

2. The oil phase agglomeration method could be used to further concentrate these metals from the tailings to such an extent that their recovery by the conventional method, e.g. electrodynamic processing could be feasible.

4. Heavy metal concentrates obtained from tailings using oil phase agglomeration method contain about 10-30% of adsorbed organic matter than can be burnt off at low temperature to avoid sintering.

4. Various factors affecting the grade and yield of heavy metal concentrates from tailings include pH, size of the mineral particles and the device used for oil phase agglomeration.

5. No significant improvements were observed in the grades of the heavy metal concentrates during refining using density differential method and magnetic separation methods.

6. Oil phase agglomeration method not only concentrates the heavy elements from tailings but recovered the oil almost quantitatively.

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DEVELOPMENT OF A DOWNHOLE STEAM GENERATOR FOR RECOVERY OF HEAVY OILS AND OIL SANDS

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INTRODUCTION

There are very large deposits of heavy oil* in Alberta. The latest estimate puts the total amount of such deposits at nearly 1,000 billion barrels (1). Most of the heavy oil deposits are in the Athabasca, Cold Lake, Peace River and Wabasca region (see Figure 1). It is believed that a similar order of magnitude of bitumen reserves may be present in the carbonates of the Peace River and Athabasca Arch (2). In general, Alberta's heavy oils and bitumens have very high viscosities (10^2 - 10^5 Pa.s) at normal reservoir conditions. Consequently their recovery by primary production techniques is impossible.

Methods by which heavy oils and bitumens can be recovered may be classified into three basic categories:

a. Mining techniques
b. In-situ processes
c. Hybrid methods.

Mining techniques comprise surface mining, hydraulic mining and modified conventional underground methods. In-situ processes include combustion, steam stimulation and the use of solvents. Hybrid processes are certain combinations of the first two.

Only a small fraction of Alberta's heavy oil reserves can be recovered economically by current surface mining techniques. Most of the deposits are at depths greater than 100 m below the ground surface (see Table 1) and conventional mining techniques can not be used economically for recovery of these deposits. New technologies must, therefore, be developed, if these vast resources are to make a meaningful contribution towards Canada's energy needs in the coming decades.

IN-SITU PROCESSES

Steam injection has been, so far, the most widely tested in-situ process for the recovery of heavy oils in Alberta. Combustion has been less widely used, although several pilot projects have either been completed, or are underway, by major oil companies. The latter method has also been the subject of extensive laboratory scale tests during the past eight years.

The sucess of any in-situ oil recovery process depends on a number of important physical parameters such as access, initiation of communication, mobilization of the oil, displacement of the oil and capture of the oil. Heavy oil formations have very low permeability to injected fluids. Therefore, one of the first obstacles to overcome is to establish communication between the injection and production wells. Communication may be achieved by various means such as fracturing of the formation by air, water or steam, or by the more sophisticated techniques of horizontal drilling and electrolinking. Oil mobilization (viscosity reduction) may be achieved by steam injection, hot water injection, steam/solvent injection, or by combustion. Displacement of the oil may be accomplished by air (combustion) or by steam.

* Including oil sands and similar heavy hydrocarbon mixtures.