DOE/MC/30251 -- 5029
(DE96000566)

High-Volume, High-Value Usage of Flue Gas Desulfurization (FGD) By-Products in Underground Mines
Phase 1 -- Laboratory Investigations

Quarterly Report
January - March 1995

June 1995

Work Performed Under Contract No.: DE-FC21-93MC30251

For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

By
Center for Applied Energy Research
Lexington, Kentucky 40511-8433

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, 175 Oak Ridge Turnpike, Oak Ridge, TN 37831; prices available at (615) 576-8401.

Available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, VA 22161; phone orders accepted at (703) 487-4650.

DOE/MC/30251 -- 5029

HIGH-VOLUME, HIGH-VALUE USAGE OF FLUE GAS DESULFURIZATION (FGD) BY-PRODUCTS IN UNDERGROUND MINES
PHASE 1 -- LABORATORY INVESTIGATIONS

DOE

DOE/MC/30251 -- 5029
(DE96000566)
Distribution Category UC-105

High-Volume, High-Value Usage of Flue Gas Desulfurization (FGD) By-Products in Underground Mines
Phase 1 -- Laboratory Investigations

Quarterly Report
January - March 1995

Work Performed Under Contract No.: DE-FC21-93MC30251

For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
P.O. Box 880
Morgantown, West Virginia 26507-0880

By
Center for Applied Energy Research
3572 Iron Works Pike
Lexington, Kentucky 40511-8433

June 1995

High Volume--High Value Usage of Flue Gas Desulfurization (FGD) By-Products in Underground Mines

Phase I: Laboratory Investigations

Cooperative Agreement No. DE-FC21-93MC30251

Quarterly Report for the Period January 1, 1995 to March 31, 1995

Summary of Progress for the Period January 1, 1995 to March 31, 1995

The study of the kenetics of the mineral transformations which take place after the FGD materials are hydrated was continued this quarter (Task 2, Subtask 2.2). Based on X-ray diffraction data, the anhydrite was found to have essentially disappeared by the fifth day of the study, while gypsum was found to maximize in the first 14 days of the study. The relative abundance of ettringite increased throughout the period of observation (40 days). Ettringite was found to nucleate primarily on or near fly ash particles, while gypsum was found to be more mobile, readily filling in cracks and fractures.

A second kinetic study was initiated during the period with an experimental setup which is similar to the current effort. The focus of this study will be to determine the effect of moisture conditions on the rate and types of mineralogical reactions which occur.

Column leaching studies (Task 2, Subtask 2.4) on the ADM material were initiated during the quarter. Two columns were packed with fly ash and one with bottom ash. One of the columns was blanketed with CO_2 (2.5%) to model the effects of soil gas on the leachate. The samples are being moisturized to model field conditions. Leachate analysis will be available during the next quarter.

Work on the field site (Task 6) to establish background data for the demonstration continued. The proposed demonstration site at the Pleasant Valley mine was found to be displaying the effects of severe weathering. An alternate mine site will be explored.

TASK 2 LABORATORY STUDIES

Subtask 2.2 Chemical and Mineralogical Characterization

Kinetics Study Investigating Hydration Reactions

Continuation of Previous Study The kinetic study that was initiated during the last reporting period (Oct. - Dec., 1994) was continued this quarter. During this reporting period, one sample was analyzed on Day 38 of the study, and comprised one of the pre-hydrated ADM CFBC cylinders (2.65 cm long by 2.6 cm i.d.) that have been curing since 2-5-95 in a temperature-controlled water bath at 25° C. The Day 38 sample was removed from the water bath and placed into a plastic bag (to minimize moisture loss) prior to x-ray diffraction sample preparation.

The XRD data indicate that anhydrite abundance remained more-or-less constant in the ADM by-product, with diffraction peaks that had decreased to nearly baseline intensity by Day 5 of the study (Figure 1). Similarly, the gypsum diffraction peak intensities were comparable to, if not less than, those from the 6 - 15 day analyses (Figure 2), supporting the earlier data which showed that the rate of gypsum formation reached a maximum by the 14th day. Portlandite abundance has remained relatively constant from Day 1 to Day 38 (Figure 3), whereas ettringite content continued its monotonic increase with time of curing (Figure 4).

The experimental results support earlier interpretations that gypsum formation occurs at different locations within the system. Hydration of anhydrite leads to the formation of primary gypsum which takes place when the anhydrite crystals recrystalize to gypsum via incorporation of water molecules into the crystal structure which is accompanied by a volume increase. This hydration reaction is not a solid state replacement, but a dissolution-reprecipitation reaction where the dissolving anhydrite crystals act as nucleation surfaces for the gypsum crystals. Secondary gypsum, on the other hand, may precipitate anywhere in the system wherever the concentration of Ca^{2+} and SO_4^{2+} ions is sufficient to exceed the gypsum solubility product. Additional Ca^{2+} ions may be supplied in the dissolution of $Ca(OH)_2$. The relatively constant amounts of $Ca(OH)_2$ in the

aging materials (Figure 3), however, suggest that anhydrite crystals are the primary source for gypsum in the ADM samples up to this point in time in the experiments.

The solubility of anhydrite ($CaSO_4$) at 25° C is $K_{sp} = 4.2 \times 10^{-5}$, while that of gypsum ($CaSO_4 \cdot 2H_2O$) is $K_{sp} = 2.5 \times 10^{-5}$. The equilibrium constant for the conversion of anhydrite to gypsum is:

$CaSO_4(s) = Ca^{2+} + SO_4^{2-}$	$\log K_{sp(anhy)} = -4.38$
$Ca^{2+} + SO_4^{2-} + 2H_2O = CaSO_4 \cdot 2H_2O$	$\log K_{sp(gyp)} = 4.60$
$CaSO_4(s) + 2H_2O = CaSO_4 \cdot 2H_2O$	$\log K = 0.22$

Anhydrite is relatively more soluble compared to gypsum. Nearly all of the anhydrite crystals dissolved in the experimental system by Day 5 (Figure 1), supersaturating the pore fluids with respect to gypsum. Preferentially gypsum formation occurs at interparticle contacts, which causes swell at these locations. Gypsum precipitation can occur in pores and cracks within the material and at external sites, e.g. on the surface of the water bath and the container walls. The variability in gypsum formation, therefore, makes it difficult to obtain consistent, representative samples on each sampling day, thus resulting in scattering of the gypsum diffraction intensity data (see Figure 2).

Conversely, the small degree of variability in the ettringite diffraction data suggests that the mineral is forming consistently *in-situ*, in proximity to the glassy fly ash surfaces. Thus, it is easier to acquire representative, more homogeneous samples with respect to ettringite abundance. Ettringite and gypsum crystals compete for available nutrients, Ca and SO_4. In the case of ettringite formation that occurs concurrently with that of gypsum formation, the rate-limiting step in the precipitation reaction is not the availability of sulfate ions, but rather the availability of aluminum ions. Aluminum ions are supplied by the dissolving fly ash spheres. However, the

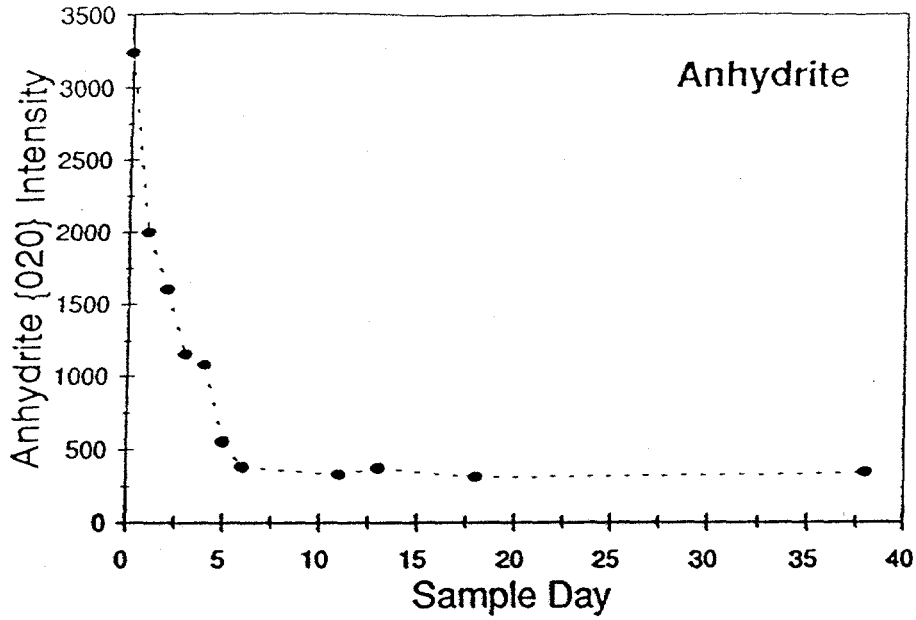


Figure 1. Anhydrite abundance as a function of curing time

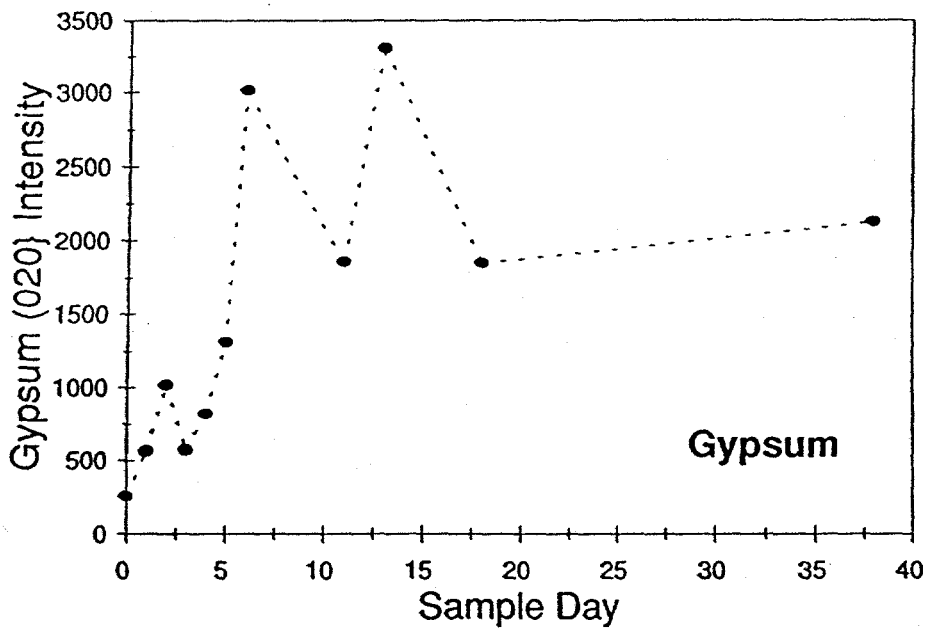


Figure 2. Gypsum abundance as a function of curing time

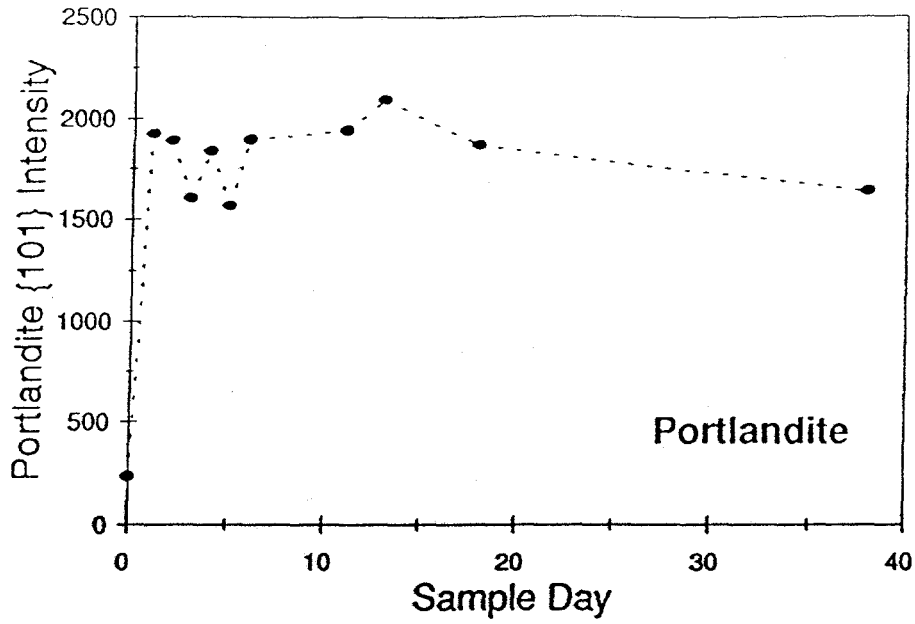


Figure 3. Portlandite abundance as a function of curing time

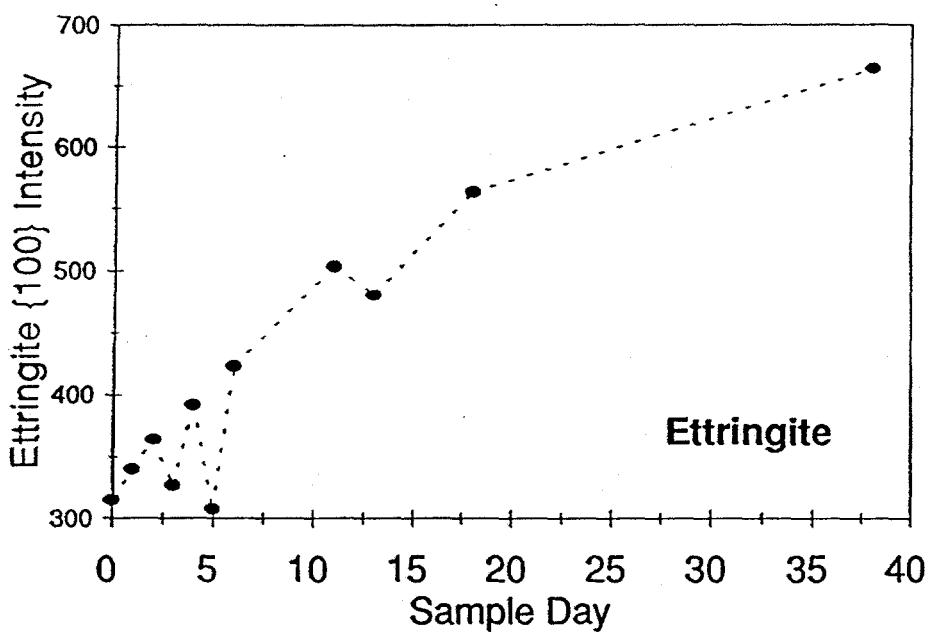


Figure 4. Ettringite abundance as a function of curing time

mobility of dissolved aluminum ions in the pH-buffered solutions (pH~12 due to $Ca(OH)_2$ buffer) is only small, suggesting that transport of the Al ions in pore solutions may control the location where ettringite needles will be able to form. Ideally, ettringite precipitates on, or in close proximity to, Al-rich surfaces. The dissolution of the glassy Si-Al spheres may be compared to the solubility of crystalline aluminum silicate phases, but probably occurs more briskly than that of the latter. Dissolution may occur incongruently due to the extremely high pH conditions of the system (Stumm and Morgan, 1981). The dominant aluminum hydrolysis species under high pH conditions is $Al(OH)_4^-$. The dissolution of the glassy spheres and that of some quartz crystals controls the upper limits of dissolved aqueous silica. Under the highly alkaline conditions the solubility of SiO_2 becomes enhanced because of the formation of monomeric and multimeric silicates. Lagerstrom (1959) and Ingri (1959) indicated that multinuclear species such as $Si_4O_2(OH)_6^{2-}$ are present in the solution phase, while under slightly alkaline conditions only the $Si(OH)_4$ species occur. Under local equilibrium, Al-Si-rich gels may precipitate from the solution phase, providing additional nucleation surfaces for ettringite crystals.

Because of the availability and mobility of dissolved silica, ettringite in this system is expected to substitute various amounts of Si in its crystal lattice. However, the XRD analyses in this study are not suitable to determine the degree of Si-substitution. This should be investigated in detail in a separate study, as the degree of Si-substitution may impact on the stability of the ettringite crystals.

The kinetic study was accompanied by a physical characterization of some of the materials to obtain free vertical swell (similar to ASTM. D 4546 Method B) and unconfined compressive strength (similar to STM D 2938). The free vertical swell was measured to characterize the swell potential of the materials in different curing environments and develop an approximate relation between the free vertical swell and unconfined compressive strength. The physical characteristics were described in detail in the previous report.

Initiation of New Study In order to both verify results of the kinetic study thus far, and to gain

better control of the experimental variables, a second kinetic study was initiated. In this study the sample preparation was similar to that for the previous study, but with different curing conditions. It is expected that changing concentration of dissolved species and fluctuations in solution pH govern the hydration reactions. The main objective of this new study, therefore, was to precisely control the solution:solid ratio, as it may influence the rates of reactions as well as the type of mineral formation. In the previous study, all samples were placed in a common water bath with a relatively high solution:solid ratio. Upon aging of the sample molds and extraction of individual molds from the water bath the solution:solid ratios continuously changed as did the equilibrium conditions. To better understand the aging processes that might occur in a mine emplacement situation with relatively constant free available moisture, the solution:solid ratios of the experiments were kept the same for all samples by preparing individual sample containers (jars). The by-product from the ADM CFBC plant was pre-hydrated with 12 percent (by weight) water, and cooled for approximately 1 hour until the temperature returned to ambient. The material (690 g) was then thoroughly mixed with 310 g of water (31% of total weight) and packed into 2.65 cm sections of 2.05 cm diameter pvc pipe. These small cylinders were placed individually into polypropylene jars, and 50 ml of distilled water was added to cover the samples. The jars were then sealed with screw-type plastic lids to prevent evaporation. X-ray diffraction and thermogravimetric analyses will be conducted on these samples every day for two weeks, followed by increasingly longer intervals for one year.

Prior to XRD and TGA analyses, the hydrated CFBC material plus pvc mold are first weighed, followed by extrusion of the solids from the mold and weighing of the pvc alone. These weights, along with the known added moisture, will facilitate the calculation of water:solid ratio for each sample. The pH of the water is then measured, followed by filtration and collection in a 50 ml glass vial, which is subsequently sealed with a foil-lined screw-type lid. The solid (approximately 15 - 16 grams) is then ground in a mortar and pestle, and returned to the polypropylene container.

X-Ray Diffraction (XRD) Approximately 2 grams of material is sampled from the container for x-ray diffraction analysis. As a semi-quantitative standard, 5 wt% TiO_2 is added prior to final

preparation. The ADM material plus standard are then thoroughly ground in an agate mortar and pestle. The diffraction analysis is obtained with a Philips APD 3500 x-ray diffractometer, using Cu-Kα radiation (λ = 1.5418 nm), a scan speed of two counts/second, an increment of 0.1°, over a 2θ range from 7 to 40°.

Thermogravimetric Analysis (TGA) Approximately 50 to 100 mg of material is obtained for the TGA analysis. The analyzer is a TA Instruments Hi-Res 2950 TGA interfaced with a P.C., and has been programmed to measure weight loss from 50° C to 900° C. Ettringite, gypsum, and portlandite dehydrate over this temperature range, and calcite decomposes to calcium oxide and CO_2.

As of this reporting period the experimental setup has been completed, as have the initial XRD and TGA analyses. Results from the first 3 months of this kinetic study will be presented in the next reporting period, April 1, 1995 to June 30, 1995.

Subtask 2.4 Laboratory Lysimeter Studies

Overview In an effort to evaluate the leaching characteristics of waste samples from the Archer Daniel Midland (ADM) utility boiler, three laboratory lysimeters were fabricated and packed with ADM wastes during this reporting period. Two of these columns were packed with samples of ADM fly ash and the third with a sample of bottom ash. One of the fly ash columns is blanketed with room air whereas the other with an atmosphere enriched in CO_2 (2.5 vol%). All three are packed to a height of 24" at a relatively low packing density in order to improve flow characteristics. Because of the manner in which the columns are packed, these tests are believed to represent a worst case scenario in terms of leachate production since the method used to pack the lysimeters intentionally provides a relatively high permeability. This high permeability results in higher percolation rates of water through the columns compared to the rates anticipated for comparable materials which will be placed in the mine at both higher density and thickness.

To serve as a basis of comparison, additional lysimeters were packed with FGD wastes from another midwestern utility; commercial and in-house waste pellets prepared from a blend of fly ash, FGD waste, and lime; and a locally marketed light-weight natural aggregate. Selected lysimeters from this group will also be blanketed with CO_2-enriched atmospheres. There are a total of 36 lysimeters included in this study.

During the twelve months following construction and packing, a fixed amount of distilled water (46.5 mL, the average weekly rainfall measured at a weather station in East Central Kentucky) will be added to the ADM columns on a weekly basis. The added water will make a single pass through the packed bed then collect in a reservoir at the bottom of the column from where it will be drained immediately prior to the next water addition.

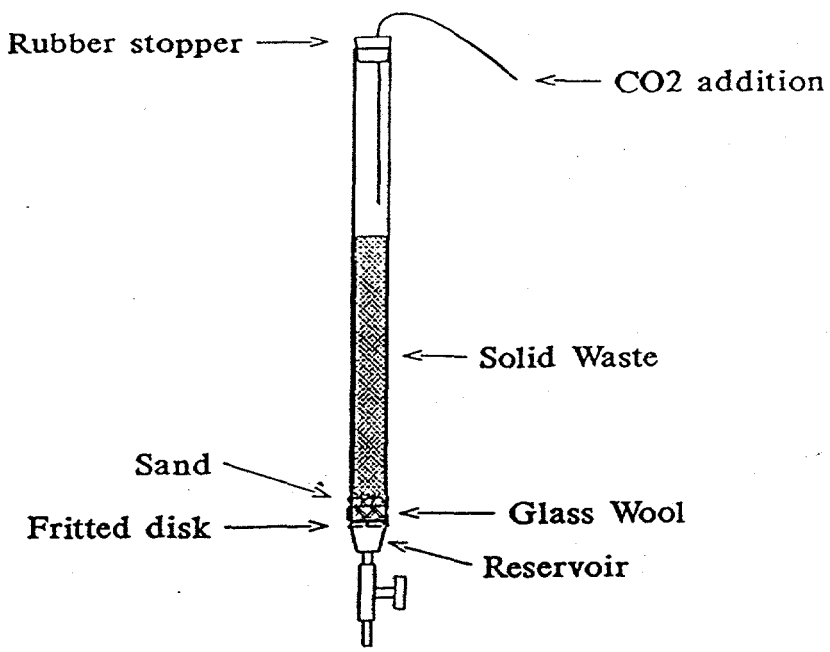


Figure 5. Schematic of a laboratory leaching column.

Lysimeter Description A schematic of the laboratory columns fabricated for this study is shown in Figure 5. The leaching columns are constructed from clear acrylic tubing that is 39" (1 m) in length, 2" inner diameter, and ~1/4" wall thickness. A plexiglass frit is sealed in the bottom of each column inside a PVC sleeve. The sleeve is in turn connected to a PVC reducing connector followed by a plastic valve. The plexiglas frit is overlain with a one-inch layer of glass wool followed by one inch of Ottawa sand to prevent blockage of the drain holes in the frit. The void volume of the

column from the valve to the top of the sand layer is approximately 100 mL. Thus, leachate waters pass through the column and collect in the void space at the bottom from where they will be drained and weighed once per week.

Packing Procedures Packing the laboratory lysimeters entailed weighing dry sample to a 2 L stainless steel mixing bowl to which was added a measured amount of distilled water for prehydration. Prehydration of the dry samples was necessitated by fact that the alternative, adding water to dry samples within the columns, can result in column melting or cracking due to the heat evolved during hydration and/or sample swelling, respectively. The sample and water were blended with a Kitchen-Aide™ mixer for approximately five minutes (or until the prehydrated sample had a homogeneous granular appearance). For the two ADM fly ash samples, a targeted weight of the prehydrated sample (2.138 lb) was transferred to a preassembled lysimeter. The column was then held vertically and tamped until a column height of 24" was attained. This provided a dry density of 49 lb/ft^3 which had been determined to be optimum for other FGD wastes included in the study.[4] The prehydrated bottom ash sample was transferred to the third lysimeter until a height of 24" was attained without compaction. This approach yielded a dry density of 71 lb/ft^3 for the bottom ash.

The three ADM columns were capped with rubber stoppers. For the bottom ash and one of the fly ash samples, this was a solid rubber stopper which served to suppress evaporation. The third sample was capped with a two-hole stopper with compressed gas containing 2.5 vol% CO_2 being delivered through one of the holes and exiting through the other at a rate of ~15 cm^3/min.

Leachate Analysis Analysis of the leachate waters will include pH, alkalinity, conductivity, anions (including but not limited to SO_4, SO_3, Cl, NO_3, and Br), and cations/metals (Ag, Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, Se, Si, Ti, V, and Zn). All analyses will be conducted as soon as practical following collection, particularly for alkalinity and anion concentration (same day). Portions of each water will be treated with acid on the day of collection to stabilize the sample prior to metals (cation) analysis. Time permitting, this latter

SAMPLE	Lysimeter #	Water Feed (mL/wk)	% CO2	Dry Wt (lb)	Prehydration Water (% dry basis)	Column height (in)	Dry Density (lb/cu ft)
ADM-fly ash	22	46.5	0	2.138	40.4	24.0	49.0
ADM-fly ash	23	46.5	2.5	2.138	40.4	24.0	49.0
ADM-bottom ash	24	46.5	0	3.136	22.1	24.0	71.9

Table 1. Test matrix for the lysimeters packed with ADM wastes.

analysis will also be conducted on the day of collection. It is anticipated that the column leaching studies will continue for a minimum of one year and as long thereafter as potentially useful data is being generated. At the conclusion of the leaching study, plugs of the leached solids will be removed from the laboratory lysimeters for XRD and SEM analysis.

The test matrix and packing parameters used for the ADM waste samples is shown in Table 1. The three lysimeters listed in Table 1 will often be referenced in this report as LC22, LC23, and LC24 which corresponds to the order shown, i.e., ADM Fly Ash, ADM Fly Ash blanketed with CO_2, and ADM Bottom Ash.

Results

Flow rates. Due mostly to the manner in which water has been added to the laboratory columns, little analytical data are available at this time. Unlike previous column leaching studies conducted at the CAER in which the columns were maintained under saturated conditions from the start, for this study, a predetermined amount of water is being added to each column each week. What this means is that *breakthrough* of the water does not occur for several weeks into the study. In

addition to the problem of not having leachate samples available for several weeks for analyses, the sheer volume of data that has since been generated from the 36 lysimeters being monitored has created a backlog of data awaiting reduction and computer entry. This is in spite of the fact that

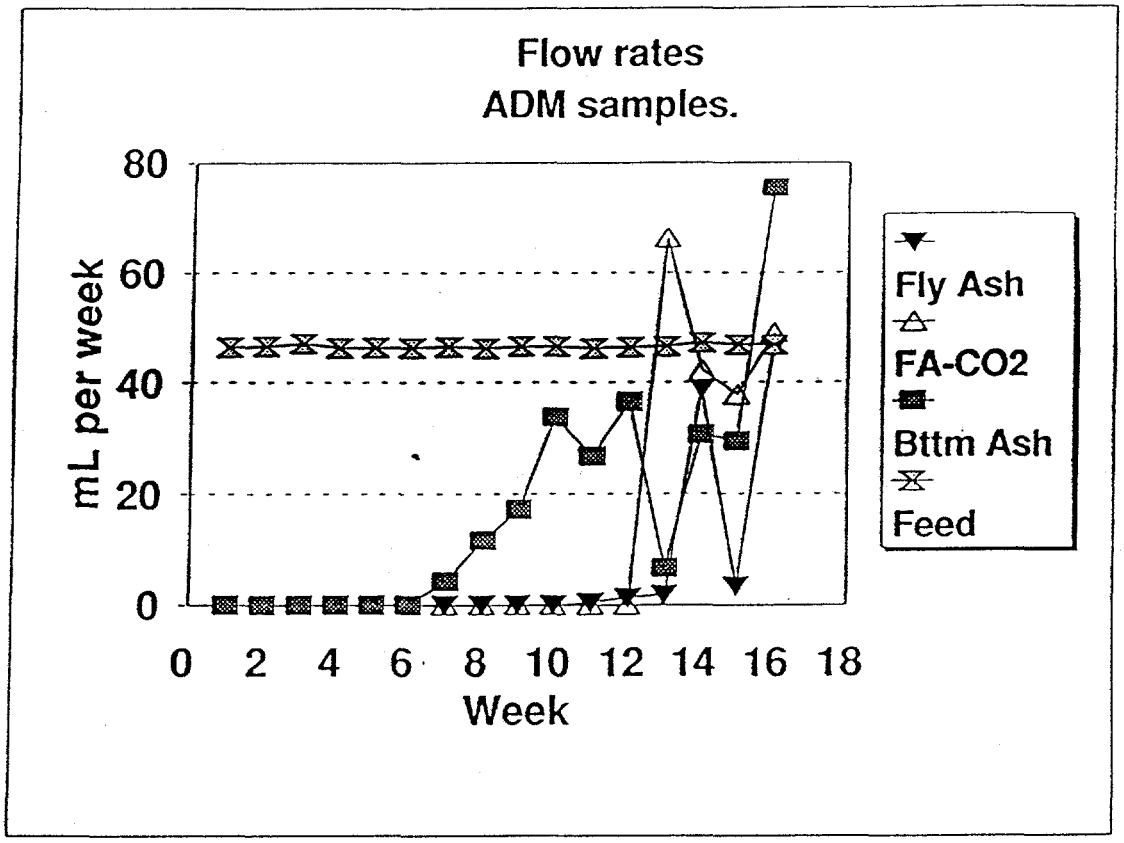


Figure 6. The rate of water addition and collection through the laboratory lysimeters packed with ADM wastes.

the analyses are being conducted within a reasonable period following collection (1-2 days) for those columns which have begun to flow.

Both feed rates and collection rates are shown for the three ADM columns in Figure 6. This plot shows the delay between the initiation of water feed and breakthrough of the leachate. The column packed with bottom ash (LC24) was the first to flow with the initial leachate collection

made during Week 7. LC23 containing ADM Fly Ash did not flow until Week 13 at which time a relatively large slug of water was collected. Water flow through each column is still rather erratic at this time. The significant point is that all three columns are now flowing. This has not always been the case in previous studies, particularly when the solid wastes were loaded at a higher compaction density. All three columns have exhibited adequate flow since about Week 14 for the full suite of analyses to be conducted. However, the anticipated decline in the concentration of various ions in the leachate over time may force the combination of two or more weeks collection later in the study in order to obtain sufficient sample for analysis.

pH. pH values for the column leachates are shown in Figure 7. All three leachates exhibit relatively high pH values at this time due most likely to the presence of free lime or $Ca(OH)_2$ in the ADM wastes. The pH of the bottom ash leachate is very high on an absolute basis but slightly lower than that of the fly ash leachates, due perhaps to more abundant NaOH and KOH in the fly ash wastes.

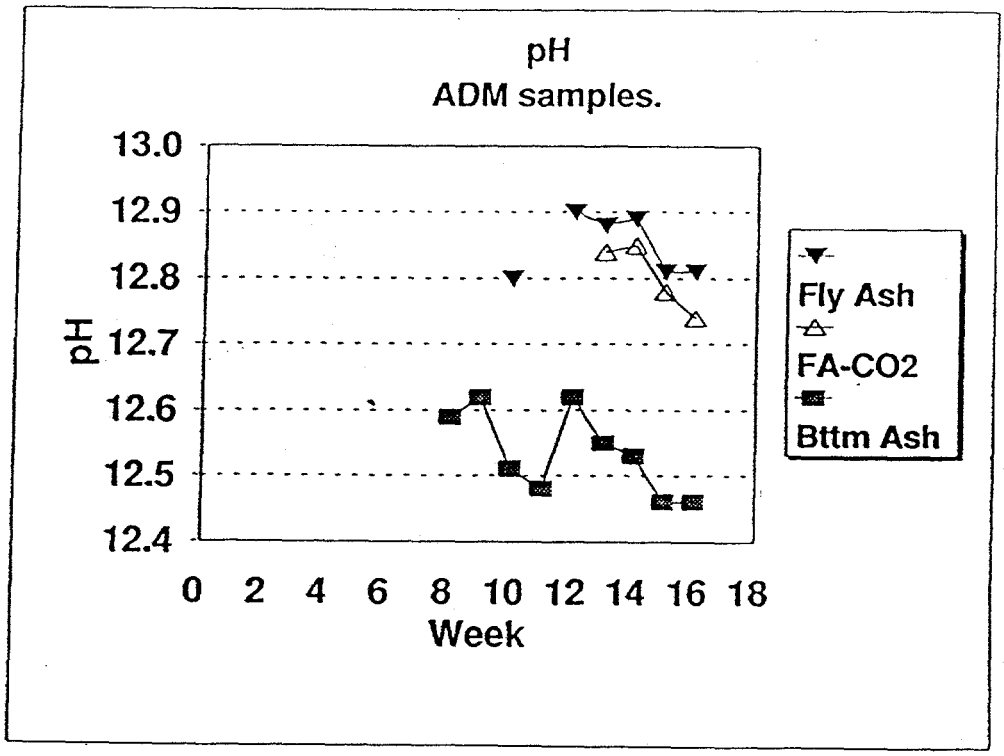
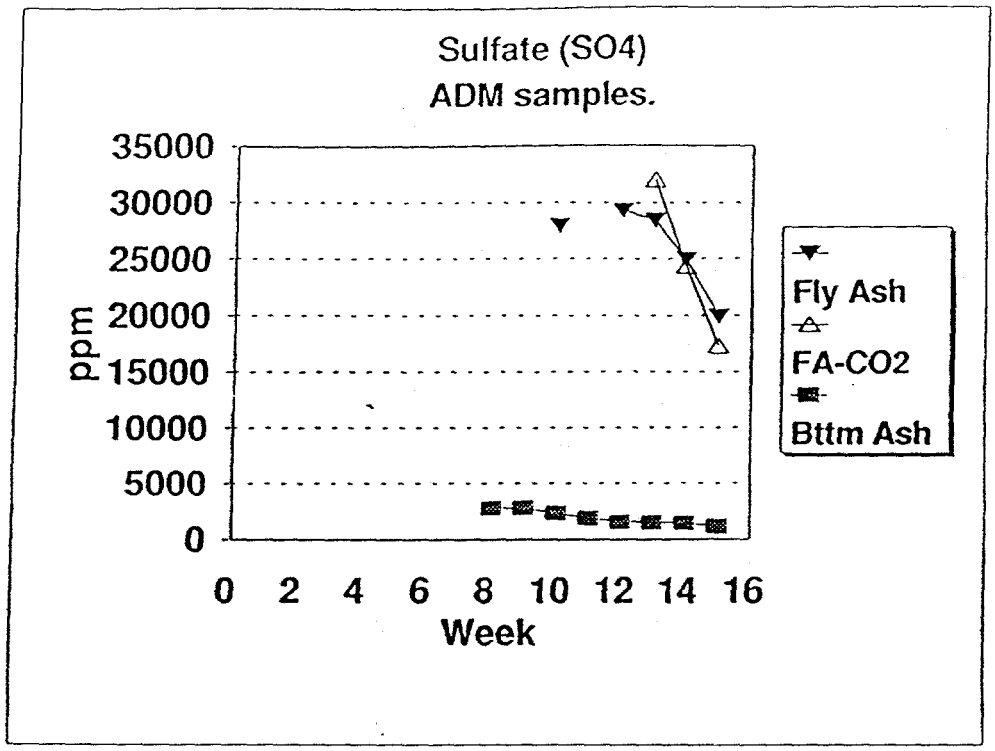


Figure 7. pH of the leachate from columns packed with ADM wastes.



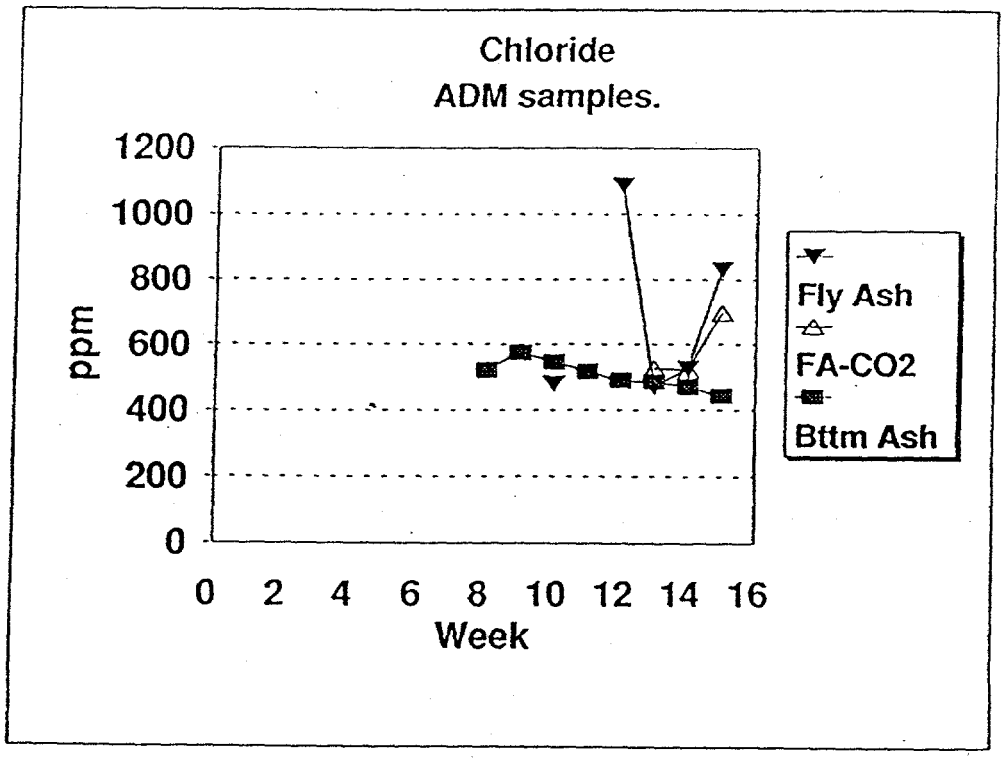


Figure 8. Major anions in the leachate from the ADM columns (Sulfate-top; Chloride-bottom).

Anions. The major anions detected in the leachate waters are shown in Figure 8. Sulfate concentrations are very high in the leachate from the columns packed with fly ash and substantially greater than in the bottom ash leachate. In contrast, chloride concentrations are reasonably similar in all three with the exception of what may be anomalous readings at Weeks 12 and 15 for the leachate from LC22 (Fly Ash).

Other Analyses Though numerous other analytical tests have been conducted to date (26 cations/metals, conductivity, alkalinity) too little of these data have been reduced and entered into the data base to make them appropriate for presentation at this time. These latter analyses will be given during the next reporting period.

Summary It is too early in this phase of the study to conduct an extensive evaluation of the leachate analyses. Certain trends in column behavior have emerged but only additional testing will verify if these are long-term trends or merely spikes in the data. It is believed that more reliable conclusions can be drawn about long-term behavior in the next quarterly report. It must again be noted that the most significant result to date is that all three columns are flowing. Thus, a major hurdle that has plagued previous studies has been successfully evaded by modifications made to the column-packing procedures.

TASK 4 BACKGROUND DEVELOPMENT FOR FIELD STUDIES

Subtask 4.2 Finalize Hydrologic Monitoring Plan and Install Wells

Weather Station The field site was visited in April in order to attempt to set up the weather station. Inspection of the parts shipped to the CAER by North Dakota EERC revealed that critical parts were missing, delaying the establishment of the station.

Site Condition An equally important development at the site was the determination of the condition of the site. The black and gray shale above the coal is weathering rapidly. Shale rubble

now covers the coal. The weathering and caving of the shale is accentuating the overhang of the sandstone. Two dangerous situations now exist. The sandstone ledge will, unless it falls prior to mining, create a situation where men should not be near the highwall. Even without the latter situation, the condition of the shale will make the first portion of the entry unstable. With a mining and FGD emplacement plan requiring roof bolting, the mine site deterioration must be addressed in the coming months.

REFERENCES

1. Ingri, N. (1959) *Acta Chem. Scand.*, 13, 758.
2. Lagerstrom, G. (1959) *Acta Chem. Scand.*, 13, 722.
3. Stumm, W. and J. J. Morgan (1981), *Aquatic Chemistry; An Introduction Emphasizing Chemical Equilibrium in Natural Waters*, 2nd Ed. John Wiley & Sons, New York.
4. *Coolside Waste Management Research: Annual Techn. Progress Report for period October 1991 through Sept. 1992*, prepared by the Univ. of Kentucky Center for Applied Energy Research and Kentucky Transportation Center for the USDoE under Contract No. DE-AC21-91-MC28162, Oct. 1992.