DOE/PC/88910--T1

DE89 014503

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Received by OSTI

JUN 19 1989

JUL 03 1989

Quarterly Technical Report to the U.S. Department of Energy

Project DE-FG22-88PC88910
Detoxification and Generation of Useful Products from Coal Combustion Wastes

During September we arranged for shipping of samples of high sulfur, Eastern coal waste products from Ohio Edison. Six buckets of dry flyash, seven buckets of wet bottom ash, and eight buckets of desulfurization gypsum slurry were provided from one of their power plants. We also contacted Mr. Walter Dees with Arkansas Power and Light and made arrangements to obtain dry flyash and dry bottom ash from their White Bluff Power Plant.

The samples from Ohio Edison arrived by Greyhound Freight on 10-3-88 and were held by Greyhound until 10-12-88 because of a mix-up in payment of shipping costs. Since that time the samples have been stored outside at the Arkansas Mining Institute where cool weather has kept down bacterial growth.

The desulfurization gypsum slurry was decanted and the settled solids scooped out of the bucket and placed in an oven where they were dried at approximately 60°C for 48 hours. This resulted in a porous, blocky material which could be ground very rapidly in a pulverizer. The resulting lightweight powder had +95 percent passing a 100 mesh screen. The bottom ash was also dried at less than 60°C, crushed to -2 mm, and then passed through a pulverizer and reduced to +80 percent passing a 100 mesh screen. The flyash was already -100 mesh and no further

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crushing or grinding was performed on it. After drying and pulverizing, the samples were stored in buckets until they were ready for mixing with the hardening agents.

Mineralogical Examination of the Flyash, Bottom Ash, and Desulfurization Gypsum:

Because of delays in obtaining the upgrade to our x-ray diffractometer, no x-ray diffractometer scans of the material were performed during this quarterly period. However, samples of flyash, bottom ash, and desulfurization gypsum were x-rayed using 114.6 mm powder diffraction camera to determine any crystalline phases present in the samples. The flyash and bottom ash consisted almost entirely of amorphous material as evidenced by a broad background halo in the low angle 2Θ region. No readily determinable crystalline phases were found to be present in either ash. The desulfurization gypsum consisted almost totally of calcium sulfite dihydrate with only minor amounts of calcium sulfate dihydrate (gypsum). When the x-ray unit is fully upgraded to a diffractometer, further studies of the mineralogical characteristics of the flyash, bottom ash, desulfurization gypsum and hardening-test reaction products will be carried out.

Chemical Analysis of the Flyash, Bottom Ash, and Desulfurization Gypsum:

During this quarter of the project several hundred hours were spent effecting repairs to the x-ray fluorescence generator and water supply. Once the generator was fully operational, the existing x-ray fluorescence tubes (1 each, chromium, tungsten, molybdenum) were examined for operability and all were found to be gassy. None of the tubes on hand could be reconditioned or made operational. This has caused us to have to order a new x-ray fluorescence tube which had not arrived in time to carry out bulk chemical analyses on pressed pellets of the flyash, bottom ash, and desulfurization gypsum and on the subsequent reaction products. These bulk analyses will be carried out as soon as the new tube can be received and the equipment aligned.

Use of the Ion Chromatograph to Examine Leachates from Flyash, Bottom Ash, and Desulfurization Gypsum and from Hardened Reaction Products Leached with Acid/Alkaline and Neutral Aqueous Solutions:

Anion Analysis:

In order to achieve adequate separation of anion peaks with minimal interference, a sodium hydroxide/sodium benzoate eluant was selected for use with the ion chromatograph and anion cartridge. Sodium hydroxide at 5 mM and .1 mM sodium benzoate were prepared from stock .1 molar solutions by adding 50 ml sodium hydroxide stock and 1 ml sodium benzoate stock to 1 liter of distilled water, respectively.

After testing several extracts in the ion chromatograph with rather indifferent results, we determined that the anion column in use was the wrong one and consisted of a silica-based quaternary ammonium rather than a resin-based column that was supposed to be installed. Unfortunately, two days of testing using the alkaline eluant destroyed this column. We attempted to regenerate the column using potassium hydrogen pthalate 5 mM solution; but the column was too far gone. We have ordered a replacement silica column and the proper resin-based column for subsequent testing.

Cation Analysis:

The transition metal cations were determined using 1.5 mM ethylene diammonium and 2 mM tartaric acid eluant and a resin-based cation cartridge. The cations were detected using a post column colorimetric detector with .2 mM PAR in a 3 M ammonium hydroxide, 1 M acetic acid solution. Detection was at 530 nanometers.

Results were excellent using this technique; however, sensitivity problems were encountered using PAR. The lack of sensitivity for Pb, Cd, and Ni can be corrected by using a modified PAR-Zn EDTA reagent. Better separation of eluted peaks can also be achieved by switching to a reverse phase column. Initial results of cation analysis are illustrated in fig. 1 and 2.

Hardening Tests:

An initial set of 120 tests of hardening agents using mixtures of lime, lime plus calcium chloride, lime plus aluminium sulfate, lime plus aluminum sulfate plus sodium silicate in combination with flyash, bottom ash, and desulfurization gypsum, and mixtures of flyash, bottom ash and desulfurization gypsum were carried out. Tests of water slurries of desulfurization gypsum, flyash, and bottom ash indicated the following pH:

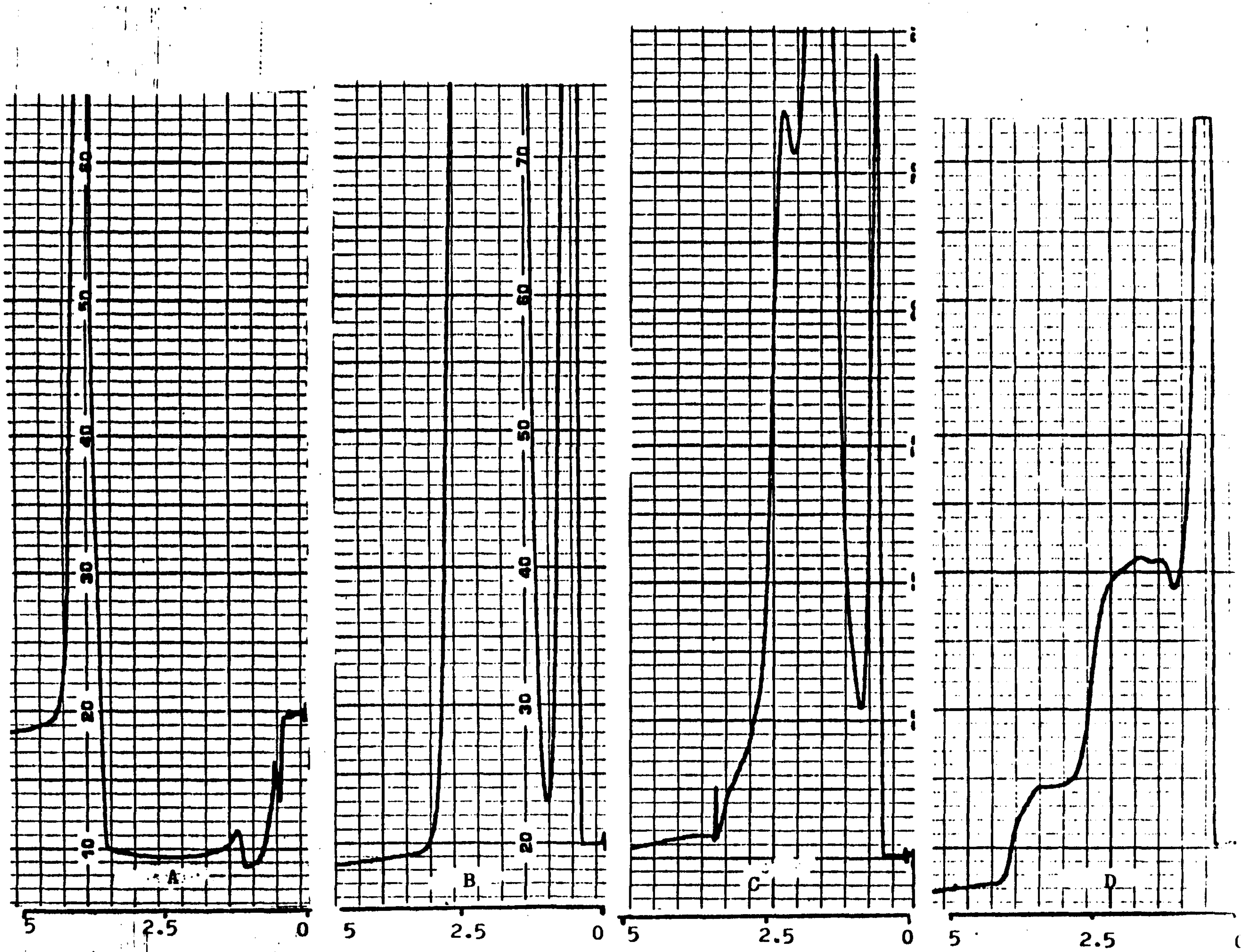

Fig. 1 Ion chromatographic analysis of extractable cations from fly ash, bottom ash, and DSG sludge. 1.5 mM EDA + 2 mM tartrate eluant with PAR postcolumn detection. Wescan resin column (269004). Eluant flow rate 2ml/min. PAR flow rate 1.4 ml/min. (A) DSG sludge extracted with 1.0 N NaOH (Note matrix interferences) (B) Bottom ash extracted with 1.0 N HCL (C) Fly ash extracted with 1.0 N HCL (D) DSG sludge extracted with 1.0 N HCL. All peaks detected are >100 ppm Fe and Mn.

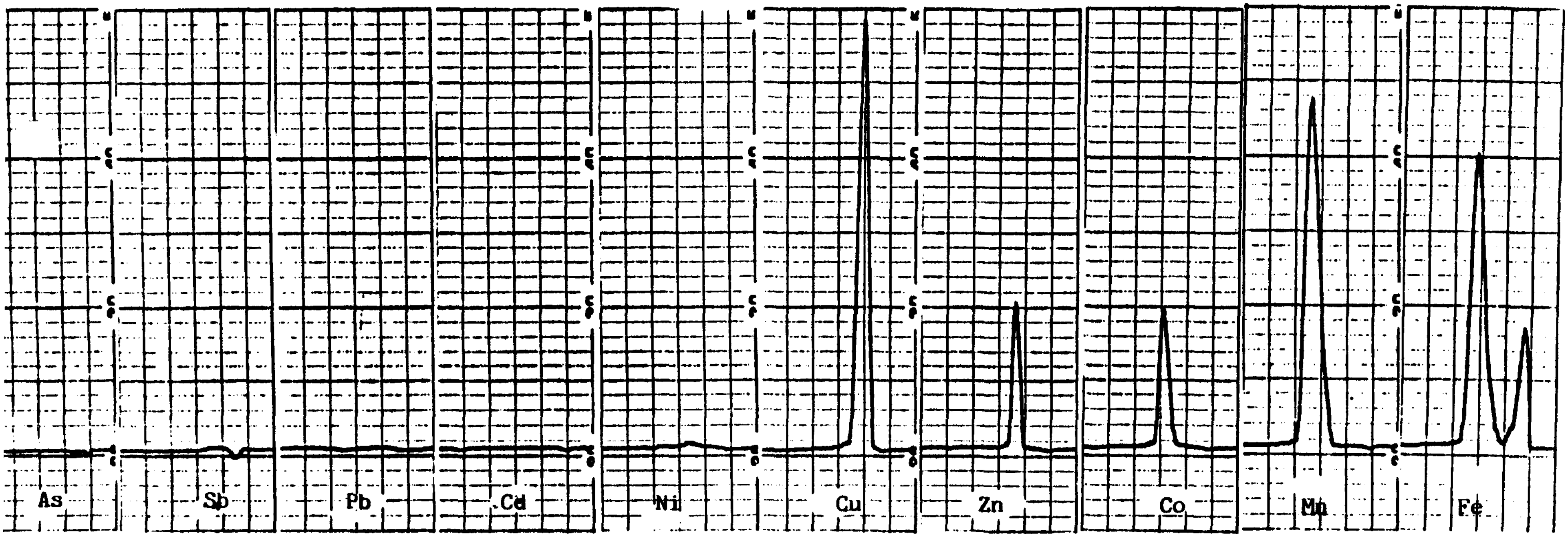

Fig. 2 10 ppm standards. Conditions same as in Fig. 1. Each chromatogram is 2.5 min. long. Lack of detectability of Pb, Cd, and Ni are evident. Resin based column give faster, but less precise separations.

DSG	8.80
Flyash	3.00
Bottom ash	7.58

The weights of flyash, desulfurization gypsum, and bottom ash and hardening agents used in the 120 tests are given in table 1.

The dry ground flyash, desulfurization gypsum, and bottom ash were mixed with the powered chemical reagents and placed in ziplock bags. They were thoroughly mixed by shaking the powdered components together. Between 50 and 100 ml of distilled water was then added to each bag until a plastic slurry was achieved. The amount of water added varied depending on the content of desulfurization gypsum, with less water being required for the somewhat coarser bottom ash and for the relatively non-absorbent flyash. The bags were then sealed and placed in boxes to harden at room temperature.

The results of the initial hardening tests were somewhat disappointing. After 24 hours, only the flyash and bottom ash and mixtures thereof had shown any significant hardening. Mixtures containing desulfurization gypsum remained in a plastic or semi-hardened state. At the end of one week, some additional hardening had taken place but the desulfurization gypsum continued to act as an inhibitor to the hardening process.

Results of the Initial Hardening Tests:

The initial hardening tests were somewhat disappointing in that the desulfurization gypsum tended to act as a hardening inhibitor rather than an accelerator. This problem was traced to a very low calcium sulfate content and very high calcium sulfite content of the material. The solubility of calcium

Table 1

Proportions of Fly Ash, Bottom Ash, and Desulfurization Gypsym (DSG) Sludge and Hardening Agents Used in Test of Ohio Edison Waste Products. Hardening Results: N = Nil (Plastic after 1 week), W = Weakly Hardened, M = Moderately Hardened, H = Hardened (Resists Crushing)

Power Plant By-Product Tested	Lime $Ca(OH)_2$			1 Part Lime/1 Part Calcium Chloride $Ca(OH)_2/CaCl_2$		
	1 g	5 g	10 g	1 g	5 g	10 g
100 g Fly Ash	N	W	W	N	W	M
100 g DSG Sludge	N	N	N	N	N	N
100 g Bottom Ash	N	M	W	N	W	M
50 g Fly Ash + 50 g DSG Sludge	N	N	N	N	N	N
20 g Fly Ash + 80 g DSG Sludge	N	N	N	N	N	N
50 g Fly Ash + 50 g Bottom Ash	N	N	N	N	N	N
50 g Bottom Ash + 50 g DSG Sludge	W	N	N	N	N	N
20 g Bottom Ash + 80 g DSG Sludge	N	N	N	N	N	N
33 g Fly Ash + 33 g Bottom Ash + 34 g DSG Sludge	N	N	N	N	N	N
14 g Fly Ash + 14 g Bottom Ash + 72 g DSG Sludge	N	N	N	N	N	N

Table 1 Continued

Power Plant By-Product Tested	5 Parts Lime/1 Part Aluminum Sulfate $5\ Ca(OH)_2/1Al_2(SO_4)_3$ 1 g	5 g	10 g	5 Parts Lime/1 Part Aluminum Sulfate/2 Parts Sodium Silicate $5\ Ca(OH)_2/1Al_2(SO_4)_3/2\ Na_2SiO_3 \cdot 5H_2O$ 1 g	5 g	10 g
100 g Fly Ash	N	N	W	N	H	H
100 g DSG Sludge	N	N	N	N	N	N
100 g Bottom Ash	N	N	W	W	M	H
50 g Fly Ash + 50 g DSG Sludge	N	N	N	N	N	N
20 g Fly Ash + 80 g DSG Sludge	N	N	N	W	M	H
50 g Fly Ash + 50 g Bottom Ash	N	W	W	N	N	N
50 g Bottom Ash + 50 g DSG Sludge	N	N	N	N	N	N
20 g Bottom Ash + 80 g DSG Sludge	N	N	N	N	N	N
33 g Fly Ash + 33 g Bottom Ash + 34 g DSG Sludge	N	N	N	N	N	W
14 g Fly Ash + 14 g Bottom Ash + 72 g DSG Sludge	N	N	N	N	N	W

sulfate is 0.209 grams per 100 cc of water whereas the solubility of calcium sulfite is only 0.0043 grams per 100 cc of water. This low solubility inhibits the conversion of the sulfite to sulfate in the reacting products and inhibits the growth of ettringite.

There are two possible solutions to this dilemma which will be tried in the next round of hardening tests. One is to add calcium sulfate dihydrate to the reaction mixtures so that the ettringite will be able to form rapidly during the initial hydration and will act as a cement to hold the calcium sulfite together until its delayed reaction can take place. A second and probably less desirable solution is to dehydrate the calcium sulfite to calcium sulfite hemihydrite (similar to plaster of paris) and add this to the reacting mixtures. The hydrating mixture would allow an early strength set to the material which, on being kept wet, would promote the formation of ettringite as the sulfite oxidizes to sulfate. Both of these techniques will be attempted during the next quarter's hardening tests.