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

Quarterly Report
October - December 1994

March 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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Research under Subtask 2.2, Chemical and Mineralogical Characterization, included further refinement of mineralogical transformation and the initiation of a kinetic study. The expansion of the FGD materials during moistening is attributable to three reactions: the hydration of portlandite to slaked lime; the formation of ettringite from fly ash and anhydrite, and; the formation of gypsum from anhydrite. The sequence of these reactions are being examined in a kinetic study. Completion of the first 15 days of study finds the steady decrease in anhydrite with concomitant formation of ettringite (on fly ash surfaces) and gypsum (pore and crack infillings). Geotechnical characterization (Subtask 2.3) focused on swell experiments which will model in situ emplacement. Specimens of FGD material have been stored in 3-inch diameter pipe and, after 39 days, 0.5% of axial swell has been recorded with material strengths of 600 to 1,000 psi. Experiments to determine the amount of moisture loss due to the heat of hydration indicate about 9 to 10% of the water is lost. Confined swell tests are also underway with pressures of 15 to 20 psi recorded at 25 days.

Work performed under Task 4 (Background for Phase II) included determination of the compressive strengths for the experimental mine roof rock. Values in the 5,000 to 7,500 psi range were found, which is typical for this type of strata in the region. Work on the hydrologic monitoring program (Subtask 4.2) included completion of the hydraulic conductivity assessment of the strata, as well as completion of the monitoring well plan. The highest hydraulic conductivity was found for the Princess No. 3 coal seam with values of $1 \times 10^3$ feet/min. The weathered sandstone over the coal had conductivities in the $10^{-4}$ to $10^{-3}$ feet/min. range.

**TASK 2 LABORATORY STUDIES**

**SUBTASK 2.2 Chemical and Mineralogical Characterization**

**Objectives**

The objectives of the research are to (1) determine immediate and long-term reactions that lead to cementitious reactions, strength formation, infilling of available pore space to decrease permeability; (2) determine effects of mixing ratios on mineralogical reactions including optimum amounts of additives (fly ash, water) to form strength and swell enhancing minerals and; (3)
recommend ideal materials mixing ratios to obtain desired mineralogical reactions. Analyses in this study made use of XRD and SEM applications.

**Mineralogical Reactions Affecting Swell**

Early swell, which results in a decrease in strength, is controlled by the mix design. Mixing ratios affect the rates of cementitious reactions between particles, which can lead to the destruction of early mineral bonds when expansion occurs rapidly after partial solidification of the materials has taken place.

Swelling of the materials has been determined in previous work to predominantly consist of three phases:

**Phase 1: Swell caused by hydration of lime.** The swell in Phase 1 may be controlled by adequate pre-hydration of the materials prior to solidification. Early free access to moisture is critical to obtain good strength.

**Phase 2: Swell caused by formation of ettringite.** Ettringite formation takes place immediately after hydration of the materials, and the rates and amounts of ettringite formed depend on the availability of Al, Si, and SO₄. This study suggests that the rates and amounts of ettringite in the materials may be influenced by additions of fly ash to the admixtures, as additional Al and Si are readily supplied by fly ash surfaces. SEM images of early formation of ettringite indicate preferential formation of the ettringite needles on fly ash substrate surfaces. This is due to the low mobility of Al ions in the pore solutions which restricts the formation of ettringite crystals to zones where the concentration of Al ions are high, such as on or near fly ash surfaces and/or Al-Si-rich gel surfaces. Once ettringite crystals nucleate on substrate surfaces, further growth occurs that leads to infilling of available pore space. Continued growth of ettringite causes swell, but also leads to strength gain due to the interlocking of crystals.

**Phase 3: Hydration of anhydrite to gypsum.** Gypsum precipitates from the sulfate-rich solutions after dissolution of anhydrite. Anhydrite is considerably more soluble than gypsum. Calcium ions for the formation of gypsum are derived from both calcium hydroxy hydrate and anhydrite crystals. Ettringite and gypsum reactions compete for the sulfate ions. Both Ca and SO₄ ions are mobile and, unlike ettringite that depends on the availability of Al and Si ions, gypsum crystals can form anywhere from the Ca-SO₄-saturated solutions. Gypsum crystals grow in pores or heal cracks, but their continuous growth causes a volume expansion that may have detrimental effects on the strength of the hardening materials.

The effects of free swell of the materials are tested on samples that were completely submerged in water. Submersion yields poor strength which was shown in XRD analyses to be caused by tremendous growth of gypsum and ettringite crystals. Better results in the unconfined
compressive strength of prehydrated materials compared to non-prehydrated materials after 30 days and 60 days aging could be related to early mineral bond breakage due to continued hydration reactions after primary solidification. Prehydration causes some mineral reactions to be completed prior to solidification and minimizes bond breakage caused by early swell. Swell in all samples could be related to enhanced gypsum and ettringite growth.

To understand the importance of early mineralogical reactions, mineral growth rates and early swell forming phases, a kinetic study was performed. This study is an ongoing project and results up to this date are summarized below.

**Experimental Design** Samples for the kinetic study included pre-hydrated ADM materials that were placed in plastic tubing to restrict free flow of water to only the top and bottom areas of the tubes while the sides did not receive any moisture. Sample size was 1 inch in diameter and 1.5 inches in height. Samples inside the plastic tubes were placed into a temperature controlled water bath (25°C) and individual samples were recovered for XRD analyses after predetermined time intervals. A TiO₂ standard was admixed to all samples prior to the X-ray analyses to obtain quantitative information on mineral growth and dissolution rates. Sampling occurred 24 hours after putting the tubes into the water bath and was continued for the first 15 days on a daily basis. After that time, samples will be taken after longer time intervals. This report includes data up to the 15th day of the experiments.

A comparison of the results showed that the amount of anhydrite crystals in the materials continuously decreased with aging of the materials in the water bath (Figure 1). Complementary SEM investigations of the aged samples revealed that all anhydrite crystals showed dissolution cavities and etch pits. The amount of gypsum crystals was recognized in the XRD data to increase with continuous aging; however, unlike the anhydrite, gypsum showed fluctuations in its growth over time as determined by XRD. Gypsum crystals were precipitated from the saturated pore solutions, infilling pores and cracks. Simultaneously with the gypsum, ettringite formation occurred and also increased with time (Figure 2). Ettringite crystals competed with the gypsum crystals for available sulfate and calcium; however, ettringite growth rates were controlled by the availability of Al and Si in the materials. The relatively low solubility of Al in part restricted the precipitation of the ettringite to location near Al-rich surfaces in the FGD materials, which can be either fly ash particles or Al/Si-rich gel surfaces.

The amounts of ettringite in the XRD results were less than expected from SEM investigations, which indicated abundant ettringite to be present throughout the samples. Ettringite crystals give only poor X-ray intensities due to the quasi-amorphous structure at early growth and, thus, a small change in X-ray intensity may be the reflection of a large change in abundance. Also, the best diagnostic peak for ettringite is at a relatively low angle and our equipment is not particularly sensitive in this region. Recrystallization of the materials over time may enhance the XRD peak intensities.

The equilibrium between calcium hydroxy hydrate and the pore solutions controls the pH of the pore fluids. Monitoring of the samples over time suggests that the amounts of Ca(OH)₂ do
Figure 1. X-ray Diffraction Data for Original Materials in a Dry, Prehydrated (~15% moisture) and Fully Hydrated (35% moisture) state (Upper). Changes in Mineralogy as a Function of Time for Fully submerged Samples. E=Etrtringite, P=Portlandite, G=Gypsum, A=Anhydrite, T=Thumasite and C=Calcite.
not vary significantly over the first 15 days of the experiments. The hydration of lime in the pre-hydration step determines the amounts of calcium hydroxide in the materials before aging.

Materials that were prepared for triaxial tests were also analyzed using XRD applications to better understand the mineral kinetics that control early strength and swell formation in the materials. Effects of hydration observed for the materials from triaxial testing were very similar to those observed in the unconfined compressive strength tests. As in the earlier studies, mobile phases (gypsum) and immobile phases (ettringite) competed for the available sulfate ions. Longer time intervals are required for detailed comparisons of the results.

Long-term studies are required to determine the stability of the materials. Important mineral reactions include the disintegration of ettringite, formation of secondary gypsum, formation of calcium carbonate, etc. Disintegration of ettringite is expected to be accompanied by a reduction of the unconfined compressive strength of the materials.

Recommended future studies include an investigation of the effects of fly ash additions to the FGD materials to further the formation of Ca-Al-silicate gels between mineral grains to act as nucleation sites for ettringite and to lower the permeability of the materials. Ca-Al-silicate gels may also recrystallize to form Ca-Al-silicate phases which increase the strength. TGA investigations need to be initiated for all kinetic experiments and results will be helpful in the interpretation of the XRD and SEM results.

ADM Kinetic Study

![Graph showing mineralogic changes with time for submerged samples.](image)

Figure 2. Mineralogic Changes With Time for Submerged Samples.
TASK 2 LABORATORY STUDIES
SUBTASK 2.3 Geotechnical Characterization

Background

The preliminary geotechnical characterization indicated promising mechanical properties for the optimum mix prepared from the prehydrated FGD materials from the Archer Daniel Midland No. 6 plant. The results of the chemical and geotechnical studies also suggested that the formation of gypsum in the cemented matrix during curing would result in high swell. Gypsum formation during laboratory curing was dramatically accelerated by full submergence of partially cured specimens in a water bath, and the studies found that, as the total swell increased during curing, the modulus and unconfined compressive strength decreased to unacceptable levels. Based on these findings, it was concluded that the formation of hydrated phases must be restricted or free swell prevented so that strength and stiffness due to swelling loss does not occur.

The actual in situ conditions will likely provide much less access of free water to the emplaced mix than that simulated in the water bath in the laboratory, and significant confining pressures in the filled adit should help to further reduce a tendency towards excessive swell. Under these conditions, it is surmised that the optimum mix design should prove adequate for the project. The final testing program for the geotechnical characterization was developed to provide a better understanding of the mechanical behavior of the emplaced mix under in situ curing and stress conditions.

Development of Testing Methodology for Second Phase

Several testing methodologies are under development to: (1) prepare specimens under curing conditions believed to be most representative of in situ conditions; (2) bound the potential range of swelling pressures and strengths; and (3) characterize important mineralogical and mechanical changes in the materials with time. Activities in the development of testing methodologies relevant to these three objectives are summarized below.

Curing parameters to simulate in situ conditions The in situ curing will feature vertical swell only, as lateral swell will be prevented by the webs between the adits. As noted above, excessive swell is undesirable, but some vertical swell is required to assure that the adits will be filled during curing. An upper bound of allowable vertical and volumetric swell of four percent is recommended for the ADM6 FGD. Localized swell of higher percentages to fill gaps in the roof will be permissible, but the average overall swell should be maintained at approximately 4 percent. This swell limitation is being simulated in specimens currently curing in the Civil Engineering Materials Research Laboratory at the University of Kentucky.

The access of water to the mixture after placement will be limited by the permeability of the mixture and the hydraulic gradient in the filled zone. Data to assess the hydraulic gradient are not available, but the hydraulic gradient would be expected to vary with location in the adit, surrounding stratigraphy, and seasonal fluctuations in the ground water environment. Under most
conditions, a very low hydraulic gradient is anticipated across the filled section. For this reason, submersion of cylindrical specimens in water baths with access to water at the ends only was judged to be suitable for modeling in situ infiltration and availability of water during curing.

The method of placement will affect the mechanical properties to some extent. Since most of the strength in the materials is due to the formation of cementing bonds between particles, the strength will be a function of the strength of the cementations and the number of bonds. The cementations' strength in the laboratory will likely be similar to the strength in situ, but the number of bonds will be a function of the density of the mix. No placement data is currently available to provide insight to expected densities, although most of the methods under consideration involve some amount of placement energy that will increase density and thus strength and modulus. To provide a conservative simulation of in situ placement densities, no specimens prepared in the laboratory are compacted during placement in the specimen forming molds. Not only does this result in looser specimens, but in some specimens it leads to a larger percentage of open air voids which further reduce the strength and stiffness and increase the measured permeability, leading to conservative estimates of these significant geotechnical parameters.

A series of specimens are curing in 3 inch I.D. PVC pipe with end caps placed on the pipe so as to permit no more than approximately 4 percent free axial swell during curing. The end caps were perforated to allow free access of water, and the specimens have been curing submerged in a water bath at 55°F. Three of the specimens were selected after 39 days curing in the water bath for study. The specimen dimensions were measured to determine the free axial swell that occurred during the curing, and the specimens were then subjected to unconfined compression testing. The results indicated approximately 0.5% free axial swell had occurred over the 39 days. The approximate unconfined compressive strengths were on the order of 600 to 1,000 psi. These results support the earlier conclusions that, when curing occurs under conditions believed to be more representative of field conditions, suitable strengths and stiffness can be achieved.

**Bounding the significant geotechnical characteristics** The unconfined compression testing performed in the first phase of the geotechnical characterization provided conservative upper and lower bounds for the strength and stiffness of the prehydrated ADM6 FGD. The triaxial testing described later herein will further refine the reasonable bounds for the strength and modulus of these materials for varying confining pressures. The free swell tests performed for the first phase geotechnical characterization provide evidence of the swell potential present in the materials under no significant confinement, but the pressure the materials are capable of exerting on the mine ceiling when confined has not been measured. For this reason, a series of confined swelling pressure tests are currently under way in the University of Kentucky Civil Engineering laboratories. The curing conditions described above are maintained on these specimens, with the exception that no vertical swell has been permitted in the materials. This will provide an accurate
estimate of the swelling capacity of the materials under optimum conditions. The results that were available from these four ongoing tests at the time of this report are shown in Figure 3. The data indicate a generally constant rate of increasing confined swell pressure over the first 25 days of testing.

Variation of properties with time and confining stress It became clear in the first phase of the geotechnical characterization that strength testing under conditions of varying confinement and stress history would be necessary to provide thorough material characterization. Triaxial testing is a common method employed in both the geotechnical and mining fields to assess the strength under such conditions. The triaxial testing methodology used in rock mechanics is inappropriate for the material characterization in the early "soil-like" stages of curing, so a testing methodology similar to that used for geotechnical engineering was employed for sample preparation and testing. The triaxial testing currently under way in the University of Kentucky Civil Engineering laboratories is also incorporating measurement of the permeability of the mixtures, so the variation of this important parameter with time is also being determined. Finally, the testing is being coordinated with a series of X-ray diffraction studies at the University of Kentucky Center for Applied Energy Research so that mineralogical changes can be correlated to the strength, permeability, and modulus development over time. Due to the unusual nature of the material, considerable effort has been extended toward the development of testing procedures and equipment. Several successful triaxial tests have been recently performed, but the results are too preliminary to be included in this report.

Other Significant Findings

During the recent testing, several material characteristics of note have been observed. These are summarized below.

Effect of heating on percent prehydration Measurements are being made to provide a more accurate estimate of the actual prehydration rate that occurs in the specimens. During prehydration, the specimens achieve temperatures in excess of boiling, so some water is lost due to vaporization. Careful measurement of mass lost during prehydration is a good indication of the quantity of water lost. Some typical measurements are shown in Figure 4. This data indicates that, although the initial mix water is 12 percent of the total initial mass, losses due to vaporization result in only 9.5 to 10 percent prehydration occurring.

Consolidation of the emplaced fill During recent testing, careful observation of the loosely placed mixture in the specimen molds immediately after placement has shown consolidation of the mixture on the order of 1 to 3 percent, with "ponding" of water from the consolidation occurring on the top of the specimens. This settlement of the mixture may not be observed in the adit due to higher compactive placement, but it certainly merits consideration in the estimation of the necessary vertical swell to contact the mine ceiling. This unavoidable consolidation of the mix could reduce the total height of the fill placed in the adit on the order of 3 to 5 percent shortly after placement in the mine, so the emplacement technology will likely have to provide nearly full
Figure 3. Confined Swell Pressure Data.

Figure 4. Water Mass Loss During Prehydration.
contact with the mine ceiling to assure that no more than the previously suggested upper bound swell of 4 percent is permitted during curing.

**TASK 4.0 BACKGROUND FOR PHASE II**

**Subtask 4.1 Mine Selection.**

Five samples were taken from the immediate roof in Core Hole HW2 and six samples were taken from the immediate roof in Core Hole HW3 (Figure 5). The depth of each sample is given in Table I. All of the samples in HW2 were described as gray shale. Five of the samples in HW3 were described as sandy shale and the sample immediately above the coal was classified as gray shale. Uniaxial compressive strength data for each sample are listed in the attached table. The average uniaxial compressive strength of the gray shale in HW2 is 5282 psi and the corresponding value for the sandy shale in HW3 is 6577 psi. The single sample of gray shale immediately above the coal in HW3 has a compressive strength of 3720 psi.

The stress-strain relationship was also determined for samples from each core hole (Figures 6 and 7). The Young's Modulus for the gray shale in HW2 has been determined to be approximately $3.45 \times 10^5$ psi and the value for the sandy shale in HW3 is approximately $5.26 \times 10^5$ psi. These values fall within the typical range for the coal-bearing strata in this region.

**TASK 4.0 BACKGROUND FOR PHASE II**

**Subtask 4.2 Hydrologic Monitoring Plan**

Efforts during the quarter centered upon work to develop final plans and a bid package for drilling and reduction of data from hydraulic conductivity tests.

**Estimation of Hydraulic Conductivity**

Estimates of equivalent porous media hydraulic conductivity in the horizontal direction were obtained from pressure-injection tests conducted in three core holes (HW2, HW3, and B1) drilled along the web between two test entryways (Figure 5). Two inflatable packers separated by a perforated five-foot-long pipe were lowered to the bottom of each hole. Water was injected into the five-foot-long test interval at a known pressure for a specified time period. The packer assembly was raised five feet after each successive test to obtain a conductivity profile at five-foot intervals for each hole. The test apparatus is shown in Figure 8. Hydraulic conductivity was calculated using the following formula:

\[ k = \frac{Q}{A \Delta t} \]

U.S. Bureau of Reclamation, 1974, The design of small dams: Technical Publication
\[
K = \frac{Q}{2\pi LH} \ln \frac{1}{r} \text{ where } L > 10r
\]

where:
- \(K\) = hydraulic conductivity
- \(Q\) = the constant rate of flow into the interval
- \(L\) = length of the test interval (5 feet)
- \(r\) = radius of the hole
- \(H\) = the total head of water (gravity head plus applied pressure head where gravity head is the distance from the water swivel to the midpoint of the test interval).

The distribution of hydraulic conductivity for the three holes is shown in Figure 9. This figure relates the elevation of the test interval to general stratigraphy along the cross section. The most conductive unit at the site is the Princess 3 coal bed (seam to be backfilled). Calculated hydraulic conductivity (approximately \(1 \times 10^{-3}\) feet/minute) in this seam is highest in core hole HW2, which is closest to the outcrop. Conductivity in the Princess 3 coal bed is approximately ten times less in core hole HW3, located about 200 feet behind the highwall. Other thin coals in the section have conductivity values that range between \(10^{-4}\) and \(10^{-6}\) feet/minute. Weathered sandstone at shallow depths in core holes HW2 and HW3 have conductivities ranging between \(10^{-4}\) to \(10^{-5}\) feet/minute.

Layered stratigraphy typical of coal-bearing regions results in hydraulic layering where low conductivity units are surrounded by units that have conductivities that are orders of magnitude higher. Conductivity extremes create a situation where flow is predominantly downward in the low conductivity units (shales and sandstones) and primarily horizontal in the high conductivity units (coal beds). Consequently, coal beds are the primary water-transmitting stratigraphic horizons.

**Monitoring Well Installation**

The proposed monitoring well network has been downsized to reflect current financial support available. This plan is designed to monitor locations where leachate will most likely be detected if it occurs. If water-quality changes are detected in these wells after emplacement, it may be necessary to implement a more intensive plan to determine the extent of leachate migration and its potential impacts.

The proposed monitoring network contains three four-inch wells (MW1, MW2, and MW3) that will be installed in the Princess 3 coal bed. Two wells will be installed in the web
Figure 5. Location of Core Holes and Proposed Monitoring Well Sites.
Figure 6. Stress-Strain Relationship for Samples from Core HW2.

Figure 7. Stress-Strain Relationships for Samples from Core HW3.
Figure 8. Equipment used for Pressure-Injection Tests.
Figure 9. Distribution of Hydraulic Conductivity For Mine Site Stratigraphic Units.
between the two entries and the third well will be installed on the down-gradient side of the entries (see Figure 7). The wells will be installed as follows:

1. drill 8-inch hole to targeted depth
2. slotted PVC screen (0.010 slot size) and riser pipe (4-inch diameter) installed using centralizers if deemed necessary
3. coarse quartz sand (.033 - .046") emplaced surrounding and above the screen using a tremie pipe to prevent sloughing of borehole materials into the sand pack
4. 1-foot of fine quartz sand (.008 - .012") emplaced on top of coarse sand using a tremie pipe
5. approximately 20 feet of bentonite granules or pellets installed above fine sand
6. remainder of bentonite seal (slurry acceptable if large fractures are not encountered)

Bentonite seals will completely surround each riser. Slurry will be placed by means that will limit mixing and dilution with water standing in the hole. Holes with standing water will require that slurry be pumped through a pipe that extends to the top of the bentonite seal.

No materials that will alter the ground-water quality (such as cement) will be used as a sealant. Concrete will be used to anchor a lockable steel protective casing over each monitoring well following its completion, but should in no case extend to such a depth that it will affect water quality in the monitoring wells.

Holes will be drilled without water to minimize introduction of water into the formation unless needed to facilitate cuttings removal. However, all water used for drilling (if needed), slurry mixing, washing, and decontamination will be chlorinated, potable water.

All materials connected with well installation are to be maintained in a clean condition. Plastic will be laid on the ground surface so that all materials that will be installed in the monitoring well, such as, but not limited to, sand, well production casing, and well screens, can be stored on this plastic. Plastic will also cover the top of such materials to minimize contamination by foreign materials until they are installed in the well. PVC production pipe and well screens that are packaged in self-contained plastic bags or coverings will be used if possible. Buckets, water tanks, tremie pipes, and other devices used to carry and emplace materials in the hole will be kept clean of foreign materials. Cutting of the completed riser shall be accomplished in such a manner that no PVC shavings are introduced into the well or annulus.

Following installation of the monitoring well in each hole, a locking steel casing will be cemented into place to protect the riser pipe at the surface. This protective casing will extend approximately 2 to 3 feet above land surface and will be securely anchored in place in the ground with concrete. Well installation is planned for in the first quarter of 1995 or early in the beginning of the second quarter.
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