Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Recovery of Organics from Tailings Pond Sludge Using Coke for Agglomeration

A. Kumar[a]; B. D. Sparks[a]; A. Majid[a]
[a] Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada

To cite this Article Kumar, A. , Sparks, B. D. and Majid, A.(1986) 'Recovery of Organics from Tailings Pond Sludge Using Coke for Agglomeration', Separation Science and Technology, 21: 3, 315 — 326
To link to this Article: DOI: 10.1080/01496398608058380
URL: http://dx.doi.org/10.1080/01496398608058380

SEPARATION SCIENCE AND TECHNOLOGY, **21**(3), pp. 315-326, 1986

Recovery of Organics from Tailings Pond Sludge Using Coke for Agglomeration

A. KUMAR, B. D. SPARKS, and A. MAJID

DIVISION OF CHEMISTRY
NATIONAL RESEARCH COUNCIL OF CANADA
OTTAWA, ONTARIO, CANADA K1A OR9

Abstract

The effect of various process variables on the recovery of organics from sludge using an agglomeration technique was studied. Factorial design procedures were used to determine the important variables and their interactions on recovery of organics. It was observed that higher amounts and smaller particles of coke produced higher recoveries. A reasonable correlation between the surface area of coke and recovery of organics was observed. Furthermore, significant improvements in recoveries were obtained by using inexpensive additives during agglomeration.

INTRODUCTION

A large amount of sludge is generated by Suncor and Syncrude as a waste stream in the hot water process used to extract bitumen from Alberta oil sands. The sludge is stored in large, diked ponds which present a potential environmental hazard. The sludge contains appreciable amounts of residual bitumen and naphtha, which tend to stabilize the sludge, resulting in a substantial quantity of water being no longer available for recycling. It has been estimated that up to 11.9% of the bitumen originally present in the oil sand remains with the sludge, which represents 2930 tons of bitumen lost per day for a plant producing 16,000 m^3 (100,000 barrels) of synthetic crude oil per day (*1*). There is, therefore, great commercial interest in extracting the residual bitumen and naphtha from tailings pond sludge.

 0149-6395/86/2103-0315$3.50/0

It has been shown (*2*) that the value of recovered bitumen from sludge could more than offset the cost of mechanical dewatering procedures if the clays in sludge are first converted to calcium forms (*3*). Several groups have reported the extraction of bitumen from sludge by dilution-induced destabilization and/or gas sparging. Patents have been issued on the use of air (*4*) or air/CO_2 (*5*) as the sparging medium and water for dilution (*6, 7*). Addition of a variety of surface-active agents, inorganic chemicals, polyelectrolytes alone or in combination followed by agitation have been reported to promote separation of bitumen from sludge (*8–11*). Camp (*8*) has claimed that cationic surfactants, low pH, and high temperature aid destabilization of the sludge. Yong et al. (*9*) have suggested that wet-grinding reduces flocculant requirement by creating reactive surfaces through a complex mechanism involving neutralization of electrical repulsive forces, precipitation of voluminous flocs, and bridging of particles by high polymers. Specken (*10*) claimed that by adding a combination of $CaSO_4$ or $KMnO_4$ and a flocculant the agglomeration of clay particles was facilitated. However, all of the above processes require substantial quantities of fresh water which might not always be readily available at plant locations. Also, the use of various chemicals might be of concern in assessing the process economics.

Workers at the National Research Council, Ottawa, have reported (*12–15*) the use of hydrophobic materials for extraction of bitumen and naphtha from sludges by the spherical agglomeration process. A variety of agitating devices has been employed (*16*) for the purpose. The process has the following advantageous features:

1) Little additional process water is required
2) Hydrophobic materials, e.g., coke and sulfur, are available at the plant site
3) Virtually complete recovery of bitumen/naphtha is obtained
4) Bitumen could be extracted from the resulting agglomerates or they could be burned with improved combustion characteristics
5) After separation of the bitumen and naphtha, the sludge showed improved settling behavior (*15*), thereby allowing greater water recycle

The present work is part of a systematic study on the separation of bitumen/naphtha (organics) from sludge by agglomeration, using a blender as the mixing device. The effects of various process variables and their interactions were studied. The use of certain additives to enhance organics recovery was also explored.

EXPERIMENTAL

Materials

Suncor sludge was obtained in 1-gallon containers from the Alberta Research Council sample bank. The sludge was well stirred before taking the sample to maintain its homogeneity. Suncor delayed coke was also obtained from the same source. The coke was ground and sized using a Brinkmann Centrifugal Grinding Mill ZM-1.

Procedure

About 100 g of homogenized sludge was placed in a Waring Blendor, the desired amount of coke and water was then added, and blending was continued for a specified time at 120 rps. Coke-organics agglomerates were washed with water over a screen to remove free mineral matter. For the purposes of analysis, the organics from the agglomerates were extracted in benzene by agitation on a paint-shaker for 15 min.

The solutions were subsequently centrifuged for 2 h at 66.6 rps. The organic layer was used for the analysis. An identical procedure was used to extract organics from sludge.

Several preliminary experiments were performed to determine the range of variables to be investigated (e.g., speed of blending and order of adding the ingredients). As a result, the type and range of variable to be investigated was established as described in Table 1.

The sludge was first mixed for 25% of the total blending time, then 50% of the coke was added, followed by 50% of the process water. Blending was continued for another 25% of the blending time, at which point the rest of the coke and process water were added. Blending was then

TABLE 1
Codes and Range of Variables for 2^{4-1} Factorial Design

	Variable/Code	−1	+1
X_1	Blending time (min)	20	40
X_2	Amount of coke (wt%)	20	30
X_3	Particle size of coke (100% passing, mm)	0.5	2.0
X_4	Amount of added water (mL)	25	50

continued until the required time was completed. At the end of blending the agglomerates were washed on a screen and removed for analysis.

Analysis

NMR proton spectroscopy was used to determine the total organics (*17*). Bitumen was determined by filter paper (*18*) or spectrophotometric (*19*) methods. Organics extracted in benzene from the sludge itself were used for calibration. BET surface area of coke was measured using a Ströhlein Areameter. The elemental composition (w/w) of coke was as follows: C, 82.8%; H, 3.5%; N, 1.4%; S, 5.9%; 0, 3.0%, and ash, 3.4%. The composition of the tailings pond sludge was found to vary from time to time. A typical sludge sample was found to have the following composition (w/w): Bitumen, 6.0%; naphtha, 1.3%; solids, 23.7%; and water, 69.0%.

RESULTS AND DISCUSSION

Effects of Process Variables

Based on the preliminary experiments, it was decided to study the effect of four variables. The experimental strategy involved using a two-level fractional factorial design (type 2^{4-1}) to find the relative importance of the variables and their possible interactions in relation to the recovery of organics (referred to as recovery) from sludge. The variables were coded as described in Table 1, a positive as well as a negative defining relationship was used, and experiments along with replicates were performed in randomized order. Only binary interactions were considered, as ternary and higher interactions are usually insignificant. Using a 95% confidence interval for the true values of parameters, the following reduced model fitting the data was arrived at:

$$\text{Recovery (\%)} = 75.5 + 8.0X_2 - 7.6X_3 + 4.9(X_1X_2 + X_3X_4) \qquad (1)$$

It is clear from the above model that X_2 and X_3 are relatively important variables. Furthermore, to maximize the recovery, the variables X_1, X_2, X_3, and X_4 should be assigned the codes 1, 1, -1, and -1, respectively.

The two more important variables (amount and particle size of coke) were studied in more detail while the remaining two variables (time of blending and amount of added water) were fixed to give maximum recovery as mentioned in the previous paragraph. Accordingly, the effects on recovery of two additional particle sizes and larger amounts of coke were investigated. The results are plotted in Fig. 1. It is evident from the figure that recovery was improved as both the particle size of coke was reduced and the amount increased. The effect of particle size on bitumen recovery is shown in Fig. 2. A general increase in bitumen recovery is observed with an increase in amount of coke while no regular trend was observed with an increase in particle size.

Recovery and Surface Area

As discussed in the preceding section, the recovery of organics or bitumen from sludge did not show a good correlation with particle size of coke. As the first step in agglomeration is the oil-wetting of particles, it is likely that surface area of the particles would have a more important influence on the process. Consequently, plots of recovery of organics and

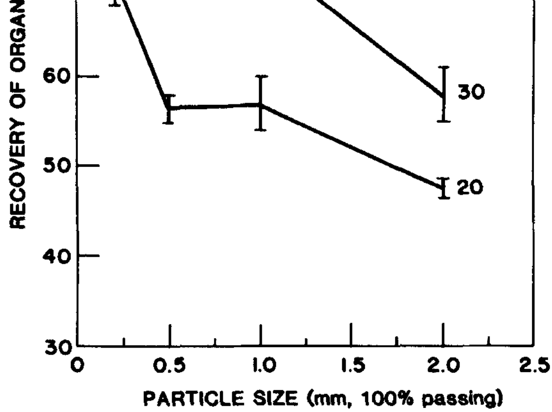

FIG. 1. Effect of particle size on recovery of organics for various amounts of coke.

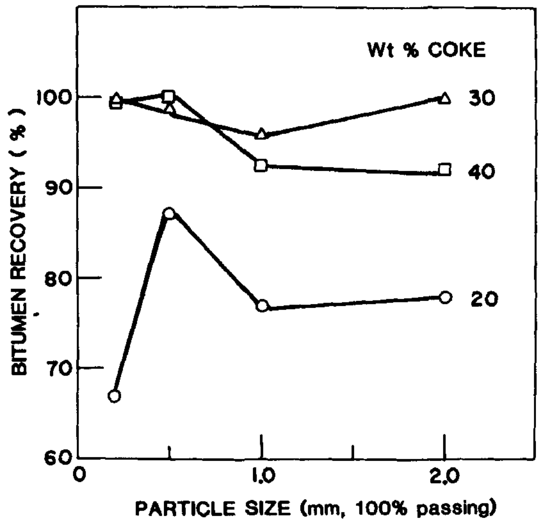

FIG. 2. Effect of particle size on recovery of bitumen for various amounts of coke.

bitumen were constructed as a function of particle surface area (Figs. 3 and 4). A linear relationship between recovery of organics and BET surface area was observed. Also, the discrepancy in Fig. 1, where only a small variation in recovery was observed between particles of 0.5 and 1 mm diameter, is explained by the fact that the BET surface area values are comparable in both cases. However, in the case of bitumen recovery (Fig. 4), no regular trend is observable. It is speculated that certain sites on particles are not wetted by bitumen as easily as by naphtha during the process of agglomeration.

When the total collection area ((surface area/unit weight) × amount used) of the coke particles was plotted against recovery, for each of the experiments carried out under the same mixing conditions, then it was found that all the points fell close to the same curve, Fig. 5. Although there is a general trend of improved organic recovery with increasing total collecting area, it is apparent that the relationship is not a simple one. An initial rapid rise in recovery upon addition of coke gradually tails off to a plateau, representing the maximum attainable recovery under the given set of experimental conditions.

However, surface area is not the only criterion to be considered in successful operation of the process. It is a requirement for satisfactory particle growth that there be sufficient oil on the surface of the coke particles to provide a continuous fluid network within the matrix of

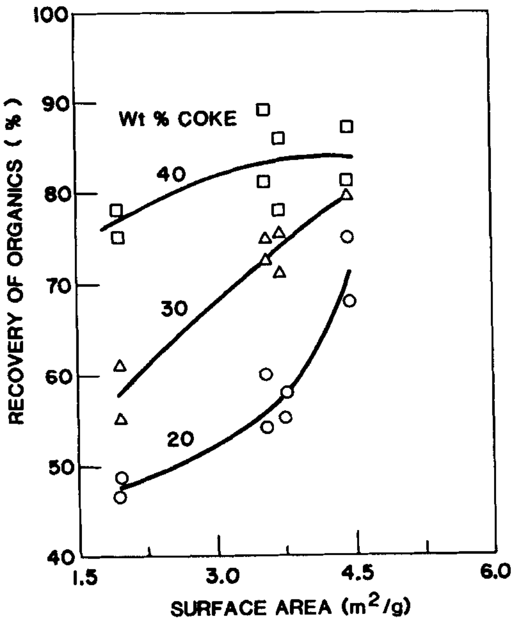

FIG. 3. Effect of BET surface area on recovery of organics for various amounts of coke.

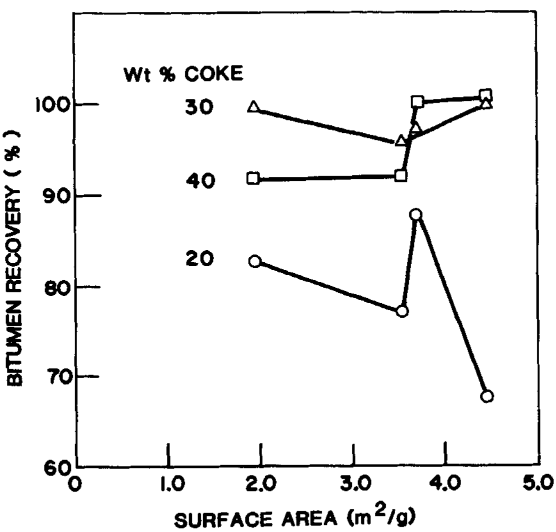

FIG. 4. Effect of BET surface area on recovery of bitumen for various amounts of coke.

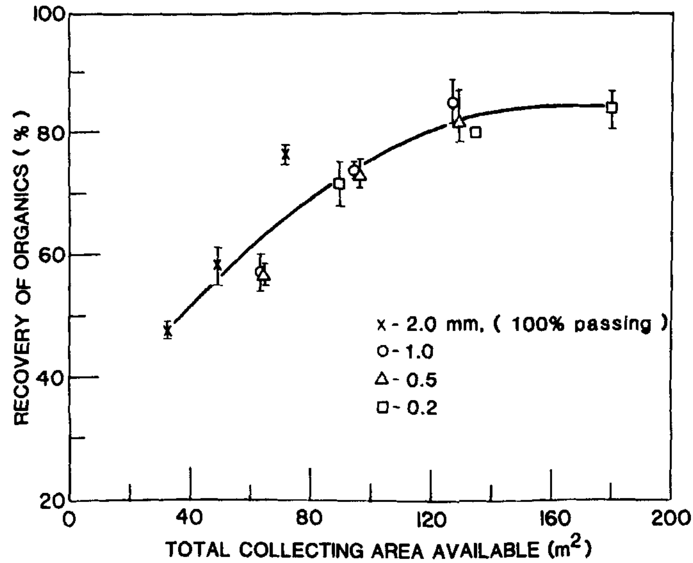

FIG. 5. Effect of total collecting area on recovery of organics.

agglomerating particles. If the available surface area is too large, the oil will be spread too thinly and consequently interparticle bonding will be weak, resulting in inadequate agglomeration. Thus, even though the oil may be completely collected by the coke particles, recovery will drop because it will be difficult to achieve a clean separation of finely agglomerated coke from the bulk of the suspension. Consequently, conditions must be defined to allow an optimum balance between adsorption and agglomeration requirements. As the total surface area consists of two major components (particle size and amount of adsorbent), then these two components can be adjusted to give the best results in the most economical manner.

Effects of Additives

As discussed in the Introduction, several workers (*8–11, 16*) have reported on the utility of chemical additives in the recovery of organics from aqueous sludge. Two additives were chosen for this study: 1) sodium silicate which is relatively inexpensive and has been reported to improve

TABLE 2
Codes and Range of Variables for 2^3 Factorial Design

	Variable/Code	−1	+1
X_1	Type of additive	Lignosulfonate	Sodium silicate
X_2	Amount of coke (wt%)	20	30
X_3	Amount of additive (wt%)	0.1	0.4

recovery (*16*), and 2) a crude lignosulfonate which is extracted from abundantly available waste (sulfite spent liquor) from a Canadian pulp and paper company. The latter has been reported to modify the interfacial properties of oil/water/salts systems (*20*). The experimental strategy involved the use of a two-level factorial design (type 2^3); the range and codes of the variables studied are listed in Table 2. The rest of the variables were selected to give recoveries lower than 60% without the use of additives. The size of coke, time of blending, and amount of added water were fixed at 2 mm, 40 min, and 25 mL, respectively, in all experiments. Experiments with replicates were performed in randomized order. Using a 95% confidence interval for the true values of parameters, the following reduced model fitted the data:

$$\text{Recovery (\%)} = 61.6 + 6.0X_1 + 7.5X_2$$

It is apparent from the above model that higher recovery is obtained by assigning code 1 to X_1 and X_2, i.e., sodium silicate and larger amounts of coke. The amount of additive (X_3) was found to have no significant effect on the recovery in the range studied. The data are presented in Figs. 6 and 7. It is clear from the figures that a significant increase in recovery is obtained by using chemical additives even at a 0.1% level. The observations here support the views of several workers (*8–11, 16*) about the effect of destabilizing the sludge and facilitating the release of organics from sludge by modifying the surface behavior.

Quality of Agglomerates

The separated agglomerates varied in appearance from a very clean and regular shape to a sticky mass; usually the best recoveries were associated with the former variety. Some arbitrary tests showed that the

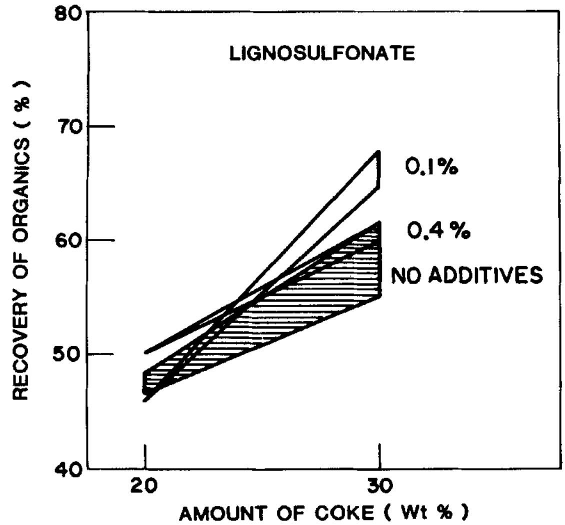

FIG. 6. Effect of lignosulfonate addition on recovery of organics.

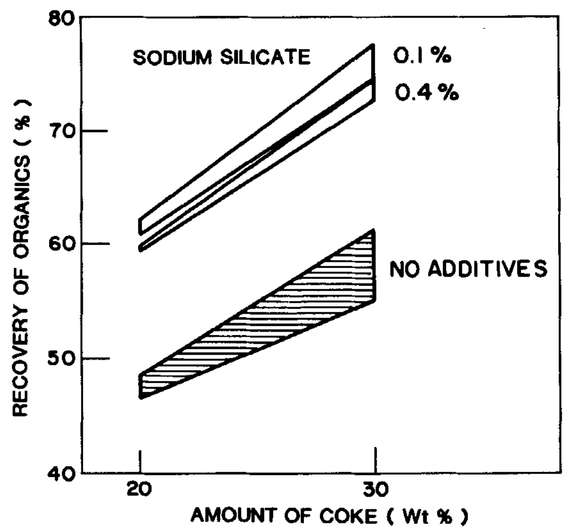

FIG. 7. Effect of sodium silicate addition on recovery of organics.

organics could be reextracted from the agglomerates with minimal agitation even in concentrated solution of bitumen in naphtha (50% w/w). The extracted coke could then possibly be reused in the agglomeration process.

CONCLUSIONS

1) In extraction of organics from sludge, the amount and particle size of coke are the most important variables.
2) There is a linear correlation between recovery of organics and BET surface area of the coke particles or total collection area (BET surface area × amount of coke) in the range of variables studied.
3) A significant increase in recoveries was obtained by using 0.1% (w/w) of sodium silicate or crude lignosulfonate as additive.
4) Good quality agglomerates were actually associated with higher recoveries.

Acknowledgments

The authors are thankful to Professors G. Neale and V. Hornof for supplying the lignosulfonate samples.

REFERENCES

1. E. S. Hall and E. L. Tollefson, *Energy Process.*, *72*, 38 (1980).
2. D. J. McConaghy, Alberta Research Council, Unpublished Report, 1978.
3. M. A. Kessick, *Int. Miner. Process.*, *6*, 277, (1980).
4. H. J. Davitt, Canadian Patents 975,696, 975, 697, 975, 699, 975, 700 (October 1977).
5. D. A. Vendrinsky, Canadian Patent 1,022,098 (December 1977).
6. F. A. Bain and J. O. L. Roberts, U.S. Patent 4,018,664 (April 1977).
7. R. B. Roth and W. H. Seitzer, Canadian Patent 1,146,898 (May 1983).
8. F. W. Camp, Canadian Patent 891,472 (January 1972).
9. R. N. Yong, A. S. Baweja, and B. P. Warkentin, Canadian Patent 1,085,762 (September 1980).
10. G. A. Specken, Canadian Patent 1,030,674 (May 1978).
11. C. E. St. Denis and M. A. Kessick, *Can. J. Chem. Eng.*, *60*, 675 (1982).
12. A. F. Sirianni and J. A. Ripmeester, Canadian Patent 1,088,445 (1980).
13. A. Majid and J. A. Ripmeester, *J. Sep. Process Technol.*, *4*, 20 (1983).
14. A. Majid, A. F. Sirianni and J. A. Ripmeester, *Proceedings, 2nd Congress Chemical Engineering, Montreal*, Vol. 2, 1981, p. 434.

15. J. A. Ripmeester and A. F. Sirianni, *J. Can. Pet. Technol., 20*, 131 (1981).
16. A. Majid, J. A. Ripmeester, and B. D. Sparks, Presented at the 4th International Symposium on Agglomeration, June 2–5, 1985, Toronto, Canada.
17. A. Majid and B. D. Sparks, *AOSTRA J. Res., 1*, 21 (1984).
18. D. L. Ball, E. D. Cooke, J. M. Colley, M. C. Hamilton, and R. Schutte, *Can. J. Chem., 59*, 1527 (1981).
19. M. S. Patel, *Anal. Chem., 46*, 794 (1974).
20. A. Kumar, G. Neale, and V. Hornof, *Pulp Pap. Can., 85*(7), 19, (1984).

Received by editor April 15, 1985