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 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 fourth quarter, characterization and oxidation tests were done on Upper Freeport coal from the Troutville #2 Mine, Clearfield County, Pennsylvania. In addition, standard test methods for characterizing pyrite-bearing materials were studied.

EXPERIMENTAL WORK

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. Sample characterization

1.0g samples were characterized by proximate and total sulfur analysis, using a LECO MAC 400 proximate analyzer and a LECO-SC-132 sulfur analyzer. Table I shows the results of proximate analysis for the -147 + 104μm size fraction.

Table I: Proximate analysis of -147 + 104μm fraction of Upper Freeport coal.

<table>
<thead>
<tr>
<th></th>
<th>Dry basis, except moisture</th>
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<tbody>
<tr>
<td></td>
<td>Sample 1, %</td>
</tr>
<tr>
<td>Volatiles</td>
<td>1.49</td>
</tr>
<tr>
<td>Ash</td>
<td>26.45</td>
</tr>
<tr>
<td>Fixed Carbon</td>
<td>17.64</td>
</tr>
<tr>
<td></td>
<td>55.91</td>
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</table>
Figure 1 shows the total sulfur content of the respective size samples; it should be noted that the total sulfur content in each size fraction decreases with decreasing particle size, probably due to the fact that pyrite is significantly harder than the coal.

The -147 + 104µm size fraction was characterized by sulfur type analysis in triplicate by ASTM Method D2492-84; this contained 0.66% pyritic sulfur, 0.01% sulfate, and 0.49% organic sulfur (calculated by difference). Reliable determination of the sulfur forms in coal is of fundamental importance to this research project. The reliability of ASTM Method D2492-84 is questionable on two counts. First, it is difficult to verify that complete oxidative dissolution of pyrite has occurred for a coal sample, and second, it is questionable whether calcium sulfate (or similar sulfates) would dissolve in the initial, non-oxidizing HCl leach. This could lead to overestimation of the organic sulfur content, since this is obtained by calculating the difference between the total sulfur, and the sulfate plus pyritic sulfur. Thus it was considered necessary to evaluate this test method, and to compare it with other static and kinetic test methods that are used for characterizing pyrite-bearing materials. The methods and results are described in detail in the attached publication. ASTM Method D2492-84 was found to be reliable only if the sample was boiled with nitric acid for 30 minutes. The alternative procedure, involving overnight treatment at ambient temperature, did not give complete dissolution of pyrite.

c. Oxidation tests

Peroxide (batch): Ore pyrite samples are frequently analyzed by oxidation with 30% hydrogen peroxide. Upper Freeport coal was subjected to this oxidation procedure. The resultant solution was analyzed for total iron, by atomic absorption, and for acid released, by titration with NaOH to pH 7. The titration results were analyzed by assuming that all Fe(III), as determined in the atomic absorption analysis, would consume three equivalents of OH⁻, and the residual OH⁻ consumption was due to the single hydrogen ion released by the reaction:

\[
\text{FeS}_2 + 15/2 \text{H}_2\text{O}_2 = \text{Fe}^{3+} + 2\text{SO}_4^{2-} + 7\text{H}_2\text{O} + \text{H}^+ 
\]

(1)

Table II: Percentage of total pyrite in Upper Freeport coal reacted during oxidation with peroxide-assessed by AA analysis of total iron, and titration with NaOH to pH 7.

<table>
<thead>
<tr>
<th></th>
<th>Temp uncontrolled</th>
<th>Temp ≤ 40°C</th>
<th>Temp ≤ 10°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe</td>
<td>Total OH⁻</td>
<td>Fe</td>
</tr>
<tr>
<td>Sample 1</td>
<td>8.94</td>
<td>374.7</td>
<td>8.18</td>
</tr>
<tr>
<td>Sample 2</td>
<td>8.40</td>
<td>357.5</td>
<td>8.34</td>
</tr>
<tr>
<td>Mean</td>
<td>8.67</td>
<td>366.1</td>
<td>8.26</td>
</tr>
</tbody>
</table>
Both analyses were converted to percentage of total pyrite oxidized on the basis of 0.66% pyritic sulfur in the coal, and are reported in Table II. Whereas both analyses are highly consistent for ore pyrite, there is a huge discrepancy for coal, and an unreasonably high release of acid. Vigorous, exothermic reactions were observed between coal and the hydrogen peroxide. It is thought that this corresponds mainly to oxidation of the coal by hydrogen peroxide, forming both soluble and surface acidic groups; the former account for the high release of acid, whereas the latter complex much of the iron that is released by pyrite oxidation. Extensive further studies are planned to characterize directly the processes occurring on oxidation of coal with 30% hydrogen peroxide.

**Kinetic oxidation tests:** Figure 2 shows the percentage of pyrite dissolution from Upper Freeport coal on oxidation with 1.97M HNO₃ at ambient temperature as a function of time; comparison with the complete dissolution within 30 minutes at 100°C demonstrates a strong dependence of rate on temperature and hence a high activation energy for oxidation. Figure 3 shows that all pyritic sulfur was dissolved (as assessed by AA analysis of Fe) after 10 hours during treatment with 5% hydrogen peroxide. The difference in behavior on reducing the H₂O₂ concentration is probably due to the fact that there was no generation of surface acidic groups that could complex any iron released by pyrite oxidation. Again, extensive work is planned to characterize coal treated by dilute peroxide, and to systematically study oxidation as a function of time of the type and concentration of oxidant.

**PLANS FOR NEXT QUARTER**

During this period, we will continue with the study of oxidation of Upper Freeport PA coal using hydrogen peroxide, ferric sulfate, and nitric acid as aqueous oxidants, as discussed above. Oxidized samples will be characterized by infrared, surface titration, and other studies, while the soluble oxidation products will be analyzed by HPLC. In addition, electrodes will be prepared from coal pyrite samples, in order to characterize the electrochemical oxidation behavior. Studies will include rest potential measurements, anodic and cathodic polarization and cyclic voltammetry experiments in different potential ranges. The composition of the pyrite electrodes will be determined by microprobe analysis and x-ray fluorescence.


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Figure 1: Total sulfur content in each size fraction of ground Upper Freeport coal.
Figure 2: Percentage of Coal pyrite dissolved by 1.97M HNO₃ at room temperature. 33.33 g/l Upper Freeport coal (-147 + 104µm)

Figure 3: Percentage of coal pyrite dissolved by 5% H₂O₂. 33.33 g/l Upper Freeport coal (-147 + 104µm).