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Characterization and Separation of Ash from CANMET Coprocessing Residue by Oil Phase Agglomeration Techniques

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INTRODUCTION

CANMET's coal/heavy oil coprocessing reactor yields a solid residue that contains most of the ash-forming components originally associated with the feed coal as well as the reacted catalyst solids. The residue amounts to about 10-20% of the product stream. For both economical and environmental reasons it is desirable to beneficiate this material in order to minimize wastage by producing a value added product suitable as an asphalt binder or electrode coke. Alternatively, removal of the ash would make it possible to recycle the material through the coprocessing reactor to increase the production of lighter oils. In the latter case it would be desirable to separate selectively the siliceous matter so that the iron content of the catalyst is retained for recycle with the pitch.

The liquid phase agglomeration technique, developed at the National Research Council of Canada, has the potential to play a major role in the beneficiation of finely divided carbonaceous solids (1-4). This technique has the advantage of being able to separate selectively fine solids while maintaining high recovery of the combustible, carbonaceous material. The principle of selective liquid phase agglomeration is based on the preferential wetting of a specific solid component, in liquid suspension, by a second, immiscible liquid (bridging oil in this case). The formation and growth of oil agglomerates is governed by the amount of oil present in the capillary interstices between the fine particles of the solids.

Surface chemical effects play an important role in the selective separation of one component from a complex mixture like coprocessing residue (3). The surface characteristics of toluene extracted solids separated from the coprocessing residue were studied using Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Analysis (EDXA), and X-ray photoelectron spectroscopy (XPS), in order to evaluate their separation potential using oil phase agglomeration.

Also, ash dissemination size is a primary determinant for separation. The degree to which a carbonaceous material can be beneficiated by agglomeration is limited by the extent to which the ash can be liberated from the material (5). Washability characteristics derived from float-sink analysis and/or specific-gravity fractionation (6), usually provide a good measure of the degree of dissemination of the ash associated with coal. In this investigation we have used float-sink tests on the toluene extracted solids from coprocessing residue to determine empirically the level of ash separation attainable. These results have been compared with the actual beneficiation results obtained by oil phase agglomeration.

EXPERIMENTAL METHODS

Materials

The vacuum residue used in this investigation was obtained from a bench scale CANMET coal-oil coprocessor. Table 1 lists the composition of this test sample.

Scanning electron micrographs were recorded using a JEOL model JSM-5300 instrument operated at 10 kV. The samples were coated with a thin carbon layer to impart conductivity. Energy dispersive X-ray analysis was performed with a Link model QX2000 system attached to the scanning electron microscope. X-ray photoelectron spectroscopy was performed with a Physical Electronics (Perkin Elmer, Eden Prairie, MN, USA) model 550 instrument. Mono chromatic Al $K\alpha$ radiation was used.

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Table 1.
Composition of CANMET Coprocessing Residue

C	77.5 w/w%
H	6.2 w/w%
N	1.2 w/w%
S	4.4 w/w%
Toluene insoluble solids (TIS)	19.7±1.3 w/w%
Ash at 600°C (feed)	11.8 w/w%
Ash at 600°C (TIS)	37.3 w/w%
Major ash constituents	Al, Si, S, Ca and Fe
Al	4.3 w/w% of ash
Fe	20.5 w/w% of ash
Si	3.0 w/w% of ash
Average particle size of the ash	10 μm

The dry samples were pressed into Indium foil for analysis. Survey spectra were collected using pass energies of 188 eV, while high resolution spectra were recorded with a 22 eV pass energy. An electron flood gun was used to neutralize the charge during the experiment. Bonding energies were referenced to the carbon-carbon bond which was assigned a binding energy of 284.6 eV. Atomic compositions were estimated by standard programs provided with the instrument. During analysis, the pressure inside the instrument was always lower than 5×10^{-9} torr.

Float-Sink Tests

Triplicate samples of coprocessing residue were extracted with toluene in a Dean and Stark Soxhlet extraction apparatus. The sample was wrapped in three layers of Whatman No. 2 filter paper to ensure no solids were lost into the extracting toluene. Also, the toluene extract was diluted and centrifuged to ensure it contained no additional solids. Three extractions on each of the samples were conducted to ensure the removal of all of the organic material.

Float-sink tests were carried out on the extracted solids using "Certigrav" at specific gravities of 1.3, 1.4, 1.5, 1.6, 1.8, 2.0 and 2.2. Each separated fraction was analyzed for ash using a Leco Mac 400 Proximate Analyzer. Size analyses were conducted on the extracted feed material and on the specific gravity fractions using a Malvern Particle Sizer M 3.1.

Agglomeration Procedure

Pitch samples (100g) were dispersed in distilled water (500 mL) and ground using a 2 kg charge of 0.25" zirconia balls in a 10 cm porcelain ball mill. The average particle size of the ground material was determined to be 9.8 ± 1.4 μm using a Malvern Master Particle Sizer M 3.1. A slurry, containing about 20 g of pitch, was first conditioned with an appropriate reagent by agitating in a Waring Blendor at 250 rps for one minute. After this time the agitation speed was lowered to 150 rps. An agglomerating liquid was then added drop-wise, with mixing, until discrete agglomerates formed. At this stage the blending speed was raised to 200 rps for 2-3 minutes to facilitate ash liberation. The agglomerated pitch was then separated from the aqueous phase on a 100 mesh screen, washed several times with distilled water, dried at 100°C and then ashed to determine the degree of beneficiation.

RESULTS AND DISCUSSION

Washability studies using float-sink tests are routinely carried out to determine the relative ease of separation of coal from refuse (6). These studies are usually very helpful in determining the efficiency of a separation process and/or what might be done to improve its performance. Our experience with coal beneficiation by oil phase agglomeration is also consistent with the usefulness of these tests in determining the amenability of oil phase agglomeration technology for cleaning different types of coals (7).

Float-Sink Tests

The float-sink process can be subdivided into two processes involving ash liberation and coal cleaning (6). In the liberation process the bonds between coal and impurities are frac-

Table 2.
Float and Sink Data for Toluene Extracted Solids from Coprocessing Residue

(1) Specific gravity	Individual fractions			Cumulative Float			Cumulative Sink			Ordinate
	(2) yield %	(3) Ash %	(4) C %	(5) w %	(6) Ash %	(7) C %	(8) w %	(9) Ash %	(10) C %	Z (11)
1.4 x 1.5 Float	12.3	3.1	19.1	12.3	3.1	19.1	100	37.3	100	6.2
1.5 x 1.6	1.5	10.1	2.1	13.8	3.9	21.2	87.7	42.1	80.9	13.1
1.6 x 1.8	8.3	19.0	10.7	22.1	9.5	31.9	86.2	42.7	78.8	18.0
1.8 x 2.0	17.8	26.0	21.0	39.9	16.9	52.9	77.9	45.2	68.1	31.0
2.0 x 2.2	25.7	39.4	24.8	65.6	25.7	77.7	60.1	50.8	47.1	52.8
Sink 2.2	34.4	59.4	22.3	100	37.3	100	34.4	59.4	22.3	82.8

tured, and in the separation process the resulting liberated particles are sorted using a dense media. One fraction is a float product which is rich in coal while another is a reject which is high in ash components. These tests provide information on the theoretically attainable separation, although in any actual coal cleaning process, the separation may be incomplete. In actual separation processes, some sink material will always report to the clean coal product and some float material to the refuse (8).

Table 2 summarizes the float-sink analysis data for the toluene extracted solids from coprocessing residue. No material floated below a specific gravity of 1.4. As the specific gravity was increased from 1.5 to 2.2, successive samples of float material, with increasing ash contents, were removed from the starting material. The product qualities of these separated fractions were very different from those of typical coprocessing fuel coal. In all cases, the ash content of the material separated at any specific gravity was much less than the ash content of typical unreacted coal separated at the same specific gravities. One possible explanation for this is that more of the vitrain lithotypes, which are contained in the feed coal, have been converted to liquid products, leaving more unreacted fusain in the coprocessing solid residue. Representative properties of lithotypes are shown in Table 3 (8).

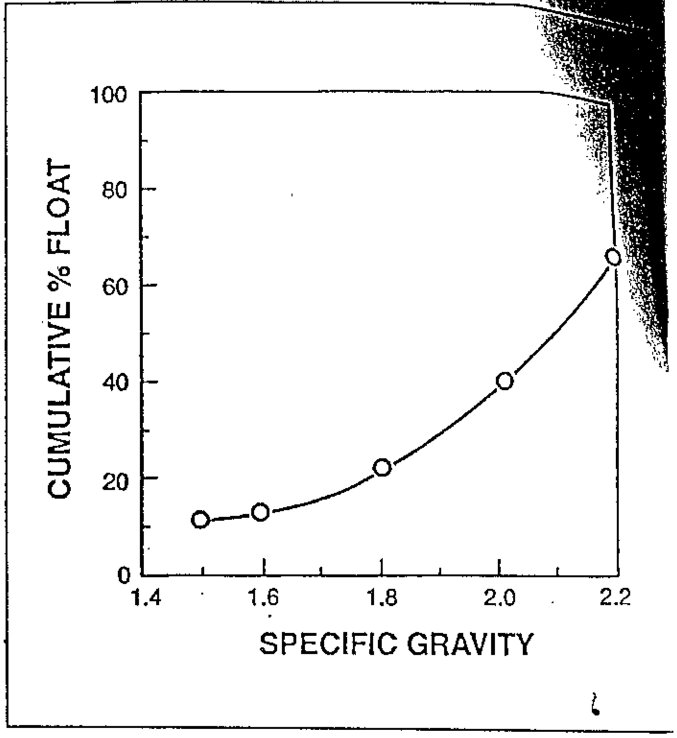

Figure 1. Washability curve showing the yield of float product separable at different specific gravities.

Experience with the oil agglomeration process has shown that particles with specific gravities above 2 cannot be oil wetted and collected as agglomerates, indicating that these particles are too hydrophillic to be wetted by oil. If it is assumed that the particles in the coprocessing residue behave in a similar manner, then it should be possible to predict the amount of coprocessing residue solids that can be removed from the oil phase. The data from the float-sink tests presented in Table 2 has been plotted graphically in Figures 1-3 as washability curves. Figure 1 is a plot of the cumulative percent weight float data and specific gravity fractions (columns 5 vs. 1). This curve shows the theoretical yield of washed product from the toluene extracted solids for any specific gravity of separation. It is obvious from this curve that a maximum of about 60 weight percent of solids have a specific gravity more than 2 and therefore, are possibly transferable to the aqueous phase.

Figure 2 shows two washability curves plotting the cumulative ash in the float product (columns 5 vs 6) and the sink (columns 8 vs 9). These curves give the theoretical percent ash of the washed product and the sink at any given yield of the washed product. These plots suggest that about 50 weight percent of the total ash is contained in the 60 weight percent float product separated at specific gravity above 2. These results suggest that theoretically it might be possible to reduce the ash content of the pitch by 50% provided that the sample could be ground to the ash liberation size which is less than 10 microns. It might therefore, be better to remove the high ash content solids from the reactor prior to coprocessing.

The plot shown in Figure 3, known as the elementary ash curve (6), is a derivation of the cumulative percent ash in the float material and is intended to show the rate of change of the ash content at different specific gravities or yields. The curve is designed to show the highest ash content of any individual particle found in the float product at any specific

Table 3.
Some Representative Properties of Coal Lithotypes

Lithotypes	General Appearance	Specific Gravity	Ash
Vitrain	Uniform shiny black bands	≈ 1.3	0.5-1% (mainly plant ash)
Clarain	Laminated: composed of shiny & dull bands	~ 1.3	0.5-2.0%
Durain	Dull, nonreflecting, poorly laminated	1.25-1.45	1-5% (much extraneous ash)
Fusain	Charcoal-like fragments	soft fusain 1.35-1.45, Hard Fusain ≥ 1.6	≥ 5-10%

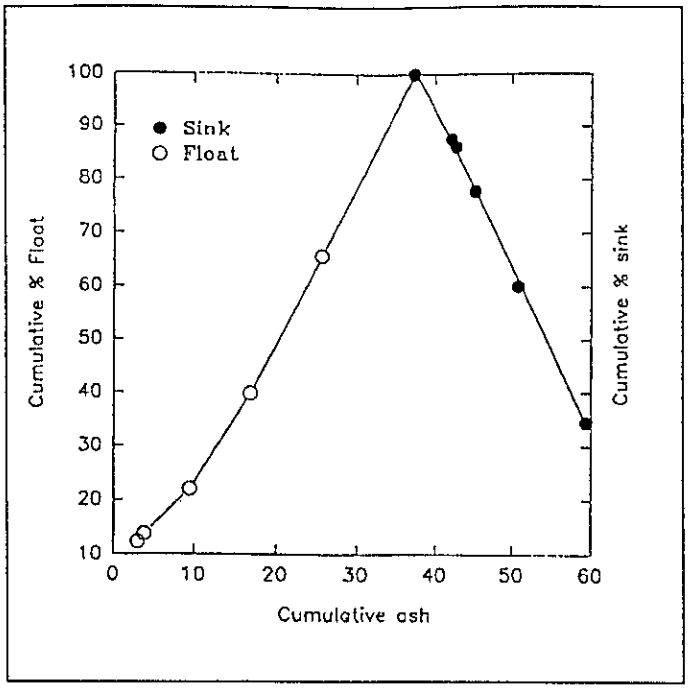

Figure 2. Washability curve showing cumulative ash in the float and sink specific gravity fractions.

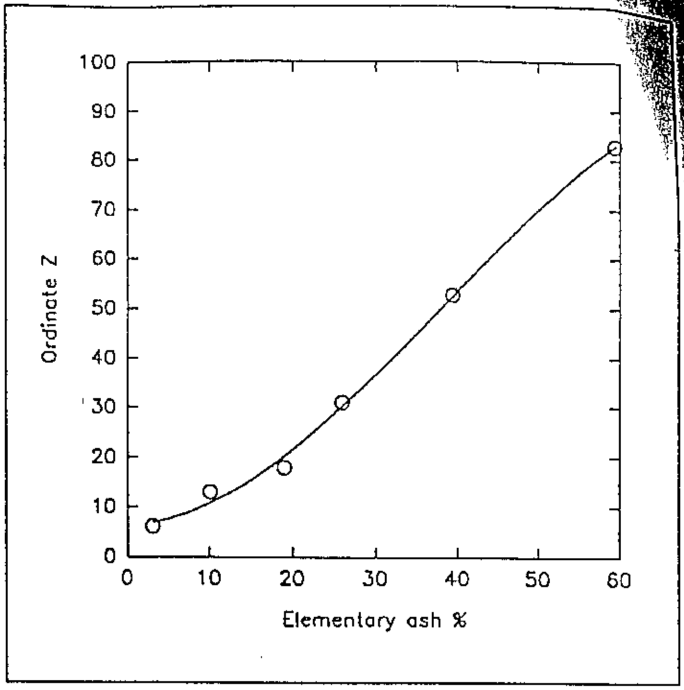

Figure 3. Elementary ash curve showing the rate of change of the ash content at different specific gravities.

gravity. This curve is constructed by finding a new ordinate Z and plotting the new ordinate value against the actual ash value of each specific-gravity fraction as the abscissa. The value of ordinate Z is found by solving the following equation:

$$Z = X + Y/2$$

where X is the cumulative weight percent float of all materials of lower specific gravity and Y is the weight percent of the material at the given specific gravity directly above X. Z is then the new ordinate value, shown in Table 2, column 11, and is plotted against the percent ash of each gravity fraction (columns 11 vs. 3).

The slope of the elementary ash curve indicates the relative ease of separation of the coal from the refuse (6). Steep slopes represent relatively small ash differences for large differences in yield, whereas a flat slope indicates an easy separation. An examination of the curve in Figure 3 suggests that the float product separated below specific gravity of 2 will have ash that is more tightly associated with the coal and thus difficult to separate. The ash from the float product obtained above specific gravities 2 will be relatively easy to separate. This is consistent with our previous data (7).

The particle size distribution of the solids separated at various specific gravities were also determined. In general, the high ash content fractions separated at specific gravities of 1.8 and higher, had lower mean particle size (10 ± 1 µm) compared to the low ash fractions obtained at lower specific gravities (25 ± 5 µm). This suggests that the sample has to be ground to an ash liberation size of ≤10 µm in order to achieve separation.

Characterization of Float-Sink Fractions

The lightest and the heaviest gravity fractions (1.5 float and 2.2 sink respectively) were analyzed by Scanning Electron Microscopy (SEM), Energy Dispersive X-ray analysis (EDXA) and X-ray Photoelectron Spectroscopy (XPS). Figure 4 shows the SEM micrographs of the samples 1.5 F (float) and 2.2 S (sink) respectively. Both samples are made of agglomerates of swollen particles. However, differences in the surface texture of the two samples are clearly seen. Sample 1.5 F is made of particles having diameter varying within the

Table 4.
Atomic Concentrations of Various Elements from XPS

Table 4. Atomic concentrations of various elements from XPS

Element	Concentrations (Atomic %)	
	1.5 F	2.2 S
C	91.5 ± 0.5	85.2 ± 0.5
O	3.9 ± 0.2	8.7 ± 0.4
N	3.6 ± 0.3	3.9 ± 0.3
S	1.0 ± 0.1	1.7 ± 0.2
Ca	< 0.05	0.5 ± 0.1

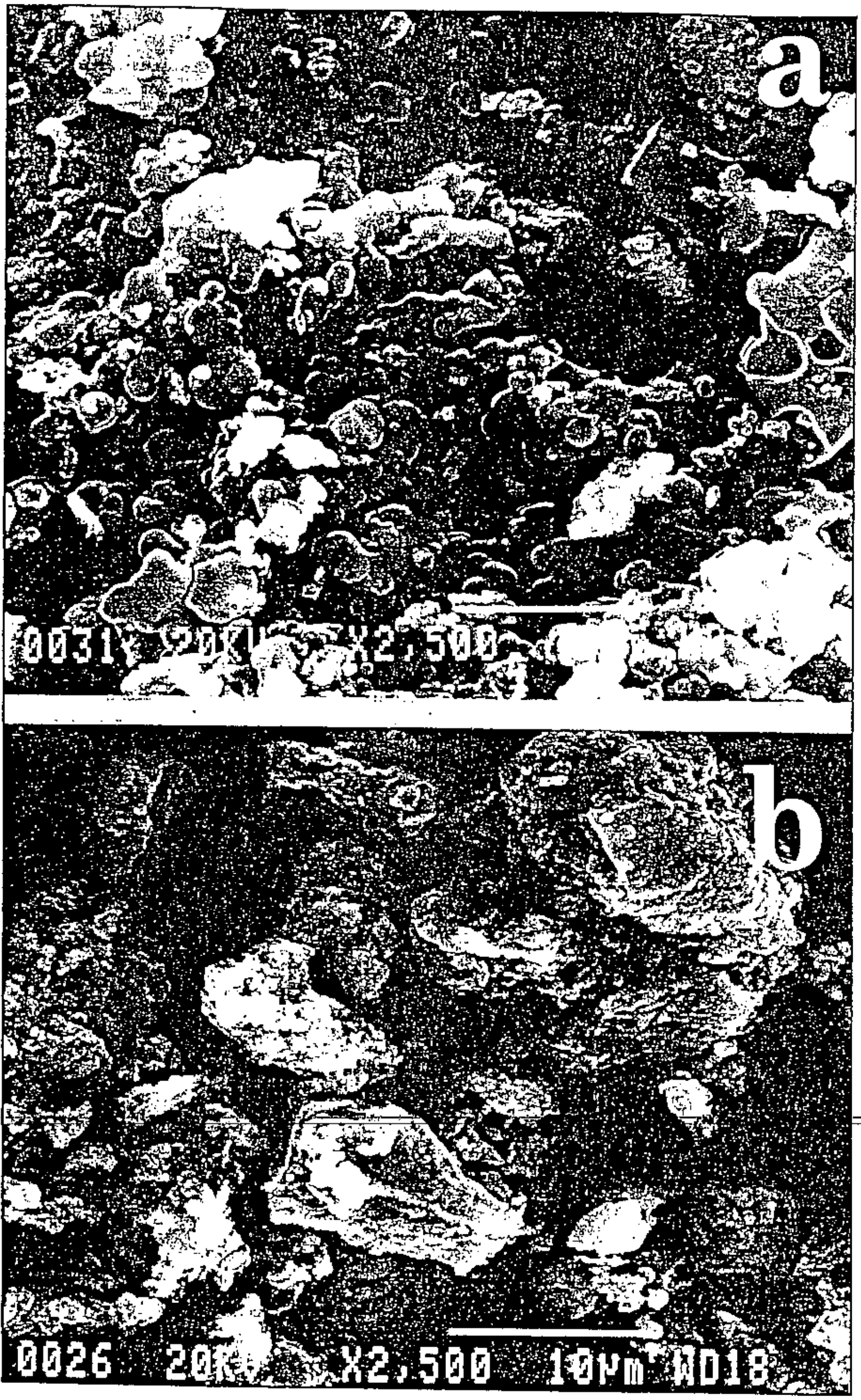

Figure 4. Sem micrographs of, a) 1.5 float, b) 2.2 sink.

range of 0.1-3 microns. The surface of the particles is smooth, with a round shape. The sample 2.2 S has a much rougher surface compared to sample 1.5 F. The aggregates in sample 2.2 S seem to be made of much smaller particles with no particular shape.

EDXA spectra of samples 1.5 F and 2.2 S are reproduced in Figure 5. This technique can only detect elements with Z >11, therefore it is not sensitive to carbon and oxygen. For both samples Al, Si, S, Ca, Fe and Cu are detected, but the intensity of the peaks is different for each sample. The concentration of most of the elements is much higher in the 2.2 S sample compared to the 1.5 float, suggesting that most of the ash is associated with the sink fraction. XPS survey spectra of both samples are shown in Figure 6. Both spectra show similar features. Peaks for S, C, N and O are observed. The atomic concentration of each element is listed in Table 4.

The combination of SEM, EDXA and XPS provides us with some information that allows us to speculate on the structure of the samples. XPS provides information on the top 10 nm of the surface. The fact that no Fe, Cu, Al or Si is seen in the XPS spectra suggest that the particles are covered by a layer of organic material. This organic layer is made mostly of carbon atoms with small amounts of O, N, and S, suggesting that some functionalities such as C-OH, C=O, HO-C=O, C-NH_2, C-SH could possibly be present. The high resolution spectra of the carbon peak also suggests the possibility of some functionalities being present. There is some calcium detected in sample 2.2 S, accordingly a higher oxygen concentration is observed, suggesting the presence of $CaCO_3$, or oxides of calcium. The fact that Ca is seen may suggest that the organic layer covering the particles is thinner or less uniform (patchy) in the sample 2.2 S. Note that even in this sample no Fe or Cu is detected.

Contrary to XPS spectra the EDXA spectra clearly show Fe, Al, Cu and Si. This is because EDXA probes much deeper into the samples providing information in the top 2-3 microns of a surface. For particles smaller than 2-3 microns it probes the whole particle. Based on these observations it can be inferred that the particles in sample 1.5 F consist mostly of Al, Si and Fe covered with uniform organic layer (91% carbon) having small amounts of functionalities. Note that it is also possible that quantities of carbon atoms be present inside the particles as well. The sample 2.2 S is essentially similar to 1.5 F sample with the exception that it is richer in inorganic elements particularly Fe and Ca. The presence of the Ca signal suggests that the organic coating is either thinner or nonuniform. Note that a $CaCO_3$ precipitate on the organic layer could also lead to a similar signal.

The results of washability studies as well as surface analysis data

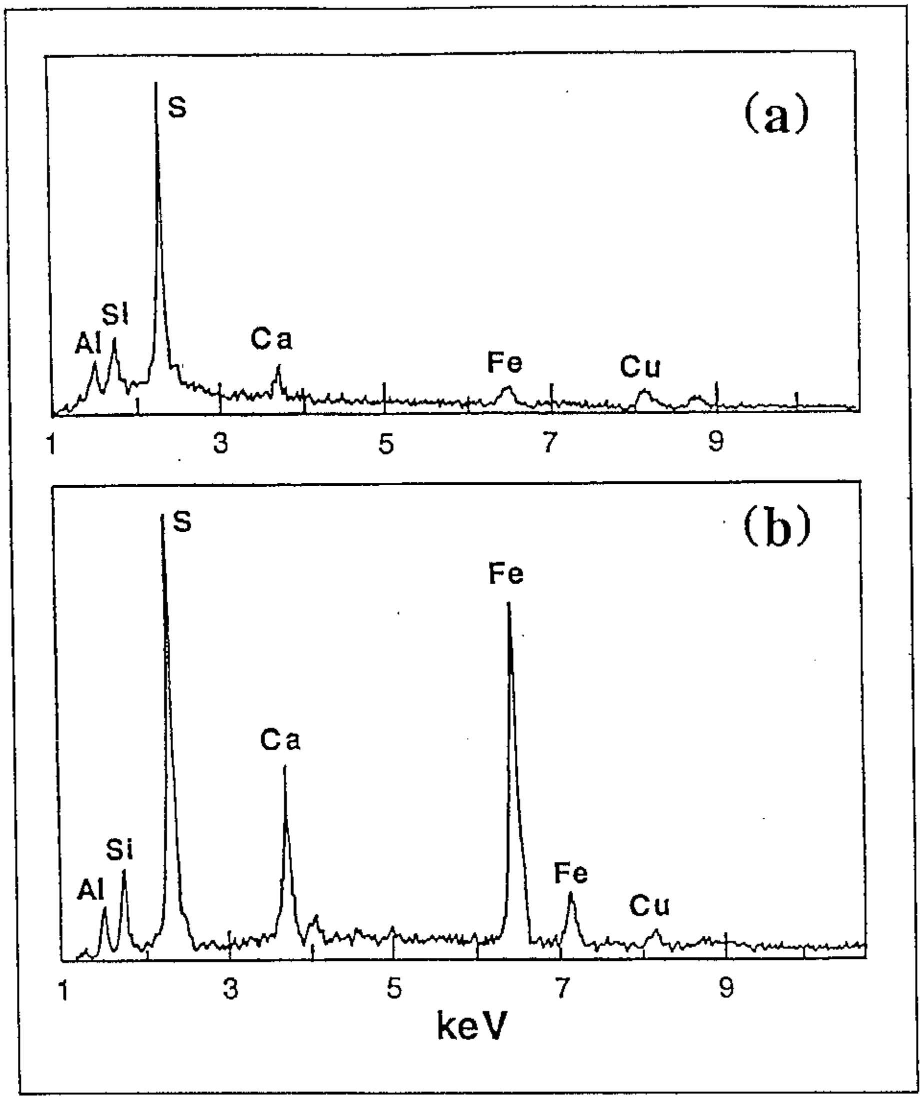

Figure 5. EDXA spectra of, a) 1.5 float, b) 2.2 sink

suggest that the ash is finely disseminated and the sample would have to be ground to an ash liberation size of less than 10 microns, in order to beneficiate the pitch. Spherical agglomeration techniques are well suited to handle solids in such a finely divided state (5,9). Several tests were carried out to agglomerate the carbon from a wet ground pitch sample (Average particle size, 9.8 ± 1.4 μm) slurried in water, using either Stoddard solvent, No. 4 fuel oil or octane as bridging liquids (11). The levels of ash rejection in these tests ranged from 20% to 40% with carbon recovery being between 80-90%. These results are in general agreement with the theoretically predicted levels of ash rejection from the washability studies. This also suggests that the remaining ash is still tightly bound to the carbon and the sample would have to be ground much finer than 10 microns for it to be liberated.

Distribution of Iron in Ash and Agglomerated Products

SEM and EDXA results for the agglomerated product and the reject material suggested that all of the iron was associated with the oil agglomerates. These results also showed that the agglomerates, obtained under optimum ash rejection conditions, did not contain any siliceous matter. However, the ICP (Inductively Coupled Plasma) analysis of the ash from these samples (Table 5) shows that although the amount of iron in the agglomerates is higher than that in the reject, a considerable amount of iron still remains in the latter material.

It is likely that two types of iron species are associated with the pitch. The first species is derived from iron sulphate catalyst added to the coprocessor and which would be expected to be present on particle surfaces as adsorbed iron. Other iron species, originating from the ash present in the feed coal could most likely be present within the solids. On agglomeration the catalytic iron species appear to be preferentially transferred to the agglomerates while the bulk iron from the original coal feed does not separate. This is consistent with our previous experience concerning the separation of pyritic sulphur from coal, which is difficult to separate from a hydrophobic matrix due to their own hydrophobic character (10,12). This preferential separation of catalytic iron could be beneficial because it reduces catalyst make-up requirements if the pitch is recycled.

CONCLUSIONS

The results of washability studies suggest that the ash particles associated with the coprocessing residue pitch are finely disseminated and that

Table 5.
Ash and Iron Content of Various Fractions of Pitch

Sample	Ash (w/w%)	Iron (w/w%)
Feed	11.8	24 ± 1
Agglomerated product	6.9	29
Reject from agglomeration	34.1	19
Aqueous phase ash from agglomeration	100	0
HCl/HF treated sample	1.6	15

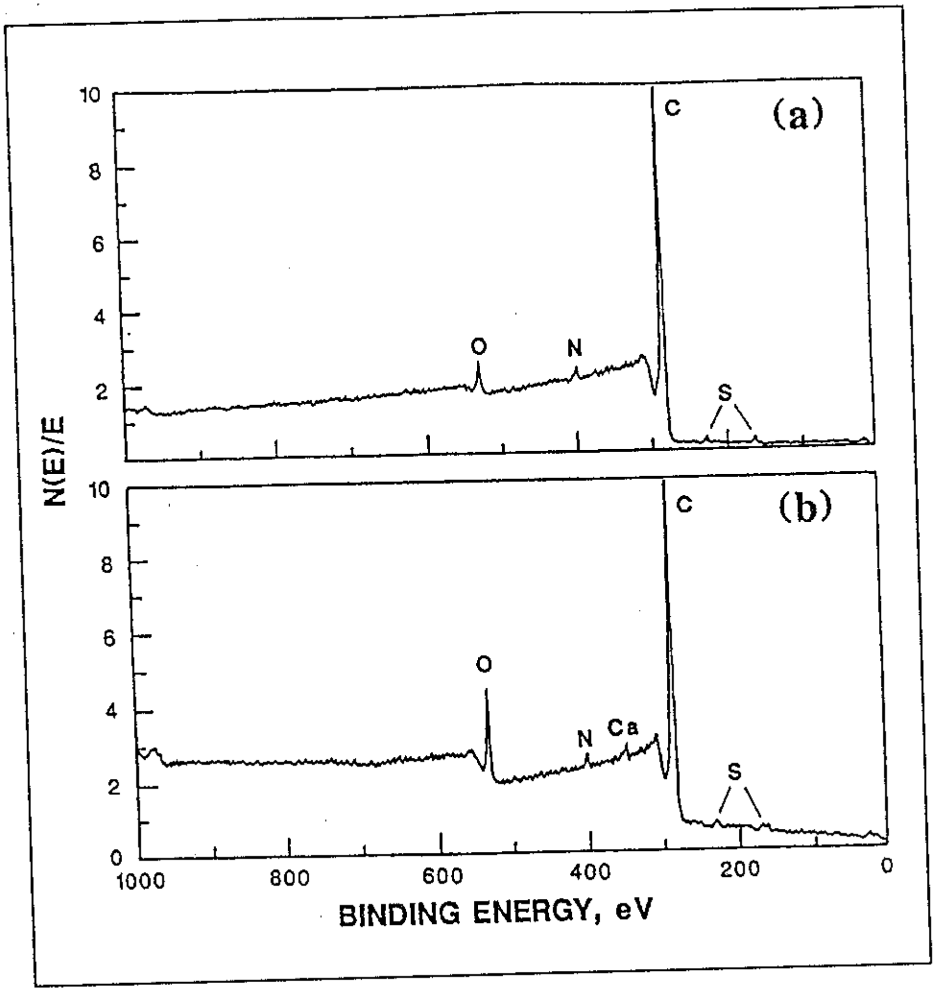

Figure 6. XPS survey spectra of, a) 1.5 float and b) 2.2 Sink

the ash liberation size is less than 10 microns. The data also predict the theoretically possible levels of ash reduction of about 50 w/w% provided the sample is ground to an ash liberation size of less than 10 microns. Better results would be possible after grinding to finer sizes. SEM, EDXA and XPS spectroscopic analysis results on the gravity separated fractions suggest that these solids consist mostly of Al, Si and Fe with an organic material coating. The lighter fractions have a thicker layer of organic matter coatings compared to the heavier fractions. Liquid phase agglomeration techniques were applied to the coprocessing residue pitch for the selective separation of the organic matter and iron from added catalyst as agglomerates. Over 40 w/w% ash rejection levels were achieved. SEM and EDXA analysis of the agglomerated product and the reject material and Inductively Coupled Plasma (ICP) analysis of the ash from both materials suggest that most of the iron from the added catalyst is retained in the agglomerates. Analysis of the ashed agglomerates showed an iron content of 29 w/w%. This is beneficial because it would reduce catalyst make-up requirements if the pitch were to be recycled. These results also show that very little if any, siliceous matter remains with the cleaned pitch. This suggests that most of the undesirable components of the solids present in CANMET coprocessing pitch residues can be removed by an oil phase agglomeration technique.

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