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RECOVERY OF ORGANICS FROM TAILINGS POND SLUDGE USING COKE FOR AGGLOMERATION

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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. However, a model expressing recovery of organics as a function of porosity parameters of coke gave better results. 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, dyked ponds which present a potential environmental hazard. The sludge contains appreciable amounts of residual bitumen and naphtha, which tends 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 16000 m³ (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.

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/CO₂ (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 CaSO₄ or KMnO₄ 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 have been employed (16) for the purpose. The process has the following advantageous features:

- (i) Little additional process water is required.
- (ii) Hydrophobic materials e.g. coke and sulphur are available at the plant site.
- (iii) Virtually complete recovery of bitumen/naphtha is obtained.
- (iv) Bitumen could be extracted from the resulting agglomerates or they may be burned with improved combustion characteristics.
- (v) After separation of the bitumen and naphtha, the sludge showed improved settling behaviour (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 Blender, 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 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 Area-meter. A Micromeritics mercury porosimeter (Pore Sizer 9305) was employed to determine the pore size distribution of coke particles. The elemental composition (w/w) of coke was as follows: C, 82.8%; H, 3.5%; N, 1.4%; S, 5.9%; O, 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-2⁴⁻¹) 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 negative defining relationship was used and

TABLE 1 Codes and range of variables for 2⁴-1 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

experiments alongwith 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:

$$\text{Recovery } (\bar{X}) = 75.5 - 8.0 x_2 - 7.6 x_3 + 4.9(x_1 x_2 + x_3 x_4) \quad (1)$$

It is clear from the above model that x_2 & x_3 are relatively important variables. Furthermore, to maximize the recovery the variables x_1 , x_2 , x_3 and x_4 would 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 increase in amount of coke while no regular trend was observed with 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 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 diameter 0.5 and 1 mm 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) x 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 mixing 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 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.

Recovery and Pore Size Distribution

As mentioned in the preceding section surface areas of coke samples of different particle sizes did not adequately correlate with their ability to recover organics from sludge. Therefore, an attempt was made to characterize various coke fractions more accurately by determining the porosity and pore size distribution, using mercury porosimetry. This technique has been employed by several workers (20-23) to characterize porous materials (clays, shales). In this regard the work of Winslow and Lovell (23) is of particular interest where pore size parameters of shales were used to correlate with their durability index for highway construction applications. The parameters considered by Winslow and Lovell (23) were: cumulative porosity (ϵ), median pore diameter (d_m , μ m) and spread factor ((S), ratio of 25 percentile pore diameter to median pore diameter). The effects of these parameters, derived for various coke fractions, on the recovery of organics from sludge, are shown in Figures 6-8. A maximum in recovery was apparent at a cumulative porosity (sum of inter and intra particle porosity) value of 0.4 (Fig. 6). It is clear from Fig. 7, that higher recoveries were observed for coke fractions having lower median pore diameter. However, an increase in recovery was observed with increase in spread factor for various coke samples (Fig. 8). To find the combined effect of these parameters on recoveries a Winslow-Lovell type of model, as described below, was tested.

$$\text{Recovery } (\%) = 1 + n/\epsilon + p/d_m + q/S$$

where ϵ , d_m and S are cumulative porosity, median pore diameter and spread factor as described earlier. n , p and q are regression coefficients.

The data from the present work adequately fitted the above model. It is clear from Fig. 9 that difference between actual and predicted recoveries is within $\pm 5\%$.

The above procedure might be helpful in screening coke and other materials for their potential application to recover organics from sludge.

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 recovery (16) (11) 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 (24). The experimental strategy involved the use of a two level factorial design (type 2³), the range and codes of the variables studied are listed in Table 2. The rest of the

TABLE 2 Codes and range of variables for 2³ 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

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:

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

It is apparent from the above model, that higher recovery is obtained by assigning code 1 to X₁ and X₂ i.e. sodium silicate and larger amounts of coke. The amount of additive (X₃) was found to have no significant effect on the recovery in the range studied. The data are presented in figures 10 and 11. 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 behaviour.

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 organics could be re-extracted 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 $\times$ amount of coke) in the range of variables studied.
3. Pore size parameters (cumulative porosity, median pore diameter and spread factor) of coke particles determined by mercury porosimetry were adequately correlated to recovery of organics.

4. A significant increase in recoveries was obtained by using 0.1% (w/w) of sodium silicate or crude lignosulfonate as additive.
5. Good quality agglomerates were usually associated with higher recoveries.

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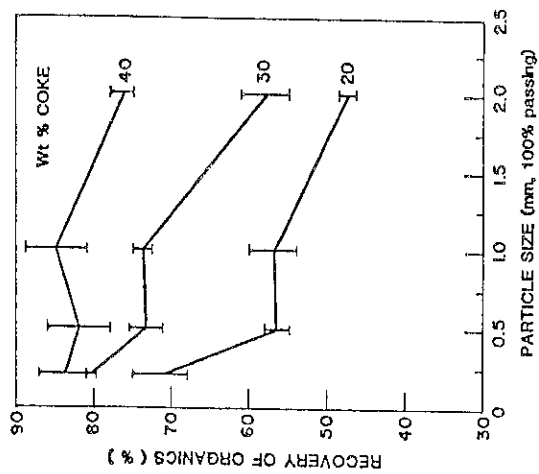


Figure 1. Effect of particle size on recovery of organics for various amounts of coke.

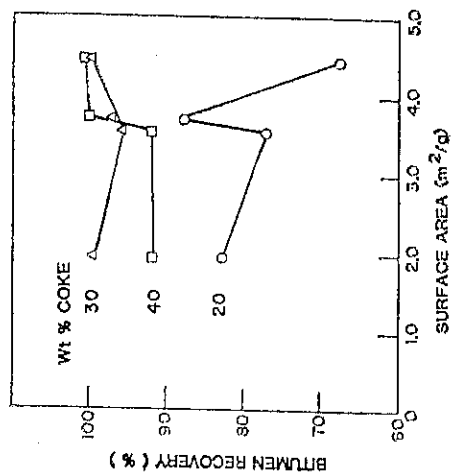


Figure 2. Effect of particle size on recovery of bitumen for various amounts of coke.

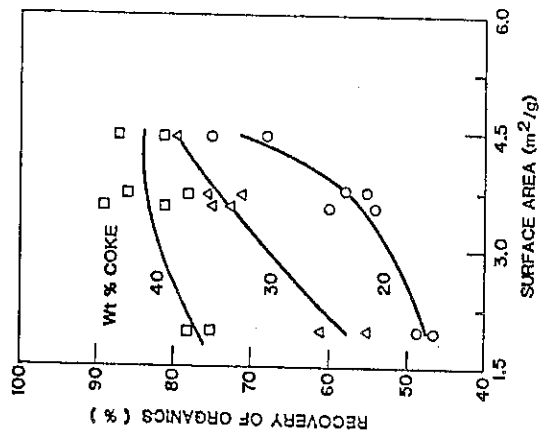


Figure 3. Effect of BET Surface area on recovery of organics for various amounts of coke.

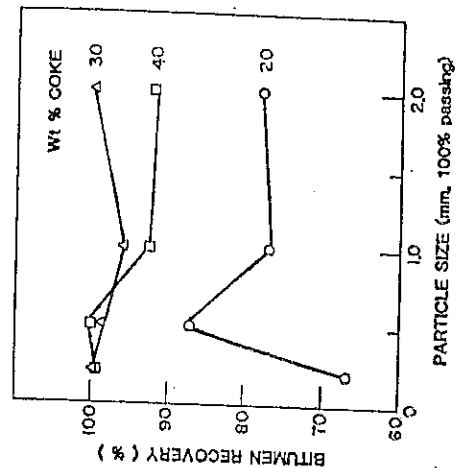


Figure 4. Effect of BET Surface area on recovery of bitumen for various amounts of coke.

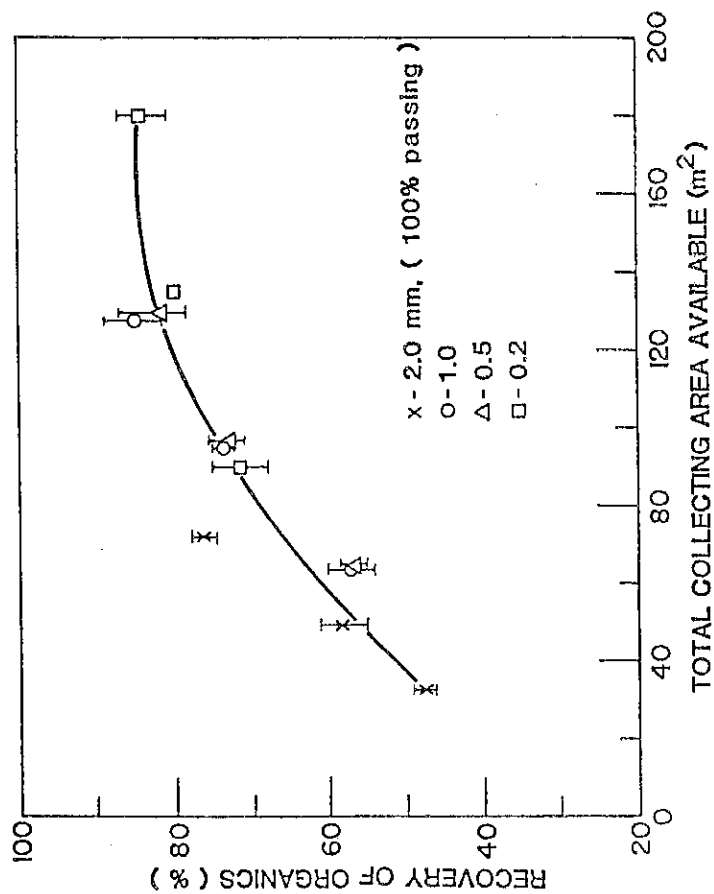


Figure 5. Effect of total collecting area on recovery of organics.

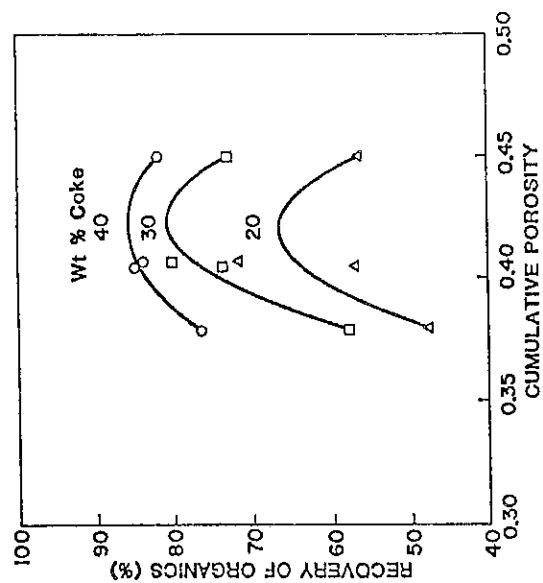


Figure 6. Effect of cumulative porosity on recovery of organics.

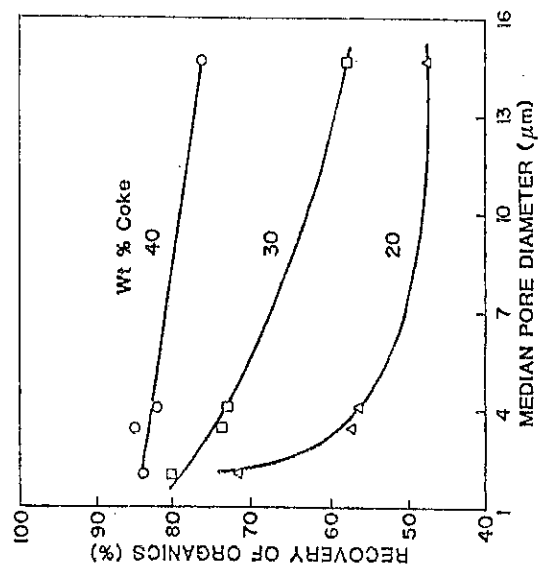


Figure 7. Effect of median pore diameter on recovery of organics.

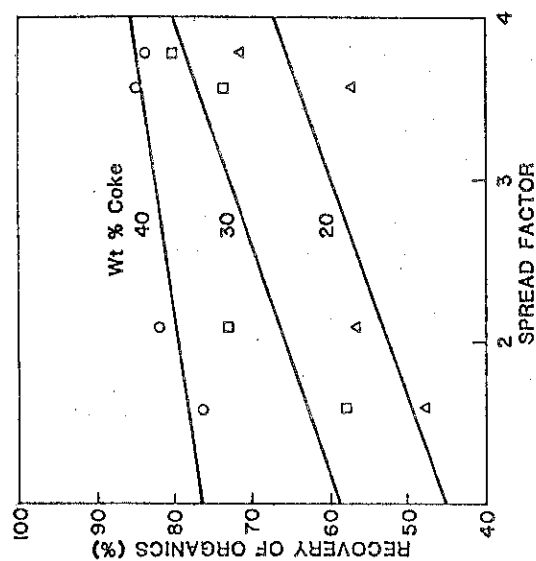


Figure 8. Effect of spread factor on recovery of organics.

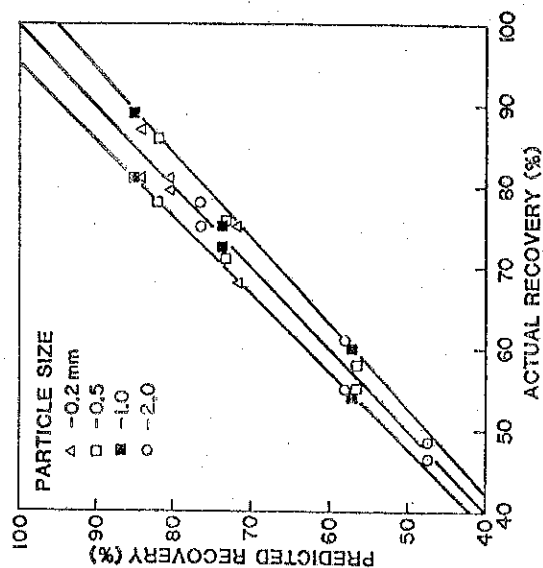


Figure 9. Plot of actual vs model-predicted recoveries of organics.

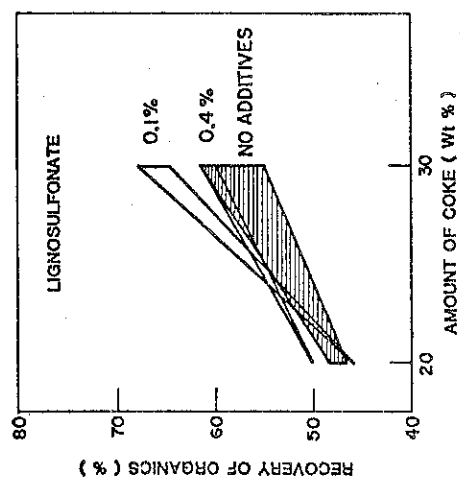


Figure 10. Effect of lignosulfonate addition on recovery of organics.

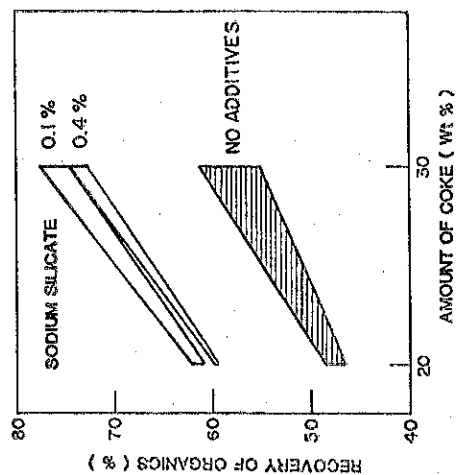


Figure 11. Effect of sodium silicate addition on recovery of organics.



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