OXIDATION OF COAL AND COAL PYRITE
MECHANISMS AND INFLUENCE ON SURFACE CHARACTERISTICS
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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 ninth 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. Scanning electron microscopy and energy dispersive X-ray analysis were done to characterize the morphology and composition of the surface of as-received coal, oxidized coal and coal pyrite. In addition, electrokinetic tests were done on Upper Freeport coal pyrite.

EXPERIMENTAL METHODS AND RESULTS

a. Rest Potential Measurements

Upper Freeport and Pittsburgh coal pyrite electrodes were prepared as reported in our March 31, 1992 report. The potential of the coal pyrite electrodes was measured as a function of time for 24 hours, in a pH 9.30 borate buffer (0.025 M Na2B4O7·10H2O), a pH 10.50 borate buffer solution (0.0125 M Na2B4O7·10H2O in 0.02425 M NaOH) and a pH 1.0, H2SO4 solution. The potentials were measured against a saturated calomel electrode (SCE), using an EG&G Model 273 potentiostat, and then converted to the SHE scale. Table 1 shows the results obtained from the mean of three values for each pyrite electrode. The potentials measured initially were relatively high, then decreased, albeit to different extents. After 24 hours, the potentials were fairly steady. Since there was no oxidant or reductant in the systems, there should not have been any reaction, but the change in potential indicates that some change, either a reaction or a physical transformation, must have been occurring. Recognizing this, we designate the potential after 24 hours as the "rest potential", with the caveat that this might not be characteristic of true equilibrium. These potentials are shown on the Eh-pH diagram overleaf for the Fe2S-H2O system, supplementing data shown in our last report. The potentials of the Upper Freeport and Pittsburgh coal pyrite samples at each pH have been marked, and designated as UF and P respectively. The subscripts 0 and 24 refer to the potentials at zero and 24 hours.

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Table 1: Potentials of coal pyrite electrodes at pH 1.00, 9.30 and 10.50.

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>Initial Potential, mV SHE</th>
<th>Potential at 24 hr, mV SHE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upper Freeport coal pyrite</td>
<td>1.00</td>
<td>727.0 ± 10</td>
<td>311.2 ± 10</td>
</tr>
<tr>
<td></td>
<td>9.30</td>
<td>600.0 ± 10</td>
<td>272.5 ± 10</td>
</tr>
<tr>
<td>Pittsburgh coal pyrite</td>
<td>1.00</td>
<td>645.0 ± 10</td>
<td>551.5 ± 10</td>
</tr>
<tr>
<td></td>
<td>9.30</td>
<td>360.0 ± 10</td>
<td>249.0 ± 10</td>
</tr>
<tr>
<td></td>
<td>10.50</td>
<td>305.0 ± 10</td>
<td>205.0 ± 10</td>
</tr>
</tbody>
</table>

Eh-pH diagram for the Fe-S-H₂O system at 25°C. Activities of Fe ions: 10⁻¹ and 10⁻⁶ M, sulfur-containing species, 10⁻¹. UF₀ and UF₂₄ denote potentials of Upper Freeport pyrite samples initially, and after 24 hours. P₀ and P₂₄ denote potentials of Pittsburgh pyrite initially and after 24 hours. (Diagram from R.C.H. Ferreira, in Leaching and reduction in hydrometallurgy, Ed. A.R. Burkin, Institution of Mining and Metallurgy, London, 1975, pp. 67-83)

In all cases the potentials of the pyrite samples were well above the region of thermodynamic stability for pyrite. As discussed in our last report, one reason for this non-equilibrium behavior is that the pyrite surface may become oxidized during grinding, despite all attempts to exclude oxygen, and form oxide films. Alternatively, the grinding procedure might introduce a large number of defects that alter the stability of the surface layers of pyrite. The differences observed in the initial potentials of the two pyrite samples are more likely to be due to differences in the level of trace oxygen impurities during grinding, or to differences in damage, than to intrinsic characteristics of the pyrite samples. At pH 1.00, oxide films would be expected to dissolve, which could account for the reduction in potential of both pyrite samples over 24 hours. However, the failure to reach the region of stability for pyrite suggests that there is also some influence from grinding defects, or that a polysulfide layer formed by acid dissolution during the "equilibration"
period. Moreover, there is a marked difference in the behavior of the Upper Freeport and Pittsburgh coals. At pH 9.30 the final potentials of both coal pyrite samples were close, but not as similar as had been observed in a phosphate buffer at pH 7.4, where the phosphate appeared to be replacing the original oxide coating (discussed in our September 30, 1992 report). The potentials of both pyrite samples decreased with increasing solution pH, which is consistent with the thermodynamics of the system.

b. Cyclic Voltammetry Experiments

For each experiment a selected pyrite sample was used as the working electrode. The 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 10.5 borate buffer solution or pH 1.00 H$_2$SO$_4$, under argon. The samples were scanned at 20 mV/s for five cycles in each test, starting in the anodic direction from the rest potential. Voltammograms were obtained after contacting the electrode with the electrolyte solution for either 2 or 24 hours.

Figure 1 shows the cyclic voltammograms of Pittsburgh coal pyrite after contacting for 24 hours with a pH 9.3 borate buffer. The cycles are numbered 1-5. On the first cycle, the current was low initially, then increased dramatically at about 0.40 V SHE. A major cathodic reaction was becoming established at -0.750 V when the scan direction was reversed back to the anodic direction. As discussed in our last report, from the Eh-pH diagram it is likely that this was a reduction of FeS$_2$ to FeS, with a release of H$_2$S, although there may only have been partial reduction to a non-stoichiometric sulfide, as proposed by Biegler, 1976:

$$\text{FeS}_2 + 2x\text{H}^+ + 2xe = \text{FeS}_{2-x} + x\text{H}_2\text{S}$$  (1)

The anodic peak II is probably due to reversal of this reaction. The difference in magnitude between the anodic peak and the cathodic peak is due to the fact that some of the H$_2$S generated in reaction 1 would diffuse away from the electrode, preventing quantitative reformation of pyrite. The surface generated, presumably sub-stoichiometric pyrite, passed a higher anodic current density in the potential range of 0.240 - 0.750V than had the original pyrite surface. Again, a large increase in current density was observed at about 0.40V, probably due to the formation of an oxide layer. On the second cycle a very small cathodic shoulder (I) appeared at about -0.40 V, and its magnitude was constant on subsequent cycles. Peak I could be due to the reduction of the stable oxide layer that formed at the highest potentials.

Figure 2 shows the 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 slow initially, then increased dramatically at about 0.400 V. Again, a cathodic reaction given by reaction 1 was becoming established at -0.750 V when the scan direction was reversed.
However, the cathodic current was much lower than that in Figure 1, suggesting that less pyrite was reduced to a non-stoichiometric sulfide according to reaction 1. The anodic peak II, due to reversal of reaction 1, was also smaller than that in Figure 1. Again there was a large increase in current density at about 0.350 V due to formation of an oxide layer. On the second and subsequent cycles the cathodic current was lower than on the first cycle.

Figure 3 shows the cyclic voltammograms obtained with the Pittsburgh coal pyrite electrode after 24 hours in contact with pH 10.5 borate buffer solution. On the first cycle, the current was low initially, then increased at about 0.300V. The cathodic and anodic peaks I and II were observed, as in Figures 1 and 2. Figure 4 shows the electrode behavior after 2 hours of contact with pH 10.5 borate buffer. The voltammograms are similar to those in Figure 3, in contrast to Figures 1 and 2, indicating that at pH 10.5 the behavior of the electrode on cycling is less sensitive to the conditioning time.

Figures 5 and 6 show the cyclic voltammograms obtained with the Upper Freeport coal pyrite electrode after 24 and 2 hours in contact with a pH 9.30 borate buffer solution. The voltammograms are remarkable because even at relatively high potentials, the electrode is passing a cathodic, rather than the thermodynamically favorable anodic current. Even at the "rest" potential, a substantial cathodic current was being passed. Also, the currents observed for the Upper Freeport coal pyrite were less steady than those for the Pittsburgh coal, under all conditions, suggesting that semiconductor or insulating layers were forming under certain conditions and giving erratic responses. This pyrite clearly has a very low propensity for oxidation, in marked contrast to the Pittsburgh coal. Such differences would be extremely important in determining the ability to desulfurize each coal after weathering. However, this behavior was not observed using a phosphate buffer at pH 7.3, and we are now doing studies to determine whether the behavior is due to the pyrite, or to the borate buffer.

Figure 7 shows the cyclic voltammograms obtained with the Upper Freeport coal pyrite electrode after 24 hours of contact with pH 1.0 H2SO4. On the first cycle the anodic current was extremely low up to about 0.600V, when oxidation occurred. A cathodic reaction was observed at about -0.400V that was probably due to dissolution of the oxidized layer, possibly a polysulfide. On the second anodic scan, the anodic current density started increasing at about 0.300V, and higher anodic currents were passed on subsequent scans, indicating that the electrochemical character of the pyrite surface changed during the course of cycling. The cathodic current was lower on the second and subsequent scans than in the first cycle.

c. Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) analysis of coal samples.

The results of dry oxidation tests on Upper Freeport coal pyrite were presented and discussed in our September 30, 1992 report. SEM/EDX analysis was done to study the morphology and the composition of the oxidized samples. Samples were mounted on carbon disks and coated with carbon, then examined using a JEOL JSM-355F SEM Model with a KEVEX EDX analyzer. For each coal sample, one particle was selected for EDX analysis. Figure 8 shows the EDX spectrum of raw coal. C, O, Al, Si and S are clearly visible. It should be noted that the peak heights are not directly proportional to the quantity of material present; quantitative analysis requires normalization of the peak heights with
respect to the peak sizes obtained for standard materials. The carbon, oxygen and sulfur are from coal; and the aluminum and silicon are probably from ash minerals. Copper and zinc were from the brass SEM sample holder. Any iron present was below the detection limit of 1.0%. Figure 9 shows the EDX spectrum of coal oxidized at 95°C after 35 days. Comparing Figure 8 with Figure 9, there is no clear increase in the oxygen peak, indicating that the EDX spectrum was not sensitive to the slight increase in the amount of carboxylic groups that had been detected by ion-exchange. Similar EDX analysis results were obtained with coal samples oxidized at room temperature and different humidity conditions.

SEM/EDX analysis was also used to study the morphology and the elemental surface composition of Upper Freeport coal pyrite and Pittsburgh coal pyrite. Coal pyrite samples were hand picked from broken coal. Figure 10 shows the surface of an Upper Freeport coal pyrite crystal; the surface is very rough and porous, with some granular material. Figure 11 shows the surface of Pittsburgh coal pyrite; the surface is more uniform than the Upper Freeport coal pyrite, with granular masses on the surface. Figures 12 and 13 are the corresponding EDX spectra. The Upper Freeport pyrite shows trace impurities of aluminum and silicon, whereas the Pittsburgh pyrite had traces of calcium.

d. Electrokinetic Studies

To study the zeta potential of coal pyrite samples, Upper Freeport coal pyrite was freshly ground to -400 mesh with a ceramic mortar and pestle under an argon atmosphere. 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 grams of coal pyrite in 100 ml of electrolyte solution were used in each experiment. In order to find the appropriate conditioning time, the zeta potential of Upper Freeport coal pyrite was determined as a function of time at pH 5.0. The zeta potential of each sample was measured in a model 501 Lazer Zee Meter, using 25.0 ml of pyrite suspension and a potential of 100 mV. Measurements were made in triplicate for each pyrite sample. The results in Figure 14 are the average of three measurements. Clearly, the zeta potential decreased for the first two hours of conditioning time and then remained constant at about -20.0 mV. This value is in the range of other values observed at pH 5.0 in the literature (Fornasiero et al., 1992). Three hours of conditioning time will be used in future electrokinetic studies to allow an electrical charge to develop fully on the coal pyrite surfaces.

PLANS FOR THE NEXT QUARTER

During the next quarter we will continue our long term studies on dry oxidation of Upper Freeport coal. 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 of the samples 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. SEM/EDX analysis will be done to study variations in the morphology of different coal and coal pyrite samples. Other coal pyrite samples will be studied electrochemically, to determine their anodic and cathodic polarization behavior, and cyclic voltammetry
experiments will be done over more extensive potential ranges and different scan rates. Electrokinetic studies will be done on different coal pyrite samples.

REFERENCES


Figure 1: Cyclic voltammogram for Pittsburgh coal pyrite after 24 hours in contact with a pH 9.30 borate buffer solution at 20 mV/s.

Figure 2: Cyclic voltammogram for Pittsburgh coal pyrite after 2 hours in contact with a pH 9.30 borate buffer solution at 20 mV/s.
**Figure 3:** Cyclic voltammogram for Pittsburgh coal pyrite after 24 hours in contact with a pH 10.5 borate buffer solution at 20 mV/s.

**Figure 4:** Cyclic voltammogram for Pittsburgh coal pyrite after 2 hours in contact with a pH 10.5 borate buffer solution at 20 mV/s.
**Figure 5**: Cyclic voltammogram for Upper Freeport coal pyrite after 24 hours in contact with a pH 9.30 borate buffer solution at 20 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 20 mV/s.
Figure 7: Cyclic voltammogram for Upper Freeport coal pyrite after 24 hours in contact with a pH 1.00 H$_2$SO$_4$ solution at 20 mV/s.
Figure 8: Energy dispersive spectrum of as-received Upper Freeport Coal.

Figure 9: Energy dispersive spectrum of Upper Freeport Coal, oxidized for 35 days at 95°C.
Figure 10: Micrograph of Upper Freeport coal pyrite

Figure 11: Micrograph of Pittsburgh coal pyrite
Figure 12: Energy dispersive spectrum of Upper Freeport coal pyrite.

Figure 13: Energy dispersive spectrum of Pittsburgh coal pyrite.
Figure 14: The effect of conditioning time on the zeta potential of Upper Freeport coal pyrite in 0.002 M sodium nitrate solution at pH 5.0