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

**Quarterly Report
April - June 1995**

September 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
University of Kentucky
Lexington, Kentucky

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

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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 April 1, 1995 to June 30, 1995

Summary of Technical Progress

The kinetics study which is investigating hydration reactions of the ADM by-product (Subtask 2.2) was continued this quarter. This study further aided in gaining information on mineral precipitation and dissolution reactions during hydration of the ADM materials. The information is of importance for a comprehensive understanding of the factors that control strength and long-term stability during aging of FGD materials.

The decision was made by Addington, Inc., DOE, and the University of Kentucky that the originally selected mine site for the emplacement demonstration must be changed, mainly for safety reasons. Mine selection will be a priority for the next quarter (Jul.-Sep., 1995).

Another activity during this reporting period was related to Subtask 4.3, the selection and testing of the transport system for the FGD material. A laboratory-scale pneumatic emplacement test unit (ETU) for dry FGD materials was built at the CAER to generate data so that a final selection of the field demonstration technology can be made. A dry pneumatic system was chosen for laboratory testing because the equipment and expertise available at the CAER matched this sort of technology best. While the design of the laboratory system was based on shotcrete technology, the physical properties of the emplaced FGD material is expected to be similar for other transport techniques, either pneumatic or hydraulic. In other words, the selection of a dry pneumatic transport system for laboratory testing does not necessarily imply that a scaled-up version will be used for the field demonstration. The ETU is a convenient means of producing samples for subsequent chemical and physical testing by a representative emplacement technology. Ultimately, the field demonstration technology will be chosen based on the laboratory data and the suitability of locally available equipment.

TASK 2 LABORATORY STUDIES

Subtask 2.2 Chemical and Mineralogical Characterization

Kinetics Study Investigating Hydration Reactions

In order to gain better control of the experimental variables during the FGD-hydration reactions, a kinetic study was initiated and the experimental parameters, objectives and early results were already discussed in the previous report. In this reporting period additional results are compared and interpreted below. To better understand the important aging processes that might occur in an FGD mine emplacement situation with relatively constant free available moisture, the solution:solid ratios of the experiments were kept constant for all samples by preparing individual sample containers (jars). The samples were aged for 160 days (and continuing). X-ray diffraction and thermogravimetric analyses were conducted on these samples every day for two weeks, followed by increasingly longer intervals (of up to one year).

A comparison of the results in Figure 1 indicates that the amount of anhydrite crystals and Ca(OH)_2 (portlandite) in the materials continuously decreased with the aging of the materials in the water bath while ettringite and gypsum continued to grow. There is a negligible amount of gypsum, but large quantities of anhydrite crystals present in the ash prior to hydration. Ettringite is already observed in the raw material and may have formed as a result of interaction of the ash with some moisture in air. The sample is rich in calcium hydroxyhydrate (Ca(OH)_2). Figure 1 shows the XRD results after the ADM FGD by-product was aged from one day up to 160 days in the kinetic experiment. Gypsum crystals were detected immediately after hydration (i.e., after one day of exposure to moisture). Ettringite crystals continued to grow both in abundance and size while portlandite and anhydrite started to dissolve. After 160 days into the experiments (see Figure 1), ettringite crystals are abundantly present in the hardened materials while anhydrite, and portlandite are depleted to a large extent. Although ettringite formation occurred immediately after hydration of the materials (Figure 3) and continued throughout the entire experiment up to day 160, the rate at which ettringite needles formed was much faster in the first 30 days of the experiments and decreased thereafter, probably because most of the gypsum crystals were consumed in the reactions and the amounts of gypsum decreased to near base-line values about 50 days into the experiments. Figures 2-5 illustrate in great detail the time dependant changes in mineral dissolution and precipitation reactions for anhydrite (Figure 2), gypsum (Figure 3), ettringite (Figure 4), and portlandite (Figure 5) as occurring in the aged ADM FGD material upon continuous hydration. It can be seen that although anhydrite is abundantly present in the raw material, hydration during the first two weeks dissolved almost all of the anhydrite crystals. Complementary SEM investigations of the aged samples revealed that all anhydrite crystals showed dissolution cavities and etch pits. After the 15th day of the kinetic experiment, the amounts of anhydrite approached a plateau. The dissolution of anhydrite provides Ca and SO_4 ions for the formation of both gypsum and ettringite which compete for the sulfate ions. Figure 3 shows that exposure to moisture for one day lead to the onset of gypsum formation.

At day 15 of the experiments a maximum amount of gypsum was recorded (Figure 3) after which gypsum crystals started to be used up in the ettringite formation (Figure 4). Gypsum concentration in the hydrated ADM material upon aging continued to decrease after day 15 and reached a plateau after 50 days into the experiments. Figure 5 suggests that the concentration of portlandite crystals in the first three weeks is relatively constant and starts to decrease after 25 days into the experiments. The decrease in portlandite continues up to day 100 after which an increase in portlandite concentration was recognized. A drop in portlandite concentration after day 120 up to day 160 was monitored. Fluctuations in portlandite concentration are affecting the solution pH (see Figure 6). It is of paramount importance to further monitor the portlandite concentrations as dissolution of portlandite directly contributes OH groups to buffer the pH of the pore solutions. If the pH of the pore solutions drops below a value of 12, the stability of ettringite crystals may be affected. If so, this could have some impact on the long-term stability of the ADM FGD materials as ettringite crystals contribute to the strength of the materials. Ettringite crystals would begin decaying in an environment that has a pH less than ~12. Although this decay may be relatively slow, it should raise concern about long-term stability of the emplacement materials.

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 CO₂. TGA analyses aided in the understanding of the early ettringite and gypsum growth rates.

Figure 1 Illustration of mineralogical changes in aging ADM FGD material after exposure to moisture

Figure 2 Anhydrite abundance as a function of curing time

Figure 3 Gypsum abundance as a function of curing time

Figure 4 Ettringite abundance as a function of curing time

Figure 5 Portlandite abundance as a function of curing time

Figure 6 Illustration of variations in solution pH in aging ADM materials

TASK 4 BACKGROUND FOR PHASE II

Subtask 4.1 Mine Selection

As reported last quarter (Jan.-Mar., 1995), visits to the mine site for the hydrologic work revealed that the face of the highwall at the Pleasant Valley Mine in Greenup County, KY had deteriorated. In consultation with Addington, Inc. and DOE officials it was decided that the originally selected mine site for the emplacement demonstration was too dangerous and must be changed. Selection of a new mine site will be a major activity during the next quarter.

Subtask 4.3 Selection and Testing of Transport System

Overview of Pneumatic Emplacement Technology (Shotcrete)

With the exception of lower solids throughput, the laboratory-scale pneumatic emplacement test unit (ETU) at the CAER (Figure 7) is functionally identical to commercially-available dry-mix shotcrete equipment. In dry-mix shotcrete (also referred to as 'gunite'), dry solids are pneumatically transported and then mixed with water in a nozzle at the end of the pipe to produce a liquid/solid jet that will collect and harden on surfaces normal to the jet, regardless of orientation relative to gravity. In other words, it is possible to deposit cementitious solids on vertical and overhead surfaces using the shotcreting technology. This sort of emplacement flexibility makes shotcreting ideal for backfilling mines where the use of forms would not be practical. Shotcreting can also refer to the pneumatic emplacement of wet materials. In this case, the solids and water are mixed before pneumatic conveyance, and high pressure air at the end of the pipe is used produce a high-velocity jet that is similar to the dry-mix system. In general, dry-mix and wet-mix shotcrete produce similar results, but there are differences that can make one technique better suited than the other for certain applications. While the laboratory research at the CAER will focus on the dry-mix technique, the wet-mix technique will also be considered for the mine demonstration. A comparison of the dry- and wet-mix processes are provided in Table 1.

System Description

The emplacement test unit (ETU) was designed using major pieces of equipment that were available at the CAER. This approach minimized equipment expenditures and resulted in a system that is tailored for laboratory-scale operation, that is well instrumented, and that can be easily modified.

The source of pneumatic air for the ETU (Figure 7) is a vortex blower with a capacity of 220 ft³/min @ 0 psig and 50 ft³/min @ 7.9 psig. Therefore, the system is limited to low pressure operation. A pitot tube is used to measure the air flowrate at the inlet of the blower. A metered stream of water can be added at the inlet of the blower to create a mist of water, if

Figure 7. Diagram of the pneumatic emplacement test unit (ETU) at the CAER.

desired. The air flowrate is controlled by a gate valve downstream of the blower. The temperature and pressure are measured at the outlet of the blower to provide a secondary measure of the air flowrate from performance curves provided by the blower manufacturer. Pressure is measured just downstream of the controlling gate valve to monitor the system for blockages.

Solids are injected into the two-inch schedule-40 steel pipe by a rotary valve. The valve can deliver FGD material at a rate of up to 6 lb/minute. A sealable hopper with a volume of 0.86 ft³ supplies solids to the valve. Purge air is injected into the bin at three points to fluidize the solids and facilitate the feeding of the solids through the valve. An electric vibrator is mounted on the bin to alleviate problems with solids flow in the hopper. Addition of solids to the hopper during operation is not possible with the system in this configuration.

Solids are then pneumatically transferred over a distance of approximately 50 ft within a straight section of 2-inch schedule-40 steel pipe which is covered by 0.5 inches of foam

Table 1 Comparison of Dry- and Wet-Mix Shotcrete Processes. Taken from "ACI Manual of Concrete Practice, Part 5-1994", Guide to Shotcrete, ACI 506R-4, American Concrete Institute, Detroit, Michigan.

Dry-Mix Process	Wet-Mix Process
1. Instantaneous control over mixing water and consistency of mix at the nozzle to meet variable field conditions.	1. Mixing water is controlled at the delivery equipment and can be accurately measured.
2. Better suited for placing mixes containing lightweight aggregates, refractory materials and shotcrete requiring early strength properties.	2. Better assurance that the mixing water is thoroughly mixed with other ingredients.
3. Capable of being transported longer distances.	3. Less dusting and cement loss accompanies the gunning operation.
4. Start and stop placement characteristics are better with minimal waste and greater placement flexibility.	4. Normally has lower rebound resulting in less material waste.
5. Capable of higher strengths.	5. Capable of greater production.

insulation. The pipe is insulated so that the extent of hydration reactions involving free lime (CaO) may be estimated when water is present during pneumatic conveyance. Thermocouples are located at 20-ft intervals to monitor any increase in temperature caused by hydration reactions. Stresses between the rigid pipe and the 'gun' cart are relieved by a flexible metal hose. The pressure drop across the straight run of pipe is measured to monitor the air and solid flowrates.

The flexible metal hose connecting the last pipe section to the main run of pipe serves to permit the manual positioning of the nozzle. The nozzle must be maneuvered so that the FGD shotcrete is evenly distributed over the sample panel. A thermocouple is placed through the bottom of the sample panel at its mid point so that it minimally intrudes in the path of the shotcrete jet.

The nozzle is constructed of 1.5-inch Schedule 40 PVC pipe and fittings (1.61 inch inside diameter). Water is injected radially inward through a ring of 24 holes (each 0.0145 inches in diameter) in the pipe. The length, diameter, and internals (if any) of the mixing zone after the point of water injection will be adjusted to optimize the performance of the nozzle.

ETU Experimental Plan

The basic goal of the experimental plan is to evaluate the performance of this FGD material as a function shotcreting parameters so that the requirements for the mine demonstration technology can be specified. This experimental plan will focus only on the physical and chemical aspects of forming an optimized shotcrete jet, not robotic positioning of the shotcrete nozzle. It is assumed that once the important shotcreting parameters are determined for this material that a robotic vehicle based on state-of-the-art mining technology can be fitted with a shotcrete nozzle for remote emplacement. The demonstration of remote, robotic emplacement during this project will depend on the cooperation of a mining company to provide equipment and expertise. If required, the demonstration of shotcrete emplacement can also be safely performed by non-remote means.

While any new material to be considered for shotcrete emplacement must be experimentally evaluated, the high free lime (CaO) content of the FGD material makes testing doubly important. Substantial amounts of heat are generated during the hydration of CaO to form Ca(OH)_2 . If most of this heat is released after deposition in the adit, then ignition of a nearby coal seam is possible. The heat generated could also cause steam explosions within pockets of free moisture that have not yet reacted with the FGD material. Aside from these safety considerations, hydration of CaO in the presence of excess moisture has been shown to decrease the strength of sample pellets. By prehydrating the FGD material with only enough water to hydrate the CaO, the subsequent strength of the pellets was improved. Therefore, it appears critical that the CaO hydration reactions take place prior to entering the nozzle. The experiment plan addresses several scenarios regarding CaO hydration sequences, including the addition of water mist to the pneumatic transport pipe. The potential advantages of pre-

wetting the FGD material during pneumatic transport are that the solids can be cooled by external heat exchange prior to emplacement and that the nozzle performance will be improved. The success of prehydration during transport will rely on extremely rapid hydration kinetics to occur.

Several shakedown runs have been successfully completed using aged ADM FGD material which had been air-slaked during storage. The aged material was used for shakedown tests to avoid the complications of CaO hydration. A fresh sample of non-hydrated FGD material will be utilized for the subsequent test matrix. The parameters to be evaluated during which are:

- Water/Solid/Air Proportions
- Use of Pre-wetting Water at Blower Inlet
- Nozzle Design
- Air Velocity
- Nozzle Distance from Collection Surface
- State/Composition of Solids (non-prehydrated, prehydrated, fly-ash admixtures, etc.)

It is anticipated that the most influential parameters will involve the amount and location of water addition. The number of experiments to be performed with regard to each of the listed parameters will be determined once the sensitivity of each to shotcrete properties is found.

For each test, a full hopper (0.86 ft³) of FGD material will be used. Complete mass balances will be impossible to achieve because the system is not closed, permitting the escape of dust and mist. Nevertheless, estimates of overspray, rebound, and dust loss will be attempted. For each test involving non-prehydrated materials, the temperatures in the pneumatic pipe and the sample slab will be recorded. The FGD shotcrete will be directed onto a vertically mounted panel for subsequent testing. The thickness of the sample slabs will be approximately three inches. Each sample slab will be stored under identically moist, constant-temperature conditions to simulate the curing environment in the mine. Cubes or cores will be cut from the slabs for strength and chemical analysis.

Application of Laboratory Results to Mine Emplacement Demonstration

It is anticipated that commercial shotcreting equipment with a capacity of approximately 10 tons/hour will be leased for the mine emplacement demonstration. The lab results will be essential in providing information for the optimal water ratio and all other shotcreting parameters. A plan for hydrating the free lime will also be a result of the laboratory work. This could involve a separate prehydrating step, partial hydration during pneumatic transport with heat exchange, or some combination of the two. The method of nozzle positioning, whether manual or robotic, is yet to be determined. At this point, however, it appears unlikely that robotic emplacement will be attempted.