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TECHNICAL REPORT
September 1 through November 30, 1991

Project Title: The use of FBC wastes in the reclamation of coal slurry solids

DE-FG22-91PC91334

Principal Investigator: Gary B. Dreher, ISGS
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John D. Steele, ISGS
Project Monitor: Dan Banerjee, CRSC

## ABSTRACT

Fluidized bed combustion (FBC) is a relatively new technology that is used commercially for the combustion of coal. In Illinois, this technology is valuable because it allows the combustion of Illinois high sulfur coal without pollution of the atmosphere with vast quantities of sulfur oxides. In FBC, coal is mixed with limestone or dolomite either before injection into the combustion chamber or in the combustion chamber. As the coal burns, sulfur in the coal is oxidized to $SO_2$ and this is trapped by reaction with the limestone or dolomite to form gypsum ($CaSO_4 \cdot 2H_2O$). Solid by-products from FBC are generally a mixture of calcium oxide, gypsum, coal ash, and unburned coal. The present research project is designed to provide initial data on one possible use of FBC waste. FBC wastes from five different locations in Illinois are mixed with coal slurry solids from two different coal preparation plants at Illinois coal mines. In mixtures of FBC waste and coal slurry solids, the alkaline components of the FBC waste are expected to react with acid produced by the oxidation of pyrite in the coal slurry solid. An objective of this research is to determine the chemical composition of aqueous leachates from mixtures of FBC wastes, generated under various operating conditions, and the coal slurry solids. These data will be used in future research into the ability of such mixtures to support seed germination and plant growth. The ultimate of this and future research is to determine whether mixed FBC waste and coal slurry solids can be slurry pond reclamation.

Five FBC waste samples and two coal slurry solid samples have been donated to this research project by various FBC operators and coal mining companies in Illinois. One slurry solid is from the Illinois No. 5 coal seam and the other is from Illinois No. 6 coal seam. The slurry solids were air dried then the FBC wastes and the coal slurry solids were divided into representative subsamples of appropriate sizes by use of a riffle sampler. The subsamples will be used for chemical and mineralogical characterization and in laboratory leaching and outdoor weathering experiments. An analytical chemical method for estimating the amount of pyrite in the coal slurry solids was implemented.

## DISCLAIMER



This project is funded by the U. S. Department of Energy (METC) and by the Illinois Department of Energy and Natural Resources as part of their cost-shared program.

## EXECUTIVE SUMMARY

The overall objective of this proposed research project is to develop an environmentally acceptable method for disposing of coal fluidized bed combustion (FBC) waste. One method of disposing of FBC wastes might be to mix it with coal slurry solid from a coal preparation plant. In this disposal method, the alkaline components of the FBC waste are expected to buffer the acid generated by the coal slurry solid as its contained pyrite is oxidized. This objective will not be met in one year of research, because it will require both greenhouse and field studies in addition to the current laboratory research.

The present goals are to:

(1) determine how well wastes from five different FBC operations in Illinois buffer the acidity generated by two different coal slurry solids; and

(2) determine the nature and chemical composition of leachate passing through mixtures of FBC waste and coal slurry solid.

The present method of disposal of FBC wastes is, principally, to return the FBC waste to the mine from which the coal was purchased for disposal on the mine property. Disposal is either by landfilling in the backfill of a surface mine, or by dumping in mined out rooms in a underground mine.

The objectives of the present research project are being met by conducting laboratory experiments in which FBC wastes from five different FBC operations in Illinois are mixed in proportions necessary to satisfy the lime requirements of two different coal slurry solids from Illinois coal mines. Water is added weekly for six months to the mixtures in fixed amounts. Leachate is collected from each mixture and analyzed for chemical composition.

A second set of experiments will test mixtures of FBC waste and coal slurry solids by outdoor weathering. The mixtures will be exposed to outdoor conditions for the six month period from January through June, 1992. Any leachate collected from the mixtures will be analyzed for chemical composition.

At the beginning and end of both the laboratory and outdoor weathering experiments, the solids will be analyzed for chemical and mineralogical composition.

To date, grab samples of the FBC wastes and the coal slurry solids have been collected, and split into appropriately sized subsamples that are representative of the collected sample. The coal slurry solids were air-dried prior to splitting. The FBC wastes were passed through a No. 6 (3.36 mm) to remove large particles that otherwise could have unduly biased the experiments.

The pyrite contents of the two coal slurry solids are being estimated according to the hydrogen peroxide estimation method of Finkelman and Giffen (1986).

During the second quarter chemical and mineralogical characterization will be continued, limestone for control experiments will be purchased, and both laboratory and outdoor weathering experiments will be begun.

REFERENCE

Finkelman, R. B. and D. E. Giffen, 1986, Hydrogen peroxide oxidation: An improved method for rapidly assessing acid-generating potential of sediments and sedimentary rocks, Reclamation and Revegetation Research, vol. 5, pp. 521-534.

## OBJECTIVES

The overall objective of this proposed research project is to develop an environmentally acceptable method for disposing of coal fluidized bed combustion (FBC) waste. The disposal method under study is to mix FBC waste with coal preparation plant slurry solids in order to prepare a medium suitable for growing plants after the closure of a slurry pond. The overall objective will not be met in one year of research. It will require a laboratory study to characterize the materials, then a greenhouse study conducted under the guidance of a soil ecologist, followed by an agronomic field study at a coal preparation plant.

The scope of the present project is to determine (1) the efficacy of FBC waste in buffering the acidity generated by the oxidation of pyritic coal slurry solids, and (2) the nature and chemical composition of effluent passing through mixtures of FBC waste and coal slurry solids. Another objective is to provide information on the potential leaching of groundwater contaminants, and on the chemical composition of the "soil" solution which, in turn, may determine the types of plants used for reclamation in future studies.

## INTRODUCTION AND BACKGROUND

In the fluidized bed combustion of high-sulfur coal, powdered limestone is injected into the fluidized bed to serve as a trap for sulfur dioxide emitted from the coal as a result of combustion. When the sulfur dioxide reacts with the calcium carbonate of the limestone, it forms gypsum. Typically, the limestone is not completely converted to gypsum in the process, so much of the waste material may consist of calcium oxide. However, the waste will also contain mineral matter residue from the combusted coal, and possibly some uncombusted coal.

Presently, most of the fluidized bed combustion wastes from central Illinois are returned to the mine that supplied the coal, presumably for disposal in the backfill, in the case of a surface mine, or in abandoned rooms, in the case of an underground mine. This research project is a laboratory study of the suitability of the fluidized bed combustion waste as a neutralizing or buffering agent in the reclamation of coal slurry solids.

Coal slurry solids arise in the removal of pyrite and rock fragments in the process of cleaning the coal. Fine, pyritic, coaly particles and clay-rich particles are removed from the coal and are discharged in a water stream to a slurry pond. The water is drained from the slurry and it is

recycled. Eventually, the slurry pond reaches its solids-holding capacity and its use has to be discontinued. At this point, the mine operator must reclaim the remains of the pond in some manner.

A possible means of reclamation is to buffer the coal slurry solids with alkaline fluidized bed combustion wastes and grow plants on it to provide some stability against erosion. The major concerns in this application are the leachability of trace inorganic species from the waste into groundwater and the ability of the fluidized bed combustion waste to buffer the potential acidity produced by the oxidation of pyrite in the coal slurry solids. These aspects will be addressed by means of appropriate aqueous extractions of mixtures of five fluidized bed combustion wastes with two coal slurry solids.

## EXPERIMENTAL PROCEDURES

In any proposed waste disposal method, the effect of that waste on the immediate environment should be known. In co-disposing FBC waste with coal slurry solids, the principal environmental effects will be those caused by aqueous leachates from the waste products. As atmospheric precipitation falls on such a waste deposit, snow melt or rain water will either infiltrate the material or run off. The components of the leachate or runoff will affect groundwater, surface water, plants, or animals. The first step in determining the effects of aqueous leachate is to determine its composition, which will probably change with time as chemical reactions within the waste deposit occur.

This research project is designed to characterize the original wastes, the aqueous leachates from laboratory leaching and outdoor weathering experiments, using mixtures of FBC waste and coal slurry solids, and changes in the mixed wastes as a result of leaching and weathering.

The coal slurry solid contains pyrite, which upon oxidation, produces acid. The FBC waste is high in unreacted calcium oxide from the calcination, during the combustion process, of calcium carbonate (limestone). It is expected that in mixtures of the two materials the acid produced by pyrite oxidation will be buffered by the alkaline components of the FBC waste.

In this research program the pyrite content and the exchangeable acidity of the coal slurry solids and the calcium carbonate equivalent, of the FBC wastes are determined. When these quantities are known, the amounts of each waste to mix together to maintain a pH of 6.0 to 6.5 are calculated. Appropriate portions of the coal slurry

solid and FBC waste are then mixed together for use in laboratory leaching experiments. The mixtures are transferred to plastic containers. Deionized water is added weekly to each mixture. Leachate from each container is collected and analyzed by inductively coupled plasma emission spectrometry (ICP), flame and graphite furnace atomic absorption spectrometry (FAAS and GFAAS), ion chromatography (IC), and carbon dioxide specific ion electrode.

A similar set of experiments is conducted outdoors to determine the effects of outdoor weathering over the six month period from January through June.

## RESULTS AND DISCUSSION

FBC wastes were collected at five FBC plants in Illinois and coal slurry solids samples were collected at two coal preparation plants in Illinois. One coal slurry solid originated from the Illinois No. 5 coal seam, the other originated from the Illinois No. 6 coal seam.

The operating parameters of the five FBC plants are listed in Table 1. We were unable to obtain much information from the supplier of FBC-1. Information about the two coal slurry ponds are listed in Table 2.

Wastes from two of the FBC plants (FBC-1 and FBC-2) were collected as separate fly ash and bottom ash fractions. Samples for our use have been mixed in our laboratory in the proportion 25% bottom ash and 75% fly ash, according to the operator's estimate of the theoretical ash production from the plant. The other three wastes were collected as composited grab samples of fly ash and bottom ash, directly from the outflow of the respective ash silo. We were unable to collect statistically representative samples of any entire ash silo. All samples were collected in plastic pails. The pails were capped immediately after collection. The amount of each FBC waste collected is shown in Table 1.

Each FBC waste was passed through a No. 6 (3.36 mm) sieve to remove large particles of shale, unburned coal and limestone that might bias experimental results. The weight percent of each FBC waste that was greater than 3.36 mm is shown in Table 1. The FBC wastes were split into appropriate masses by means of a riffle sampler.

A grab sample of each coal slurry solid was collected from a "dry" location at each of two coal slurry ponds. Approximately 250 pounds of coal slurry solid was shoveled into five five-gallon plastic pails and the pails were tightly capped. The coal slurry solid was spread onto

polyethylene film in a laboratory for about two weeks to air dry. The material was mixed by hand during the period to hasten drying. The air-dry coal slurry solid was split to appropriate masses using a riffle sampler. The air-dry percent moisture and bulk density of each coal slurry solid are shown in Table 2.

Apparatus for the outdoor weathering experiments was designed. Leaching columns will be constructed from 9-inch inside diameter Schedule 40 PVC pipe and gasketed pipe caps. A pipe-threaded tubing adapter will be fitted through the center of each pipe cap to serve as a drain for leachate. Mixtures of coal slurry solid and FBC waste will be placed in each column, and leachate from rainfall or snowmelt will be collected in linear polyethylene bottles. Leachate will be analyzed by ICP, FAAS, GFAAS, IC, and $CO_2$ electrode. Seven columns will be placed in each of two wooden cabinets constructed for this project. Each leaching column and each cabinet top will be covered with 1.18 mm nylon mesh to keep leaves, insects, and other debris out, but to allow rainfall and snowmelt to contact the waste mixtures.

The pyrite content of the two coal slurry solids are being estimated by the hydrogen peroxide ($H_2O_2$) estimation procedure of Finkelman and Giffen (1986) and ion chromatography. In the hydrogen peroxide method, 15% $H_2O_2$ solution is added to a sample containing pyrite. The $H_2O_2$ oxidized the pyrite to produce acid. The pH of the solution is monitored during the reaction, and the rate of change of pH is indicative of the pyrite content of the solid. A family of curves of pH versus time was generated using various weights of 99.9% $FeS_2$ (m.p. 1171°C).

## FUTURE WORK

During the second quarter, further characterization of the coal slurry solids will be done, and characterization of the FBC wastes will begin (Task 2). Commercial agricultural limestone will be purchased and sized to be used as controls in leaching experiments (Task 2). Both laboratory leaching and outdoor weathering experiments will be started and leachates from both types of experiments will be analyzed (Tasks 3 and 4).

## PROJECT QUALITY ASSURANCE PLAN

The enclosed project quality assurance plan was written in fulfillment of Task 1.

## REFERENCE

Finkelman, R. B. and D. E. Giffen, 1986, Hydrogen peroxide oxidation: An improved method for rapidly assessing acid-generating potential of sediments and sedimentary rocks, Reclamation and Revegetation Research, vol. 5, pp. 521-534.

TABLE 1
Operating characteristics of fluidized bed combustion plants

| Operating Characteristics | FBC-1 | FBC-2 | FBC-3 | FBC-4 | FBC-5 |
|---|---|---|---|---|---|
| Type FBC | circulating (5 units) | circulating | forced air | AFBC | circulating (2 units) |
| Coal | Ill. No. 6? | Ill. No. 5 | Ill. No. 5 | Ill. No. 5 | Ill. No. 5 |
| Sorbent | Limestone | Limestone | Limestone | Limestone | Limestone |
| Particle Size | | | | | |
| Coal | | 0.5"x0 | 0.25-1.25" | 0.5-1" | <2 mm |
| Sorbent | | -30 mesh | | 8x20 mesh | <2 mm |
| Sorbent/Coal Ratio | | 2.4-2.7 | 1.4 | 2.5 | 4 |
| Feed Rate | | | | | |
| Coal | 590 T/d per unit | 1.8 T/hr | | 4.5 T/hr | 10 T/hr |
| Sorbent | | 14 T/hr | | 1.8 T/hr | 6-6.5 T/hr |
| Combustion Temperature (°F) | | 1550-1650 | 1500-1700 | 1510-1530 | 1700 |
| Operating Pressure (psig) | | 400 | 50 | 685 | 1300-1400 |
| Air Input (lbs/hr) | | 1°:88,000<br>2°:55,000 | | 85,000-86,000 | 350,000-400,000 |
| % $O_2$ in Stack Gas | | 3.75-6.5 | | 3.5-4.5 | 4 |
| Size of FBC | 425,000 lbs steam per hr per unit<br>24.6 MW | 125,000 lbs steam per hr | | 120,000 lbs steam/hr<br>3500kW | 30 MW per unit |
| Manufacturer/Model of FBC | | Alstrom/ Pyro Power | Stone-Johnson/ Fluid Fire | Foster-Wheeler | Riley Stoker |
| Ash Collection Points | | •baghouse<br>•bottom ash<br>•economizer<br>•boiler banks | •baghouse<br>•bottom ash | •baghouse<br>•economizer<br>•surge hopper<br>•multiclones<br>•superheater hoppers | •baghouse<br>•air heater hoppers<br>•ash coolers |
| Total Daily Ash Amount | 700-800 T<br>(75% fly ash, 25% bottom ash) | 70 T flyash<br>50 T bottom ash | | 82 T | 435 T |
| Current Ash Disposal Method | back to coal mine | back to coal mine | local ash heap | back to coal mine | back to coal mine |

TABLE 1
Operating characteristics of fluidized bed combustion plants

| | | | | | |
|---|---|---|---|---|---|
| Amount Collected (kg) | flyash: 13.4<br>bottom ash: 30.2 | flyash: 16.3<br>bottom ash: 26.3 | 19.7 | 14.5 | 13.8 |
| % ≥3.36 mm | 0.86 | 5.0 | 6.7 | 1.5 | 0.07 |

TABLE 2
Characteristics of coal slurry ponds

| Slurry Pond Characteristic | Coal Mine Preparation Plant | |
|---|---|---|
| | CSS-A | CSS-B |
| Coal Seam | Ill. No. 6 | Ill. No. 5 |
| Slurry Pond Volume(MM $yd^3$) | 23 | 8-9 |
| Remaining Useful Life of Pond (yrs) | 8-9 | 10 |
| Reclamation Plan | soil cover, revegetation | thin soil cover, revegetation |
| % of Coal Stream Represented by Slurry Stream | 20-30 | |
| % Moisture, as received | | 15 |
| Dry Bulk Density ($g/cm^3$) | 0.83 | 1.45 |

# PROJECT MANAGEMENT REPORT
September 1 through November 30, 1991

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## COMMENTS

Ms. Lettie Schmitt was hired as a part-time hourly employee effective September 4, 1991 through August 31, 1992 to work on this research project.

We unexpectedly had to collect a second coal slurry sample because there was insufficient quantity in our sample library of one we intended to use. This has caused a delay in sample preparation and characterization, and set-up of laboratory leaching experiments (Milestones C, D, and E). Other Milestones are on schedule.

This project is funded by the U. S. Department of Energy (METC) and by the Illinois Department of Energy and Natural Resources as part of their cost-shared program.

# END

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