TECHNICAL REPORT
September 1 through November 30, 1994

Project Title: NEAR-NEUTRAL OXIDATION OF PYRITE IN COAL SLURRY SOLIDS

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ABSTRACT

In this research project we plan to determine the rate of oxidation of pyrite associated with coaly particles (coal slurry solid) when the pH of the surrounding environment is held at approximately 7.8. Coaly particles that contain pyrite are generated during the preparation of Illinois Basin coal for market. These particles are discharged to an impoundment, which eventually must be reclaimed. The purpose for reclamation is either to prevent the generation of acidic solution as the pyrite in the coal slurry solid reacts with air, or to prevent the migration of the acidic solution to a groundwater aquifer. The reclamation is usually accomplished by covering the impoundment with a four-foot-thick layer of topsoil.

One possible alternative method for reclamation of a coal slurry impoundment is to mix in alkaline residue from the fluidized-bed combustion of coal. This codisposal would slow the production of acid and would also neutralize any acid produced. If the codisposal method is found to be environmentally acceptable, it will save the coal mining companies part of their cost of reclamation, and also provide a safe and useful disposal outlet for a portion of the residue that is generated by the fluidized-bed combustion of coal.

During this quarter we purchased and set up two automatic titrators, which will be used in determining the rate of pyrite oxidation at nearly neutral pH. The titrators will provide a means for maintaining the pH at the desired level. The rate at which sulfate ion is produced as a result of pyrite oxidation will be used to measure the amount of pyrite oxidized over time.

U.S. DOE Patent Clearance is NOT required prior to the publication of this document.
EXECUTIVE SUMMARY

This research project is part of an overall research program that addresses the codisposal of residue from the fluidized-bed combustion (FBC) of Illinois Basin coal with coal slurry solids (CSS) generated during the cleaning of coal in preparation for market. This cleaning process is conducted principally to remove pyrite from the coal, but other minerals, such as calcite and clay minerals, are removed to some degree as well. The waste stream from the coal preparation plant is discharged into a coal slurry impoundment, which eventually must be reclaimed, normally by covering with a minimum four-foot-thick soil cover.

The coal cleaning process is not 100% efficient, so additional methods are used in coal combustion to prevent the emission of sulfur dioxide to the atmosphere. One such combustion method is fluidized-bed combustion. In the fluidized-bed combustion process, pulverized coal is combusted in the presence of pulverized limestone. At the temperature of the combustor, the limestone loses carbon dioxide and produces calcium oxide. The calcium oxide reacts with sulfur dioxide, a reaction product of pyrite oxidation at high temperature, to produce calcium sulfate or anhydrite. The FBC residue, then, consists of unreacted calcium oxide, calcium sulfate, and a relatively minor amount of uncombusted coal particles.

The calcium oxide in the FBC residue, when exposed to water or water vapor, produces calcium hydroxide. The pH of an aqueous solution of calcium hydroxide is about 13. Calcium hydroxide, in turn, quickly reacts with carbon dioxide from the atmosphere to produce calcium carbonate, which in aqueous solution, yields a buffered solution with a pH of about 7.8.

The codisposal of alkaline FBC residue with potentially acidic coal slurry solids appears to be a method for disposing two residues in a mutually beneficial process. A portion of the generated FBC residue is disposed of and the rate of production of acidic leachate from the coal slurry solid is decreased.

In research just completed (Dreher et al., 1994) we began developing a mathematical model to calculate the rate of oxidation of pyrite in the presence of calcium carbonate. The expected use of this model will be by those who design or monitor coal slurry...
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impoundments. Other researchers (Moses and Herman, 1989; 1991)\textsuperscript{2,3} have determined the rate of oxidation of pure pyrite, but the oxidation rate of pyrite in CSS is unknown. To effectively use the model, the latter should be known.

We will obtain the needed data by allowing pyrite in CSS to oxidize under controlled pH conditions. The pH of the solution will be controlled by balancing the delivery of acidic and basic solutions to the reaction medium by using two automatic titrators. CSS, from which calcium carbonate and sulfate have been removed, will be maintained at a pH of 7.8 for a predetermined time, then the solid and solution will be separated and the solid will be allowed to partially air-dry. The solid will again be exposed to the pH-controlled solution for another time period, then allowed to partially air-dry. Each separated solution will be analyzed for concentration of sulfate, from which the amount of pyrite oxidized will be calculated.

A second set of experiments will be conducted in which the time periods will be randomized between 0 and 10 days, in order to determine whether the regulation of wetting and drying times has an effect on the pyrite oxidation rate.


OBJECTIVES

This research project is part of a multi-year program, the overall goal of which is to reclaim coal slurry impoundments by codisposal of residues from the fluidized-bed combustion of coal with the coal slurry solids from a coal preparation plant. The specific objective of the research project being conducted this year is to develop data on the rate of pyrite oxidation in the codisposal mixture.

The tasks required to meet this objective are to expose samples of coal slurry solid to regular or random cycles of wetting and drying. The pH during the wetting phase will be maintained at $7.8 \pm 0.2$ by titration of either dilute HCl solution or dilute NaOH solution. The amount of sulfate ion generated during the oxidation will be assumed to represent the amount of pyrite oxidized. From these data a rate law for pyrite oxidation will be calculated.

INTRODUCTION AND BACKGROUND

In the Illinois Basin, most of the coal mined contains pyrite at concentrations that are higher than are acceptable for regulation of sulfur dioxide emission to the atmosphere during combustion. For this reason, sulfur is removed from Illinois Basin coal prior to marketing it.

For years, the principal method for removing sulfur from Illinois Basin coal has been gravity separation, although this method does not remove all the pyrite. The resulting coal slurry solid (CSS), which consists of coal particles, pyrite, and other minerals, is discharged into a coal slurry impoundment. A coal slurry impoundment is typically constructed on the surface in the case of an underground mine; or in the case of a surface mine, the coal slurry solid might be discharged into a dammed, abandoned mining cut. The particles settle out in the impoundment and the water is recycled through the coal preparation plant circuit. Eventually, the impoundment will reach its solids-holding capacity. When that occurs, the impoundment must be reclaimed by an acceptable method, preferably one that prevents either the formation or the migration of acidic leachate. The presently accepted method is to cover the coal slurry solids with a minimum four-foot-thick soil cover.

Even though much of the pyrite can be removed from Illinois Basin coal by the preparation process, sulfur remains in the marketed product. Further efforts to prevent sulfur dioxide from entering the atmosphere must be taken in the combustion of the coal. One such method for combusting Illinois Basin coal, and which we expect to become more widespread, is the fluidized-bed combustion (FBC) process, in which pulverized coal is combusted in the presence of pulverized limestone in what is termed a "fluidized bed." The purpose of the limestone is to react with sulfur dioxide that is generated as the sulfur in the coal is released and oxidized during combustion. Because the limestone is not combustible, large quantities of combustion residues are generated. These residues must be disposed of in an environmentally acceptable manner.
FBC residue typically consists of 10% to 30% calcium sulfate and 25 to 45% calcium oxide and/or hydroxide. These materials can yield strongly alkaline solutions (pH 12 or higher) when mixed with water. Calcium hydroxide is readily converted to calcium carbonate (calcite) on exposure to air. A mixture of calcite and water typically has a pH of approximately 8.

The oxidation of pyrite in a coal slurry solid and the consequent generation of acid, is appreciably slowed by the addition of alkaline material to the pyrite-bearing material, especially under water-saturated conditions. We demonstrated that pyrite oxidation can occur under unsaturated conditions, but the presence of FBC residue neutralized the acid generated (Dreher et al., 1992). If the two residues can be codisposed, both residues would be acceptably treated and a potentially deleterious environmental effect would be avoided.

If mixtures of FBC residue and CSS will support seed germination and plant growth, the current requirement of a four-foot thick soil cover on a reclaimed coal slurry impoundment might be circumvented. This, of course, is subject to regulatory acceptance and approval of the codisposal method.

One of the objectives of the overall research program is to mathematically model the oxidation of pyrite, the neutralization of generated acid, and the migration of the resulting solutes through a reclaimed coal slurry impoundment (Dreher et al., 1994). Some of the information required to understand the processes that occur in the codisposal situation is documented in the literature. There is information in the literature on the oxidation of pure pyrite under nearly neutral conditions (Moses and Herman, 1989; 1991), but information about the rate of pyrite oxidation in a coaly matrix at slightly alkaline pH is lacking. These data are required for the development and application of the predictive computer model.

EXPERIMENTAL PROCEDURES

Four samples of pyrite-bearing coal slurry solids will be used in this research. The samples to be used were collected during previous phases of the research program. We have two grab samples of coal slurry solids from each of two coal slurry impoundments. These samples have been designated CSS-1, CSS-1a, CSS-2, and CSS-2a. Samples CSS-1 and CSS-2 were collected in September 1991; samples CSS-1a and CSS-2a were collected in September 1993. Samples CSS-1 and CSS-1a originated from the Illinois No. 6 coal seam, and CSS-2 and CSS-2a from the Illinois No. 5 coal seam.

The CSS samples will be washed with warm, dilute hydrochloric acid to remove calcium carbonate and sulfate. The acid washing will be followed by water washing, and finally by washing with acetone. The acid-washed and dried samples will be stored under nitrogen in a desiccator, to prevent further oxidation before the experimental work is begun.
In the first task, each of the four CSS samples will be exposed to a regular, predetermined sequence of wet-dry cycling. During each wetting period, the pH of the solution phase will be maintained at a pH of $7.8 \pm 0.2$ by titrating dilute NaOH or HCl solution from automatic titrators into the reaction vessel. At the end of the wetting period the sample will be filtered and allowed to air dry for a predetermined amount of time. Each wet-dry cycling period will last up to two months. Two samples will be allowed to oxidize at a time. While one sample is in its drying period, the other sample will be in its wetting period, thereby making full use of the titrators.

In the second task, one sample from each of the two coal slurry impoundments will be selected for wet-dry cycling of random period lengths. A random number table will be used to choose the lengths of the wetting and drying periods of between 0 and 10 days. This will allow us to determine whether the pyrite oxidation rate determined in the previous task is independent of the regular wet-dry cycling periods.

In both tasks, the concentration of sulfate in the separated solution will be taken as an indicator of the degree of pyrite oxidation. Because of the relatively short lifetime of sulfoxy intermediates, such as di- or tetrathionate, and the relatively long duration of the wet and dry cycling steps in these experiments, we do not expect sulfoxy intermediates to interfere with the determination of the pyrite oxidation rate. However, as a check, initial extracts will be analyzed for sulfate before and after treatment with hydrogen peroxide solution. The hydrogen peroxide will oxidize sulfoxy intermediates to sulfate. According to the following overall chemical equation for pyrite oxidation, two moles of sulfate are generated for each mole of pyrite oxidized:

$$\text{FeS}_2 + \frac{15}{4} \text{O}_2 + \frac{7}{2} \text{H}_2\text{O} + \text{Fe (OH)}_3 \rightarrow 2\text{SO}_4^{2-} + 4\text{H}^+$$

The acid generated during the drying step will be neutralized by addition of NaOH solution during the wetting step.

**RESULTS AND DISCUSSION**

Two Mettler Model DL-21 general purpose titrators were purchased. In addition, two bidirectional data output boards were purchased and installed in the titrators. A 286 personal computer was interfaced with the titrators. We are currently learning how to program the titrators through the computer for automatic, unattended operation.

The next steps will be to prepare and standardize the HCl and NaOH solutions, prepare the CSS samples, and begin the experiments.
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REFERENCES


