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OXIDATION OF COAL AND COAL PYRITE
MECHANISMS AND INFLUENCE ON SURFACE CHARACTERISTICS

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TECHNICAL PROGRESS REPORT (6/30/92)

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 result 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 seventh quarter, electrokinetic, humic acid extraction and film flotation tests were done on oxidized samples of Upper Freeport coal from the Troutville #2 Mine, Clearfield County, Pennsylvania. Scanning electron microscopy and energy dispersive X-ray analysis was done to characterize the morphology and composition of the surface of as-received coal, oxidized coal, oxidized coal after extraction of humic acids and humic acid extracted from oxidized coal. In addition, electrochemical studies were done on electrodes prepared from coal pyrite samples.

EXPERIMENTAL METHODS AND RESULTS

a. Sample Preparation

Monosized fractions of the Upper Freeport coal were prepared using a mortar and pestle, followed by sieving. Both grinding and sieving were done in an argon-filled glove box, to prevent oxidation.

b. Electrokinetic Studies

In order to study the effect of pH on the zeta potential on Upper Freeport Coal, coal particles were ground to minus 4000 mesh ($<38 \mu\text{m}$) with a mortar and pestle in a nitrogen-filled glove box. A 0.002M sodium nitrate solution was used as the electrolyte, because nitrate ions do not form complexes with metal ions commonly found in coal suspensions. Sodium hydroxide and nitric acid were used to adjust the pH. Samples containing 0.02 grams of coal with 100 ml of electrolyte solution were conditioned for 16 hours, then redispersed ultrasonically. The zeta potential of each sample was measured in a Model 501 Lazer Zee Meter, using 25.0 ml of coal suspension and a potential of 100 mV. Triplicate

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measurements were made for each coal sample. The results in Figure 1 are the average of three measurements versus the final pH after conditioning.

Figure 1 shows that the effect of increasing oxidation temperature (the oxidation procedures were reported in our 3/31/92 report) is to lower the potential at a given pH. For coal oxidized at 150°C for 24 hours, the PZR dropped from its original pH value of 4.8 to about pH 2.8. Samples oxidized at higher temperatures were negatively charged at all pH values tested. This is attributed to the formation on oxidation of acidic surface functional groups that are dissociated even at low pH.

c. Humic Acid Extraction Tests

During electrokinetic testing at pH 12 of coal samples that had been oxidized at 200 and 230°C, the pulp acquired an intense brown color, because of the dissolution of humic acids. Dissolution of humic acids might also be responsible for the fact that the zeta potential of these samples remained constant in the alkaline range, whereas that of the less oxidized samples continued to drop. These humic acids were extracted from 0.3g of Upper Freeport Coal, previously oxidized at 230°C for 24 hours, by stirring with 500 ml of 0.1M NaOH solution in an inert atmosphere at room temperature for 16 hours, decanting and filtering. The filtrate was then acidified with 0.1M HCl solution to pH 2.0. After stirring for 16 hours the humic acid precipitate was separated by centrifuging and filtering. The humic acids were washed repeatedly with distilled water to remove any HCl or NaCl, until the filtrate was nearly colorless. Then the humic acids were dried overnight at room temperature in a vacuum desiccator, to minimize oxidation.

Humic acids formed on the coal surface during oxidation make the coal more hydrophilic. Figure 2 shows the film flotation partition curves of raw coal, coal oxidized at 230°C and coal oxidized at 230°C after extraction of humic acids (the film flotation method was reported in our 3/31/92 report). Clearly, the removal of hydrophilic humic acids partially restores the intrinsic wettability of the coal.

d. Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) analysis

SEM/EDX analysis was done to study the morphology and the elemental composition of raw coal, oxidized coal, oxidized coal after extraction of humic acid and humic acids. Samples were mounted on carbon sample holders and coated with carbon for SEM examination using a JOEL JSM-35SF scanning electron microscope with a KEVEX energy dispersive X-ray analyzer. The analyses were carried out at an accelerating voltage of 10 kV and a beam current of 10 nA with an X-ray take off angle of 28°. The SEM instrument has a resolution of the order of 40 - 60Å.

Figure 3 shows the surface of a raw coal particle (+63µm -75µm fraction) coated with small particles of mineral matter. The surface of coal shows little macroporosity and moderate roughness. Figure 4 shows the surface of a coal sample oxidized at 230°C for 24 hours. Although one cannot generalize from examination of two particles, the morphology and structure seem to be preserved on oxidation, but the surface roughness appears to be slightly more pronounced. Figure 5 shows the surface of coal oxidized at 230°C for 24 hours

after the extraction of humic acids. The particle is very regular in shape, with an even surface, to which are attached small, lamellar particles. Figure 6 shows the surface of humic acid extracted from coal that had been oxidized at 230°C for 24 hours. The surface is rugged, with some elongated, sheet-like aggregates.

For each coal or humic acids sample, one particle was selected for EDX analysis. Figure 7 shows the energy dispersive spectrum of raw coal. C, O, Al, Si and S are clearly visible. The carbon, oxygen and sulfur are from the coal; and the aluminum and silicon are probably from ash minerals. Copper and zinc were from the SEM sample holder. Any iron was below the detection limit of 1.0 wt%. Figure 8 shows the energy dispersive spectrum of coal oxidized at 230°C for 24 hours. Comparing Figure 8 with Figure 7, there is a marked increase in the intensity of the oxygen peak, demonstrating the formation of oxygen-containing functional groups. Figure 9 shows the energy dispersive spectrum of coal oxidized at 230°C for 24 hours after extraction of humic acids. The oxygen peak is dramatically lower than that in Figure 8, due to the removal of the carboxylate groups of the humic acids. The energy dispersive spectrum of humic acid, shown in Figure 10, shows an oxygen peak that is very strong, comparable with the carbon peak.

e. Rest Potential Measurements

The potential of coal pyrite electrodes was measured as a function of time in an electrolyte of 0.01M sodium borate in 0.49M sodium sulfate at pH 7.8. The electrode preparation procedure, and the rest potential measurements at pH 1.0 were reported in our March 31, 1992 report. Electrode potentials were measured against a saturated calomel reference electrode (SCE), using an EG&G Model 273 potentiostat, and then converted to the SHE scale. Figure 11 compares the rest potentials of mineral and coal pyrite electrodes. At pH 1.0, the rest potential of a coal pyrite electrode is lower than a mineral pyrite one, close to the potential at which oxidation is thermodynamically favorable. Also, the rest potential of coal pyrite at pH 7.7 is lower than the rest potential of coal pyrite at pH 1.0, but to a lesser extent than would be expected from the Eh-pH diagram for the Fe-S-H₂O system.

PLANS FOR NEXT QUARTER

During the next quarter we will continue studying the oxidation of Upper Freeport Coal using different procedures, focussing on characterization techniques that reveal more about the mechanism of oxidation. These studies will incorporate the 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. Coal pyrite electrodes will be studied to determine the anodic and cathodic polarization behavior and cyclic voltammetry experiments will be done in different potential ranges.

Figure 1 Effect of oxidation on the zeta potential of Upper Freeport Coal (-400 mesh) in 0.002 M sodium nitrate solution as a function of pH

Figure 2 Film flotation partition curves of Upper Freeport Coal (200 x 250 mesh) as received, oxidized at 230 °C and after humic acid extraction.

Figure 3 Micrograph of Upper Freeport Coal, as received, +63 μm - 75 μm fraction

Figure 4 Micrograph of Upper Freeport Coal, +63 μm - 75 μm fraction, oxidized for 24 hours at 230°C.

Figure 5 Micrograph of Upper Freeport Coal, +63 μm - 75 μm fraction, oxidized for 24 hours at 230°C, after extraction of humic acid.

Figure 6. Micrograph of Humic acid extracted from Upper Freeport Coal after oxidation for 24 hours at 230°C.

UCB MSME EDS
Cursor: 0.000keV = 0

Figure 7 Energy dispersive spectrum of as-received Upper Freeport Coal.

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Cursor: 0.000keV = 0

Figure 8 Energy dispersive spectrum of Upper Freeport Coal, oxidized for 24 hours at 230°C.

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Figure 9 Energy dispersive spectrum of Upper Freeport Coal, oxidized for 24 hours at 230°C, after extraction of humic acid.

UCB MSME EDS
Cursor: 0.000keV = 0

Figure 10 Energy dispersive spectrum of humic acid extracted from Upper Freeport Coal, after oxidation for 24 hours at 230°C.

Figure 11 Potential of mineral and coal pyrite samples as a function of time.

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