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SUBJECT — SUJET

DEASHING OF VACUUM RESIDUE FROM THE CANMET COPROCESSING UNIT PART II: AGGLOMERATION AND FLOTATION METHODS

FOR — POUR

ENERGY RESEARCH LABORATORIES
CANMET, ENERGY, MINES AND RESOURCES

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ABSTRACT

This is the second part of a report summarizing the results of an investigation of deashing vacuum residue from the CANMET coal-oil coprocessing unit. The results of a number of preliminary experiments involving agglomeration and flotation methods are reported. Levels of ash rejection in these experiments was low (15-40%) compared with the emulsification/ demulsification experiments reported in Part I ($64.5 \pm 16\%$). However, it is anticipated that with proper conditioning and process optimization it will be possible to achieve better results.

INTRODUCTION

Vacuum residue from the CANMET coal-heavy oil coprocessing unit contain all the ash originally associated with the feed coal as well as the iron compounds formed from the catalyst precursor. The objective of this investigation was to explore the potential for the economical deashing of this residue so that it can be recycled to extinction.

In earlier work by SNC and NRC (1,2) a technique was developed for deashing light, coprocessing oil products. The approach involved emulsification of the oil in water and transfer of the solids into the aqueous phase for separation. Application of this approach to the vacuum residue fraction requires the use of high temperatures ($>150^{\circ}\text{C}$) in order to mobilize the oil to allow emulsification to occur. This temperature requirement makes it necessary to carry out the process in a pressure vessel. Some preliminary testing has been carried out using equipment provided by CANMET. Details of this aspect of the programme will be described in Part III of this report.

Compared to the lighter oils the vacuum residue required relatively severe conditions for emulsification, and consequently it was deemed appropriate to test other less energy intensive treatment schemes. Where it is possible to exploit differences in surface properties both flotation and the oil agglomeration techniques (3-7) provide an effective means of deashing hydrophobic materials. In the coprocessing reactor the iron sulfate catalyst precursor is eventually converted to pyrite and/or pyrrhotite. Iron sulphides cannot be readily separated from a hydrophobic matrix due to their own hydrophobic character (7). This factor may be utilized to advantage in the case of vacuum deashing where it is beneficial to leave the iron compounds with the cleaned oil, thereby reducing catalyst make-up requirements. In this report a series of tests are described in which oil agglomeration or flotation was used for the selective deashing of vacuum residue from a coprocessing reactor. A number of conditioning treatments designed to improve selectivity in ash removal are also described.

EXPERIMENTAL

Materials. Vacuum residue used in this investigation were obtained from the bench CANMET coal-oil coprocesser. The residue was ground to -100 mesh size using a Brinkman Centrifugal Grinding Mill ZM-1. The ash content of the ground residue was $14.3 \pm 1.7\%$. Varsol (stoddard solvent) and dodecane were used as agglomerating aids and were of technical grade. Fuel oil No. 4 was a 50/50 mixture of fuel oil No. 2 and fuel oil No. 6. A surfactant, Pluronic L-61, was obtained from BASF and had an HLB value of 3.0. The Frother, Aerofroth 73 was obtained from American Cyanamid Co. H_2O_2 (30-35%) was of technical grade and was purchased from Fisher Scientific.

Procedures.

a) Agglomeration in a Waring blender. Ground vacuum residue and distilled water were mixed in a 1 litre pyrex glass Waring blender jar. The pH was adjusted to the required level with NaOH or H_2SO_4 . An agglomerating aid was added dropwise while agitating the suspension at 100 rps until discrete agglomerates formed. At this stage the blending speed was raised to 200 rps for 2 to 3 minutes to facilitate ash liberation. The agglomerates were separated from the aqueous phase on a 100 mesh screen. After drying at $100^\circ C$ the agglomerates were ashed to constant weight at $600^\circ C$.

b) Flotation in a Waring blender. Ground/conditioned vacuum residue were dispersed in distilled water contained in a Waring blender operated at 150 rps. Aerofroth 73 (1-5 drops) was added to the suspension and agitation continued for 5-10 minutes. After this time the mixture was allowed to stand undisturbed for 15-30 minutes. The froth was then removed with a spoon and washed on a 400 mesh screen. All material passing through the sieve was recombined with material in the blender jar. The froth was first dried at $100^\circ C$ and then ashed at $600^\circ C$.

c) Conditioning with H_2O_2 . Ground vacuum residue were added to 0.02% NaOH solution at $95^\circ C$ in a blender jar and then dispersed by mixing at 150 rps for 10 minutes. Tests both with and with-

out added surfactant were carried out. At the end of the agitation period, the contents of the blender jar were transferred to hot H_2O_2 solution (90°C) and boiled for 2-3 hours. After this time the suspension was cooled, and filtered through a medium porosity frit in a glass crucible, washed with water and then dried at 110°C . Ash content was determined by combustion at 600°C .

RESULTS AND DISCUSSION

Table 1 lists a number of experiments carried out for the removal of ash from coprocessing vacuum residue. An examination of the data for the ash content of the products from these treatments leads to the following conclusions:

1. Heating the vacuum residue with H_2O_2 causes over 40% of the ash to be rejected. This probably results from partial oxidation of the ash constituents thereby rendering them more hydrophilic.
2. Grinding in the presence of NaOH followed by separation into different size fractions, results in the accumulation of ash into the coarser fractions.
3. Between 15-30% ash rejection was achieved using froth floatation.

These experiments were of a preliminary nature and with proper conditioning and process optimization it should be possible to achieve higher ash rejection levels.

Beneficiation Using Oil Agglomeration

The result for the beneficiation of vacuum residue using oil agglomeration are listed in Table 2. Ash rejection in these preliminary experiments ranged from 25-36%. Again proper conditioning of the ash constituents to render them more hydrophilic, will improve the ash rejection levels during agglomeration processing.

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Table 1. Miscellaneous Experiments for the Beneficiation of CANMET Coprocessing Vacuum Residue

Exp. No.	Ref. No	Description	Ash	Content	Remarks
			Product	Reject	
T-1-A	4301-08 Blank	----	----	----	Ash content of feed = $14.3 \pm 1.7\%$
T-1-1	4197-194	Dispersed in distilled H ₂ O and ground in a ball mill using 6mm Al ₂ O ₃ balls.	15.0	----	Ash red
T-1-2	4197-194-1	-400 mesh material from above dispersed in distilled water and agitated in a waring blendor in presence of 5 drops of Aerofroth 73 frother. -Froth -Sink	14.4	21.9	Ash red Ash very red
T-1-3	4197-194-2	As above in presence of 5 drops of 2% Na ₂ SiO ₃ +2 drops of Aerofroth 73 frother. -Froth -Sink	11.5	13.1	Ash red Ash very red
T-1-4	4197-194-3	+30 mesh material from experiment T-1 was treated with 1 drop of Aerofroth 73 frother in a Waring blendor. -Froth	11.6		
T-1-5	4197-194-3-2	Residue from above treated again as in T-4. -Froth	11.2		
T-1-6	4197-194-3-3	Residue from T-5 treated again as in T-4. -Froth -Sink	11.9	53.4	
T-1-7	4197-190	Dispersed in 0.05% NaOH and ground in a ball mill using 6mm Al ₂ O ₃ balls. +30 mesh +400 mesh -400 mesh	14.6 12.6 8.3		
T-1-8	4197-191-2	+400 mesh material was conditioned with humic acid and then floated with Aerofroth 73 frother in a Waring blendor. -Froth	9.1		
T-1-9	4197-191-2	Heated with H ₂ O ₂ in presence of NaOH	7.5		
T-1-10	4197-189	Dispersed in distilled water containing NaOH and pluronic L-61 surfactant. Agitated for 10 minutes in the Waring blendor and then heated with H ₂ O ₂	7.7		

Table 2. Beneficiation of CANMET Coprocessing by Agglomeration

Exp No	Ref. No	Agglomeration Aid and Amount	Conditioner	Agitation Mode and Time	Ash Content of the Agglomerates
T-2-1	4301-08 Blank	————	————	————	14.3±1.7
T-2-2	4197-185-1	Dodecane, 25ml/28.8g of vacuum residues	————	Ball mill, 10 hrs	10.1
T-2-3	4197-185-2	Dodecane, 25ml/28.8g of vacuum residues	NaOH	Ball mill, 10 hrs	10.0
T-2-4	4197-192	Varsol, 25ml/25.0g of vacuum residues	H ₂ SO ₄ , pH 1.75	Ball mill, 10 hrs	10.1
T-2-5	4197-191-1	Varsol until discrete agglomerates	NaOH	Waring blendor, 10 minutes	8.7
T-2-6	4197-186-4	Fuel oil No.4, until discrete agglomerates	————	Waring blendor, 10 minutes	10.1
T-2-7	4197-194-4	Varsol, until discrete agglomerates	————	Waring blendor, 10 minutes	14.7%