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DOE/PC/89758--T13

**SURFACE ELECTROCHEMICAL
CONTROL FOR FINE COAL AND PYRITE SEPARATION**

DOE Project No. DE-AC22-89PC89758

SEP 11 1992

Technical Progress Report
April 1, 1992 - June 30, 1992

DOE/PC/89758--T13

DE92 040541

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KINETIC STUDY OF FINE COAL AND COAL PYRITE FLOTATION

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ABSTRACT

A series of fine coal kinetic tests were carried out on three coals. It was found that the rank of flotation rates for the three coals tested were: Upper Freeport > Pittsburgh No. 8 > Illinois No. 6. In the case of Pittsburgh No. 8, the contained coal-pyrite was found to float more slowly than the coal itself when xanthate was used as the collector. In kinetic modeling, first order kinetic models produced large errors for long flotation times. It was found that a modified first order kinetic model with slow and fast rate constants was appropriate for fine coal flotation. A log-log plot of $1/(R_i - R)$ versus t forms a straight line for the test conditions of this study. The Lai proportionality flotation model was found to apply from the start and extending over a very broad time range.

INTRODUCTION

Understanding fine coal flotation kinetics is essential for improving flotation results. Coal and pyrite have not only different floatabilities but also different flotation rates, which may be utilized in the separation of coal and coal-pyrite [1]. This study presents kinetic results of fine coal flotation for three coals: Upper Freeport, Pittsburgh No. 8 and Illinois No. 6.

The early application of kinetics to particle flotation was based on the analogy between a chemical reaction (collision of molecules) and the underlying flotation mechanism; collision of hydrophobic particles and air bubbles generated in the pulp volume. The simplest and most basic model is the first order rate equation, given in equations 1 and 2.

$$\frac{dR}{dt} = K(R_i - R) \quad (1)$$

or

$$R = R_i (1 - \exp(-K \cdot t)) \quad (2)$$

Where: R_i is the ultimate yield
 t is the flotation time (minutes)
 K is the flotation rate constant
 R is the yield at time t

The first order kinetics is mainly used in the early days, there is a lot modification after the first order kinetics[2-6]. Ralph W. Lai discover a proportionality law of process[2,7,8], and use it to analyze and interpret a multitude of kinetic phenomena, the mathematical form is:

$$\frac{dR}{dt} = K \frac{(R_i - R)}{t} \quad (3)$$

or in the integration form:

$$\ln\left[\frac{1}{(R_i - R)}\right] = K \ln(t) + \ln(c) \quad (4)$$

The examples of this equation's application are given in fields as divers as chemical kinetics, extractive metallurgy and froth flotation[2].

It was observed during the experiments that about 80 percent of coal was floated during the first few minutes. When the process approaches the completion the flotation is very slow. Actually it could be better to think about that the feed of coal simply consists of two kind of materials: the fast floated and the slow floated. The corresponding modified first order kinetics for fine coal flotation is [6]:

$$R = R_i[\phi \cdot \exp(-K_s \cdot t) + (1 - \phi) \exp(-K_f \cdot t)] \quad (5)$$

where: ϕ is the fraction of the slow floated materials,
 K_f is the flotation rate constant of the fast floated materials,
 K_s is the flotation rate constant of the slow floated materials.

The objective of this paper is to collect flotation kinetics data and finds out the differences between the coal and coal-pyrite, and try to determine the kinetics equation of the fine coal flotation.

DATA COLLECTION AND ANALYSIS

Flotation experiments were conducted in a laboratory batch flotation cell for three coals: Upper Freeport, Pittsburgh No. 8 and Illinois No. 6 coal. The collector was xanthate and dodecane. The concentrates were collected from half minutes to 96 minutes. The particle size of sample was -100 + 325 mesh.

In order to determine the constants in the kinetics equation, A numerical fitting method (NLF program) and graphic method were used. NLF basically is a computer program which automatically finds the constants in the equation using non linear fitting technique. The plotting method is to plot the yield versus time by using different transformations. If the resulted plot is a strait line, and then the strait line could be described by a simple equation.

RESULTS AND DISCUSSION

The flotation kinetics for the coal and coal-pyrite of Pittsburgh No.8 was shown at Fig.1 with xanthate as a collector. The coal has higher floatability than the pyrite. This indicates that for Pittsburgh No.8 coal it is difficult to float pyrite from coal using reverse flotation and it seems that the xanthate causes agglomeration of the coal.

The long time, complete flotation kinetics data for the three coals was given at TABLE 1 using dodecane as a collector. The three kinetics equation were evaluated in this study: first order, modified first order and Lai's proportionality law. The kinetics parameters were listed at TABLE 2. It can be seen from the TABLE 2 that the rank of rate constants for the three coals is: Upper Freeport > Pittsburgh No.8 > Illinois No.6.

First order kinetics equation

The observed and calculated yields using first order kinetics equation were given at Fig.2. The yield calculated by the first order did not change after 16 minutes, in fact the flotation was continuing, the yield was continuing to increase. It only fits flotation at short times, at longer time it always underestimates flotation yields.

TABLE 1

Kinetic data of fine coal flotation

Time, minute	Yield, %					
	Dodecane: none			dodecane: 0.13 ml/l		
	Illinois	Pittsburgh	Upper	Illinois	Pittsburgh	Upper
0.5	9.52	13.72	33.31	11.93	17.54	63.30
1.0	26.90	27.43	50.29	26.96	31.51	78.39
2.0	37.88	43.56	72.11	38.96	55.48	87.51
4.0	59.30	62.54	80.76	59.32	70.53	92.92
8.0	72.54	77.65	87.91	79.52	84.72	95.57
16.0	80.43	84.56	90.34	85.86	91.25	96.74
32.0	85.72	88.32	92.83	90.25	93.77	97.21
64.0	89.22	90.25	93.55	91.58	94.25	97.65
96.0	91.56	91.79	94.27	92.32	95.62	97.75

Lai's proportionality law

Fig.3 to Fig.5 is the log-log plot for Upper Freeport, Pittsburgh No.8 and Illinois No.6 coal. In all these cases the plots are straight lines. It shows that the completed fine coal flotation kinetics follows the proportional law for the tested conditions. The comparison of the observed yield and the calculated yield was given at Fig.6. The observed and calculated yields show good agreement. The proportional law of flotation kinetics is applicable over a very long time range.

Modified first order

The results of the evaluation of the two-component kinetics equation are shown at Fig.7, the observed and calculated yields are very close. This is an indication that the modified first order equation is a good approximation for fine coal flotation kinetics.

TABLE 2

The kinetics parameters of the fine coal flotation

	First order		Modified first order				Lai's proportionality	
	R_i	K	R_i	K_s	K_f	ϕ	R_i	K
Upper	95.2	1.96	96.28	0.69	2.46	0.21	98.00	0.96
Pittsburgh	92.6	0.40	94.41	0.39	0.67	0.18	97.50	0.98
Illinois	89.9	0.28	90.82	0.75	0.94	0.22	95.50	0.77

CONCLUSIONS

The Pittsburgh No.8 coal has higher floatability than coal-pyrite. The rank of flotation rate constants for the three coals is: Upper Freeport > Pittsburgh No.8 > Illinois No.6. Lai's proportionality law and modified first order kinetics equation are suitable for the fine coal flotation.

ACKNOWLEDGEMENT

The author acknowledge the financial assistance from U.S. Department of Energy under project No. DE-AC-89PC-89758

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(b) Xanthate $2.5 \times 10^{-6} \text{ M}$
 ■ Coal
 ○ Coal pyrite

(a) Xanthate 0.00 M
 ■ Coal
 ○ Coal pyrite

Fig.1 The flotation kinetics of Pittsburgh No.8 coal and coal-pyrite with xanthate as a collector

Fig. 2. First order kinetics
 ■ Upper Freeport seam
 ○ Pittsburgh No.8 seam
 * Illinois No.6 coal
 — Calculated

Fig. 3. The log-log plot of flotation kinetics of Upper Freeport coal
 ○ Dodecane: 0.00 ml/l
 ■ Dodecane: 0.13 ml/l

Fig. 4. The log-log plot of flotation kinetics of Pittsburgh No.8 coal
 ○ Dodecane: 0.00 ml/l
 ■ Dodecane: 0.13 ml/l

Fig. 5. The log-log plot of flotation kinetics of Illinois No.6 coal
 ○ Dodecane: 0.00 ml/l
 ■ Dodecane: 0.13 ml/l

Fig. 6. Lai's proportional law
 ■ Upper Freeport seam
 ○ Pittsburgh No.8 seam
 * Illinois No.6 coal
 — Calculated

Fig. 7. Modified first order kinetics
 ■ Upper Freeport seam
 ○ Pittsburgh No.8 seam
 * Illinois No.6 coal
 — Calculated

SURFACE ELECTROCHEMICAL CONTROL FOR FINE COAL AND PYRITE SEPARATION

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DOE Project No. DE-AC22-89PC89758

October 19, 1989 - October 20, 1992

OBJECTIVE

The overall objective of this research is development of quantitative fundamental information related to premium coal production. The study is focused on the characterization of the surface electrochemical properties of coal pyrite to ascertain the possibility for advanced coal beneficiation processing. Further, electrochemical modification and control of coal/pyrite surfaces are to be applied to flotation practice.

ACCOMPLISHMENTS AND CONCLUSIONS

Transpassive Oxidation of Pyrite

In two previous papers (1,2), the results of our cyclic voltammetry studies of both mineral and coal pyrite were presented. At the mineral pyrite surface, three anodic peaks at about -0.8 V, -0.1 V and +0.5 V (versus SCE) were detected along with their corresponding reduction peaks, as shown in Figures 1 and 2, for quiescent and stirred solutions respectively. The first two peaks (peak 1 and 2) correspond to Fe⁰/Fe(II) and Fe(II)/Fe(III) oxidation. The reactions are:

A third peak, at a higher oxidation potential (+0.5 V, peak 3) corresponds to transpassive oxidation of pyrite. The proposed reactions are as follows:

The main reaction products are Fe(III) oxides and sulfate ion with residual partially oxidized sulfur intermediates (S_x^{2-} , S^0 and $S_xO_6^{2-}$). The majority of the polysulfides, elemental sulfur and polythionates would continue to oxidize to sulfate but those remaining on or near the surface would be reduced to HS^- on the return cathodic cycle. Surface ferric hydroxide, formed in the transpassive region, is reduced to metallic iron. These studies indicate that HS^- (surface) is strongly adsorbed on the iron, forming FeS_x during the next anodic scan.

The excess iron oxidizes to ferrous hydroxide (equation 1). These two reactions are characterized by two dominant anodic peaks observed in the lower potential region. They are peak 1, the ferrous hydroxide peak and peak 1a, the iron sulfide peak (Figure 2). Thus, the magnitude of peak 1a correlates directly with the quantity of sulfur intermediates formed in the transpassive region. The greater the amount of reaction forming peak 1a, the greater the expected hydrophobicity and floatability of pyrite particle.

Continuing research has centered on transpassive oxidation of pyrite. A series of voltammograms were performed in sodium borate/sulfate solutions at pH 9.2 with rotating disk electrodes to examine the conditions affecting the intensity of peak 1a and to show the difference in response between mineral and coal pyrite. Based on these voltammograms, a plot of peak current density versus electrode rotation speed is shown in Figure 3. The integrated charges associated with peak 1a versus anodic scan reversal potential and electrode pre-condition time are shown in Figures 4 and 5 respectively.

The effect of rotation speed was markedly different for mineral pyrite compared to Illinois coal pyrite. For mineral pyrite, at lower rotation speeds, peak 1 was predominant and peak 1a was relatively insignificant. As rotation speed increased, peak 1a increased, becoming predominant at 700 rpm, and continued to increase with further increase in electrode rotation speed. For Illinois coal pyrite, peak 1a also increased slowly with increasing electrode rotation speed, but was always much smaller than peak 1. The results for Pittsburgh coal pyrite were similar to Illinois coal pyrite. These results infer that enhanced floatability for mineral pyrite may be greater than that expected for coal pyrites following electrochemical alteration.

For both mineral and Illinois coal pyrite, the intensities of peak 1a increased with increasing anodic scan reversal potential and reached maximum values at about 0.85 to 0.9 V and 0.75 V respectively. The charge associated with peak 1a is much less for Illinois coal pyrite than for mineral pyrite. These results identify the potential range where the reaction forming partially oxidized sulfur intermediates predominate.

When the electrode was pre-conditioned at a threshold potential (0.6 V for mineral pyrite, 0.4 V for Illinois coal pyrite) for increasing time periods, peak 1a was continuously enhanced. For mineral pyrite, the charge of peak 1a increased with increasing electrode pre-condition time and tended to level off after 30 sec., probably indicating saturation of the surface. For Illinois coal pyrite, the electrode pre-condition time required to obtain the same magnitude of peak 1a was much longer than that for mineral pyrite (about 10 times). The total peak charge was observed to decrease when the pre-condition time was prolonged.

Mineral and Illinois coal pyrite also may be compared upon examining the voltammograms illustrated in Figure 6. Again, the effect of electrode rotation speed and anodic scan reversal potential was less pronounced for coal pyrite compared to mineral pyrite. These results are consistent with the enhanced reactivity observed for coal pyrite in the transpassive region compared to mineral pyrite. The disulfide ion in coal pyrite is oxidized more readily all the way to sulfate with fewer partially oxidized sulfur intermediates.

Raman Spectroscopy

The formation of sulfur and polysulfides in the transpassive region was identified by Raman spectroscopy in-situ as shown in Figure 7 for mineral and Illinois coal pyrite. After a certain time, new diagnostic peaks centered at about 150, 210 and 470 cm^{-1} were observed. The first two peaks are characteristic of elemental sulfur and are attributed to the S-S-S bending mode (3). The broad peak between 440 and 480 cm^{-1} contains a number of separate peaks and they are attributed to the S-S stretching mode of various polysulfide species (3).

A minimum potential was required to form sulfur or polysulfides on pyrite surfaces. The minimum potential for sulfur to be detected changes with the solution pH. For both acid (pH 2.6) and weak alkaline (pH 9.2) solutions, the observed value was 0.6 V, whereas for neutral solutions the value was 0.4 V. In strong alkaline solutions (pH 12.2) sulfur could not be detected at any potential.

Higher potentials, however, do not necessarily produce more sulfur or polysulfides. The intensity of the sulfur spectra is defined here arbitrarily as the integration of the broad peak at about 470 cm^{-1} with respect to the frequency shift. The sulfur intensity varies with the charge passed to the pyrite electrode as illustrated in Figure 8. Figure 8 shows that at higher potentials, above 0.8 V, less and less sulfur or polysulfides are formed.

The transformation of sulfur and polysulfides to sulfates may be the reason for the decline of the sulfur intensity with applied potentials. At higher potentials, oxygen begins to form and newly formed oxygen species may be extremely reactive as sulfur oxidants. The oxidation products appear to dissolve into the solution and therefore cannot be detected by surface Raman spectroscopy. The higher the potential, the greater the amount of oxygen produced. The unreacted oxygen molecules form and leave as visible bubbles and thus accelerate the transport of the sulfoxy ions away from the surface.

Flotation and Electrochemical Pretreatment of Coal Pyrite

It was observed that both mineral and coal pyrite floated very well in acid medium with potassium amyl xanthate as collector, but were depressed in alkaline solution (4). Figure 9 shows the floatability (percent floated) of mineral and Pittsburgh coal pyrite as a function of pH in the medium with and without Na_2SO_4 and $\text{Na}_2\text{B}_4\text{O}_7$ electrolyte. The experimental conditions are listed in Table 1. For both mineral and coal pyrite in solutions without electrolyte, there is low floatability at pH values around 4, which are close to the natural pH of the pulps. Results in the

Table 1. Conditions for Flotation Experiments

No.	Sample	Solution (M)		
		Xanthate	Na ₂ SO ₄	Na ₂ B ₄ O ₇
1	Mineral Pyrite	0.66×10^{-5}	0.00	0.00
2	Mineral Pyrite	0.66×10^{-5}	0.49	0.01
3	Coal Pyrite	1.32×10^{-4}	0.00	0.00
4	Coal Pyrite	1.32×10^{-4}	0.49	0.01
5	Coal Pyrite	1.32×10^{-4}	Lime added for pH control	

absence of electrolyte are consistent with results observed by Fuerstenau et al.(5). The floatability of mineral and coal pyrite is enhanced in the presence of electrolyte and the depressed floatability around their natural pH disappears. It may be concluded that sodium sulfate and sodium borate are effective activators for mineral and coal pyrite in xanthate system in the pH range of 2 to 8. Figure 9 also shows the effect of lime addition on the flotation recovery of coal pyrite. With small addition of lime for pH control significant reduction in the floatability of coal pyrite is noted (6).

Figures 10 and 11 illustrate the effect of applied potentials on floatability of coal pyrite. Na₂SO₄ and Na₂B₄O₇ were added to the solution as supporting electrolyte. The highest floatability of coal pyrite occurred in the potential range from +0.8 V to +1.0 V. Considering the higher resistance of the particle bed compared to solid electrode, these results agree well with those from electrochemical studies and Raman spectroscopy.

Figure 12 illustrates the effect of electrochemical pretreatment and xanthate dosage on the floatability of coal pyrite. The flotation behavior of pyrite pretreated at potential -1.5 V is similar to that for untreated pyrite. This situation may be due to the formation of iron hydroxides on the surface of pyrite or the surface of pyrite remaining unchanged.

Conclusions

The electrochemical oxidation of pyrite forming elemental sulfur and polysulfides takes place in the potential range, +0.4 to +1.1 V (SCE). Optimum sulfur formation occurs near +0.8 to +0.9 V for mineral pyrite and near +0.7 to +0.8 V for Illinois coal pyrite. These reactions are affected by electrode rotation speed, anodic scan reversal potential and electrode pre-condition time more significantly for mineral pyrite and less pronounced for Illinois coal pyrite.

Raman spectroscopic techniques were used successfully to study the electrochemically oxidized pyrite in-situ. The spectra obtained for several fixed potentials, indicated the presence of sulfur and polysulfides on surfaces of pyrite electrode. The results obtained are in good

agreement with those from electrochemical measurements.

Enhanced floatability of coal pyrite has been shown to occur when the pyrite has been exposed to potentials which form elemental sulfur and polysulfides; but, only when electrolyte is present. This has been confirmed by a series of flotation experiments using an electrochemical flotation cell.

OTHER RESEARCH

Besides the studies reported above, other work is ongoing on this project. These include characterization of coal pyrites, floatability evaluation of three typical US coal samples and mathematical modeling of coal flotation.

PLANS

Funding for this project will end October 20, 1992. The kinetics of sulfur formation will be studied based on previous results. A model will be developed to explain the flotation behavior of coal pyrites and the differences observed in flotation kinetics between coal and mineral pyrites in terms of the observed electrochemical properties. Laser Raman spectroscopy will be used to verify the conditions under which a sulfur-rich layer is formed on the pyrite surfaces in the presence of flotation reagents.

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Figure 1. Mineral Pyrite in Quiescent Solutions.

Figure 2. Mineral Pyrite in Stirred Solution.

Figure 3. Effect of Electrode rpm on Peak Current Density.

Figure 4. Integrated Charge of Peak 1a for Various Anodic Limits.

Figure 5. Integrated Charge of Peak 1a for Various Pre-condition Times.

Figure 6. Comparison of Mineral (a) and Illinois Coal Pyrite (b).

Figure 7. Raman spectra of oxidized pyrite at 1.0 V (0.5 M NaCl, pH 9.2).

Figure 8. Effect of potential on Raman intensity of sulfur and polysulfides.

Figure 9. Floatability of pyrite as a function of pH.

Figure 10. Effect of potential on pyrite floatability.

Figure 11. Effect of potential on pyrite floatability.

Figure 12. Effect of xanthate and potential on pyrite floatability.

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