Preliminary assessment of agglomeration techniques for bitumen separation from storage tank sludge

Majid, Abdul; Sparks, Bryan D.

Publisher's version / Version de l'éditeur:

Proceedings of the 1986 Tar Sands Symposium, 1986-07-10

PRELIMINARY ASSESSMENT OF AGGLOMERATION TECHNIQUES FOR BITUMEN SEPARATION FROM STORAGE TANK SLUDGE*

by

Abdul Majid 1/
Bryan D. Sparks 1/

ABSTRACT

The authors have developed a novel technique for the recovery of hydrocarbon components lost to the tailings streams of existing and proposed bitumen separation plants. This involves the use of hydrophobic materials as collectors for 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 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. Storage tank sludge from a heavy oil project has been evaluated for the recovery of residual bitumen employing this technique. Preliminary results indicate 80-90% recovery of residual bitumen. The quality of the agglomerated solids in terms of undesirable components, such as water and inorganic minerals was also investigated. Also, the treated slurries gave faster solid settling rates and improved drying characteristics for the thickened sediment. About 35% of the original water could be recovered from the treated samples after only 2-3 hours of settling.

INTRODUCTION

All bitumen separation processes, both in situ and surface mine, currently in operation in Alberta have the disadvantage of producing large volumes of aqueous tailings partly in the form of stable sludge suspensions, containing significant quantities of bitumen (Camp 1977; Kessick 1978; Hall et al. 1980, 1982).

In several previous publications (Kumar et al. 1985; Majid et al. 1982, 1983, 1985, 1986; Sirianni et al. 1980, 1981) the authors have investigated a novel technique for the recovery of hydrocarbon components lost to the tailings streams of existing and proposed bitumen separation plants. Addition of finely divided hydrophobic 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. The process has the following advantageous features:

- Little additional process water is required.
- Hydrophobic materials, e.g., coal,

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

* Issued as NRCC #25701.

- Coke and sulfur are available at or near the plant site.
- Virtually complete recovery of bitumen/naphtha is obtained.
- Bitumen can be extracted from the resulting agglomerates or they may be burned with improved combustion characteristics compared to refinery coke alone.
- After separation of the bitumen and naphtha, the sludge showed improved settling behaviour (Ripmeester et al. 1981), thereby allowing greater water recycle.

In the present work a storage tank sludge from an in-situ heavy oil project has been evaluated for residual bitumen recovery by agglomeration techniques. The investigation also included an assessment of the quality of the coke-oil agglomerates in terms of undesirable components, such as water and inorganic materials. The potential for bitumen recovery from the coke oil agglomerates has been examined and a means of reducing sulfur dioxide emissions on burning coke-oil agglomerates is proposed.

EXPERIMENTAL METHODS

Materials

A 2 gallon sample of a storage tank sludge from an in-situ heavy oil project was obtained from Petro Canada Ltd. Before using, the sample was stirred vigorously to allow for more homogeneous sampling from the bulk. Samples of Syncrude and Suncor refinery cokes, for use as collectors, were obtained from the Alberta Research Council sample bank. The coke was ground and sized using a Brinkman Centrifugal Grinding Mill ZM-1.

Agglomeration Procedure

Typically 50-100g of the sludge was mixed with varying amounts of refinery coke (100-200μm diameter). The contents were then agitated to allow the hydrophobic carbon to scrub organic material from the suspension. Agitation was continued until the collector and hydrocarbons together produced an organic phase, in a form allowing ready separation from the remaining tailings by screening. The oil agglomerates/oil phase were then thoroughly washed with water to remove entrained mineral matter.

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. 2000 rpm for 2 hours. Both bitumen and naphtha from the oil agglomerates were thus extracted into the benzene. This benzene solution was used for the quantitative determination of bitumen using a combination of the spectrophotometric, and filter paper methods described elsewhere (Ball et al. 1981; Majid et al. 1984). The solids remaining in the polypropylene flask were washed until 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. On visual inspection, when no coke was found in the reject, it was assumed that all of it was associated with the organic phase. However, in cases where some coke was lost in the reject the amount of coke associated with the organic phase was estimated from the loss on ignition of the dry solids.

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 sample jar which was sealed tightly using a polyethylene gasket. The jars were agitated on a paint shaker for 30 minutes and the organic phase was separated by centrifuging at 2000 rpm for 2 hours. Bitumen and naphtha were then estimated as described above. Solids were determined gravimetrically after drying and water by difference.

Recovery of Residual Bitumen from Storage Tank Sludge

Table 1. Tank Sludge Composition.

Bitumen (w/w%)	Solids (w/w%)	Water (w/w%)
14.2±0.2	59.4±2.3	26.4±2.4

The composition of the storage tank sludge is shown in Table 1. This sludge has a substantially higher bitumen and solids content compared to the sludges obtained from mineable oil sands tailings ponds, which were treated in earlier work. Two approaches were used for the recovery of bitumen from the sludge. One involved the solvent extraction of bitumen while agglomerating the solids, with the addition of sufficient limestone to balance the water content, while the second technique made use of the reverse agglomeration mode by using hydrophobic refinery coke to collect bitumen from the sludge. The results from both studies are discussed below.

I. Agglomeration with Suncor Coke

All experiments were carried out in a Waring blendor after diluting the sludge with an equal volume of water. This resulted in 0.5-1 mm agglomerates that were readily separable from the slurry by screening.

Effects of Process Variables

a) Ratio of Coke to Bitumen

The results in Table 2 demonstrate the effect of the amount of added coke on the recovery of bitumen from sludge.

Figure 1 is a graphic representation of the results. It is evident from curve (a) that recovery is improved progressively with increasing amounts of added coke until a plateau is reached corresponding to the maximum attainable recovery under the prevailing conditions. This is consistent with previous findings (Kumar et al. 1985; Majid et al. 1985) for other types of sludge.

As is seen from the results in Table 2, considerable quantities of undersized coke agglomerates can end up in the

Table 2. Effect of Coke to Bitumen Ratio on Recovery.*

Exp. #	Ratio of Coke to Bitumen	Recovery w/w% of Total: Bitumen	Recovery w/w% of Total: H_2O	w/w% of Coke in Reject	Composition of Coke-Oil Agglomerates w/w%: Total Combustibles	Composition of Coke-Oil Agglomerates w/w%: H_2O	Composition of Coke-Oil Agglomerates w/w%: Minerals
1	0.7	14.0	-	59.6	72.7	12.1	15.2
2	1.1	50.4	37	33.6	83.0	8.3	8.7
3	2.8	79.0	18.5	6.4	84.8	8.1	7.1
4	3.5	76.3	37	10.2	79.2	13.8	7.0

* All experiments were carried out in the presence of 0.1% Na_2SiO_3 in a Waring blendor at 17000 RPM for 5 minutes; Ratio of sludge to added water = 1:1.

reject. There is a correlation between the total amount of coke added and the amount of coke in the reject as seen from Figure 1b which is a plot of % recovery against the amount of coke in the reject. When the amount of coke is small, most of it is adsorbed into the dispersed bitumen without affecting the size of the bitumen droplet. Hence on screening most of the coke will pass through the screen along with bitumen, thus resulting in poor recovery of bitumen. With increasing amounts of coke, the surface area of hydrophobic solid is more in balance with the available bitumen and binding of coke particles together to form physically separable particles becomes possible. Collection efficiency is also affected by the amount of inert material in the system (inert in the sense of not interacting with bitumen). In this case the water dispersible particles can impede contact between oil wetted coke particles thereby preventing agglomerate growth to a suitable size. In many previous investigations it has been demonstrated that the removal of the bulk of the oil phase from a sludge frees the entrapped water (Majid et al. 1982, 1983, 1985; Sirianni and Ripmeester 1981). This greatly improves the rate of settling and enhances the evaporation of water from the resulting solid sediment. In the present investigation clean sludge obtained after the removal of bitumen was left to settle overnight in graduated cylinders. From the volume of clear surpernatant containing less than 0.1% fines the amount of water recovered over and above the dilution water was estimated as a percentage of the water originally present in the sludge. These results are also shown in Table 2. When the recovery of bitumen was less than 20% only the dilution water was separated. In all other cases the amount of recovered water originally associated with the sludge ranged from ≈15-40%. However, there is no correlation between the recovery of bitumen and the amount of water separated.

b) The Degree of Agitation

Results in Table 3 illustrate the effect of the degree of agitation. With increase in mixer rotational speed the recovery of bitumen goes up initially and then tapers off. This is shown graphically in Figure 2a. Also, for equivalent amounts of bitumen recovered, less time is required at higher agitation speeds than at the lower agitation speeds.

A linear correlation between the amount of coke rejected and the speed of agitation shown in Figure 2b appears to be the result of the better mixing at higher agitation speeds. Good mixing of the sludge is important to both bitumen collection and interaction between the oiled collection particles. As agglomeration conditions improve the amount of coke passing to the screen underflow will decrease.

Table 3. The Effect of the Degree of Agitation.*

Exp. #	Agitation Speed RPM	w/w% of Bitumen Recovered	w/w% of Coke in Reject	Composition of Coke-Oil Agglomerates w/w%		
				Total Combustibles	H_2O	Minerals
1	10,000	71.9	19.8	76.5	12.9	10.6
2	13,500	78.3	16.4	76.2	14.6	9.2
3	17,000	76.3	10.2	79.2	13.8	7.0

* All experiments were carried out in the presence of 0.1% Na_2SiO_3; Ratio of Coke to bitumen = 3.5; Time for agitation 5 minutes.

The quality of coke oil agglomerates in terms of mineral matter content was improved with the increase in the degree of agitation. This is evident from the linear correlation between the speed of agitation and the mineral matter content of coke oil agglomerates shown in Figure 2c. As a result of the destructive forces due to agitation agglomerates are continuously breaking and reforming. This results in the exposure of the entrapped hydrophilic mineral matter solids thus allowing their rejection into the aqueous suspending phase. At higher agitation speeds, this will happen more frequently than at lower speed, explaining the lower mineral matter content of the coke oil agglomerates formed at higher speeds.

The degree of agitation does not appear to have a significant effect on the water content of coke oil agglomerates as seen from the plot of w/w% water in agglomerates versus agitation speed, shown in Figure 2d.

c) Effects of Additives

As discussed above we have found some chemical additives beneficial in the recovery of organics from aqueous tailings. Three additives were chosen for this study; sodium silicate, sodium pyrophosphate and a commercial silicone glycol surfactant wetting agent from Dow Corning Canada Inc. The results are listed in Table 4 below. A significant increase in recovery is obtained by using either Na_2SiO_3 or $Na_4P_2O_7$ as additives even at a 0.1% level, with none of the coke remaining unagglomerated. Also the quality of coke oil agglomerates in terms of mineral matter content is improved by the use of these two additives. The use of X2-5150 on the other hand is not as beneficial. The quantity of X2-5150 required for equivalent recoveries is much greater and the mineral matter content of coke oil agglomerates, obtained using X2-5150, is much higher than for the other two additives.

II. Agglomeration of Mineral Matter

A few experiments were carried out to agglomerate the mineral matter after dissolving the bitumen in stoddard solvent. Since the water content of the sludge was substantially higher than the bridging liquid requirements of solids initially present more solids were added in the form of ground limestone. The results are given in Table 5.

As seen from the results, simple solvent extraction followed by centrifugation gave much better results than the solvent extraction spherical agglomeration using limestone. Recoveries of both the bitumen and the solvent were best in the former case compared with the latter. The recovery

Table 4. The Effect of Additives.*

Exp. #	Additive and its Conc	Recovery w/w% of Total		w/w% of Coke in Reject	Composition of Coke-Oil Agglomerates w/w%		
		Bitumen	H_2O		Total Combustibles	H_2O	Minerals
1	-	77.5	-	3.0	85.4	6.3	8.3
2	Na_2SiO_3-0.1%	88.7	37	-	87.7	6.2	6.1
3	$Na_4P_2O_7$-0.1%	87.3	37	-	86.6	7.4	6.0
4	X2-5150-0.05%	77.5	37	10.8	76.2	11.2	12.6
5	X2-5150-0.5%	82.5	37	12.8	75.6	5.2	19.2

* Ratio of Coke to Bitumen = 3.5:1; Speed of agitation = 9000 rpm; Time for agitation = 15 minutes.

Table 5. Agglomeration of Mineral Solids from Sludge.

Exp. #	Ratio of limestone to sludge	Overall w/w% Recovery Bitumen	Solvent	Experimental Conditions
1	-	65.3	81.5	Agitated with solvent and then bitumen solution decanted.
2	0.53	78.3	90	Agitated the solids from above with added limestone. Additional bitumen solution released decanted.
3	-	86.4	93.4	Agitated with solvent, centrifuged and bitumen solution decanted.
4	0.25	86.5	94.4	Agitated the solids from above with added limestone.
5	0.25	67.6	83.7	Agitated with solvent, added limestone and bitumen solution decanted.
6	0.5	65.7	84.8	Same as above.

of hydrocarbons did not improve any further on agglomeration of solids obtained after decanting the centrifuged bitumen solution. However, the compact agglomerates are much easier to transport and dispose of compared with the slushy mass before agglomeration.

Removal of most of the bitumen solution prior to the addition of limestone resulted in better hydrocarbon recovery compared with the agglomeration in the presence of bitumen solution. This is because the amount of hydrocarbons available for occlusion by the solids will be less in the former case.

The ratio of limestone to sludge does not appear to affect significantly the hydrocarbon recovery. However, there is an effect on agglomerate strength. At low limestone addition the agglomerates are very wet and weak compared with dry and strong agglomerates obtained when the ratio of water to solids is brought into the most appropriate range.

As is evident from the results in Table 5, five to fifteen percent of the solvent is lost to the solids. This is a disadvantage for solvent extraction techniques because the refined solvent is more expensive than the bitumen recovered and would necessitate an additional step for the recovery of solvent from solid agglomerates.

Recovery of Bitumen from Coke-Oil Agglomerates

After collecting bitumen from tailings streams using coke, it would be desirable to recover this bitumen from coke oil agglomerates for further processing. This aspect is currently under investigation and the results will be reported in a future publication. Preliminary results indicate that over 50% bitumen can be recovered by solvent extraction followed by centrifugation at 800-2000 G force for 10 minutes with the coke being recycled to collect more bitumen.

Coke-Oil Agglomerates as Fuel

Agglomeration of coke, using residual bitumen from tailings streams, increases its thermal value and volatile content. If the bitumen associated with coke oil agglomerates cannot be recovered economically then its use as a fuel might be more desirable. However, high sulfur content of both bitumen and coke could lead to unacceptable sulfur emissions. The use of coke oil agglomerates as a source of fuel thus would require either elaborate and expensive sulfur dioxide removal equipment or a means of binding the sulfur with the ash forming components. This second aspect is currently under investigation. Formation of coke oil agglomerates in the presence of limestone or lime is part of this study. We believe that the incorporation of limestone or $CaCO_3$ into the agglomerates will lead to reduced sulfur emissions that will be environmentally acceptable. Preliminary results are encouraging.

Conclusions

Coke/Bitumen Agglomeration.

- The recovery of residual hydrocarbons from aqueous tailings and the quality of coke oil agglomerates depend on such factors as the mode and degree of agitation, mixing time, ratio of coke to total hydrocarbons in the tailings, pulp density and pH of the slurry.

- Pulp density of the slurries had a significant effect on the recovery of bitumen as well as the quality of coke oil agglomerates. In general higher pulp densities leads to poorer recoveries and lower quality agglomerates.

- Increasing the mixer rotational speed reduces the time required for good bitumen recoveries.

- Under high shear agitation, continued agitation beyond an optimum time leads to lower recoveries because of the dominance of destructive forces.

- Over 50% bitumen can be solvent extracted from coke oil agglomerates and the resulting coke can be recycled to collect more bitumen.

- Removal of oil greatly improves the rate of settling of the sediment thus freeing additional water. However, no correlation was found between the recoveries of bitumen and water.

Solids/Water Agglomeration.

- Solvent extraction followed by centrifugation recovered more hydrocarbons than solvent extraction alone or in combination with the agglomeration of mineral solids.

- About 5-15% of the solvent is lost to the solids in solvent extraction processes for the recovery of residual bitumen from storage tank sludge.

Captions for Figures

Figure 1 a) Effect of Coke: Bitumen on the bitumen recovery.
b) Amount of coke rejected as a function of bitumen recovery.

Figure 2 Effect of the degree of agitation on:
a) w/w% bitumen recovered.
b) w/w% collector coke in reject.
c) w/w% inert solids in agglomerates.
d) w/w% water in agglomerates.

REFERENCES

Ball, D.L.; J.M. Cooley, M.C. Hamilton and R. Schutte. 1981. A rapid method for the determination of bitumen, water, and solids in oil sands. Can. J. Chem. 59:1527-1530.

Camp, F.W. 1977. Processing Athabasca Tar Sands - Tailings Disposal. Can. J. Chem. Engin. 55:581-591.

Hall, E.S. and E.F. Tollefson. 1980. Recovery of residual bitumen from the aqueous tailings from hot water extraction of oil sands by air sparging. Energy Processing Canada. 39-46.

Hall, E.S. and E.F. Tollefson. 1982. Stabilization and destabilization of mineral fines-bitumen-water dispersions in tailings from oil sand extraction plants that use the hot water process. Can. J. Chem. Engin. 60:812-821.

Kessick, M.A. 1978. Clay slimes from the extraction of Alberta oil sands, Florida Phosphate matrix and other mined deposits. CIM Bulletin. 80-88.

Kumar, A.; B.D. Sparks and A. Majid. 1985. Recovery of organics from tailings pond sludge using coke for agglomeration. Proc. Can. Chem. Engin. Conf. 5:214-219.

Majid, A. and J.A. Ripmeester. 1982. Recovery of organics from aqueous effluents. NRC Special Report #C1094-82S.

Majid, A. and J.A. Ripmeester. 1983. Recovery of organics from aqueous effluents using refinery coke. J. Separ. Proc. Technol. 4:20-22.

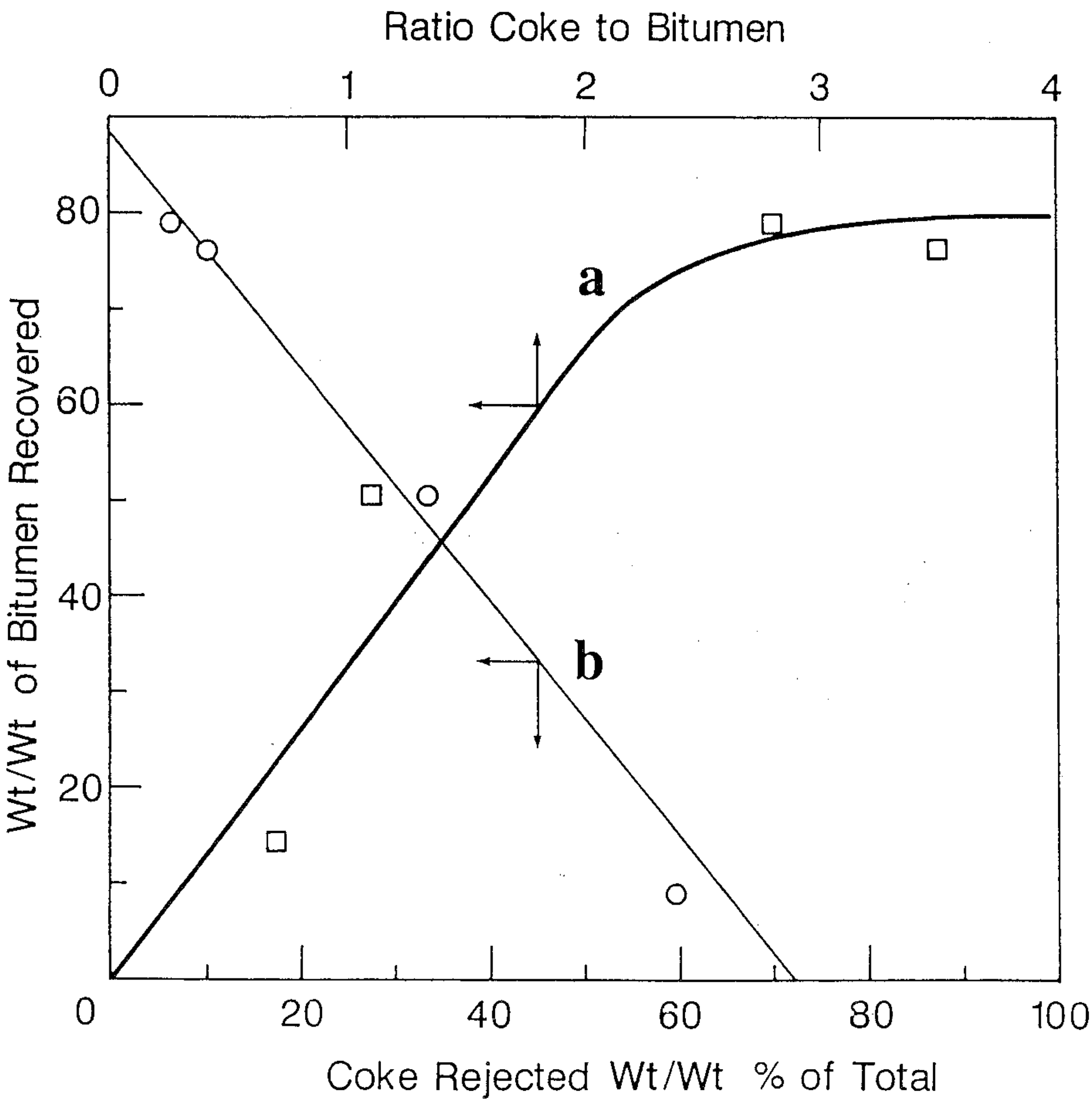
Majid, A. and B.D. Sparks. 1984. Total analysis of mineral wastes containing bitumen, solvent, water and solids. AOSTRA J. of Res. 1:21-29.

Majid, A.; J.A. Ripmeester and B.D. Sparks. 1985. Recovery of organics from aqueous effluents using hydrophobic materials. Proc. 4th Intern. Symp. on Agglomeration. 927-935.

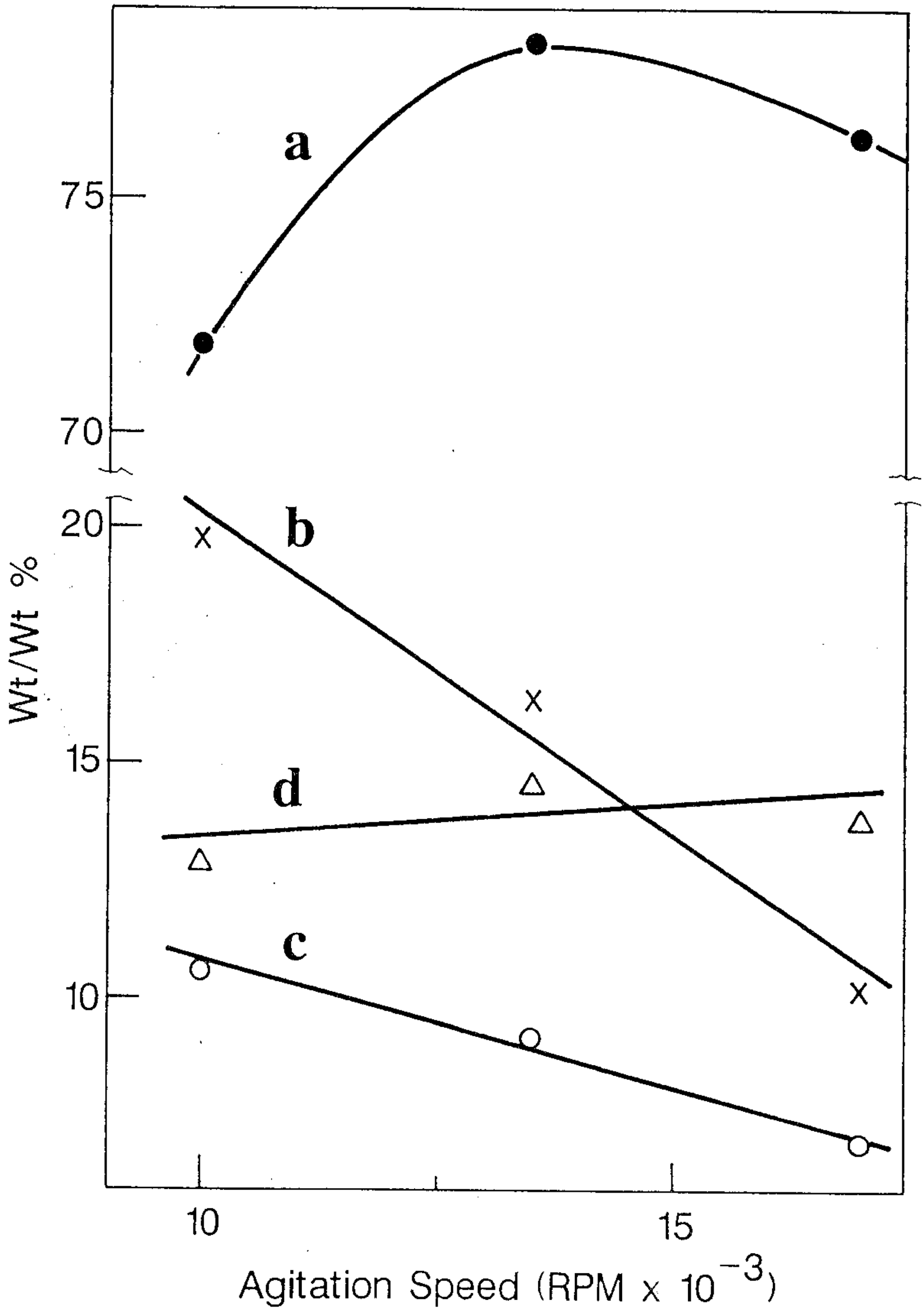
Majid, A.; A.F. Sirianni and J.A. Ripmeester. 1986. Recovery of organic and heavy metal components from aqueous dispersions. Can. Patent #1200778.

Sirianni, A.F. and J.A. Ripmeester. 1980. Tar sand bitumen recovery from aqueous effluents. Can. Patent #1088445.

Sirianni, A.F. and J.A. Ripmeester. 1981. Recovery of water and bitumen from the Athabasca oil sand tailings ponds. Can. J. Pet. Technol. 131-133.



Ratio Coke to Bitumen
0
1
2
3
4
80
60
40
20
a
b
Wt/Wt of Bitumen Recovered
0
20
40
60
80
100
Coke Rejected Wt/Wt % of Total



a
b
c
d
75
70
20
15
10
Wt/Wt %
10
15
Agitation Speed (RPM x 10^{-3})

36

DOE

TAR SAND

SYMPOSIUM

SPONSOR:
U.S. DEPARTMENT OF ENERGY

JULY 7-10, 1986

HOST:
WESTERN RESEARCH INSTITUTE

JACKSON, WYOMING