

IMPROVED SULFUR REMOVAL FROM COALS BY REDOX POTENTIAL CONTROL OF SURFACES DURING GRINDING.

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ABSTRACT

Control of the redox potential of an Upper Freeport run-of-mine coal slurry during wet grinding and subsequent beneficiation gave better sulfur removal, with no decrease in coal recovery, than either potential control during grinding or beneficiation alone. Sodium dithionite, a reducing agent used to depress the sulfur, also gave substantially better results than pH control alone, irrespective of whether the physical beneficiation was by oil agglomeration, foam flotation, or microbubble batch flotation. Three-phase contact angle measurements and pulp potential measurements suggest that slow electrochemical reactions at the particle surfaces may be responsible for the improved results obtained when the reductant is added at the grinding stage.

INTRODUCTION

The purpose of this work was to alter the surface properties of coal and/or associated mineral particles during grinding to enhance the removal of sulfur-bearing minerals during the beneficiation process. This was done by using reducing agents to alter the electrochemical potential during grinding and beneficiation. The fact that sulfide ores can be depressed by electrochemical techniques is well catalogued in the literature(1-5). Studies(6-9) also have shown that electrochemical effects due to "galvanic interaction" of grinding media during size reduction can affect the flotation of sulfide minerals. In this study, however, electrochemical effects were imposed during grinding by the addition of a chemical reagent. It was presumed that the generation of fresh surfaces, improved contact with the freshly generated surfaces, and the presence of an energy-intensive environment, would all contribute towards promoting surface reactions that could result in enhanced beneficiation.

It should be emphasized that adding oxidizing or reducing agents and monitoring the system by measuring the potential of the pulp relative to a reference electrode, yields a potential which has no real thermodynamic significance. However, it may be used as a guideline, and it has been shown to correlate with laboratory flotation results(10).

EXPERIMENTAL

Materials

a) Feed Coal.

A run-of-mine coal sample from the Upper Freeport Seam, Lucerne Mine No. 6, Helvetia Coal Company, Indiana County, Pennsylvania, was used. The sample was dried and reduced to a nominal top size of 9.5 mm (3/8 in) by the Pittsburgh Energy Technology Center. It was further reduced to minus 176 μm in a hammermill, riffled into aliquots, purged with argon, and sealed until use. Its properties are listed in Table 1.

Table 1. Upper Freeport run-of-mine coal, 'as received.

Moisture %	Ash %	Total Sulfur %	Pyritic Sulfur %	Organic Sulfur %	Sulfate Sulfur %	Heating Value Btu/lb	Hardgrove Grindability (0.7% Moisture)
0.85	32.65	2.41	2.04	0.36	0.01	9970	87

b) Additives.

Reagent grade sodium hydroxide, sulfuric acid, and sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$) were used. Kerosene was employed as a conditioner and as an agglomerating oil; Dowfroth 150, Accofroth 76, and methylisobutylcarbinol (MIBC) were used as collectors.

Experimental procedure

Grinding.

Samples of the 176- μm feed coal were wet ground (40% solids by weight coal) for 15 minutes in a stirred ball mill using 1/8-in stainless steel balls as the grinding media. The final average particle size was about 10 μm .

Separations.

After grinding in the stirred ball mill, each slurry was separated from the balls and divided into aliquots for separation by three techniques.

1) Microbubble Frit Flotation

The slurry was diluted to 10% solids, conditioned with kerosene (collector) and MIBC (frother), and placed in a flotation cell. Microbubbles were formed in the flotation cell by admitting a regulated gas flow through a porous glass frit at the bottom of the cell. The coal particles, being hydrophobic, attached themselves to the microbubbles and were thus carried to the top of the cell in a fine froth. The overflowing froth (or concentrate) and the material remaining in the flotation cell (i.e., the tailings) were collected, filtered, dried, and analyzed.

2) Microbubble Foam Flotation

In this process the conditioned pulp was transferred to a flotation tube and a microbubble foam was introduced at the bottom of the tube. The foam was prepared by adding either Accofroth 76 or Dowfroth 150 to water in a modified blending chamber at high speed. The concentrate and the tailings were filtered, dried, and analyzed.

3) Oil Agglomeration

A 10% percent coal/water slurry was agglomerated with 15% (by weight of coal) kerosene in a 500-ml blending chamber for 3 minutes at low shear. The agglomerates were separated from the tailings using 100- and 200-mesh test sieves. They were then filtered, dried, and analyzed.

Variations in pretreatment during comminution in the stirred ball mill included the use of NaOH and H_2SO_4 for pH adjustments and $\text{Na}_2\text{S}_2\text{O}_4$ for control of the pulp potential (ϵ). Tests were also conducted with no additives and with the same additives introduced after grinding.

Float/Sink

In another series of tests, portions of the feed coal sample were subjected to float/sink separation using Certigrav at a specific gravity of 1.4 to obtain an organic-rich fraction with a

low mineral content and a mineral-rich fraction with a high mineral content. After separation, the samples were dried at 107°C until no odor of Certigrav remained. The float fraction thus obtained contained 4.7% ash and 0.78% sulfur, and the sink fraction contained 55.4% ash and 8.8% sulfur. Since the ideal separation conditions are those in which the organic fractions are more hydrophobic and the mineral fractions are more hydrophilic, by separating the feed coal into organic-rich and mineral-rich fractions, each fraction may be tested separately to determine the surface characteristics under the conditions used. Flotation results, conducted with coal samples soaked in Certigrav and then dried, were compared with flotation results from samples that had not been soaked in Certigrav to assure that exposure to the Certigrav liquid did not affect the particle surfaces.

Contact angle measurements

Three-phase (solid-liquid-water) contact angle measurements at various values of pH and also for an aqueous phase containing sodium dithionite were made using compressed pellets of organic-rich and mineral-rich coal fractions of the Upper Freeport coal which were obtained from the float-sink separation. The pH of the water drops placed on the pellets was adjusted using NaOH and H₂SO₄. A 0.1 M solution of sodium dithionite (Na₂S₂O₄) was used. A Rame-Hart contact angle goniometer was used, and the contact angles were measured from enlarged photographs of the drops using a protractor. The contact angles thus obtained were accurate to within 5 degrees, which is the best accuracy that may be expected from a heterogeneous substance like coal.

Potential Measurements

Zeta potential measurements were made with a Komline Sanderson Model 12S zeta meter. Measurements were made for both organic-rich and mineral-rich fractions of coal obtained by float-sink separation in solutions of various concentration of sodium dithionite. The pH and the pulp potential (ϵ) were monitored with an Orion Microprocessor Ion Analyzer (Model 901) using a combination pH electrode and a combination Pt-Ag/AgCl electrode (0.044±0.001V vs.SCE).

RESULTS

Beneficiation

In the grinding and beneficiation tests, the sample was ground both with and without pH control. The samples ground at pH 3 and pH 7 were each separated at both pH 3 and pH 7. Those ground at the natural pH of 5.5 and at pH 11 were separated at the same pH as during grinding. The results, presented in Table 2, show that under most conditions, the coal recovery was high but with only moderate sulfur reductions and rather poor ash reduction. Since the blender flotation technique yielded poor recoveries, particularly at low pH, some of these tests were repeated using Dowfroth 150 as the frother instead of Accofroth 76. Sulfur removal was poor with Dowfroth, although a slight improvement in coal recovery was obtained.

Table 3 shows the results obtained in replicate runs when sodium dithionite was present during both grinding and separation. This produced significant improvement in the sulfur reduction over those experiments where only pH control was used (Table 2). Average

sulfur reduction values obtained with pH control are compared to those obtained when sodium dithionite was used during both grinding and separation in Figure 1. Figure 2 shows an equally important result; when sodium dithionite was used in only one step, either grinding or separation, lower sulfur reduction was obtained. However, the values still tended to be better than those found during pH control.

Table 2. Results of separations performed under various conditions of pH during grinding and separation.

Grinding pH	Separation		% S Conc.	% S ^a Redn.	% Ash ^b Conc.	% Ash ^c Redn.	% Coal ^d Recov. (additive)
	Type ^e	pH					
Feed			3.64	-	31.3	-	-
Natural	Foam Frit Agg	Natural ~5.5	2.20	39.2	15.9	51.3	84.1 (Accofroth)
			2.20	39.2	19.9	39.0	97.6 (MIBC)
			2.32	35.9	13.4	58.9	95.5 (Kero)
7	Foam Frit Agg	7	2.24	38.1	14.3	56.2	90.3 (Accofroth)
			2.11	41.7	17.6	46.0	97.0 (MIBC)
			2.39	34.0	13.3	59.3	96.0 (Kero)
3	Foam Frit Agg	3	2.19	39.5	15.4	52.8	65.6 (Accofroth)
			2.22	38.7	19.9	32.1	97.7 (MIBC)
			2.27	37.3	12.8	60.8	94.1 (Kero)
3	Foam Frit Agg	3	2.59	28.9	19.3	38.4	89.9 (Dow Froth)
			2.30	36.8	14.3	54.3	88.0 (MIBC)
			2.25	38.1	14.3	54.3	94.1 (Kero)
3	Foam Foam Frit Agg	7	2.22	39.07	16.4	47.8	88.7 (Accofroth)
			3.20	12.41	24.5	15.5	98.7 (Dow Froth)
			2.50	33.1	15.4	50.8	95.9 (MIBC)
			2.34	35.6	14.2	54.8	96.1 (Kero)
11	Foam Frit Agg	11	2.60	28.6	16.5	47.4	95.3 (Accofroth)
			2.31	36.4	14.8	52.6	91.7 (MIBC)
			2.43	33.3	13.5	56.8	96.4 (Kero)

a % S Reduction = $\frac{\% \text{Feed S} - \% \text{Product S}}{\% \text{Feed S}}$ (all DAF)

b Ash reported on a moisture-free basis; sulfur reported on a moisture- and ash-free basis.

c % Ash Reduction = $\frac{\% \text{Feed Ash} - \% \text{Product Ash}}{\% \text{Feed Ash}}$, moisture free.

d % Coal Recovery = $\frac{100 \times (100 - \% \text{Product Ash}) (\text{Product wt})}{(100 - \% \text{Feed Ash}) (\text{Feed wt})}$

e Foam, Frit, and Agg indicate the type of separation technique used: foam flotation, microbubble frit flotation, or oil agglomeration, respectively.

Table 3. Results of separations performed using 0.1 M sodium dithionite during both grinding and separation^a. Replicate runs for each technique are shown.

Grinding Condition	Separation		% S Conc.	% S Redn.	% Ash Conc.	% Ash Redn.	% Coal Recov.	
	Type	Condition						
		pH						ϵ (V)
Feed			3.64	-	31.3	-	-	
0.1 M $\text{Na}_2\text{S}_2\text{O}_4$	Frit	5.0	-0.39	1.56	57.1	9.3	70.3	68.6
	Frit	4.6	-0.43	2.09	42.6	13.0	59.4	92.4
	Frit	4.3	-0.40	1.96	46.3	12.8	59.3	92.6
	Frit	4.8	-0.40	1.93	46.9	16.1	48.6	90.8
	Foam	5.2	- ^b	1.89	48.3	12.8	59.1	71.5
	Foam	5.2	-	2.05	43.8	12.3	60.8	68.5
	Foam	5.2	-	1.89	48.3	12.1	61.4	65.4
	Foam	5.3	-	1.66	54.5	12.5	60.2	58.0
	Agg	5.0	-0.39	2.02	44.5	12.1	61.4	95.4
	Agg	4.9	-0.40	1.98	45.4	12.4	60.7	84.6

^a Definitions as in Table 1.

^b The foam flotation technique does not permit sufficient time for pulp potential measurements.

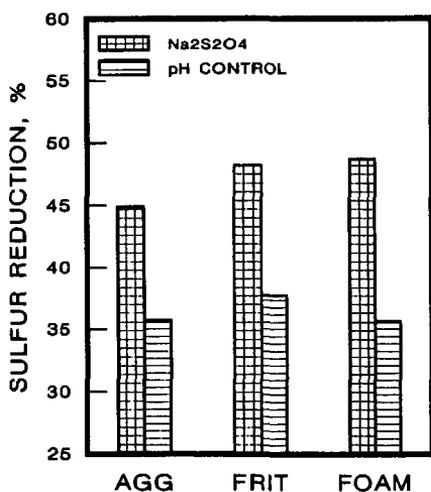


Figure 1. Average sulfur reduction values obtained when $\text{Na}_2\text{S}_2\text{O}_4$ was used during both grinding and separation compared to those obtained with pH control alone.

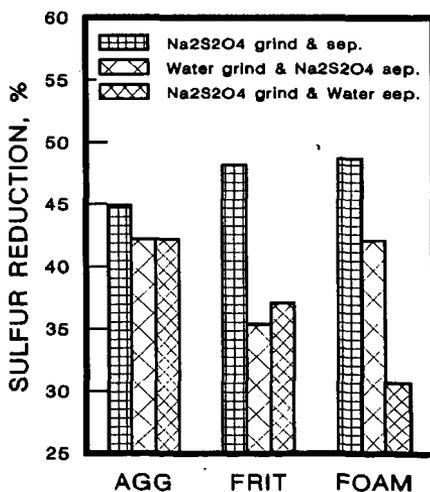


Figure 2. Results obtained when $\text{Na}_2\text{S}_2\text{O}_4$ was used either during grinding or separation only, or during both grinding and separation.

Surface Characterization Tests

Table 4 depicts the results of contact angle measurements made on pellets prepared with material from the float-sink separations. A smaller angle indicates a surface of greater hydrophobicity (see Figure 3). The contact angles measured for the mineral-rich fraction are consistently larger than those measured for the organic-rich fraction, demonstrating that the mineral-rich fraction is more hydrophilic than the organic-rich fraction. Also, the hydrophilicity of the mineral fraction was a maximum at high pH. These are expected results. However, an unexpected result was that the contact angles measured when the aqueous phase contained 0.1 M sodium dithionite were similar to those with the acidic and neutral aqueous solutions.

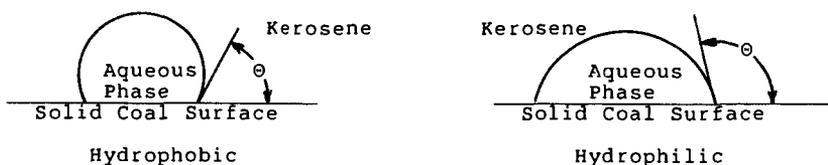


Figure 3. Contact angle measurement.

Table 4. Measured contact angles (θ) of organic-rich and mineral-rich fractions of Upper Freeport coal using the sessile drop technique. Values are averages of 'n' measurements with a standard deviation of σ .

Condition	Mineral-Rich "Sink" Fraction			Organic-Rich "Float" Fraction		
	θ	σ	n	θ	σ	n
pH 11.0	27.5	1.69	8	21.2	5.32	8
pH 7.6	27.3	3.58	8	20.3	4.56	8
pH 3.0	24.4	4.72	8	17.5	3.38	8
0.1M Na ₂ S ₂ O ₄	26.1	3.98	8	20.9	2.10	8
pH 4 Buffer	24.5	0.71	2	16.5	2.12	2
pH 7 Buffer	26.5	2.12	2	15.5	0.71	2
pH 10 Buffer	30.0	0	2	20.0	0	2

An attempt was made to determine the effect of ionic strength on the zeta potential of the organic-rich and mineral-rich fractions in solutions of varying sodium dithionite concentration. During these tests, it was found that both the pulp potential, and the pH of the slurry, changed with time. The change continued over several minutes and the rate of change was a function of sodium dithionite concentration. Thus these experiments provided no information about the effect of the ionic double layer. However, they suggest that the kinetics of reactions at the surface may be important and that slow electrochemical surface reactions may have been taking place.

DISCUSSION

The increased floatability of pyrite and other sulfide minerals is usually attributed to mild oxidation which leads to the formation

of sulfur or sulfur-like entities which enhance the particle hydrophobicity. Hamilton and Woods(11) have explained the effect as the formation of a metal-deficient sulfide; conversely, reduction produces a metal-rich sulfide on the particle surface. These authors state that the attractive interaction between water and the mineral surface is determined by the availability of metal ions in the immediate surface layer (large anions, like sulfide, are generally not hydrated). Thus, removal of metal ions from the surface reduces the opportunity for specific interaction with water molecules. Hydrophobic/hydrophilic effects in solution may also be explained in terms of the free energy of the particle surface(12). When this is done the entropy component of the free energy change of the surface is seen to be significant(12).

Guy and Trahar(13) report that for many sulfides, the oxidation reaction does not proceed rapidly. Firth and Nicol(14) state that a number of factors could affect the rate of reaction on pyrite surfaces. These include: the temperature and humidity, the size distribution and form of occurrence of the sulfides, the time of exposure, and the presence of peculiarities in the crystal lattice, such as sulfur deficiencies and the presence of polymorphs, which may serve as active sites for oxidation reactions. Castro(15) found that, over time the electrode potential of chalcocite decreased when sodium sulfide was added, indicating oxidation of the mineral. More recently, Miley(16) has shown that the electrode potential of a suspension of coal particles in an aqueous solution of a strong oxidizing agent changes over several hours. Thus, observing this change, a general picture of the oxidation process may be obtained, the change being indicative of the "oxidation state" of the coal.

One may envision that the reduction reaction, which has been studied less extensively, may display kinetic effects similar to those observed for oxidation. Chander(17) has reviewed the published literature on the mechanism of reduction of pyrite minerals and states that a unified theory is, as yet, unavailable. According to Chander(17), formation of metastable species in the solution or in the solid phase, nonstoichiometry of the solid phase, and slow reaction kinetics could all lead to nonequilibrium conditions. The variation of the pulp potential and pH with time does suggest slow reaction kinetics.

CONCLUSION

The addition of sodium dithionite to control pulp potential resulted in improved ash and sulfur removal from Upper Freeport coal as compared to pH control. The best results were obtained when the reducing agent was present during both grinding and separation. Contact angle measurements indicated that the improvement was not due to a lesser affinity for the organic portion of the coal toward the dithionite solution. The pulp potential and the pH of the slurries containing the organic-rich and mineral-rich fractions of the coal varied with time, indicating the possibility of slow reaction kinetics. This work is an example in which the grinder has been employed effectively in chemical pretreatment. The concept, often discussed in the literature, has rarely been demonstrated.

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