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Majid, A.; Ripmeester, J. A.; Sparks, B. D.

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RECOVERY OF ORGANICS FROM AQUEOUS EFFLUENTS USING

HYDROPHOBIC MATERIALS (NRCC #23879)

A. Majid, J.A. Ripmeester and B.D. Sparks

Division of Chemistry
National Research Council of Canada
Ottawa, Ontario, Canada K1A 0R9

ABSTRACT

Aqueous effluents contaminated with oils are produced by a number of industrial processes. In particular, the oil sands industry is a major source of oily wastes and sludge. The work described here was undertaken in an attempt to recover the valuable hydrocarbon components found in the tailings streams of existing and proposed bitumen separation plants. This has been accomplished by using hydrophobic materials as collectors for the residual organics.

Addition of finely divided hydrophobic particles to an agitated tailings slurry results in adsorption of the residual organic liquids by these collector solids. Continued mixing then results in agglomeration of these particles due to cohesion between the adsorbed liquid films. The agglomerated solids can be readily separated from the bulk of the slurry on the basis of their particle size. As a result of the agglomeration process the hydrocarbon residues are concentrated into a more convenient form suitable for further treatment to recover the individual components or for use as an enriched fuel source. Treated slurries gave faster settling rates and improved drying characteristics for the thickened sediment.

A number of hydrophobic materials, such as refinery coke, activated charcoal and heavy oil have been tested. The effectiveness of these materials was found to depend on such factors as particle size, surface area, degree of agitation and ratio of collector to oil. Surfactants can also be used to improve the oil affinity of the hydrophobic solids and thereby their collection capability. Under optimum conditions over 90% of the hydrocarbons originally present in the tailings reported with the agglomerate fraction.

The quality of the agglomerated solids in terms of undesirable components, such as water and inorganic minerals, depended predominantly on the size of agglomerate produced. Improved results could be obtained by recycling the

agglomerate to increase the ratio of oil to collecting solids thereby increasing agglomerate size and allowing improved drainage. Further removal of undesirable sludge solids could be achieved by washing.

INTRODUCTION

The hot water process used by Suncor and Syncrude to extract bitumen from the Athabasca Oil Sands produces large volumes of tailings (1-4). The process comprises contacting the mined material with a jet of steam and hot water and then transferring the resulting pulp to a hot separation cell. Here, sand (>44 μ m particles) settles to the bottom as tailings and a bitumen froth is recovered from the top. Sand and water which are discharged from the bottom of the cell are combined with a "water-fines" slurry from an air floatation treatment of a "middlings drag stream". This combined effluent stream is normally referred to as "Primary extraction plant tailings".

The bitumen froth from the separation and scavenger cells is diluted with naphtha to facilitate separation of water and solids in centrifuges. Centrifugation yields an organic stream containing the bulk of the naphtha and bitumen plus an aqueous slurry containing silt and clay plus traces of bitumen and naphtha, this latter fraction constitutes "Final extraction plant tailings". Both the primary and final extraction plant tailings are pumped to the retention pond for storage.

Considerable amounts of bitumen and diluent naphtha are lost in these tailings. The data reported by Camp (5) indicate that the effluent from the primary extraction plant would contain 0.63% bitumen. This represents 8.0% of the oil in the oil sand feed. Tailings from the final extraction plant is much richer in oil, but the volume of this stream is relatively small, so that the oil plus diluent naphtha content of 5.0% would represent only 3.9% of the oil in the oil sand feed. Thus, the total loss of bitumen would be approximately 11.9% or 2930 tons per day for a plant producing 100,000 barrels of synthetic crude oil per day (6).

Although long term ponding of this by-product represents a simple, relatively inexpensive and, therefore popular disposal technique, it does represent both an environmental hazard and a process deficiency. As the tailings ponds have increased in size and the seriousness of the problem has grown more apparent, the desire to find a permanent method of tailings disposal has become more urgent. Also with the continuing use of water required for the increased production of bitumen from the Athabasca Oil Sands, interest in recycling a greater proportion of the process water is mounting (2,4). From an economic point of view, the recovery of residual bitumen and solvent naphtha is significant in considering any water recovery process.

Table I - Average Composition of Aqueous Tailings

Sample	wt%			
	Mineral	Water	Bitumen	Naphtha
Sand Agglomerates				
Sample #1	82.3	12.9	1.7	3.1
Sample #2	82.0	13.0	1.5	3.5
Sample #3	82.2	11.5	1.8	4.5
Sample #4	82.2	12.0	1.1	4.7
Sample #5	87.0	9.6	0.4	3.0
Sample #6	82.0	13.2	1.7	3.1
Suncor Aqueous Sludge				
Sample #1	16.0	71.2	8.6	2.2
Sample #2	10.6	84.0	3.9	1.5

We have been interested in techniques for the recovery of valuable hydrocarbon components lost to the tailings streams of existing and proposed bitumen separation plants (7-9). Addition of finely divided collector particles to an agitated tailings slurry results in adsorption of the residual organic liquids by the hydrophobic solids. Continued mixing then results in agglomeration of these particles due to cohesion between the adsorbed liquid films.

In the present work an attempt has been made to identify the most important variables affecting the efficiency of recovery of the hydrocarbon components in various types of tailings, particularly Suncor sludge and extracted sand agglomerates obtained after the separation of bitumen from oil sands by the

Solvent Extraction-Spherical Agglomeration (SESA) process.

A number of hydrophobic materials, such as Syncrude refinery coke, Suncor refinery coke, activated charcoal and heavy oil were used as collectors. In addition the quality of the agglomerated solids in terms of undesirable components, such as water and inorganic materials was also investigated.

EXPERIMENTAL METHODS

Sample Handling: Suncor aqueous sludge was obtained in 1-gallon and 5-gallon-size lots. Before sampling, the sludge was stirred vigorously, so that a more homogeneous sample could be withdrawn from the container.

Extracted sand agglomerates were stored under naphtha. About 100 gms of agglomerates were removed from the bulk sample using a perforated strainer to allow drainage of excess solvent. The sample was placed in a 500 ml glass jar and a kimwipe tissue was placed on top of the agglomerates. The jar was inverted for 10 minutes to remove drainable solvent. 40-60 grams of these drained agglomerates were then transferred into a Waring blender and mixed with an equal amount of water at a speed of ca. 1500 revolutions per minute (rpm) for 2-3 minutes to

produce a slurry containing about 40-50% solids. This slurry was then subsequently used in the experiments to recover residual organics.

Refinery coke was ground to the desired particle size using a Brinkmann Centrifugal Grinding Mill ZM-1.

Samples of Suncor aqueous sludge, Suncor refinery coke and Syncrude refinery coke were obtained from the Alberta Research Council sample bank. Activated charcoal DXL-0-4294, 12 x 40 mesh pits cal, was obtained from Atlas Chemical Industries Inc.

PROCEDURES

a) Recovery of Residual Organics: The technique employed is one of the general class of processes known as spherical agglomeration (10). Typically 50-100 g of the tailings were mixed with varying amounts of a collector. An appropriate amount of sodium silicate or sodium pyrophosphate solution was then added, and the pH of the mixture adjusted to the desired range. The contents were then 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 naphtha present in the tailings was also adsorbed on the carbon along with the bitumen. 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 (10), 2) A ball mill, 3) A Waring blender, 4) A horizontally reciprocating shaker with a lateral travel of 10 cms and an adjustable period, 5) A paint shaker, which has a complex motion involving a lateral oscillation of 1 cm at about 500 cycles per minute (cpm) and combined with a simultaneous rotation of 15° in the vertical plane at a rate of ca. 750 cycles per minute.

b) Analyses of Oil Agglomerates: Wet, oil agglomerates were transferred quantitatively to a preweighed, 500 ml, polypropylene centrifuge bottle (Nalgene Lab Ware). A known volume of benzene was then added to dissolve the bitumen. The contents were then agitated on a paint shaker for 30 minutes. The organic and aqueous phases were separated by centrifuging at ca. 4000 rpm for 2 hours. Both bitumen and naphtha from oil agglomerates were thus extracted into the benzene. This solution was used for the quantitative determination of bitumen and naphtha using a spectrophotometric method and proton nmr respectively (11). The contents of the polypropylene flask were washed till the filtrate was colourless, then dried at 110°C to constant weight. The difference in the weight of wet agglomerates and dried solids gave the weight of total hydrocarbons plus water. Subtracting the weight of total hydrocarbons, as estimated above, from this weight gave the amount of water. Similarly the weight of mineral matter in oil

agglomerates was estimated from the weight of dried solids after subtracting the weight of coke from the total weight.

c) Analyses of Aqueous Tailings: 50-100 gms of aqueous tailings were transferred into a 500 ml preweighed dried glass jar. 100 ml of benzene was introduced into the same jar which was sealed tightly using a polyethylene gasket. The jars were agitated on a paint shaker for 30 minutes and the organic phase separated by centrifuging at 4000 rpm for 2 hours. Bitumen and naphtha were then estimated as described above. Solids were determined gravimetrically after drying and water by difference.

RESULTS AND DISCUSSIONS

Recovery of Organics from Suncor Sludge Pond Tailings

a) Effect of the Amount of Coke: Tables II and III list the results for the recovery of residual bitumen and naphtha from Suncor sludge pond tailings using Syncrude refinery coke. The results obtained, using a Waring blender for agitation, are shown in table IV. These results are also represented graphically in figures 1 and 2. The effect of the ratio of coke to total organics in the tailings is shown in figures 1a and 2a. As is evident from the figures the effect of the coke content varies with the mode of agitation. In general the recoveries are improved with increasing amounts of added coke until an optimum value is reached, beyond this point, the recovery of residual organics again decreases.

The increase in the percentage of organics recovered with amount of coke added, is more pronounced for a ball mill than a blender. Also, the decrease in the amount of organics recovered

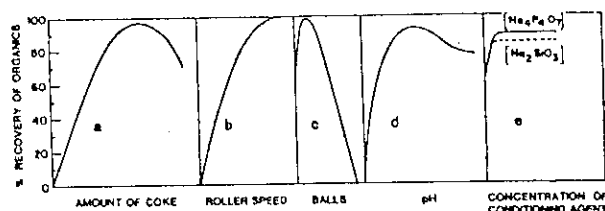


Figure 1 - Effect of: a) ratio of collector to total organics; b) roller speed, c) tumbling charge, d) pH, and e) conditioning agent on the recovery of organics from Suncor sludge pond tailings in a ball mill using Syncrude coke (200 μ m) and 0.15% sodium pyrophosphate. (Roller speed = 100 rpm for a and c-e; time of agitation = 15 hrs for b; tumbling charge was 500 g alumina balls except in c).

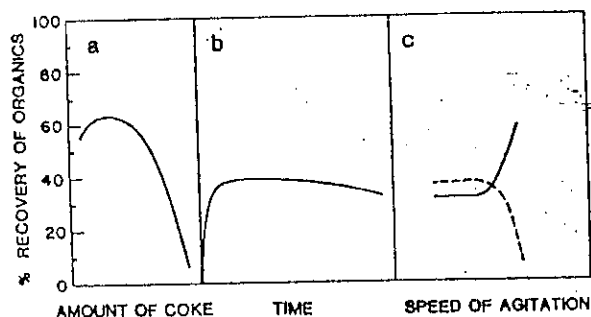


Figure 2 - Effect of: a) ratio of collector to total organics, b) agitation time, and c) agitation speed on the recovery of organics from Suncor sludge using Syncrude coke (200 m) in a Waring blender. (Blender speed a = 7200 rpm and b = 5900 rpm; agitation time a and c = 15 min; collector to organics for b and c = 4.5).

Table II - Recovery of Residual Hydrocarbons from Suncor Sludge Pond Tailings Using Syncrude Refinery Coke (200 μ m size) in a Ball Mill*

Example #	Ratio of Coke to Total organics in Tails	Roller Speed (RPM)	Time for Agitation (hours)	% Recovery			Comments
				Bitumen	Naphtha	Total	
1	2	100	15	62.5	73.8	65.5	a
2	2.5	100	15	82.5	80.0	81.4	a
3	3.0	100	15	100	100	100	b
4	5.0	100	15	100	100	100	b
5	7.0	100	15	90	80	87.3	c
6	4.0	10	20	65	78	68.6	a,c
7	4.5	50	15	100	100	100	b
8	4.5	70	10	87.5	73.3	83.6	b
9	4.0	100	6	85.0	75.0	81.7	b
10	4.25	150	4	100	100	100	b

* 500 gms of porcelain or alumina balls and 0.15% of sodium pyrophosphate were common in all the experiments.

- a) Hydrocarbon phase recovered as a sticky mass.
- b) Hydrocarbon phase recovered as a non-sticky mass.
- c) Some residual coke in the reject.

Table III - Recovery of Residual Hydrocarbons from Suncor Sludge Pond Tailings Using Syncrude Refinery Coke (200 μ m size) in a Ball Mill*

Example #	Ratio of Coke to Total organics in Tails	Conditioning Agent and its Concentration wt% of tailings	wt. of Alumina Balls gms	% Recovery			Comments
				Bitumen	Naphtha	Total	
1	4.5	-	-	20	26.7	21.8	a,c
2	3.0	$\text{Na}_4\text{P}_2\text{O}_7; 0.15$	-	70	87	74.6	a,c
3	5.0	$\text{Na}_4\text{P}_2\text{O}_7; 0.15$	-	90	89	89.7	c,b
4	5.0	$\text{Na}_4\text{P}_2\text{O}_7; 0.3$	-	57.5	60	58.2	a,c
5	3.0	$\text{Na}_4\text{P}_2\text{O}_7; 0.15$	100	100	100	100	b
6	3.0	$\text{Na}_4\text{P}_2\text{O}_7; 0.15$	500	100	100	100	b
7	3.0	$\text{Na}_4\text{P}_2\text{O}_7; 0.15$	2000	-	-	-	d
8	3.0	-	500	75	90	79.1	b
9	4.0	$\text{Na}_4\text{P}_2\text{O}_7; 0.06$	500	100	100	100	b
10	3.0	$\text{Na}_4\text{P}_2\text{O}_7; 0.05$	500	100	100	100	b
11	2.5	$\text{Na}_2\text{SiO}_3; 0.04$	500	87.7	87.7	88	a,c
12	2.5	$\text{Na}_2\text{SiO}_3; 0.24$	500	67.7	100	86.2	a,c
13	3.0	$\text{Na}_2\text{SiO}_3; 0.48$	500	90	95	91.4	c
14	3.0	$\text{Na}_2\text{SiO}_3; 0.96$	500	92	96	93.1	c
15	3.0	$\text{Na}_2\text{SiO}_3; 1.92$	500	91	96	92.4	c
16	2.5	HCl	500	4	7	4.8	d,e
17	2.5	HCl; $\text{Na}_4\text{P}_2\text{O}_7; 0.3\%$	500	7.5	13.3	9.1	d,e
18	2.5	HCl; $\text{Na}_2\text{SiO}_3; 1.6$	500	18.8	46.7	26.1	d,e
19	2.0	NaOH; pH = 8.0	500	90.8	26.7	78.2	a,c
20	2.0	NaOH; pH = 9.5	500	60	72.2	63.3	a,c
21	2.0	NaOH; pH = 12	500	70.8	80.0	73.3	a,c

* Roller speed 100 RPM; Time for Agitation 15 hours.

a) Hydrocarbon phase recovered as a sticky mass.

b) Hydrocarbon phase recovered as a non-sticky mass.

c) Some residual coke in the reject.

d) Almost all coke in the reject.

e) Slurry pH = 1.

Table IV - Recovery of Residual Organics from Suncor Sludge Pond Tailings Using Syncrude Refinery Coke (200 μ m size) in a Waring Blendor

Example #	Ratio of Coke to Total Organics in the Tailings	Blendor Speed RPM	Time for Agitation minutes	% Recovery			Comments
				Bitumen	Naphtha	Total	
1	2.5	17000	5	57.5	40.0	52.7	a,b
2	2.0	7200	20	65	40.0	58.2	b,c
3	4.0	7200	15	25	8.0	20.4	a,b
4	4.5	7200	15	30	6.7	23.6	b,c
5	4.5	6300	10	35	26.7	32.7	b,d
6	4.5	6300	15	32.2	40.0	34.6	b,d
7	4.5	4900	20	32.5	40.0	34.6	b,d
8	4.5	4900	30	25.0	26.7	25.5	b,d
9	5.0	17000	1	20.0	6.7	16.4	e
		6300	10				
10	4.0	17000	1	100.0	-	73.7	b
		4900	10				
11	3.5	4900	10	23.8	16.0	21.8	b,d
12	4.5	7200	5	47.5	33.3	43.6	e
		6300	10				
13	4.5	6300	5	42.5	13.3	34.6	d
		4900	5				
14	2.5	6300	15	31.0	13.3	26.6	a,b
		4900	15				

a) Sticky agglomerates.

b) Some residual coke in the reject.

c) Agglomerate obtained as Single Sticky lump.

d) Non-sticky agglomerates.

e) Excessive coke lost in the tailings.

beyond the optimum amount of coke is steeper and more pronounced in the Waring blender. As the degree of agitation in a blender is severe, the bridging liquid requirements necessary to maintain agglomerate size at an appropriate level for separation will be greater than for a ball mill with its milder form of agitation. Thus the optimum amount of coke required to recover the residual organics in a blender will fall in a narrow range compared with a ball mill where the slow mixing is more amenable to low ratio of collector to bridging oil. Speed and time of agitation and the load of grinding balls are some factors that determine the optimum amount of collector for maximum recovery of residual organics. In general too little coke results in incomplete recovery and a sticky organic phase, while too much coke gives a brittle mass with some unagglomerated coke ending up in the reject. This complicates the analysis of the organic phase by introducing an additional step for the estimation of residual coke in the reject.

b) Mode of Agitation: Two modes of agitation were used for the recovery of residual organics from sludge pond tailings; a ball mill and a Waring blender. In the ball mill the individual small coke/oil agglomerates eventually formed a unitary, coherent mass on prolonged agitation. No attempt was made to control the size of the agglomerates in the ball mill and all experiments were carried out to completion.

The Waring blender gave fair sized, non-sticky agglomerates. However, some of the bitumen remained stuck on the blades of the blender and had to be washed away with benzene. Addition of coke in stages produced better agglomerates. Sticky oil agglomerates could be rendered non-sticky by recycling in the presence of more coke. Washing of oil agglomerates on a screen to remove occluded mineral particles resulted in some loss of adsorbed naphtha. However, this loss was reduced when agglomerates were washed by dispersing in water and reagitating in the blender, for a few minutes.

Under the conditions investigated, recovery of residual organics, naphtha in particular, was much better in a ball mill compared to the blender. The highest roller speed for the ball mill was 150 rpm as compared to the slowest blender speed of 4900 rpm. Heat generated due to this vigorous agitation could result in evaporation of some naphtha thereby accounting for the poor recovery of this component in the blender. In these experiments mass balance closures for naphtha were poor, indicating that losses were indeed occurring.

The effect of the degree of agitation is shown in figures 1b and 2c for both a ball mill and a blender. In the latter case the results were not very reproducible owing to process difficulties. Increasing the rotational speed of the ball mill shortened the time for maximum recovery of both bitumen and naphtha. At 10 rpm a recovery of only 70% was achieved after 20 hours whereas 100% recovery was obtained at 50 and 150 rpm after 15 and 4 hours treatment

respectively. Times required for maximum recovery of organics in a blender were, on the other hand, considerably shorter and ranged from 5-30 minutes. Time did not appear to be a significant factor in the recovery level as seen in figure 2b. Increasing degree of agitation in a blender had an opposite effect on the recovery of bitumen and naphtha as is evident from figure 2b. Increasing the speed of the blender increases the recovery of bitumen but decreases the apparent recovery of naphtha, probably because of greater evaporation losses, owing to increased heat generation at higher mixing speeds. In the Waring blender experiments it was often observed that considerable amounts of coke passed through the screen during separation from the slurry. This is an indication of an insufficiency of oil for complete agglomeration of the amount of coke used under the severe agitation conditions inherent to a blender.

The effect of the degree of agitation was more pronounced on the size of agglomerates. For a constant period of agglomeration, as the speed of agitation was increased, the size of agglomerates obtained decreased. This is caused by the greater degree of attrition encountered by particles under more vigorous mixing conditions.

For ball mills an important variable is the loading of tumbling media. Although up to 75% recoveries of organics could be obtained in the absence of any media, the presence of balls did improve the results. Best recoveries were obtained by using alumina or porcelain balls in amounts of 0.5-4.0 times the weight of the slurry charge, a charge of tumbling media greater than this gave much poorer recoveries. Thus, when using a weight of balls equivalent to about 10 times the weight of the slurry charge none of the organics were recovered and all of the coke reported with the reject in a much finer state than its original condition.

c) Effect of a Conditioning Agent: Sodium pyrophosphate has long been used to release complexed organic matter from mineral matrices (12). We find that it also improves collectability of the oil components of sludge by coke. The effect appears to be more pronounced in the absence of grinding balls. Whereas only about 20% of total organics could be recovered in the absence of a conditioning agent and tumbling media, addition of a small amount of sodium pyrophosphate improved the recovery to around 75%. In the presence of tumbling media the addition of sodium pyrophosphate resulted in an increase in recovery from 80% to almost 100%. Some fine mineral components of the tailings are known to have a strongly adsorbed organic layer (13,14) capable of 'armouring' bitumen droplets in the sludge by adsorption at the bitumen/water interface thereby inhibiting coalescence of the bitumen component and interfering with collection by coke particles. Sodium pyrophosphate or sodium silicate interact with these mineral particles resulting in their release from the interface. Thus, more hydrophobic bitumen surfaces are produced with a greater propensity for coke interaction. The grinding action of the

tumbling media could have a similar effect by continuously breaking through the 'armouring' layer and exposing fresh bitumen surfaces. As is apparent from figure 1(e) the concentration of sodium pyrophosphate or sodium silicate does not appear to have any significant effect in the range studied.

d) Effect of pH: Figure 1(d) shows graphically the effect of pH on the recovery of residual organics from sludge pond tailings. Extremely poor recoveries resulted when the pH of the slurry was below 5. Best recoveries were achieved in the pH range 6.5-8 whereas a slight reduction in the amount of residual organics recovered was observed in the pH above 8. Poor recoveries of residual organics at lower pH could be accounted for by the stronger bonding between organic matter and clay particles at an acidic pH, thus making the release and corresponding recovery of adsorbed bitumen from mineral matter in sludge very difficult.

RECOVERY OF RESIDUAL BITUMEN AND NAPHTHA FROM AGGLOMERATED SAND

Results for the amount of residual bitumen and naphtha recovered from sand agglomerates, obtained after the recovery of bitumen from oil sands using the SESA process, are listed in tables V and VI. Variables investigated included the ratio of collector to total organics in the sand agglomerates, collector types and its particle size, mode and period of agitation. The organic phase recovered using a ball mill or

grease kettle was a unitary phase. All other experiments resulted in individual agglomerates that were readily separable from the slurry by screening.

The overall recoveries of residual bitumen and naphtha from agglomerated sand were significantly less than those obtained with the sludge pond tailings. The explanation for these inferior results probably resides in the fact that the agglomerate derived slurries had a significantly higher pulp density than the tailings pond (40-50 w/w% compared to 10-16 w/w%). As the water dispersible particles will tend to impede contact between oiled coke particles, a reduction in collection efficiency should be expected as the amount of inert material in the system is increased. Qualitatively it was noticed that overall recovery of organics declined as the amount of unagglomerated or partially agglomerated coke passing the screen increased.

Modes of Agitation: Modes of agitation used included a Waring blender, a ball mill, paint shaker, reciprocal shaker and a grease kettle. The degree of agitation had a significant effect on the efficiency of recovery. In general it takes longer to agglomerate all organic matter at slower rates of agitation, but beyond an optimum rate of agitation recovery becomes poor and eventually nil as the destructive forces acting on the agglomerates become dominant in the system.

Both the ball mill and grease kettle produced a unitary organic phase whereas the

Table V - Recovery of Residual Hydrocarbons from Sand Agglomerates
Mode of Agitation = Paint Shaker

Example #	Name	Collecting Agent					
		Average Particle size (µm)	Ratio of Coke to Total organics in the Tailings	Time for Agitation minutes	% Recovery		
					Bitumen	Naphtha	Total
1	Suncor Refinery Coke	850	5.0	120	50	30.9	37.3
2	Suncor Refinery Coke	>150	1.5	120	58.2	6.0	21.9
3	Suncor Refinery Coke	>150	2.0	120	50.3	37.5	41.4
4	Suncor Refinery Coke	>150	3.0	120	67.3	28.9	40.6
5	Suncor Refinery Coke	<150	1.0	120	95.4	21.2	43.8
6	Suncor Refinery Coke	<150	1.5	120	73.9	37.5	46.6
7	Suncor Refinery Coke	<150	2.0	120	94.8	45.6	60.6
8	Suncor Refinery Coke	< 75	1.5	120	76.2	19.0	39.2
9	Suncor Refinery Coke	< 75	2.0	120	81.0	52.3	62.4
10	Suncor Refinery Coke	< 75	3.0	120	82.1	28.1	47.3
11	Suncor Refinery Coke	< 75	0.65	30	100.0	21.9	36.9
		300	1.0				
12	Suncor Refinery Coke	300	1.0	60	100.0	38.1	49.4
13	Suncor Refinery Coke	<150	1.0 + Bit.	120	95.4	-	29.1
14	Syncrude Refinery Coke	< 75	1.0	120	26.8	28.9	28.3
15	Syncrude Refinery Coke	< 75	2.0	120	79.1	22.9	40.0
16	Syncrude Refinery Coke	< 75	3.0	120	100.0	64.2	80.5
17	Syncrude Refinery Coke	< 75	4.0	120	100.0	41.8	70.1
18	Activated Charcoal	< 30	0.3	60	83.4	17.2	35.6
19	Activated Charcoal	< 30	0.6	120	46.4	38.5	40.0
20	Activated Charcoal	< 30	0.9	60	65.5	73.1	71.7
21	Activated Charcoal	< 30	2.5	60	39.1	34.6	35.5

Table VI - Recovery of Residual Hydrocarbons from Sand Agglomerates
 Agitation Modes = a) Reciprocating Shaker
 b) Waring Blender
 c) Ball Mill
 d) Grease Kettle

Example #	Name	Collecting Agent		Mode of Agitation	Time for Agitation minutes	Speed of Agitation	% Recovery		
		Average Particle size (µm)	Ratio of Coke to Total Organics in the Tailings				Bitumen	Naphtha	Total
1	Suncor Refinery Coke	75	3.0	a	300	120 CPS	41.1	93.1	74.7
2	Suncor Refinery Coke	75	3.0	a	300	190 CPS	53.6	66.7	62.0
3	Suncor Refinery Coke	2 mm	5.0	a	120	120 CPS	31.1	6.0	13.0
4	Suncor Refinery Coke	2 mm	10.0	a	120	120 CPS	34.6	25.2	28.1
5	Suncor Refinery Coke	2 mm	20.0	a	60	120 CPS	86.3	29.8	47.0
6	Activated Charcoal	30	0.5	a	60	120 CPS	27.3	16.3	18.4
7	-	-	-	b	10	9000 RPM	11.5	-	3.3
8	Suncor Refinery Coke	300	4.0	b	10	9000 RPM	46.2	87.8	80.2
9	Suncor Refinery Coke	300	4.0	b	10	12000 RPM	35.8	27.0	29.6
10	Suncor Refinery Coke	300	4.0	b	10	17000 RPM	50.0	4.9	21.4
11	Suncor Refinery Coke	300	5.0	b	5 min	17000 RPM	62.1	4.6	21.9
12	Syncrude Coke	200	4.5	b	10 min	9000 RPM	37.2	6.0	16.3
13	Activated Charcoal + Bitumen	<30	2.5+0.5	b	10 min	9000 RPM	61.1	31.6	39.0
14	Activated Charcoal	<30	0.5	b	5 min	4500 RPM	29.1	21.5	23.0
15	Heavy Oil	-	2.0	c	10 hours	100 RPM	25.0	-	18.0
16	Heavy Oil + Activated Charcoal	<30	2.5+0.25	c	10 hours	100 RPM	59.4	65.9	64.1
17	Heavy Oil	-	2.0	d	10 hours	-	30.3	19.8	22.7
18	Heavy Oil + Activated Charcoal	<30	1.0+0.25	d	10 hours	-	12.0	40.0	32.2

other modes of agitation resulted in agglomerates >200 µm. Best recoveries were achieved in a paint shaker or a reciprocal shaker at 120 cpm. Recoveries in a ball mill at 100 rpm or blender at 9000 rpm were almost identical although the time required in the ball mill was considerably longer. The grease kettle produced the worst results, largely because the mild agitation produced by this equipment was inadequate to overcome the adverse effect of high pulp density.

Choice of the Collecting Agent: Various collecting agents used for the recovery of organics from sand agglomerates included: Syncrude refinery coke, Suncor refinery coke, activated charcoal, heavy oil and a mixture of heavy oil and activated charcoal. Refinery coke had the maximum efficiency of recovery and also produced suitably sized, non-sticky, coherent agglomerates. Activated charcoal and heavy oil gave poor recoveries, but a mixture of heavy oil and activated charcoal was as good a collector as

refinery coke. These results clearly demonstrate that the degree of organics recovery is related largely to the effectiveness of the agglomeration process itself. Thus, when the agglomerates are too small to be retained on the separating screen large amounts of carbon are lost to the tailings and the overall recovery of organics tends to be low. Therefore, those factors which tend to affect agglomerate size, such as collector to organic ratio, attrition due to degree of agitation and inert particle content also have a large effect on organic recovery. When heavy oil was used as a collector it became more fluid as a result of dilution by the naphtha present in the tailings. Most of the oil thus passed through the screens along with the mineral matter and so could not be recovered. Activated charcoal has a fine particle size and high surface area. Such solids are typically difficult to agglomerate because it is necessary to saturate the particle pores with bridging liquid before agglomerate growth can occur. Thus, most of the charcoal can end up in the reject, taking all the adsorbed organic matter with it.

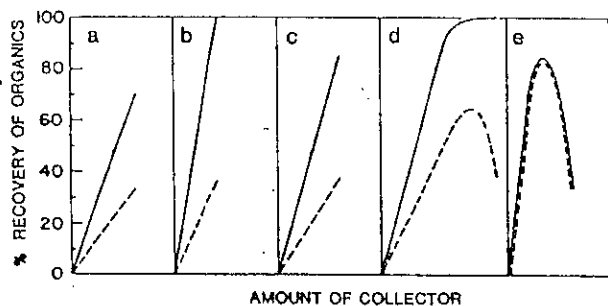


Figure 3 - Effect of the amount of collector on the recovery of bitumen (---) and naphtha (—) from sand agglomerates in a paint shaker. (Collector a-c = Suncor coke, d = Syncrude coke, and e) activated charcoal; particle size of the collector a) 200-150 μ m, b) 150-100 μ m, c-d) 75-50 μ m, and e) 30 μ m).

Effect of the Amount and Particle Size of Collector: The effect of the amount and particle size of the collector on the recovery of residual organics is shown in figures 3a-e for batch experiments in sealed jars using a paint shaker. For Suncor coke the amounts of bitumen and naphtha recovered increased with increase in the amount of coke added. However, the effect appears to be more pronounced for coke of particle size 100 \times 150 μ m compared with the coarser and finer sizes. With Syncrude coke, increasing the amount of collector quickly resulted in complete recovery of the bitumen whereas the naphtha recovery passed through a maximum in the same range. The reason for this difference in the recovery pattern for the two components is unclear. Apart from this anomaly the results for the two types of coke were very similar. It does appear however, that coke is not a particularly good collector for naphtha.

Activated charcoal is distinctively different to both the Suncor and Syncrude refinery cokes. The optimum amount of activated charcoal required for best recovery of bitumen and naphtha is much less than for coke. This can be explained on the basis of the very high surface area of activated charcoal compared with coke. Increasing the amount of activated charcoal beyond an optimum amount resulted in a decrease in the amount of both bitumen and naphtha recovered. The reason for this sudden drop in recovery is again explainable by an insufficiency of bridging liquid to satisfy the requirements of this highly porous collector.

Composition of the Organic Phase

There was considerable variation in the composition of the organic phase. The main controlling factors were found to be the agglomerate drainage time, the extent of washing, the amount of organic solvent preferentially adsorbed on the coke, mode of agitation, ratio of coke; total organics in the tailings, surface area of the coke and the type of tailings.

In general the oil agglomerates obtained from Suncor sludge pond tailings had the lowest content of water and mineral matter. Bitumen and naphtha contents of the oil agglomerates obtained from Suncor sludge ranged from 3-25% while corresponding values for oil agglomerates obtained from sand agglomerates was 0.5-10%. Water content of the two oil agglomerates ranged between 10-30% and 20-70% respectively, while the range of mineral matter content was 0.5-15% and 1-40% respectively. The poor quality of oil agglomerates obtained from sand agglomerates is partly due to the instability of the oil agglomerates produced, because of the relatively low organic content of the sand slurries, compared to the tailings slurries, and partly to the inability of coke to be agglomerated in the presence of a high concentration of sand particles.

The mode of agitation had a significant effect on the quality of oil agglomerates. Thus oil agglomerates obtained using a ball mill had a higher bitumen and naphtha content and lower mineral matter content than those obtained using a blender. This is because of the milder kneading action in a ball mill, which allows release of occluded mineral matter and water. Similarly the reciprocating and paint shakers also gave better quality agglomerates compared with the blender. Water content of the agglomerates did not appear to be markedly affected by mode of agitation.

Surface area of the coke particles was another factor controlling the quality of oil agglomerates. With hydrophobic materials of high surface area such as activated charcoal and fine coke particles the bitumen, naphtha and water content of the oil agglomerates was much higher than those for the coarser coke particles. This is caused by the higher initial absorption of naphtha and water by high surface area materials.

The quantity of mineral matter retained in the coke was found to depend on two factors. The first was the thoroughness of washing to remove water wettable occluded mineral particles and secondly the amount of hydrophobic mineral matter absorbed into the oil phase.

A few experiments were carried out in which the agglomerates were reused to collect more oil from fresh tailings. The water content of these agglomerates was found to be reduced considerably with more compact agglomerates being obtained.

SETTLING BEHAVIOUR OF THE TAILINGS

Oil coated clay particles are said to be responsible for the stability of clay sludges obtained from the hot water extraction of oil sand (3,4,8). However, removing most of the oil attached to the clay particles frees the entrapped water. This greatly improves the rate of settling and enhances evaporation of water from the resulting sediment. Water containing less than 0.1% fines can easily be recovered by decantation, filtration or centrifugation. Over 70%

of the water initially present could be recovered on free settling of the cleaned sludge during a two week period. The compacted sludge solids, obtained by decanting the water after two weeks, dried in about 10 days under ambient conditions.

CONCLUSIONS

Based on the experimental results for the recovery of residual organics from Suncor sludge pond tailings and sand agglomerates, obtained after the recovery of bitumen from oil sand using the SESA process, the following conclusions can be drawn:

1. Hydrophobic materials such as refinery coke, activated charcoal and heavy oil can be successfully used to recover residual bitumen and solvent from oil sand tailings.
2. These materials preferentially collect the specks of oil attached to clay particles and so permit trapped water to flow out, the de-oiled tailings then settle and consolidate readily.

3. By using coke to clean oil sand tailings two problems are addressed. Not only are residual organics recovered, but the coke is also beneficiated through the rejection of inorganic impurities, because of the selectivity of the agglomeration technique.
4. Refinery coke is a better collector than activated charcoal and heavy oil.
5. Degree of efficiency for recovery of residual organics depends on such factors as the mode and degree of agitation, ratio of collector to total organics in the tailings, surface area of the collector particles and the pH of the slurry.
6. Quality of oil agglomerates in terms of oil, water and mineral matter content depends on such factors as the time of agglomerate drainage, the extent of washing, the amount of organic solvent preferentially adsorbed on the coke, mode of agitation, ratio of coke: total organics in the tailings, surface area of the collector and the type of tailings.

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