SURFACE ELECTROCHEMICAL CONTROL FOR FINE COAL AND PYRITE
SEPARATION

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Technical Progress Report
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SURFACE ELECTROCHEMICAL CONTROL FOR
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DOE PROJECT NO. DE-AC22-89PC89758

Technical Progress Report

April 1, 1991 to June 30, 1991

This technical progress report, prepared in accordance with the reporting requirements of DOE Project No. De-AC22-89PC89758, covers the work performed from April 1, 1991 to June 30, 1991. The ongoing work includes the characterization of coal pyrites, the floatability evaluation of three typical U.S. coal samples, the flotation behavior of coal pyrites, the electrochemical measurement of the surface properties of coal pyrites, and the characterization of species produced at pyrite surfaces.

This report contains two sections, "A Rotating Disk Electrode Study of Pyrite", and "The Floatability of Coal and Coal Pyrite".

A ROTATING DISK ELECTRODE STUDY OF PYRITE

INTRODUCTION

The cyclic voltammetry study of mineral and coal pyrites using stationary electrodes was reported previously (1,2). The effect of solution stirring, especially in the transpassive region above 0.4V, was observed to be critical to subsequent oxidation/reduction reactions occurring in the lower potential region. This inferred that diffusion may be important to the reaction kinetics in the high voltage region. Rotating disk electrode techniques allow precise definition of mass-transport geometry. This permits quantitative examination of diffusion processes at the electrode surface. For this reason, rotating electrodes of mineral and coal pyrites (Pittsburgh and Illinois) were prepared and initial experiments were conducted to examine the effect of electrode rotation speed on the formation of the previously defined peak 1a, proposed to be due to iron sulfide formation.

EXPERIMENTAL

The solution preparation, equipment and experimental procedure were the same as described previously (1). The hydrodynamics of the system was controlled by a model 616 rotating disk electrode (RDE) manufactured by EG & G Parc, capable of rotating an electrode at speeds from 100 to 8000 rpm with a speed accuracy of better than $\pm 3\%$ for the entire range.

Working electrodes of mineral and coal pyrite were cut with a diamond core drill to $d = 1.1$ cm, avoiding inclusions, cracks and voids, and tightly fitted into a teflon disk holder. The electrical contact between the disk electrode and the rotator was through a spring connected

to the contact stud of the rotator. This made the disk electrode readily changable. The electrode surfaces were ground and polished before each measurement. The exposed surface areas of the disk electrodes were 1 cm².

RESULTS AND DISCUSSION

In the previous cyclic voltammetry study using stationary electrodes, it was observed that the effect of solution stirring in the transpassive region (from about 0.4V up to oxygen evolution) was critical to subsequent reduction and oxidation reactions. Oxidation reactions occurring in the region -0.8V to -0.7V were markedly influenced by pretreatment in the transpassive region. The two dominant peaks in this region were proposed to be related to the formation of ferrous hydroxide and iron sulfide, specified in the previous report as a double peak, peak 1 and peak 1a. It was also observed that when the electrode was pre-conditioned at 0.4V for 3 min., peak 1a was greatly enhanced and appeared for both stirred and quiescent solutions. Figures 1 and 2 are provided to illustrate the high reproducibility obtained with the rotating disk electrode when compared to results obtained with stationary electrodes (1). In Figure 1, the voltammograms were obtained at 700 rpm for only a portion of the scan. Quiescent conditions were maintained for the remainder of the scan. The results indicate again that peak 1a is dependent on electrode rotation only in the high potential region (0.0 to +0.8V). Electrode rotation in the low potential region had no influence on peak 1a formation. Figure 2 illustrates results obtained when the electrode was pre-conditioned at 0.4V at 700 rpm for 3 min. Peak 1a was greatly enhanced. These results are essentially identical to those obtained for the stationary electrode used previously (1).

The effect of electrode rotation speed on intensity of peak 1 and peak 1a in solutions at

pH 9.2 is shown in Figures 3 and 4 for mineral pyrite, 5 and 6 for Pittsburgh coal pyrite, and 7 and 8 for Illinois coal pyrite. Based on these results, plots of peak current density versus the square root of rotation speed for mineral and coal pyrites were obtained and are illustrated in Figures 9, 10 and 11 respectively. The effect of rotation speed was markedly different for mineral pyrite compared to coal pyrites. For mineral pyrite, at lower rotation speeds, peak 1 (the ferrous hydroxide peak) was predominant and peak 1a (the iron sulfide peak) was relatively insignificant (Figure 3). As rotation speed increased, peak 1a increased, becoming predominant at 700 rpm (Figures 4 and 9). For Pittsburgh coal pyrite, peak 1a also increased with increasing electrode rotation speed up to 1000 rpm (Figure 5), but decreased with further increases in electrode rotation speed, (Figure 6). Peak 1 remained predominant up to 2000 rpm (Figure 10). For Illinois coal pyrite, the effect was less pronounced. Peak 1a did not appear until 700 rpm had been attained (Figure 7). Above 700 rpm, it increased slowly with increasing rotation speed (Figure 8), but was always much smaller than peak 1 (Figure 11).

These characteristics can be correlated with observed flotation properties of mineral and coal pyrites after electrochemical alteration. As discussed in our previous report (1). The formation of peak 1a was directly related to the oxidation products, iron hydroxide and sulfur formed at high potential, which were reduced to metallic iron and hydro-sulfide during the cathodic scan. In the next anodic scan, cathodic products reacted according to the following equation to form iron sulfide (peak 1a):

These results infer that, the greater the intensity of peak 1a, the greater the tendency for oxidation of pyritic disulfide ion ($\text{S}_2^{=}$) to partially oxidized intermediates (S^0 , $\text{S}_3\text{O}_6^{=}$, etc.). These oxidized intermediates are capable of forming HS^- during the reduction cycle and thus

enhance FeS_x formation (peak 1a) during anodic oxidation. Further, the greater the reaction forming peak 1a, the greater the hydrophobicity and floatability of the pyrite particle. The results obtained for coal pyrite show that peak 1 (ferrous hydroxide formation) is favored over peak 1a (ferrous sulfide formation). This suggests that, in keeping with the higher reactivity of coal pyrite, S_2^- in coal pyrite is oxidized more readily all the way to SO_4^{2-} with fewer partially oxidized sulfur intermediates. This explains the enhanced floatability observed for mineral pyrite over coal pyrite.

REFERENCES

1. Hu, et al, "Surface Electrochemical Control for Fine Coal and Pyrite Separation", Department of Energy Technical Progress Report, April 1, 1990 to June 30, 1990, University of Utah, 1990.
2. Hu, et al, "Surface Electrochemical Control for Fine Coal and Pyrite Separation", Department of Energy Technical Progress Report, October 1, 1990 to December 31, 1990, University of Utah, 1990.

Figure 1. Mineral Pyrite in Solutions at pH 9.2 for RDE.
 Scans Initiate at 0.0V Toward Anodic.
 Scan Rate : 50 mV/s.

Figure 2. Effect of Electrode Pre-conditioning.
 Mineral Pyrite in Solutions at pH 9.2 for RDE.
 R.P.M.: 700. Scan Rate : 50 mV/s.

Figure 3. Mineral Pyrite in Solutions at pH 9.2 for RDE at Various R.P.M. Scan Rate : 50 mV/s.

Figure 4. Mineral Pyrite in Solutions at pH 9.2 for RDE at Various R.P.M. Scan Rate : 50 mV/s.

Figure 5. Pittsburgh Coal Pyrite in Solutions at pH 9.2
for RDE at Various R.P.M. Scan Rate : 50 mV/s.

Figure 6. Pittsburgh Coal Pyrite in Solutions at pH 9.2 for RDE at Various R.P.M. Scan Rate : 50 mV/s.

Figure 7. Illinois Coal Pyrite in Solutions at pH 9.2 for RDE at Various R.P.M. Scan Rate : 50 mV/s.

Figure 8. Illinois Coal Pyrite in Solutions at pH 9.2
for RDE at Various R.P.M. Scan Rate : 50 mV/s.

Figure 9. Effect of Electrode Rotation Speed on Peak Current

Figure 10. Effect of Electrode Rotation Speed on Peak Current

Figure 11. Effect of Electrode Rotation Speed on Peak Current

THE FLOATABILITY OF COAL AND COAL PYRITE

The floatability of mineral and coal pyrite was reported in previous technical reports (1-3). During this quarter, tests of floatability of coal and coal pyrite have been extended in the following areas: (1) floatability of Pittsburgh coal in xanthate, (2) floatability of coal after pretreatment by acid, (3) floatability of Pittsburgh coal and coal pyrite in hydrazene, (4) floatability of Pittsburgh coal after activation by CuSO_4 and Na_2S , and (5) floatability of mineral and coal pyrite with CO_2 gas.

FLOATABILITY OF PITTSBURGH COAL AND COAL PYRITE IN XANTHATE

It is thought that xanthate only floats pyrite, but not coal. In order to determine the floatability of coal in xanthate, flotation tests at different dosages of xanthate and a different pH were performed. Figure 1 shows the floatability of Pittsburgh coal and coal pyrite for the addition of xanthate at the natural pH. For the entire range of the experiment, the coal demonstrated better floatability than the coal pyrite. At the natural pH and 1.3×10^{-4} M xanthate, the floatability of Pittsburgh coal is nearly 100%, while that of Pittsburgh coal pyrite is only about 40%. Figure 2 shows the floatability at different pH. The trend with pH is the same for coal and coal pyrite, but the coal has better floatability. The flotation yield for coal is typically 30% greater than that for pyrite at one half the xanthate concentration. This may be due to either better adsorption of the collector xanthate by the coal or to the agglomeration of the coal upon addition of xanthate.

For many coals it is better to float the coal from the coal pyrite due to the good flotation behavior of the coal. However, it is usually preferable to float the minor component and depress

the major component. For such a reverse flotation process, an activator should be used to activate the coal pyrite and a depressant should be used to depress the coal.

FLOATABILITY OF COAL AFTER PRETREATMENT BY ACID

In previous technical reports (2,3), it was reported that acid pretreatment can remove carbonaceous matter from the surface of Pittsburgh coal pyrite, altering the pH of the pulp and improving the floatability of the pyrite. These experiments were performed on Pittsburgh coal to compare the behavior with that of the pyrite. The floatability after pretreatment with H_2SO_4 is shown in Figure 3. Acid pretreatment improved the floatability of the pyrite, but decreased the floatability of the coal. This would be favorable for a reverse flotation process.

FLOATABILITY OF PITTSBURGH COAL AND COAL PYRITE IN HYDRAZENE

Hydrazene is a strong reducing agent and is expected to increase the floatability of coal pyrite. Flotation experiment results are shown in Figures 4 and 5 for Pittsburgh coal and coal pyrite. As shown in Figure 4, the floatability of coal was not affected by the addition of hydrazene. The floatability of coal pyrite increased with the addition of hydrazene (Figure 5), but the effect of hydrazene was not great.

FLOATABILITY OF PITTSBURGH COAL AFTER ACTIVATION BY $CuSO_4$ AND Na_2S

In a previous technical report (3), it was reported that $CuSO_4$ and Na_2S increase the floatability of mineral and coal pyrite. For comparison, the effects of $CuSO_4$ and Na_2S on the floatability of Pittsburgh coal were investigated. The results are shown in Figures 6 and 7. Neither reagent has much effect on the floatability of the coal. Coal still has a better floatability

than the coal pyrite, although the reagents are activators for pyrite.

FLOATABILITY OF MINERAL AND COAL PYRITE WITH CARBON DIOXIDE GAS

In mineral flotation, it is common practice to use carbon dioxide to increase the floatability of pyrite. Flotation tests of Colorado mineral pyrite and Pittsburgh coal pyrite with CO_2 were performed. Both samples showed increased floatability and the effect was greatest for coal pyrite. However, Jin (4) reported that CO_2 enhances the hydrophobicity of coal and it is not expected to improve the separation of coal and pyrite.

CONCLUSIONS

Pittsburgh coal has a higher floatability than Pittsburgh coal pyrite in xanthate. For reverse flotation, depressants and activators should be used. Sulfuric acid increased the floatability of pyrite and decreased that of coal. Copper sulfate and sodium sulfide activated pyrite flotation, but hydrazene had a small effect. Carbon dioxide gas increased the floatability of both mineral and coal pyrite.

FUTURE WORK

Selective collectors for coal pyrite and depressants (such as dextrine and humic acid) for coal will be studied.

REFERENCES

1. Hu, et al, "Surface Electrochemical Control for Fine Coal and Pyrite Separation", Department of Energy Technical Progress Report, January 1, 1990 to March 31, 1990, University of Utah, 1990.

2. Hu, et al, "Surface Electrochemical Control for Fine Coal and Pyrite Separation", Department of Energy Technical Progress Report, October 1, 1990 to December 31, 1990, University of Utah, 1990.
3. Hu, et al, "Surface Electrochemical Control for Fine Coal and Pyrite Separation", Department of Energy Technical Progress Report, January 1, 1991 to March 31, 1991, University of Utah, 1991.
4. R. Jin, "Coal Flotation Chemistry," PhD Dissertation, University of Utah, 1989.

Figure 1 Floatability of Pittsburgh Coal and Coal Pyrite in Xanthate

Figure 2 Floatability of Pittsburgh Coal and Coal pyrite as a Function of pH

Figure 3 Floatability of Pittsburgh Coal and Coal Pyrite After Pretreatment With H₂SO₄

Figure 4 Floatability of Pittsburgh Coal with Hydrazene

Figure 5 Floatability of Pittsburgh Coal Pyrite with Hydrazene

Figure 6 Floatability of Pittsburgh Coal and Coal Pyrite Activated by CuSO_4

Figure 7 Floatability of Pittsburgh Coal and Coal Pyrite in Xanthate and Na₂S

Figure 8 Floatability of Colorado Mineral Pyrite in CO₂

Figure 9 Floatability of Pittsburgh Coal Pyrite in CO2

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