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OXIDATION OF COAL AND COAL PYRITE
MECHANISMS AND INFLUENCE ON SURFACE CHARACTERISTICS
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TECHNICAL PROGRESS REPORT (12/31/91)

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 coal 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 fifth quarter, wet chemical and dry oxidation tests were done on Upper Freeport coal from the Troutville #2 Mine, Clearfield County, Pennsylvania.

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. Wet chemical oxidation studies

Acidic ferric sulfate: 20 g of -75 +63 μ m (200x250 mesh) samples of Upper Freeport coal particles were oxidized for 24 hours at room temperature in a well stirred, Pyrex vessel through which argon was passed continuously, using 600 ml of 0.0094M, 0.0187M, and 0.0374 M, Fe₂(SO₄)₃ solutions, all adjusted to pH 1.00 $\pm$ 0.05. This corresponded to 50%, 100% and 200% of the stoichiometric Fe(III) requirement for oxidizing all the pyrite in each sample. 10 ml samples of slurry were withdrawn periodically, filtered immediately, and the coal was washed with water to remove all ferric, to halt oxidation. Both the coal and liquid fractions were stored under argon. Solution samples were analyzed by atomic absorption spectrophotometry, to determine the total iron concentration in solution. The ferric:ferrous ratio was determined from the solution potential, using calibration curves reported earlier.

Figure 1 shows that in all three oxidation tests, the solution potential, which in this medium reflects the ferric:ferrous ratio, decreased rapidly during the first few minutes, then continued to decrease more slowly over the 24-hour test period. Figure 2 shows that the

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Fe(III) concentration decreased markedly in the first few minutes, then remained almost constant, whereas the ferrous concentration increased steadily over 24 hours (Figure 3), accounting for the observed decline in solution potential. The initial decrease in Fe(III) led to an overall decrease in total dissolved iron, and hence cannot be due only to reduction to Fe(II). It is thought that the iron loss, which has also been observed in other tests, is due to chemisorption on oxidized surface functional groups, or precipitation of a hydrolyzed phase or basic sulfate compound. Diffuse reflectance infrared fourier transform analysis (DRIFT), and X-ray powder diffraction analysis are planned to identify the true mechanism.

Nitric acid: 20 g of -75 +63 μ m (200x250 mesh) samples of Upper Freeport coal were oxidized for 24 hours at room temperature in a well-stirred, Pyrex vessel, using 600 ml of 0.10M or 3.00M HNO₃. Samples were taken and treated as described above. The total iron in solution was determined by atomic absorption. As-received coal, and samples oxidized for 24 hours were analyzed by the sodium acetate ion-exchange method described by Brooks and Sternhell, to determine the surface carboxylate species (Brooks, J.D., and Sternhell, S., *Aust. J. Appl. Sci.*, 1957, 8, 206): One gram of sample was purged with nitrogen, and shaken with 100 ml of 3.0M sodium acetate for 24 hours. The method assumes that all the surface carboxylic acid groups will be converted to their sodium salts on exposure to sodium acetate, releasing hydrogen ions into the solution:

where (s) denotes a surface species. The slurry was then filtered, and the acid in a 30 ml aliquot was determined by titration with 0.2M NaOH. The results are shown in Table I. 0.1M HNO₃ gave a slight increase in the carboxylate oxygen content of the coal, whereas 3.0M HNO₃ gave an appreciable increase.

Table I: Weight percent carboxylate oxygen in coal samples subjected to different treatments

Coal Treatment	Weight % carboxylate oxygen
As received coal	0.68
0.1M HNO ₃ , 24 hrs	0.81
3.0M HNO ₃ , 24 hrs	1.87

Although reproducible results were obtained using potentiometric titration, it is questionable whether the ion exchange reaction shown above will go to completion; thus this method could seriously underestimate the surface carboxylic acid concentration. This uncertainty is now being investigated.

Figure 4 shows the percentage of coal pyrite dissolved by HNO₃ as a function of time. At either 0.1M or 3.0M HNO₃ there was rapid initial oxidation; the former eventually oxidized 64% of all pyrite in the coal sample, whereas the latter had oxidized all pyrite within 5 hours. It is clear from the solution potentials in each case (Figure 5), that oxidation halted at the lower nitric acid concentration because of the low potential.

c. Dry oxidation tests

5 g samples of -75 +63 μ m Upper Freeport coal, spread to a depth of about 1 mm, were oxidized in a convection oven at 100°, 150°, 200° and 230°C, for 24 hours, to investigate the effect of oxidation temperature. Samples were also oxidized at 230°C for 1, 2, 4, 8, and 24 hours, to investigate the oxidation rate. The surface carboxylate concentration of the oxidized samples was determined by the ion-exchange method outlined above.

Figure 6 shows that the extent of oxidation after 24 hours was relatively insensitive to temperatures up to 150°C, but increased dramatically at 200 and 230°C. Figure 7 shows a steady increase in the extent of oxidation with oxidation time, at 230°C; it is evident that equilibrium had not been achieved by 24 hours. The rate of oxidation (Figure 8) appeared to be at a maximum after 2 hours.

PLANS FOR NEXT QUARTER

During the next quarter we will continue studying the oxidation of Upper Freeport coal using different aqueous oxidants. Diffuse reflectance infrared fourier transform analysis (DRIFT) will be done to investigate the change in in nature and concentration of surface functional groups, as a function of time, and nature of the oxidant. The dry oxidation studies will be continued, with sample characterization by DRIFT, surface area, ion-exchange and other methods. Film flotation tests will be done to characterize the flotability of as-received coal, and samples subjected to different oxidation procedures. Electron microscopy of the coal, and coal pyrite, is planned. Electrodes that have been prepared from coal pyrite samples will be studied to determine their rest potentials, anodic and cathodic polarization behavior, and cyclic voltammetry will be done in different potential ranges.

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Figure 1 : Solution potential during oxidation of Upper Freeport coal (200x250 mesh fraction) by ferric sulfate at pH 1.0

Figure 2 : Concentration of ferric iron during oxidation of Upper Freeport coal (200x250 mesh fraction) by ferric sulfate at pH 1.0

Figure 3 : Concentration of ferrous iron during oxidation of Upper Freeport coal (200x250mesh fraction) by ferric sulfate at pH 1.0

Figure 4 : Percentage of coal pyrite dissolved by 3.0 M HNO_3 and 0.1 M HNO_3 at room temperature, 33.3 g/l Upper Freeport coal (200x250 mesh fraction)

Figure 5 : Solution potential during oxidation of Upper Freeport coal (200x250 mesh fraction) by 3.0 M HNO_3 and 0.1 M HNO_3

Figure 6 : Effect of oxidation temperature on weight percent oxygen in the form of carboxylic groups on the surfaces of Upper Freeport coal oxidized for 24 hours

Figure 7 : Effect of oxidation time on weight percent oxygen in the form of carboxylic groups on the the surfaces of Upper Freeport coal oxidized at 230°C

Figure 8 : Rate of increase in weight percent oxygen in the form of carboxylic group on the surfaces of Upper Freeport coal oxidized at 230°C

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