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

**Quarterly Report
January 1 - March 31, 1997**

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

Phase II: Field Investigations

Cooperative Agreement No. DE-FC21-93MC30251

Quarterly Report for the period January 1, 1997 to March 31, 1997

Summary of Activities

Activities during the quarter focused on two areas: monitoring of grout strength from the field demonstration (Subtask 1.4) and construction of laboratory lysimeters to examine the leaching characteristics of the waste materials used in that demonstration (Subtask 2.4).

Two of the auger holes filled in October 1996 at the demonstration site were sampled and returned to the laboratory for compressive strength, mineralogic, and chemical testing. Construction and packing of eight laboratory leaching columns (lysimeters) was also initiated. Four columns were packed with samples of grout taken from cement-mixer trucks during the emplacement (October, 1996). A fifth column was loaded with crushed material cored from borehole #10 two months after emplacement. Samples of dry FGD material were used to prepare water/FGD waste blends that were loaded to the final three columns. Two of these latter columns were loaded with a slurry produced by blending water with the FGD waste at levels similar to those used during emplacement (~38 wt%). Differing amounts of slurry was loaded to each these columns and permitted to harden prior to initiating water additions. The final column was loaded with a blend of the dry FGD waste and a lesser amount of water (27.5 wt%) to both facilitate the percolation of water through the lysimeter and to permit subsequent comparisons to previous studies of the leaching behavior of dry FGD materials.¹ Weekly additions of 100 mL of distilled water have been initiated. However, due to a significant lag time between the initiation of water feed and leachate-water breakthrough, leaching data are not available for presentation at this time.

Task 1. Field Demonstration

Subtask 1.4 Monitoring of Grout Strength

Two of the filled auger holes were sampled on 12-6-96, using a drill equipped with a 1.5 inch i.d. coring bit. Cores of the hardened grout were acquired horizontally *in situ*, whereas vertical cores were obtained by chiseling a large block of grout from the auger hole, removing it (while preserving the orientation), and then coring it in the laboratory. All samples were immediately placed into polyethylene bags at the field site to prevent dessication. The cores were then subjected to unconfined compressive strength testing at the University of Kentucky Department of Civil Engineering facilities. Results of these tests are presented in Table 1.

Samples of the hardened grout within the auger holes were also obtained for chemical analysis and

x-ray diffraction (XRD). Major and minor elemental distributions are shown in Table 2.

XRD analysis indicates that the major crystalline phases are ettringite, quartz, gehlenite, and calcite, with a minor amount of portlandite (Figure 2). Comparison with the parent material (Figure 2) reveals that the anhydrite and lime initially present have been dissolved from the fly ash, with a corresponding formation of ettringite and minor portlandite, and possibly an amorphous 'paste'.

Task 2

Subtask 2.4 Leaching Studies

LYSIMETER DESCRIPTION.

A schematic of the laboratory leaching columns fabricated for this study is shown in Figure 1. The lysimeters are constructed from clear-acrylic cylinders that are 39" (~1 m) in length, 2" (~5 cm) inner diameter, and ~1/4" (~0.6 cm) wall thickness. A plexiglass frit is sealed in the bottom of each column inside of a PVC sleeve with PVC cement. The sleeve is in turn connected to a PVC reducing connector and plastic valve. The valve is maintained in the closed position except during sample collection. The plexiglas frit is overlain with one inch of glass wool followed by one inch of Ottawa sand to prevent blockage of the drain holes in the fritted disk. The void volume of the column from the top of the valve to the top of the sand layer is slightly in excess of 100 mL which is a sufficient volume to retain the leachate water passing through the columns each week. Thus, leachate waters pass through the column and collect in the void space at the bottom until drained and weighed one week after addition.

STUDY SAMPLES AND LYSIMETER PACKING PROCEDURES.

A total of 5 samples were selected for placement into 8 lysimeters. Table 3 shows the lysimeter number along with selected information on packing and physical characteristics.

During the field tests conducted on October 4 and October 14, 1996, replicate samples were obtained from each cement truck immediately prior to emplacement. Four *truck* samples were selected for leaching studies based on on-site slump tests and subsequent compressive strength tests of replicate samples (no testing was conducted on the material load to LC40). The samples selected for study were permitted to harden in sealed 1-gallon cans for approximately two months then crushed and sieved to -8 mesh prior to loading to the columns. The crushed samples were loaded without compacting and without water addition to lysimeters LC37-40 (Table 3).

Hardened grout cored from borehole #10 was used to fill LC41. This borehole was filled on October 14, 1996 and cored just under two months later on December 4. This sample was also crushed to -8 mesh and loaded without water addition or compaction.

A sample of dry FGD waste, taken from the storage silo from which materials used in the emplacement tests were obtained, was loaded to lysimeters 42-44. This material was used as received, i.e., without crushing or sieving. The loading procedure entailed weighing approximately

2.1 lb (~1-kg) of dry sample to a 2-L stainless-steel mixing bowl to which was added a targeted amount of distilled water (prehydration water). The sample and water were then blended with a Kitchen-Aide *Classic*TM mixer at low speed for approximately five minutes (or until the prehydrated sample had a homogeneous appearance). A relatively high water content (38%), similar to that used for the emplacement tests, was targeted for the samples loaded to LC42 and LC43. This yielded a flowable grout that was routed to the bottom of these two lysimeters by pouring a portion of the mix through a one-inch PCV pipe that was inserted into the two-inch lysimeter. Bed heights of approximately 2.0 and 4.75 inches were obtained by this approach for LC42 and LC43, respectively. Load weights were determined by weighing the lysimeter before and after loading. The materials in lysimeters LC42 and LC43 were permitted to harden for one week prior to the addition of leachate waters. This approach was selected in an effort to more closely simulate the flow and leaching characteristics of the emplaced materials.

The sample loaded to LC44 was blended with a lesser amount of water, again using the Kitchen-Aide blender. This yielded a dryer sample that was loaded loosely (without tamping) to the lysimeter with a plastic scoop. This was the loading procedure used in a prior study of the leaching characteristics of dry FGD wastes and was selected in an effort to obtain data that would be more directly comparable to the results from that study.^{2,3}

All columns were mounted in a vertical alignment and capped with solid rubber stoppers. The stoppers were used to suppress evaporative water losses and to prevent the diffusion of atmospheric CO₂ into the lysimeters. The latter is an important consideration since it has been shown that the presence of CO₂ can significantly impact the mineralogic transformations that occur over time.⁴

WATER ADDITION AND COLLECTION.

A tygon tube is attached to the drain spout of each lysimeter and routed through a snug-fitting hole drilled through the lid of a 200 mL polyethylene collection bottle positioned beneath each column. The drain valve is maintained in the closed position for all columns with the exception of LC42 and LC43 (in-situ hardened grout) which will be maintained in an open position for the duration of the study. Water additions are made at weekly intervals by removing the rubber stopper from the top of each column, adding 100 mL of deionized-distilled water, then replacing the stoppers to seal the columns. Six days after water addition, the remaining drainage valves are opened and each lysimeter permitted to drain for 24 hours. The collection bottles are then removed, the weight of the collected water determined, and the next water addition is made.

ANALYSIS.

Analysis of and the analytical protocols used for the leachate waters will be the same as conducted in a previous set of laboratory lysimeters in which FGD wastes were examined.³ Briefly, the leachate waters will be analyzed for pH, alkalinity, conductivity, anions (including but not limited to SO₄, SO₃, Cl, NO₃, 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 are treated with acid to stabilize the sample prior to metals (cations) analysis. Time permitting,

this latter test will also be conducted on the day of collection. In addition, XRD spectra were obtained for all study samples in dry form prior to initiating the leaching study and will be conducted again at the conclusion of the study.

As of this writing, all columns except for LC42 and LC43 (in-situ hardened grout), have exhibited free flow. However, analytical results to date are insufficient to merit reporting at this time. Interim leaching results will be the subject of future progress report(s). It is anticipated that the column leaching studies will continue for one year and as long thereafter as potentially useful data are being generated.

1. "Laboratory-Lysimeter Studies of dry FGD wastes from tests of the Coolside Technology" Taulbee, D.N.; Schram, W.H.; Thomas, G.A.; Rathbone, R.F.; Robl, T.L.; 1996, *Proc. 13th Annual Intl. Pittsburgh Coal Conf.: Coal-Energy and the Environment*, v.1; S.H. Chiang, ed.; Sept. 3-7; The Univ. of Pittsburgh School of Eng. Cntr. for Energy Res., Pittsburgh PA; 705-710.
2. Coolside Waste Management Research: Technical Progress Report. Contract No: DE-AC21-91MC28162; Report Period: Nov. 1, 1994 to Nov. 30, 1994.
3. Coolside Waste Management Research: Technical Progress Report. Contract No: DE-AC21-91MC28162; Report Period: July 1, 1995 to July 31, 1995.
4. "The Effect of Carbonization Reactions on the long term stability of products made from dry FGD Materials" T.L. Robl, U.M.Graham, D.N.Taulbee, W. Giles; 1996, *Preprints: Am. Chem. Soc., Div. Fuel Chem.* 41, #2, Am. Chem. Soc., Washington, DC, 549-552.

Figure 1. Schematic of a laboratory leaching column.

	Auger Hole #10 (psi)
Core #1	852
Core #2	918
Core #3	957
Core #4	1083
Core #5	811

Table 1. Unconfined Compressive strengths for samples of hardened grout taken from borehole #10.

Figure 2. XRD spectra of parent material (top) and hardened grout from Auger Hole #10.

	Auger Hole #10	Auger Hole #15		Auger Hole #10	Auger Hole #15
MgO	1.6%	0.4%	% H ₂ O	38.4%	36.6%
NaO ₂	0.1%	0.4%	% Ash	51.8%	53.7%
Fe ₂ O ₃	3.6%	3.4%	% VM	10.0%	10.0%
TiO ₂	1.3%	1.3%	% C	2.2%	2.2%
SiO ₂	36.9%	37.0%	% H	4.9%	4.4%
CaO	25.9%	24.6%	% N	<0.1%	<0.1%
K ₂ O	1.4%	1.5%	% S	1.3%	1.4%
P ₂ O ₅	0.1%	0.2%	SO ₃	7.5%	7.0%
Al ₂ O ₃	19.1%	20.1%	%C _{min}	0.3%	0.4%
Zn	72ppm	12ppm			
Cu	14ppm	57ppm			
Ni	49ppm	42ppm			
Co	10ppm	10ppm			
Cr	64ppm	66ppm			
Ba	454ppm	439ppm			
V	84ppm	89ppm			
Mn	<5ppm	<5ppm			
Mo	<5ppm	<5ppm			
Free CaO	2.4%	2.4%			

Table 2. Chemical analysis of hardened grout from Boreholes #10 and #15.

LC #	Sample Description	Bed Weight (g-dry)	Added H ₂ O (g)	Slump (in)	Compressive Strength (psi)	Bed Height (cm)	Bed density (kg/m ³ -dry)
37	Truck #1; 10/14/96	1,000	0	5	824/562/788	54.5	900
38	Truck #2; 10/14/96	1,000	0	6	824	57.0	870
39	Truck #4; 10/4/96	1,000	0	nd	nd	48.5	1010
40	Truck #4; 10/14/96	1,000	0	7	537/580	52.5	940
41	Core from borehole #10	1,000	0		852/918/957 1083/811	54.0	920
42	Hydrated FGD; 38 wt% H ₂ O	96	57			5.0	950
43	Hydrated FGD; 38 wt% H ₂ O	236	144			12.0	970
44	Hydrated FGD; 27.5 wt% H ₂ O	1,000	380			38.0	1300

Table 3. Study samples and packing characteristics for materials loaded to the laboratory lysimeters (Multiple values listed under compressive strength column represent the results from replicate tests.

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