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SURFACE ELECTROCHEMICAL CONTROL FOR FINE COAL
AND PYRITE SEPARATION

Doe Project No. DE-AC22-89PCC89758

Technical Progress Report
July 1, 1990 to September 30, 1990

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This technical progress report prepared in accordance with the reporting requirements of DOE Project No. DE-AC22-89PC89758 covers the work performed during the period, July 1, 1990 to September 30, 1990. It includes sections on cyclic voltammetry and the floatability and selectivity of coal and coal pyrite.

THE FLOATABILITY AND SELECTIVITY OF COAL AND COAL PYRITE

INTRODUCTION

Sulfur content of coal is of considerable importance from an environmental standpoint. Pyrite is a major contributor to sulfur emissions during coal combustion. Coal desulfurization processes can be divided into chemical and physical processes. In the past two decades research efforts have been directed to develop chemical processes including leaching, microwave treatment and molten salt reactions. So far they have been limited to laboratory or pilot plant scale.

Flotation and oil agglomeration are two major important physical processes based on economical and technological criteria. In practice, the flotation practice could occur in two ways: (1) selective flotation of coal from pyrite using frothers, collectors and depressants. (2) selective flotation of pyrite from the depressed coal. MICB, pine oil or cresylic acid on the order of 0.2 lb/ton are used as frothers. Fuel oil masks the hydrophilic sites arising from the heterogeneous nature of the solid coal and serves as a collector. Lime, sodium cyanide, ferrous or ferric sulfate and many chemicals have been investigated as depressants.

The flotation behavior and mechanism of mineral pyrite is best understood among all sulfide minerals. The species of xanthate responsible for flotation in the presence of short-chained xanthate is dixanthogen. Pyrite depression is made possible by using various chemicals to reduce the oxidation potential of the solution to prevent the formation of the collector, dixanthogen.

There are few investigations of coal and coal pyrite separation. The mechanism is not well understood, and processes for separating of coal and coal pyrite are still not satisfactory. Basic, systematic research on the floatability of pure coal pyrite and the selectivity between coal and coal pyrite is required. The objective of this work is to investigate the selectivity and floatability of coal and coal pyrite systematically and fundamentally in regard to the following four aspects:

- * Natural Floatability
- * Floatability in salt solution (indication of floatability under indifferent an ionic atmosphere)
- * Floatability with frother only
- * Selectivity

EXPERIMENTAL

Materials and Equipments

Three coal samples of different rank: Illinois hvCb, Pittsburgh hvAb and Upper Freeport mvb, were prepared. The preparation procedure and characteristics of the bulk coal samples have been presented in previous technical reports.

Three pyrite samples from the three coal samples were prepared by grinding and gravity concentration procedures. About 20 lbs of each coal sample was split into 500 gram batches and each batch was ground to 28 mesh using a rod mill. After grinding, pyrite was separated from the coal on a shaking table, dried at room temperature and preserved under argon for the flotation tests.

Reagent grade HCl and NaOH were used to adjust the pH of solutions, and reagent grade NaCl was used to make salt solutions of various concentrations. Reagent grade MIBC and dodecane were used as collectors for flotation.

Experimental Procedure

The floatability of the coals and coal pyrites was measured in the Hallimond tube. For each test, one gram of sample was conditioned for two minutes and floated for two minutes. The concentrate was dried, weighed and the yield calculated.

RESULTS AND DISCUSSIONS

Natural Floatability

Natural floatability may be defined as that at natural pH or at modified pH. The floatability in distilled water at the natural pH, expressed as yield of floated coal, for Upper Freeport, Illinois, and Pittsburgh coals are 43.00%, 39.40% and

42.70% respectively. The rank of natural floatability for the three coals is:

Upper Freeport > Pittsburgh > Illinois

The floatability in distilled water at modified pH without any frother or collector is given in Table 1.1 and Figures 1.1 and 1.2 for the three coals and the three pyrites. The pyrites have little natural floatability. The coals have some natural floatability.

Floatability in Salt Solution

Another indication of floatability is the floatability in salt solution (under an indifferent ionic atmosphere). The Hallimond tube tests were conducted in 3% NaCl solution. The floatability of the three coals and pyrites in salt solution are given in Table 2.1 and illustrated in Figures 2.1 and 2.2. The effect of salt on the floatability of coal and pyrite is shown in Figures 2.3 to 2.8. In almost all cases except Illinois coal the floatability increases in salt solution. The rank of floatability of the three coals in salt solution is:

Upper Freeport > Pittsburgh > Illinois

Floatability with Frother only

These tests were carried out with MIBC frother only (4300 grams/ton). The results are shown in Table 3.1 and Figure 3.1 to 3.5. From these tests it was found that the three pyrites do not have floatability with MIBC frother. The Pittsburgh, Upper Freeport and Illinois coals have a relatively good floatability.

Selectivity of Dodecane

Selectivity has two meanings: (1) the difference in flotation behavior of a collector (or depressant or activator) between two pure minerals. (2) the selective absorption of reagents on a mineral in a mixed ore. To find some selective collectors for coal and pyrite the Hallimond tube tests were performed with dodecane collector. Tables 4.1 to 4.3 and Figures 4.1 to 4.3 show the comparison of flotation behavior of coals and pyrites. There are large differences between the flotation behaviors of coal and pyrite over a wide pH range in all three cases.

CONCLUSIONS

From the work completed this quarter the following conclusions can be made:

1. The three coals have natural floatability and the rank of floatability is:

Upper Freeport > Pittsburgh > Illinois

2. In almost all cases except Illinois coal the floatability improves in salt solution. The rank of floatability of the three coals in salt solution is:

Upper Freeport > Pittsburgh > Illinois

3. The three pyrites do not show floatability with MIBC frother only. Upper Freeport and Illinois coals have relatively good floatability with MICB.

4. Dodecane can selectively float coal from pure coal pyrite in over a wide range of pH.

CONTINUOUS WORK

Investigations of the floatability of coal and coal pyrite involving different modifiers, depressants and activators and chemicals for oxidation and reduction potential regulation are in progress.

Table 1.1 Natural Floatability of Coal and Coal Pyrite

MIBC: 0 g/t
Collector:0 g/t

No.	PH	Yield(%)	PH	Yield(%)
Coal			Pyrite	
Illinois hvCb:				
Natural Flotation PH=4.54:			Natural Flotation PH=4.60	
1.	2.17	35.80	2.80	5.51
2	4.54	39.40	4.60	9.47
3	6.43	35.00	5.97	7.45
4	8.37	39.90	8.84	7.17
5	10.07	40.50	10.04	4.24
Pittsburgh hvAb:				
Natural Flotation PH=4.40			Natural Flotation PH=3.37	
1	2.11	38.40	2.18	18.51
2	4.40	42.70	3.37	5.31
3	6.87	37.90	6.60	16.58
4	8.56	34.80	7.85	19.90
5	9.90	29.10	9.89	13.84
Upper Freeport mvb:				
Natural Flotation PH=4.54:			Natural Flotation PH=3.72	
1	2.22	55.2	1.99	9.4
2	4.54	43.00	3.72	5.80
3	5.85	66.40	6.26	8.90
4	8.19	54.90	8.40	11.90
5	10.10	47.40	10.14	6.50

Fig.1.1 The Natural Floatability of coals

Fig.1.2 The Natural Floatability of Pyrites

Table 2.1 Floatability of Coal and Coal Pyrite
in Salt Solution

NaCl: 3%

MIBC: 0 g/t

Collector: 0 g/t

No.	PH	Yield(%)	PH	Yield(%)
Coal			Pyrite	
Illinois hvCb:				
1.	2.12	44.80	2.30	11.30
2.	3.40	29.30	4.20	17.50
3.	5.01	30.90	6.00	16.40
4.	7.80	33.7	7.90	23.20
5.	9.80	24.00	9.90	21.60
Pittsburgh hvAb:				
1.	2.00	56.40	2.10	22.40
2.	4.00	34.40	4.10	30.60
3.	6.00	60.40	5.95	36.30
4.	8.30	40.40	8.02	42.70
5.	10.10	49.40	9.92	22.40
Upper Freeport mvb:				
1.	2.10	59.60	2.10	17.70
2.	4.50	58.20	3.90	17.10
3.	6.00	51.80	6.10	37.80
4.	8.10	53.10	7.90	46.10
5.	9.80	50.90	10.00	29.50

Fig.2.1 The Floatability of Coals in Salt Solution

Fig.2.2 The Floatability of Pyrites in Salt Solution

Fig.2.3 The Effect of Salt on the Floatability of Illinois Coal

Fig.2.4 The Effect of Salt on the Flotability of Pittsburgh Coal

Fig.2.5 The Effect of Salt on the Floatability of Upper Freeport Coal

Fig.2.6 The Effect of Salt on the Floatability of Illinois Pyrite

Fig.2.7 The Effect of Salt on the Floatability of Pittsburgh Pyrite

Fig.2.8 The Effect of Salt on the FLoatability of Upper Freeport Pyrite

Table 3.1 The Flotation Response of Coal and Pyrite

MIBC: 1000 g/t

Aeration Rate: 25 mm/min.

No.	PH	Yield(%)	PH	Yield(%)
Coal			Pyrite	
Illinois hvCb:				
1.	2.03	48.90	2.10	06.00
2.	3.06	45.00	4.38	17.80
3.	5.39	46.50	6.16	23.10
4.	8.03	53.80	8.15	15.20
5.	9.97	02.60	9.82	18.10
Pittsburgh hvAb:				
1.	1.99	29.60	1.99	14.60
2.	2.99	08.40	2.95	15.20
3.	3.97	21.90	4.03	16.80
4.	7.01	29.50	7.90	17.90
5.	10.04	17.70	9.75	21.40
Upper Freeport mvb:				
1.	1.96	50.20	2.00	17.00
2.	2.71	55.50	3.01	09.50
3.	4.64	66.70	4.12	11.30
4.	8.43	45.50	7.75	20.10
5.	10.06	39.40	10.87	17.00

Fig.3.1 The floatability of Coals with Frother Only

Fig.3.2 The Floatability of Pyrites with Frother Only

Fig.3.3 The Comparison of Floatability of Illinois Coal and Pyrite

With Frother Only

Fig.3.4 The Comparison of Floatability of Pittsburgh Coal and Pyrite With Frother Only

Fig.3.5 The Comparison of Floatability of Upper Freeport Coal and Pyrite with Frother Only

Table 4.2 The Flotation Response of Coal Pyrite
Dodecane 17200 g/t

No.	PH	Yield(%)
Illinois hvCb: Natural Flotation PH=5.80		
1.	2.40	14.80
2.	4.00	16.80
3.	5.80	13.00
4.	8.10	13.10
5.	9.80	13.90
Pittsburgh hvAb: Natural Flotation PH=3.90		
1.	2.10	08.50
2.	3.90	21.20
3.	6.20	15.50
4.	8.20	17.70
5.	9.90	9.80
Upper Freeport mvb: Natural Flotation PH=3.60		
1.	2.20	14.90
2.	3.60	19.60
3.	5.30	19.90
4.	7.80	21.30
5.	10.00	15.80

Table 4.3 The Flotation Test of Dodecane Dosages Using
the Hallimond Tube

No.	Dosage(g/t)	Yield(%)
Illinois hvCb		
	Natural Flotation pH = 5.90	
1.	4300.00	06.80
2.	8600.00	13.00
3.	12900.00	15.90
4.	17200.00	13.20
Pittsburgh hcAb:		
	Natural Flotation PH = 3.60	
1.	8600.00	23.60
2.	12900.00	08.90
3.	17200.00	12.60
Upper Freeport mvb:		
	Natural Flotation PH = 3.70	
1.	8600.00	05.70
2.	12900.00	07.40
3.	17200.00	13.40

Fig.4.1 The Selectivity of Dodecane for Illinois Coal and Pyrite

Fig.4.2 The Selectivity of Dodecane for Pittsburgh Coal and Pyrite

Fig.4.3 The Selectivity of Dodecane for Upper Freeport Coal and Pyrite

CYCLIC VOLTAMMETRIC STUDY

INTRODUCTION

Additional cyclic voltammetry measurements have been completed this quarter to obtain further information on the results reported in the previous report.

Summary of Experiments Performed

(1) Mineral pyrite from Rico, Colorado, in borate solution. (2) Original mineral pyrite (from Ward's National Science Establishment) in $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$ solution. (3) Conditions effecting the formation and intensity of the anodic peak 1a. (4) Sweep reversal study - effect of reversing the potential at different cathodic limits.

EXPERIMENTAL

The preparation of electrodes and solutions, equipment, and experimental procedures are the same as described in the previous report.

RESULTS AND DISCUSSION

As described in the last report, at the mineral pyrite surface, three anodic peaks at about -0.8 V, -0.1 V, and $+0.5$ V (SCE) have been detected along with their corresponding reduction peaks. Peaks 2 and 5 have been detected in pyrite oxidation in many studies. Peaks 1 and 6 and peaks 3 and 4, especially the unique properties of the double peak 1 and 1a, have not been reported in previous studies. In order to rule out any accidental phenomena, such as unknown inclusions in the electrode or the peculiarity of the electrolyte used, the cyclic voltammetric measurements were repeated with a new mineral pyrite electrode from another source (Rico, Colorado) in the same solution ($\text{Na}_2\text{B}_4\text{O}_7/\text{Na}_2\text{SO}_4$) and with the original mineral pyrite electrode in 0.1 M $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$ solution. The results are shown in Figures 1 to 4. By comparison with the Figures 2 and 7 in the last report, it is evident that in both stirred and quiescent solutions, the same peaks are observed and the shapes of the voltammograms are very similar. In $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$ solution the double peak 1a appears even in quiescent solution (see fig. 4), and the current density is higher but less affected by solution stirring than that in borate solutions.

Figure 2. Mineral Pyrite (Colorado) in Quiescent Borate
Solution of pH 9.2. Scan Rate: 50 mV/s.
Anodic Reverse Potential: 0.8 V.

Figure 3. Mineral Pyrite in Stirred $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$
Solution of pH 9.28. Scan Rate: 50 mV/s.
Anodic Reverse Potential: 0.8 V.

Figure 4. Mineral Pyrite in Quiescent $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$
Solution of pH 9.28. Scan Rate: 50 mV/s.
Anodic Reverse Potential: 0.8 V.

Figure 5. Mineral Pyrite in Borate Solution of pH 9.2.
 Scan Rate: 50 mv/s.
 Scan initiates at 0.0 V towards anodic

Figure 6. Mineral Pyrite in Borate Solution of pH 9.2.
 Scan Rate: 50 mv/s.
 Scan initiates at 0.0 V towards anodic

Figure 7. Mineral Pyrite in Stirred and Quiescent Borate Solution of pH 9.2. Scan Rate: 50 mV/s. Electrode Pre-conditioned at 0.4 V for 3 Min.

Figure 8. Pittsburgh Coal Pyrite in Stirred and Quiescent Borate Solution of pH 9.2. Scan Rate: 50 mV/s. Electrode Pre-conditioned at 0.4 V for 3 Min.

Figure 9. Mineral Pyrite in Stirred Borate Solution of pH 9.2. Electrode Pre-conditioned at 0.4 V for different time. Scan Rate: 50 mV/s.

Figure 10. Pittsburgh Coal Pyrite in Stirred Borate Solution of pH 9.2. Electrode Pre-conditioned at 0.4 V for different time. Scan Rate: 50 mV/s.

Figure 11. Mineral Pyrite in Stirred Borate Solution of different pH and Electrode Preconditioned at Appropriate Potential for 3 Min. Scan Rate: 50 mV/s.

Figure 12. Mineral Pyrite in Quiescent Borate Solution of different pH and Electrode Preconditioned at Appropriate Potential for 3 Min. Scan Rate: 50 mV/s.

Figure 13. Mineral Pyrite in Stirred Borate Solution of pH 9.2. Potential Reversed at Different Cathodic Limit. Scan Rate : 50 mV/s.

Figure 14. Mineral Pyrite in Quiescent Borate Solution of pH 9.2. Potential Reversed at Different Cathodic Limit. Scan Rate : 50 mV/s.

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