APR 01 1993

**OXIDATION OF COAL AND COAL PYRITE
MECHANISMS AND INFLUENCE ON SURFACE CHARACTERISTICS
DE-FG22-90PC90287**

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DOE/PC/90287--T10

DE93 013610

TECHNICAL PROGRESS REPORT (3/31/93)

RESEARCH OBJECTIVES

The objective of this research is to develop a mechanistic understanding of the oxidation of coal and coal pyrite, and to correlate the intrinsic physical and chemical properties of these minerals, along with changes resulting from oxidation, with those surface properties that influence the behavior in physical cleaning processes. The results will provide fundamental insight into oxidation, in terms of the bulk and surface chemistry, the microstructure, and the semiconductor properties of the pyrite.

During the tenth quarter, electrochemical experiments were done on electrodes prepared from Upper Freeport coal pyrite, and Pittsburgh coal pyrite samples provided by the U.S. Bureau of Mines, Pittsburgh Research Center, Pennsylvania. Electrokinetic tests were done on Upper Freeport and Pittsburgh coal pyrite. In addition, surface area measurements were done on Upper Freeport and Upper Clarion coals.

EXPERIMENTAL METHODS AND RESULTS

a. - Cyclic Voltammetry Experiments

Upper Freeport and Pittsburgh coal pyrite electrodes were prepared as reported in our March 31, 1992, and September 30, 1992, reports, respectively.

Because of the porous, irregular nature of the pyrite electrodes, the exposed surface areas were estimated by mapping a magnified image. The estimated areas, 0.2 cm^2 for the Upper Freeport and 0.187 cm^2 for the Pittsburgh pyrite, were used to calculate the current densities. Cyclic voltammetry experiments were conducted in a three-compartment Pyrex cell, with a 12 cm^2 platinum gauze counter electrode, and a saturated calomel reference electrode, using a pH 9.3 borate buffer solution, a pH 7.4 phosphate buffer solution or pH 1.0 H_2SO_4 , under argon. Voltammograms were obtained after contacting the electrode with the electrolyte solution for 2 hours. The samples were scanned at 2.0 mV/s for five cycles in each test, starting in the anodic direction from the rest potential. This scan rate is slower than the 20 mV/s rate reported in our last report. In general, when comparing voltammograms generated at fast and slow scan rates, there are three general differences. First, the current densities tend to be much lower at slow scan rates. If there is a fixed amount of chemical reactant for a given electrochemical reaction, then there will be a fixed charge associated with the reaction. Consequently the integral of a current-time plot would be constant.

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$$\int idt = c$$

Defining the scan rate, S , as $S = \frac{dV}{dt}$, then

$$\frac{1}{S} \int idV = c \text{ or } \int idV = cS$$

i.e. it is clear that where the amount of reactant is fixed, the integral of the current density-potential curve will be proportional to the scan rate. Even if the amount of reactant is not fixed, the current tends to be higher at faster scan rates.

The second feature of different scan rates is that slow scan rates tend to be more reversible than fast rates. A given electrochemical reaction requires a certain amount of time to go to completion, regardless of the rate-controlling process. When scanning rapidly, the reaction might start at the potential where the reaction becomes thermodynamically favorable, but generally does not proceed to completion before the potential has changed considerably. Because the reaction rate increases with increasing overvoltage, the peak for a given reaction is likely to be at an overpotential, rather than at the reversible potential itself. By the time all the reacting species has been exhausted, and the current has dropped back to zero (or another reaction has started), the electrode might be at a potential significantly greater (in absolute value) than the reversible electrode potential. Because this effect occurs on both the anodic and cathodic scans, there can be considerable hysteresis in the overall current-potential loops. In contrast, at a slower scan rate the electrode stays near the reversible electrode potential for much longer, hence the reaction is likely to have enough time to go to completion near the reversible electrode potential, giving much less hysteresis. It is important to recognize that these differences are due to the dynamic nature of the cyclic voltammetry procedure, rather than the nature of the electrode reactions. Comparison of the voltammograms for fast and slow scan rates enables the reversibility of specific reactions to be assessed.

The third feature of slow scan rates is the fact that when an electrode reaction gives soluble products, the product has time to move away from the electrode by diffusion, convection or migration, and hence is not present to give the reverse reaction when the electrode is scanned in the opposite direction. This allows one to distinguish between reactions that involve soluble species and those that do not.

Figure 1 shows the cyclic voltammograms of Pittsburgh coal pyrite after 2 hours of contact with pH 1.0 H_2SO_4 . On the first anodic sweep, there was no significant anodic current until about 0.9V SHE. On reversing the scan direction, there was no cathodic peak at about 0.7-0.65V corresponding to ferric reduction, as had been observed for the same electrode scanned at 20mV/s in H_2SO_4 (Figure 3, September 30, 1992 report). This is due to the third feature of slow scan rates discussed above; at 2 mV/s, the ferric ions that dissolved at high potentials would have diffused away from the electrode to the bulk solution by the time lower potentials were reached. The cathodic peak I was probably due to the reduction of oxidation products that formed at the highest potentials. The cathodic reaction occurring at about -0.3V is probably reduction of FeS_2 to FeS , with release of H_2S , although there may only have been partial reduction to a non-stoichiometric sulfide, as proposed by Biegler, 1976 [1]:

There was no anodic peak at about 0.2V corresponding to the reversal of reaction 1, as had been observed for the same electrode at 20mV/s in H₂SO₄, because of diffusion of the H₂S from the electrode. Successive scans resulted in converging voltammograms.

Figure 2 shows the cyclic voltammograms obtained with the Upper Freeport coal pyrite electrode after 2 hours of contact with pH 1.0 H₂SO₄. Cycling started at the rest potential previously measured after 24 hours, which was lower than the potential of the electrode after 2 hours (see September 30, 1992 and December 31, 1992 reports). The cycles are numbered 1 to 5. On the first cycle, the electrode passed a cathodic current at potentials up to 0.65V, then a very small anodic current (note that the scale is different from that used in Figure 1). On reversing the scan, a small cathodic current passed down to about 0.0 V, when the current increased slightly. There was a dramatic current increase at about -0.4V, due to reduction of pyrite. When the scan direction was reversed, a small anodic current passed from 0.0 to 0.8V, indicating that the surface had been changed in such a way as to facilitate the passage of anodic current at potentials that had given cathodic currents on the first cycle. Similarly, the cathodic currents on the second cathodic scan were smaller than those on the first, with a small cathodic peak I at about 0.0V, probably due to the reduction of oxidation products. Successive voltammograms converged.

Figure 3 shows cyclic voltammograms of Pittsburgh coal pyrite after contacting for 2 hours with a pH 7.4 phosphate buffer; these are similar to the voltammograms obtained in the same buffer at 20 mV/s (Figure 1 in our September 30, 1992 report), albeit at somewhat lower current densities. On the first cycle the anodic current was initially very low, then increased dramatically at about 0.6V, and the only significant cathodic peak was at about -0.45 V (I), probably corresponding to reduction of damaged or oxidized surface layers that formed during electrode preparation or conditioning. The anodic current was higher after the first cycle. Peak III is similar in magnitude to the peaks in the voltammograms obtained at 20mV/s on the second and subsequent cycles. Although we attributed this peak to formation of pyrite by reversal of reaction 1, it is clear that this could only be true on the first cycle, which did show a larger peak. Thereafter, and on all cycles at 2 mV/s, peak III could not have involved H₂S, since this would have dissipated at the slow scan rate. Instead, the peak must be due to an electrochemical reaction involving the phosphate in the buffer solution. The cathodic peak II, which only appeared on the second and subsequent cycles in Figure 3, must be due to reduction of oxidized layers that formed at high potentials, or of phosphate species.

Figure 4 shows cyclic voltammograms of Upper Freeport coal pyrite after contacting for 2 hours with a pH 7.4 phosphate buffer. These are quite different from the voltammograms obtained in the same buffer at 20 mV/s, where an unsteady anodic current passed at most potentials (Figure 5 of our September 30, 1992 report). Here, the electrode passed a cathodic current on the first cycle up to about 0.6V, when the current reversed and increased. There was only one cathodic peak on all cycles, starting at about -0.4V, probably due to reduction of FeS₂; this decreased with cycling. The anodic peak II is probably due to the same electrochemical reaction responsible for peak III in Figure 3. An anodic current passed over most of the potential range on the second and subsequent anodic scans.

Figure 5 shows cyclic voltammograms obtained with the Pittsburgh coal pyrite after 2 hours of contact with pH 9.3 borate buffer. On the first cycle, the current was low initially, then increased dramatically at about 0.4V. A cathodic peak I started developing at -0.4V,

with a maximum at -0.5V. The cathodic current then increased again, presumably because of pyrite reduction. The anodic peaks II and III could not be due to re-formation of FeS_2 by interaction of reduced layers with H_2S , and hence must be due to electrochemical reactions involving the borate buffer. At the slow scan rate, two distinctive peaks could be resolved, whereas at the higher scan rate (Figure 2, December 31, 1992 report), there appeared to be only one.

Figure 6 shows cyclic voltammograms obtained with the Upper Freeport coal pyrite electrode after 2 hours in contact with pH 9.3 borate buffer. These are very similar to those for the Pittsburgh pyrite discussed above. On the first cycle, a cathodic current passed to about 0.45V, where the current reversed and increased. A cathodic peak I started developing at -0.4V, with a shoulder at -0.6V, probably due to reduction of oxidation products formed during electrode preparation, or reduction of borate species. This peak did not appear at the faster scan rate (Figure 6, December 31, 1992 report). A cathodic peak due to reduction of pyrite was established at -0.75V. The anodic peaks II and III are probably due to the same reaction of borate seen in Figure 5.

b. - Electrokinetic Behavior of Raw and Oxidized Coal.

3g samples of -400 mesh Upper Freeport and Pittsburgh coal pyrite, spread to a depth of about 1 mm, were oxidized in a convection oven at 230°C for 24 hours. Raw samples of Upper Freeport and Pittsburgh coal pyrite were freshly prepared by grinding to -400 mesh with a ceramic mortar and pestle under argon. A 0.002 M sodium nitrate solution was used as the electrolyte. Sodium hydroxide and nitric acid were used to adjust the pH. Samples containing 0.02 g of coal pyrite in 100 ml of electrolyte solution were conditioned for 4 hours. The zeta potential of each sample was measured using a Model 501 Lazer Zee Meter, using 25.0 ml of coal pyrite suspension and a potential of 100 mV. The results in Figure 7 are the average of three zeta potential measurements for each pH value (after conditioning). For both coal pyrite samples, there is no significant effect of oxidation upon the PZC. The PZC is consistent with values in the literature.

Upper Freeport coal samples oxidized at higher temperatures were negatively charged at all pH values tested (June 30, 1992 report). It is clear that this negative charge must be determined mainly by the acidic groups present on coal surface, rather than the oxidation products on the pyrite.

c. - Film Flotation Tests

Figure 8 shows the film flotation partition curves of as-received and oxidized coal pyrite at 230°C (the film flotation method was reported in our March 31, 1992 report). Clearly, the critical surface tension increased dramatically on oxidation, reflecting a decrease in the hydrophobicity of pyrite samples with oxidation. This is undoubtedly due to the presence of hydrophilic iron oxide or hydroxide on the surface. Clearly this change with oxidation would affect the performance of physical coal cleaning processes.

d. - Surface Area Measurements

A Micromeritics Surface Area/Pore Volume Analyzer (Model 2100D) was employed for gas adsorption experiments. In this apparatus, the quantity of adsorbed gas is

determined from volume measurements before and after each adsorption step. The operating and data analysis procedures for the instrument are described in the Micromeritics Operating Manual [2]. CO₂ adsorption experiments, followed by analysis using the Dubinin-Polanyi equation, were used in the present study. The use of the Dubinin-Polanyi equation for determination of surface areas is discussed by Marsh et al [3]. The relevant equation is:

$$\log V = \log V_0 \frac{BT^2}{\beta} \log^2 \left(\frac{P_0}{P} \right) \quad (2)$$

where V is the volume of gas adsorbed, in cm³ adsorbate per gram of adsorbent, V_0 is the micropore capacity (cm³/g), P is pressure, P_0 is the saturation vapor pressure of the adsorbate at temperature $T^\circ\text{K}$, β is the affinity coefficient of the adsorbate relative to nitrogen, and B is a constant. Thus, a plot of $\log V$ vs $\log^2 (P_0/P)$ should yield a straight line, with intercept of $\log V_0$ and slope $-BT^2/\beta$. Utilizing the calculation procedures described in the instrument manual [2], the gas volumes V and V_0 are reduced to S.T.P. The applicability of equation (2) is limited to microporous materials, where the majority of pore diameters are a few times the effective diameter of the adsorbing gas molecules. For such systems, monolayer adsorption may be assumed, so that V_0 may be used to estimate the surface area from the equation:

$$S = N_A V_0 S_a v^{-1} 10^{-20} \quad (3)$$

where S is the specific surface area (m²/g), N_A is Avogadro's number, v is the specific volume of the adsorbing gas, and S_a is the effective specific surface area per molecule of the gas at the appropriate temperature. The specific volume of CO₂ at STP is 2.23×10^4 cm³/mole and S_a has been taken as 25.3 Å²/molecule at 298°K [2]. For all adsorption experiments the samples were outgassed for 48.0 hours. The entire evacuation procedure was performed by the mechanical vacuum pump in the gas adsorption apparatus at a vacuum of about 10⁻³ mmHg. A temperature of 20°C was maintained by placing a water-filled container around the sample bulb. The time to reach equilibrium between points varied from coal to coal, but was usually between 1.5 and 2 hours. In general, 4 points were measured for each coal. For Upper Clarion coal, a -20 mesh sample was used, whereas for Upper Freeport coal, a 200 x 230 mesh sample was used. Sample weights of 1.0 to 2.0 g were used, and duplicate measurements were made for each coal sample.

Figure 9 shows the results obtained when the data for both coals were plotted by the Dubinin-Polanyi method; excellent fits to straight lines were obtained for both coals. Surface areas of 114.5 m²/g and 120.5 m²/g were obtained for Upper Clarion and Upper Freeport coals, respectively. These results show that the surface area is similar for both coals.

PLANS FOR THE NEXT QUARTER

During the next quarter we will continue studying the dry oxidation of Upper Freeport coal for more extensive oxidation time; in addition, we will study the oxidation behavior of coal samples from the Pennsylvania State Coal Bank using different procedures, focusing on characterization techniques that reveal more about the mechanism of oxidation. These studies will include analysis by diffuse reflectance infrared fourier transform analysis (DRIFT) to observe the change in type and relative concentration of surface functional

groups, as a function of both time, and nature of oxidant. Wettability studies are also planned. Other coal pyrite electrodes will be studied to determine their anodic and cathodic polarization behavior, and cyclic voltammetry experiments will also be done. Electrokinetic studies will be done on different coal pyrite samples.

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Figure 1: Cyclic voltammogram for Pittsburgh coal pyrite after 2 hours in contact with a pH 1.0 H_2SO_4 solution at 2.0 mV/sec

Figure 2: Cyclic voltammogram for Upper Freeport coal pyrite after 2 hours in contact with a pH 1.0 H_2SO_4 solution at 2.0 mV/s.

Figure 3 : Cyclic voltammogram for Pittsburgh coal pyrite after 2.0 hours in contact with a pH 7.4 phosphate buffer solution at 2.0 mV/s.

Figure 4: Cyclic voltammogram for Upper Freeport coal pyrite after 2.0 hours in contact with a pH 7.4 phosphate buffer solution at 2.0 mV/s.

Figure 5: Cyclic voltammogram for Pittsburgh coal pyrite after 2.0 hours in contact with a pH 9.3 borate buffer solution at 2.0 mV/s.

Figure 6 : Cyclic voltammogram for Upper Freeport coal pyrite after 2 hours in contact with a pH 9.30 borate buffer solution at 2.0 mV/s.

Figure 7: Effect of oxidation on the zeta potential of Upper Freeport and Pittsburgh coal pyrites (-400 mesh particles oxidized at 230°C for 24 hours) in 0.002 M sodium nitrate solution as a function of pH.

Figure 8: Film flotation partition curves of Upper Freeport and Pittsburgh coal pyrite samples (-400 mesh), as received and thermally oxidized for 24 hours at 230°C.

Figure 9: A Dubinin-Polanyi plot of Upper Clarion coal (-20 mesh) and Upper Freeport coal (200x250 mesh) as obtained by carbon dioxide adsorption at room temperature

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