DEEP CLEANING OF A hvA BITUMINOUS COAL USING A POLYETHYLENE OXIDE/POLYPROPYLENE OXIDE BLOCK CO-POLYMER

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ABSTRACT

Deep cleaning of a hvA bituminous coal using flotation process was investigated in this study. A -1/4 inch raw coal containing about 35% ash was subjected to initial flotation tests at nominal feed sizes of -600 μm and -212 μm. In both cases a clean coal product of 13% ash with a combustible matter recovery of about 80% was obtained. Since the ash content was much too high for deep cleaning, a second sample which was the product of a conventional coal preparation plant was used in subsequent studies. It contained about 7% ash. The material was wet ground to nominal feed sizes of -600 μm, -212 μm and -65 μm, respectively, and floated using n-dodecane as collector. The reduction in ash was marginal for the -600 μm and -212 μm coals. However, a clean coal product of 3.9 % ash could be obtained with a high yield using -65 μm feed. The product quality was further improved by introducing a mild oil agglomeration stage prior to flotation and by using an ethylene oxide/propylene oxide block copolymer as an additive. The ash content of the clean coal so obtained was 2.5% with a combustible matter recovery of about 76%.

INTRODUCTION

A super clean coal is considered to be of practical importance in many industrial applications such as liquefaction, coal/water slurries, etc. Liberation of combustible matter from ash forming minerals by size reduction is a necessary step in deep cleaning. In some cases fine grinding to particle sizes less than 100 μm might be required to achieve a satisfactory liberation. With decrease in particle size, the effectiveness of conventional coal cleaning methods mainly involving gravity diminishes. The coal recovery decreases, selectivity becomes poor, and medium recovery becomes a problem. Coal flotation is one of the most promising method for cleaning material at fine sizes. Use of an oily collector and other reagents is often necessary to enhance the hydrophobicity of coal and to promote its flotation. When oil is used alone it might also increase the hydrophobicity of the ash minerals and result in a decrease in the selectivity of the flotation process. It is generally recognized that selectivity of coal flotation does not improve below particle sizes of 100 μm (Crawford, 1936; Davis, 1948; Miller, 1964; Raleigh and Aplan, 1991). Two methods might be used to improve efficiency of separation: I. Decrease floatability of ash forming minerals by the use of dispersants and depressants. II. Increase the floatability of coal by reagents that make coal more hydrophobic. Method I was been demonstrated by Yancey and Taylor, 1935; Zimmerman, 1948; Miller, 1964; Choudhry and Aplan, 1990; Aplan, 1989; Perry and Aplan, 1985, 1988; Arnold and Aplan, 1989.

In this study, Method II was employed to increase the efficiency of coal cleaning by flotation. An ethylene oxide/propylene oxide (PEO/PPO) block co-polymer was used as a reagent to increase the hydrophobicity of flotation in the presence of oily collector. Utilization of a mild oil agglomeration stage prior to flotation was also investigated to further promote the ash rejection.

EXPERIMENTAL PROCEDURE

Flotation

A Wemco Model 71260-01 flotation machine was used in the flotation experiments. The stirrer speed was kept constant at 1000 rpm. The solids concentration in the flotation feed was 10% by weight. The flotation pulp was conditioned for 3 minutes to disperse the coal. Dodecane was added in required amounts as the oily collector and the pulp was conditioned for additional 3 minutes. The desired quantity of surfactant was added as an aqueous solution. After conditioning with the surfactant and dodecane, 0.5 kg/T methyl isobutyl carbinol (MIBC) was added as the frother. The slurry was further conditioned for 2 more minutes prior to introduction of air into the cell. The froth was removed at preset time-intervals for a total of 8 minutes. The natural pH of the pulp was 8.0 and no pH adjustments were made throughout the experiments. The flotation products were filtered, dried, weighed and analyzed to determine their ash content.

To prepare the flotation feed, a rod mill was used to wet grind the sample from 1/4 inches to the nominal feed sizes of -600 μm and -212 μm. To prepare the -65 μm feed, a Bleuler mill was employed. The grinding time was determined through prior grinding tests.

Mild Oil Agglomeration

A mild oil agglomeration of the coal slurry prior to flotation was performed in an attempt to further decrease the ash content. For this purpose, dodecane and a solution of block co-polymeric surfactant was emulsified in a blender for 3 minutes. A coal slurry of 400 ml (1% solid) was added into this solution and blending was continued for 3 more minutes to produce loose agglomerates of coal particles. The slurry was than transferred into the flotation cell and flotation experiments were carried out by addition of frother only.

MATERIALS

Coal Samples

The run-of-mine and clean coal samples were obtained from Emerald Mine in Pittsburgh, PA. The coal was a hvA bituminous sample of Pittsburgh seam. The ash and sulfur contents are given in Table 1.

Surfactants

Two different polymeric surfactants from BASF Cooperation were used in this study to enhance the rejection of ash minerals from coal. These were water soluble and added to the pulp as an aqueous solution. The number of hydrophobic and hydrophilic groups and other properties are given in Table 2. The molecular structure of this type of surfactants is given in Figure 1. Dodecane from Aldrich Chemical Company was used as the oily collector. The frother used in this study was methyl isobutyl carbinol (MIBC) obtained from Shell.

RESULTS AND DISCUSSIONS

Flotation of Raw Coal

Initial flotation studies were performed using a raw coal containing 35% ash from Emerald Mine, Pittsburgh at nominal feed sizes of -600 μm and -212 μm using dodecane as the collector. The results are presented in Figure 2. The decrease in ash was not satisfactory for both the -600 μm and -212 μm feed materials. A clean coal product of about 12 to 13% ash with a combustible recovery of about 80% was obtained. This observation was in agreement with other studies where no improvement in the product quality was observed with decreasing feed size (Crawford, 1936; Davis, 1948; Miller, 1964, Raleigh and Aplan, 1991). It is possible that even though grinding to a smaller sizes increased liberation, the problems associated with flotation of fine particles increased. Further cleaning of this sample was not attempted. Instead a clean coal sample from a processing plant with 7.0% ash was used.

Flotation of Precleaned Coal

Flotation studies in the presence of dodecane

The second sample tested in this study was a pre-cleaned hvA bituminous coal which was obtained from a conventional coal preparation plant and had an ash content of 7.0%. Similar to the raw coal sample, flotation studies were conducted at various feed sizes in the presence of dodecane as collector. The results of flotation studies are given in Figure 3. As one can see, the reduction in ash was minimal for the -600 μm and -212 μm feed materials. However, a clean coal product of about 3.9 % ash could be obtained with a combustible matter recovery of 75% for the -65 μm feed after 2 minutes of flotation. These results show that an increase in selectivity is possible with improved liberation. In order to further decrease the ash content of the sample two surfactants were employed for the -65 μm feed material.

Flotation Studies in the Presence of Dodecane and Block Co-polymers Surfactants

Aliquots of aqueous solutions of the PEO/PPO block co-polymers (BC3 & BC7) and the collector were added simultaneously to the flotation cell. The results are given in Figure 4 for the two polymeric surfactants. For comparison, the flotation data for dodecane alone is also included. It can be seen that the presence of the polymeric surfactants substantially enhanced the ash rejection. A clean coal with an ash content of 2.9% and a combustible matter recovery of 75% could be obtained in the presence of BC3 after 2 minutes of flotation. The corresponding ash was 3.1% for BC7. The amount of ash rejection was found to be a function of both surfactant type and concentration.

Flotation Studies Preceded by a Mild Oil Agglomeration Stage

In this series of tests, the coal slurry was agitated in a blender to produce loose agglomerates of coal particles. The surfactant, BC7, concentration was same as in previous tests. The agglomerated mass was floated and the results are presented in Figure 4. It can be seen that the product quality improved substantially. A clean coal product of 2.5% could be obtained with a recovery of 75%. A more significant advantage of the pre-agglomeration stage was a substantial increase in rate of flotation. To quantify this effect flotation rates were obtained by plotting flotation yield as a function of flotation time and the data were fitted to a first order model with a rectangular distribution of floatabilities (Huber-Panu et al., 1976; Klimpel, 1980). The mathematical form of this model is given by:

$$R_{(t)}=R_{\infty}\{1-[(1-e^{-kt})/kt]\}$$

where $R_{(t)}$ is the recovery at time t, R_{∞} is the ultimate recovery and k is a rate constant. The parameters estimated by the model are given in Table 3. The mean residual square (MRS) errors were somewhat high but the use of alternate models, namely, classical first order, first order with sinusoidal and normal distributions of floatabilities (a summary of these models is given by Miller et al., 1993) gave even higher fitting errors. It can be seen that the ultimate recovery is somewhat similar (around 100%) for all the cases. The flotation rate is between 2 and 3.5 min^{-1} for the test where flotation was employed only. Use of a mild agglomeration stage significantly accelerated the kinetics of flotation. The flotation rate obtained for this case was 10.66 min^{-1}. It is interesting to note that this increase in the rate of flotation was also accompanied with a decrease in the ash content, showing the effectiveness of the agglomeration stage.

CONCLUSIONS

Flotation processing of a hvA bituminous coal was investigated for coals ground to several feed sizes. To improve the influence of PEO/PPO block co-polymers, the selectivity of separation was studied. Based on these tests, the following conclusions were made:

- For the raw coal sample, no improvement in the ash rejection was observed with decrease in feed size. An ash content of 12 to 13% with a combustible matter recovery of about 80% was obtained.
- In case of clean coal, the reduction in ash was marginal for the -600 μm and 212 μm coals. However, for the -65 μm feed a clean coal product of 3.9% ash was obtained with a high yield.
- The clean coal quality was improved further by addition of block co-polymers. The ash content of clean coal so obtained was 2.9% for BC3 and 3.1% for BC7 with a combustible matter recovery of about 75%.
- When a mild oil agglomeration was used prior to flotation the clean coal quality improved further. The clean coal ash content so obtained was 2.5% with a combustible matter recovery of about 76%. In addition, the use of the agglomeration stage resulted in a significant increase in the rate of flotation.

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Table 1. A summary of the coal samples used in the study.

Coal samples	Ash (%)	Sulfur (%)
Pittsburgh (Clean coal)	7.0	1.32
Pittsburgh (Raw coal)	35.0	1.85

Table 2. Selected properties of the surfactants used in this study.

Surfactant	Code	Number of hydrophobic groups (PPO)	Number of hydrophilic groups (PEO)	M.W.	HLB*	Surface tension, dyne/cm
Ethylene oxide/ propylene oxide block co-polymer	BC3	30	26	2650	11	43.0
	BC7	56	60	5900	13	33.0

* *Hydrophile-lipophile balance.*

Table 3. The ultimate yields, flotation rates and mean residuals for fitting the first order kinetics equation with rectangular distribution of floatabilities.

	Dodecane (0.07 kg/T)	BC3 (0.1 g/T)	BC7 (20 g/T)	Aggl. & Flotation
R_∞	100.0	99.4	94.3	100.0
k	3.45	2.34	1.97	10.66
MRS*	3.14	8.97	25.56	17.80

* *Mean residual square*

Figure 1. Structural formula of PEO/PPO block co-polymers used in this study.

$$HO\text{-}(CH_2CH_2O)_X\text{-}(CH_2\overset{\displaystyle CH_3}{\overset{|}{C}}HO)_Y\text{-}(CH_2CH_2O)_X\text{-}H$$

EO—PO—EO

X = Number of moles of ethylene oxide
Y = Number of moles of propylene oxide

Figure 2. Combustible matter-ash recovery curves for the run-of-mine sample of Pittsburgh seam coal.

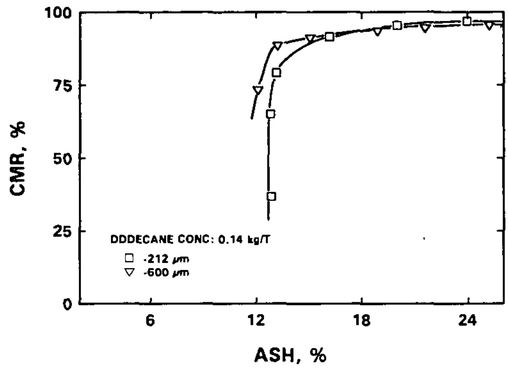

Figure 3. Combustible matter-ash recovery curves for the pre-cleaned sample of Pittsburgh seam coal.

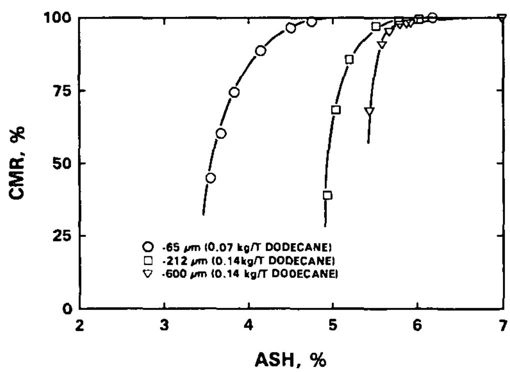

Figure 4. Effect of PEO/PPO block co-polymers on the combustible matter recovery and ash content.