

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

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**Quarterly Report
July - September 1995**

January 1996

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

MASTER

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

By
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Center for Applied Energy Research
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January 1996

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 July 1, 1995 to September 30, 1995

Summary of Technical Progress

Efforts primarily focused on Subtask 2.2, Chemical and Mineralogical Characterization and Subtask 4.3 Selection and Testing of Transport System. As part of Subtask 2.2, samples were collected from the Freeman United Crown Mine III FBC disposal facility representing a variety of ages and weathering. These samples were chemically analyzed and also subjected to X-ray diffraction analysis. The hydration of the ABC material was found to result in the rapid development of portlandite, ettringite and gypsum and the loss of calcia (lime) and anhydrite. The cementitious reactions were found to be completed early. The strength of the material was relatable to the amount of ettringite formed and the ultimate concentration of ettringite was controlled by the availability of alumina. The hydrated FGD materials undergo extensive carbonation reactions which result in high concentrations of calcite. Total sulfate decreased with weathering. Ettringite appears to be remarkably stable in the weathering environment and does not break down until after gypsum is replaced by calcite. The loss of strength in the materials is a function of carbonation reactions and not the rapid breakdown of ettringite.

A laboratory scale transport system has been built at the CAER to evaluate the potential of pneumatic transport for flue gas desulfurization material (FGDM) emplacement and to provide essential data for the mine emplacement demonstration as part of the Subtask 4.3 effort. The system is modeled after shotcreting systems and has the advantage that the material can be remotely placed without the need for forms. The test program is focusing on determining the pneumatic conditions necessary to maximize the strength of the emplaced FGDM under anticipated mine curing conditions while minimizing dust formation. A study was performed to determine the amount of mist loss as a function of air velocity and distance of the nozzle to the collection surface. During these experiments, water at a rate of 15 gal/hr was injected into the nozzle. The air/water jet then impinged onto a flat plywood surface mounted vertically so that all the water that adhered to the surface would drain into a container. The water collected compared to the amount injected into the air jet was defined as the percentage of water capture. The best results were obtained for the higher velocity runs (362 ft/sec) at a distance of 4 ft. between the collector and the nozzle. Several slabs of FGDM shotcrete, up to 3 inches in thickness, have been successfully prepared to date. Prehydrated FGDM was utilized to avoid the complications associated with free lime hydration. The FGDM adhered to the vertically positioned plywood without slumping. The samples exhibited stiffness immediately upon deposition suggesting a consistency that, in larger volumes, would be advantageous for bulk fill applications. The slabs are being cured for chemical and physical analyses.

Work on Subtask 4.1, Mine Selection, also proceeded during the quarter. A new mine site, located in the south-central section of the Pikeville quadrangle, Pike County, Kentucky, was examined for the field study. The proposed fill site is in the Middle Pennsylvanian Breathitt Formation Middle Amburgy coal bed, a coal previously mined by Costain elsewhere on the property.

Efforts on Subtask 4.2, Hydrologic Monitoring Plan, focused primarily on theoretical issues concerning the effects of the mining and backfill activity on the ground water and surface water due to uncertainties in the location of the final field site. There are three major concerns about the effects of the mining activity: changes in the ground water flow field, changes in ground water quality, and consequential induced changes on stream flow.

TASK 2 LABORATORY STUDIES

Subtask 2.2 Chemical and Mineralogical Characterization

We have been studying the hydration reactions and mineralogic and chemical transformations which take place in FGD materials as part of an effort to characterize their applicability for use as structural fill material in coal highwall mining.¹ These efforts have included previously reported lab based studies of the kinetics of hydration and mineralogic transformations in closed systems to determine the reactions controlling strength and swell characteristics. We have also been studying weathering in open systems, the topic of this section, as the environment ultimately determines the fate of the materials.

The Study Site

The study was conducted at the Freeman United Coal Company's Crown Mine III, located in central Illinois. The company has pioneered fluidized bed combustion backhaul and disposal methods at this site. In the late summer of 1990, a prototype ash handling system was set up and operated to gain knowledge of ash handling characteristics. In 1991, a permanent system was constructed and put into operation.

FBC fly ash is hauled in semi-trailer dump trucks to the mine. The ash is dumped into a hopper and metered out with screw feeders. An enclosed collection system was installed to control the dust from the trucks. A wet scrubber system was used initially for dust collection, but was later changed to a dry filtration system. The ash is withdrawn from the dump hopper and mixed with water before being pumped to the disposal site.

The mixing and pumping system is instrumented and monitored so that process upsets are controlled automatically. When in normal operation, no attendant is required. The solids are settled from the slurry and the water returned to the mixer. Work on new methods of handling ash continues and prototypes of new systems are being planned. All of the systems have been developed in-house by Freeman United.

Future systems may include injection into abandoned mines. Part of the reason for using the slurry transport system was to gain knowledge of the behavior of FBC fly ash slurries for potential underground injection in abandoned mine works. A prototype system was set up in 1993 and used to inject several truckloads of FBC ash into abandoned works at Crown Mine I.

The principal materials disposed at the Crown Mine III are circulating fluidized bed combustion (CFBC) fly and bottom ash from co-generating units operated by the Archer Daniels Midland plant in Decatur, Illinois. The ADM fly ash as received is fine and dry and is slurried with water in the system described (4:1 liquid:solid) and pumped through 8-inch diameter PVC piping to the fill. There it settles into a mud-like paste that typically hardens within days. In addition to the fly ash materials, coarser bottom ash representing about 20% of the total material received is also handled at the mine. It is disposed of dry in the landfill area and then wetted.

Study Methods and Objectives

Our investigations focused on the mineralogic transformations that occur when the ADM material is hydrated and exposed to weathering over time. Emphasis was placed on 1) examining mineralogic transformation and disintegration reactions, and 2) relating the mineralogic reactions to long-term stability factors of the emplaced material.

The material was collected and investigated at the CAER by X-ray diffraction (XRD), scanning electron microscopy (SEM) and thermogravimetric analysis (TGA). Elemental analysis was performed by X-ray fluorescence methods (Table 1). Sulfur was determined with a LECO analyzer. CO₂ was determined by TGA, and was defined as the weight loss between 550 °C and 700 °C.

Samples were collected from the dry bed ash (sample FU-15C, Table 1) and fly ash materials (FU-14C) as received and also from the fresh slurried materials from the pipe discharge (FU-2C, FU-3C). These two samples were analyzed 4 days after collection. Three samples which were approximately one month old were collected. One of these (FU-4C) was collected from near the surface of the fill and was durable and rock-like, while another was collected on the surface (FU-1C) and was weaker and more friable than the first. A third sample (FU-5C) was excavated from about 0.2 to 0.3 m in depth and was softer and moister than the others.

Older materials included a sample of friable bed ash deposited one year ago as collected from the surface of the fill (FU-8C) and samples collected from berms which were constructed during the spring (FU-10C, FU-11C, FU-13C), summer (FU-6C, FU-7C) and winter of 1993 (FU-12C). Two of these samples (FU-6C, FU-11C) were collected from the surface of the berm and were physically weak and friable. The three other samples (FU-7C, FU-12C and FU-13C) were excavated from 0.2 to 0.3 m in depth and were better consolidated. Sample FU-13C was, in particular, well indurated. Finally, a sample of pipe scale was collected (FU-9C). The plastic piping used to distribute the slurry material develops a heavy scale which is removed every 4 to 5 weeks by passing the piping through rollers and crushing the scale.

Results

The dry fly and bed ash differed in particle size, with the bed ash being sand-size and the fly ash the constituency of fine silt. The relative elemental concentrations differed between the two materials as well. The fly ash had higher concentrations of silica and alumina, (Table 1) which is a reflection of a higher proportion of ash derived from the coal. The bed ash has a higher proportion of calcium oxide derived from a higher proportion of the original limestone sorbent.

Early Hydration Reactions and Neo-Formed Minerals The comparison of the dry as-received materials with the freshly hydrated and slurried samples provides an indication of the important early reactions. The principal minerals in the unhydrated materials are anhydrite (CaSO₄), and calcia or lime (CaO), and quartz (SiO₂), minor calcite (CaCO₃) and glassy silicious ash particles. The important minerals in the freshly hydrated materials are portlandite Ca(OH)₂,

Sample #	FU-14C	FU-15C	FU-2C	FU-3C	FU-1C	FU-4C	FU-5C	FU-9C
Age	0 days	0 days	1 day	1 day	1 month	1 month	1 month	1 month
Type	fly ash	bed ash	fly ash	pipe scale				
Location	as-rec.	as-rec.	surface	surface	surface	surface	subsurf.	pipe

Chemistry

Ash	96.63	96.92	84.29	85.33	84.93	82.86	83.12	75.86
LOI	3.94	4.80	14.22	12.27	15.60	19.46	15.97	23.85
SO ₃	17.21	19.13	15.74	13.35	12.45	11.64	17.20	3.39
CO ₂	3.35	0.74	4.52	6.29	8.99	9.22	4.66	6.39
SiO ₂	23.33	8.32	17.62	23.28	23.98	29.28	14.09	3.27
TiO ₂	0.26	0.12	0.22	0.32	0.32	0.44	0.20	0.14
Al ₂ O ₃	5.63	2.28	3.88	5.77	6.09	8.77	3.05	1.59
Fe ₂ O ₃	5.78	2.14	6.04	7.02	4.45	4.96	6.51	0.97
CaO	42.36	57.36	34.79	30.56	33.18	23.67	29.27	56.75
MgO	4.01	1.96	5.46	4.88	3.81	5.26	7.71	1.18
K ₂ O	0.82	0.18	0.55	0.74	0.84	0.90	0.45	0.18
Na ₂ O	0.33	0.07	0.29	0.41	0.51	0.74	0.26	0.16
P ₂ O ₅	0.08	0.08	0.07	0.07	0.09	0.07	0.06	0.03

Mineral-2θ

Ettringite-9.09	ns	ns	2.3	2.5	3.3	3.4	2.3	ns
Ettringite-15.8	ns	ns	1.8	2.2	2.6	3.0	1.8	ns
Ettringite-22.9	ns	ns	2.1	2.7	3.2	3.9	2.2	ns
Ettringite-35.0	ns	ns	2.2	2.8	2.7	4.1	2.1	ns
Gypsum-11.6	ns	ns	6.2	3.4	2.1	2.4	4.2	ns
Gypsum-20.7	ns	ns	3.3	2.8	1.9	2.0	2.5	ns
Lime/Et-32.2*	4.8	7.0	2.5	2.9	2.6	3.6	2.3	ns
Gypsum-29.1	ns	ns	5.0	4.5	2.7	3.0	4.0	2.1
Calcite-29.4**	ns	ns	3.3	3.5	3.2	4.2	4.1	1.7
Port-18.1	ns	ns	4.2	3.0	3.4	ns	4.6	28.7
Port-34.1	ns	2.7	9.0	6.2	7.2	2.2	7.2	20.7
Anhyd.-25.4	7.0	4.5	ns	ns	ns	2.0	ns	ns
Calcia-36.0	8.2	12.3	2.1	2.1	1.9	2.3	3.0	ns
Quartz-26.7	4.4	ns	3.8	4.8	4.3	5.6	4.4	ns
Calcite-39.4	ns	ns	1.7	1.9	1.7	2.1	1.9	ns

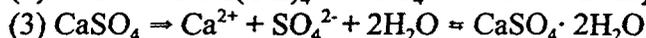
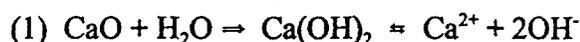
*Significant peak overlap occurs between Lime and Ettringite **Significant peak overlap with Gypsum.

Table 1a. Chemical and Mineralogic Data for Study Samples 1 Month or Less in Age. Chemical and LOI Data is on a Weight Percent Moisture Basis. Xray Data is as Peak Height Ratioed to Background Values. Must be >1.6 to be Considered Significant, Major phases are Bolded.

Sample #	FU-8C	FU-6C	FU-7C	FU-12C	FU-13C	FU-11C	FU-10C
Age	12 months	22 months	22 months	16 months	16 months	26 months	26 months
Type	bed ash	fly ash					
Location	surface	surface	subsurf.	subsurf.	subsurf.	surface	subsurf.
<i>Chemistry</i>							
Ash	81.72	74.20	75.60	80.27	72.83	74.09	79.49
LOI	17.07	21.61	16.56	17.05	31.84	20.97	16.39
SO ₃	20.54	11.94	8.69	12.63	11.76	11.00	11.44
CO ₂	5.00	24.56	22.50	14.05	13.99	14.34	10.94
SiO ₂	7.32	24.05	26.91	19.30	26.28	27.33	26.66
TiO ₂	0.13	0.35	0.45	0.27	0.43	0.45	0.46
Al ₂ O ₃	2.63	7.24	8.58	6.68	8.34	8.37	8.09
Fe ₂ O ₃	2.08	5.13	5.27	4.84	4.18	4.38	4.52
CaO	40.93	30.40	27.22	36.29	24.43	27.33	30.82
MgO	1.37	0.79	1.13	0.59	1.47	1.18	1.57
K ₂ O	0.20	0.23	0.91	0.40	0.73	0.90	0.62
Na ₂ O	0.29	0.16	0.48	0.24	0.46	0.58	0.43
P ₂ O ₅	0.09	0.09	0.09	0.11	0.09	0.08	0.09
<i>Mineralogy</i>							
Ettringite	2.4	3.5	3.9	3.5	4.0	3.7	2.6
Ettringite	1.9	2.3	2.9	3.4	3.4	3.5	2.4
Ettringite	2.0	3.3	3.8	4.1	4.3	4.0	1.7
Ettringite	2.0	2.1	2.7	4.5	4.7	5.3	5.2
Gypsum	12.3	2.6	ns	ns	ns	ns	ns
Gypsum	4.5	2.9	ns	ns	ns	ns	ns
Lime/Etrr.	2.5	2.0	2.4	4.1	4.1	4.7	4.6
Gypsum	7.5	5.1	2.7	2.4	2.8	4.5	3.8
Calcite	2.7	8.3	7.5	3.4	3.1	3.9	4.8
Portlandite	7.8	ns	ns	3.1	1.7	ns	ns
Portlandite	12.8	ns	ns	6.6	2.1	2.4	2.2
Anhydrite	ns	ns	1.7	2.2	2.2	2.5	2.3
Calcia	ns	ns	ns	ns	1.8	1.8	1.8
Quartz	ns	5.0	5.2	3.4	4.8	4.7	3.4
Calcite	ns	3.2	3.0	ns	1.7	2.0	2.2

Table 1b. Chemical and Mineralogic Data for Study Samples 12 Months or More in Age. See Caption for Table 1a for Further Description.

gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$) and minor calcite. Thus early reactions consist of the hydration of free lime (1) and its dissolution to form a highly alkaline solution, the formation of ettringite (2), and the formation of gypsum (3); or



Anhydrite is an orthorhombic mineral and is much denser (2.98 g/cm^3) and more soluble ($K_s = 4.2 \times 10^{-5}$) than gypsum (2.32 g/cm^3 and $K_s = 2.4 \times 10^{-5}$) which is a monoclinic mineral. Thus, the anhydrite-gypsum transition probably does not occur in the solid state, but anhydrite first dissolves and gypsum forms as a precipitate. This makes gypsum a mobile phase which has been found to form anywhere, rapidly filling cracks and crevices.² The formation of ettringite is a competing reaction to that of gypsum. However, it also requires alumina and hydroxide ions to form. It is typically found on, or near, coal ash particles, which are its source of alumina.

The ideal stoichiometric form of ettringite is $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$. Stoichiometric ettringite, however, is an artifact of the laboratory, and in nature it typically is highly variable in composition. Another important member of the ettringite family is thaumasite, $\text{Ca}_6\text{Si}_2(\text{SO}_4)_2(\text{CO}_3)_2(\text{OH})_{12} \cdot 24\text{H}_2\text{O}$ which contains silica in substitution for some of the alumina and carbonate for some of the sulfate. It is now believed by some that thaumasite and ettringite form a solid solution series.³ The structure of ettringite is complex, and perhaps the best definitive work was by Moore and Taylor who determined that ettringite had a trigonal hexagonal unit cell which consists of columns which have the composition $(\text{Ca}_6[\text{Al}(\text{OH})_6]_2 \cdot 24\text{H}_2\text{O})^{6+}$ which are aligned along the crystallographic c-axis (Al^{+3} ions are octahedral coordinated by $(\text{OH})^-$) and are accompanied by channels of the composition $(\text{SO}_4)_3 \cdot \text{H}_2\text{O}^{6-}$.⁴ This remarkable structure provides a high degree of flexibility for substitution of cations within the structure as well as the wholesale substitution of anionic complexes. This characteristic has attracted much research, and ettringite and the members of its family appear well suited for waste stabilization.^{5,6,7,8,9,10}

Ettringite is found to form rapidly, as it is an important mineral in the 1 day and 1 month old samples to the point of being a dominant phase in sample FU-4C. The rapid formation of ettringite has also been observed in laboratory experiments. Schwiete and Niel investigated the growth of ettringite crystals from solution and reported that ettringite formed as early as 30 seconds after hydration, and needle-like crystals could be identified after only 4 minutes.¹¹

Mikhail and Abo-El-Enein suggested, based on XRD analyses of early ettringite, that after 1 day of hydration, the intensities of ettringite peaks increased while those of the reactants tricalcium aluminate and CaSO_4 decreased.¹² At higher reaction temperatures (60°C), characteristic peaks for ettringite appear as early as 15 minutes after hydration. Muhammad, et al. found that a highly defective, but clearly identifiable ettringite formed within 3 minutes of hydration, and a fully developed ettringite in as little as 80 minutes.¹³ Thus the early rapid formation of ettringite is not surprising.

The X-ray data indicated that the best consolidated, most rock-like of the study samples, FU-4C and FU-13C had the most extensive ettringite formation. The critical role of ettringite as an important cementitious constituent has been also documented in laboratory experiments.¹⁴

Long Term Mineral Transformations and Weathering There are several important longer term reactions which are identifiable by examining the older samples. These are a substantial decrease in the quantity of gypsum and portlandite, which with two exceptions, essentially disappears, and an increase in the relative amount ettringite accompanied by a substantial increase in calcite.

Thus ettringite continues to form in the materials at the expense of both gypsum and portlandite. Gypsum is present in measurable quantities in two of the older samples, FU-8C, where it is present in abundance and FU-6C. Both of these samples also have lower ettringite contents and FU-8C has abundant portlandite as well. Ettringite formation is clearly limited by the low concentration of Al_2O_3 in this sample (2.63%). The development of ettringite is found to be generally limited by alumina availability, as a strong correlation is found between normalized X-ray intensities and alumina concentration (Figure 1).

The amount of calcite present as determined by both X-ray and TGA in the older samples is also found to be much higher (Figure 2). The hydrated fly ash samples had an average of 6.7% CO_2 versus 16.7% in the fly ash samples older than one year. Thus atmospheric CO_2 is a major reactant in the system. At very high pHs, i.e. ~12, such as developed by a solution saturated with $Ca(OH)_2$, CO_2 is readily absorbed, reacts directly with the hydroxide (4) and disassociates to the carbonate ion:



The carbonate and calcium ions form calcium carbonate, which is highly insoluble at an elevated pH.

The data (Table 1) indicates that, in the longer term, calcite is replacing gypsum (5),

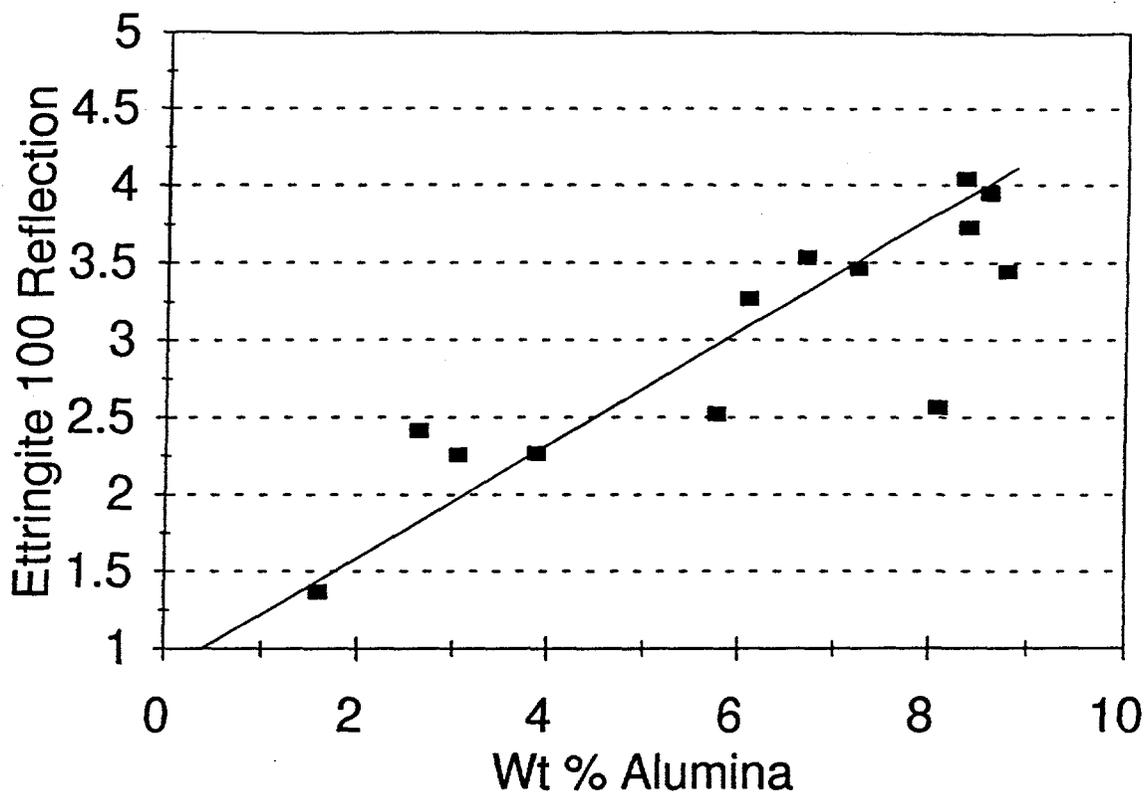
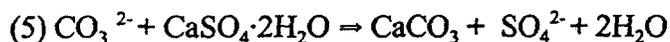


Figure 1. Plot of Al_2O_3 Concentration Versus Normalized Ettringite 100 Peak ($9.0^\circ 2\theta$) Intensity.



which all but disappears in the older samples. This is not unexpected, as under highly alkaline conditions and atmospheric partial pressures of carbon dioxide (PCO_2) calcite is less soluble than gypsum.

The above reaction is also supported by a general decrease in sulfate concentration concomitant with an increase in carbonate concentration. For example, in the 5 freshly hydrated fly ash samples the average SO_3 content was 14.1% (range 11.6 - 17.2%) and the average CO_2 to SO_3 ratio was 0.5 (range 0.3 - 0.8). In the six fly ash samples older than one year, the SO_3 content averaged 11.2% (range 8.7 - 12.6%) and had an average CO_2/SO_3 of 1.5 (range 0.95 - 2.6).

The data indicates that ettringite is highly stable in the weathering environment, as the X-ray spectra indicates that it is present in abundance in all of the older samples. The most severely weathered sample, FU-10C, falls farthest off of the Al_2O_3 -ettringite curve, contains no

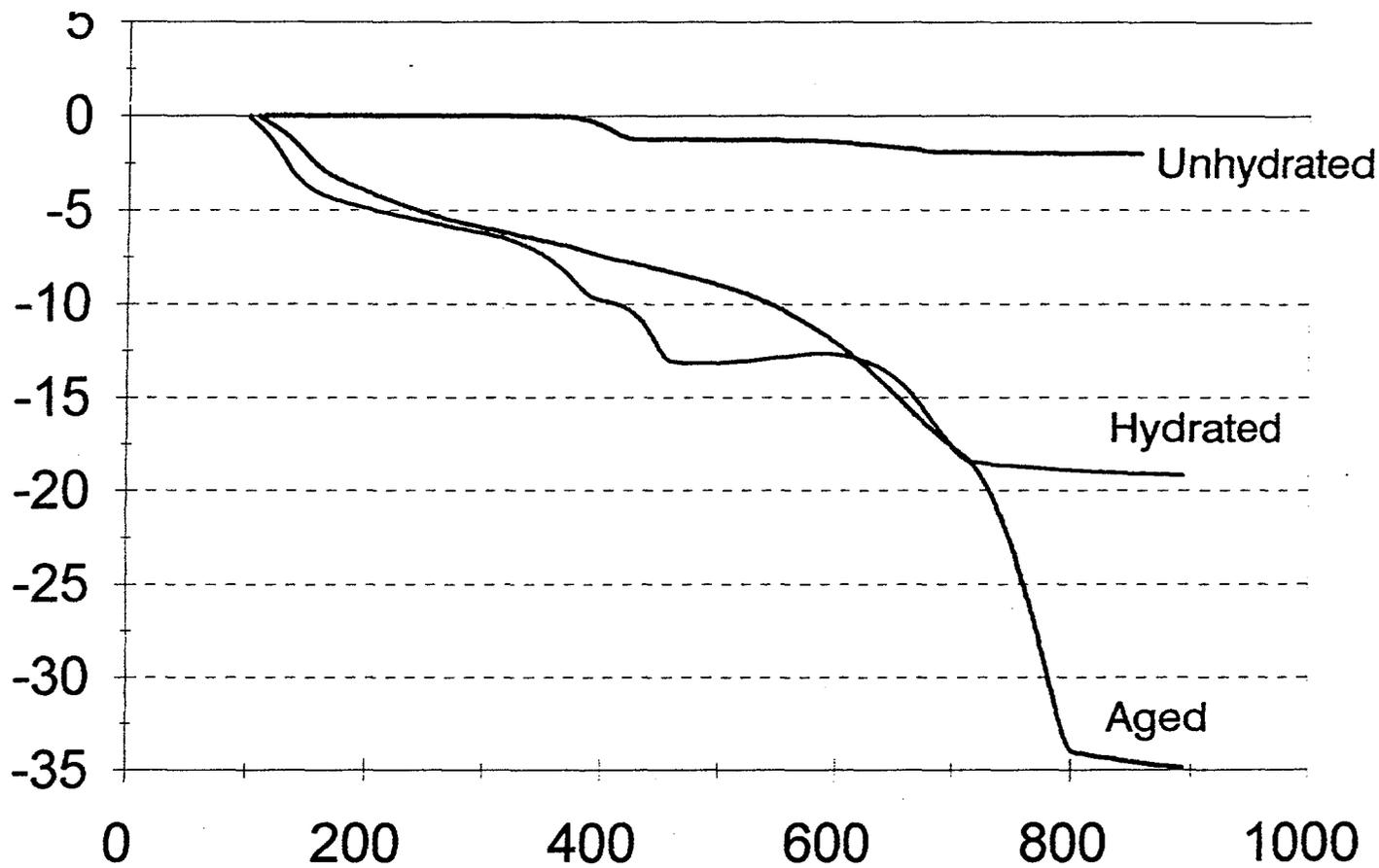


Figure 2. TGA Records of Unhydrated (FU-14C, Uppermost Curve), Freshly Hydrated (FU-3C, Middle Curve) and Hydrated and Aged (FU-6C, Lower Curve) FBC Fly Ash Material from Freeman United Disposal Area.

gypsum and does show some attenuation of the ettringite peaks relative to the other samples. Thus, the ettringite in this sample may have undergone some weathering induced decay.

Although the examination of the fresh samples suggests that the bulk of the anhydrite rapidly reacts to form other minerals, some proportion of it appears to be very slowly reactive. Most of the older samples had some proportion of anhydrite still present. The persistence of anhydrite, even in highly weathered samples, indicates that a proportion of it is either non-reactive or very slowly reactive.

The data of this study does not provide information as to whether ettringite breaks down to form thaumasite during weathering. The X-ray spectra for both minerals are similar and the only substantially different peak (211 thaumasite reflection) is masked by a strong quartz peak at this angle. Quartz is ubiquitous in these samples. The authors also do not believe that the morphologic differences observed for these minerals by SEM are sufficiently reliable to be truly diagnostic.

Conclusions

- The hydration of the AFBC material results in the rapid development of portlandite, ettringite and gypsum and the loss of calcia (lime) and anhydrite.
- The cementitious reactions are completed early and the strength of the material is related to the amount of ettringite formed.
- The ultimate concentration of ettringite was controlled by the availability of alumina.
- The hydrated FGD materials undergo extensive carbonation reactions which result in high concentrations of calcite.
- Calcite formation takes place initially at the expense of gypsum.
- Total sulfate concentration of the samples decreased with weathering induced carbonation. Ettringite appears to be remarkably stable in the weathering environment and does not break down until after gypsum is replaced by calcite.
- The loss of strength in the materials is a function of carbonation reactions and not the rapid breakdown of ettringite.

TASK 4.0 BACKGROUND FOR PHASE II

Subtask 4.1 Mine Selection

The mine site is in the south-central section of the Pikeville quadrangle, Pike County, Kentucky. Figure 3 shows the location of the backfill site on an enlarged topographic map. The mine will be developed in the Middle Pennsylvanian Breathitt Formation Middle Amburgy coal bed, a coal previously mined by Costain elsewhere on the property. The coal bed in a company

borehole in the ridge which will be mined is slightly over 3 feet thick. The immediate roof is a sandy fireclay (7 inches) overlain in succession by over 12 feet of sandstone, 3.5 feet of gray shale and underclay, and the 2.5 foot Upper Amburgy coal bed followed by the Kendrick shale (a generalized stratigraphic section is shown in Figure 4). The sandstone above the Middle Amburgy appears to be present throughout the ridge to be highwall mined. The Middle Amburgy coal bed from the latter core has 7.76% ash and 1.09% sulfur (dry basis). The Upper Amburgy has 19.25% ash and 9.73% sulfur (dry basis). While the Upper Amburgy is typically a high sulfur coal, the latter analysis is atypically high for the study area. The actual mine site will not be exposed until the first quarter of 1996. Detailed sampling of the coal and roof rock will be undertaken at that time.

TASK 4.0 BACKGROUND FOR PHASE II

Subtask 4.2 Hydrologic Monitoring Plan

Introduction Last year the study team began to investigate hydrogeologic conditions and ramifications of disposing of FGD materials at a potential site. Studies included preliminary core drilling for stratigraphic control, packer injection testing to determine intrinsic permeability in strata of various lithologies, and design of a monitoring-well network to assess the ground water flow system prior to, during, and after mining and emplacement of FGD material. Unfortunately, the site became unsuitable for further consideration due to safety reasons associated with the weathering and erosion of the highwall into which the mining was to have taken place.

At present, the suitability of the replacement site (Costain Coal Company's mine in Pike County) for field monitoring is in question. Because of the uncertainty of establishing a suitable field site to conduct pre- and post-backfill monitoring within the current project term, our research thrust will focus on theoretical issues concerning the effects of the mining and backfill activity on the ground water and surface water.

Concerns There are three major concerns about the effects of the mining activity: changes in the ground water flow field, changes in ground water quality, and consequential induced changes on stream flow. Highwall mining will generally take place in upland areas where recharge to the ground water system occurs. The aquifers in this portion of the flow system are generally the near-surface fracture system, the coal seams, permeable sandstone units, and major fracture systems that cut across the stratigraphic units. Preferential ground water flow pathways may be created, at least temporarily, by the adit excavated during the mining process, at the interface between the emplaced FGD material and the bedrock, and by fractures in the FGD material after induration has occurred. On the other hand, the indurated FGD material may become a significant artificial aquitard.

These changes in the physical framework could have the following effects on the hydrologic system:

- damming effect where the FGD material has a lower intrinsic permeability than the surrounding rocks.

- draining effect where the FGD material or its interface with the encompassing bedrock have a higher intrinsic permeability than the surrounding rocks.
- no change if the cumulative factors create an intrinsic permeability that is equal to the existing system.

Potential Hydrologic Ramifications

There are many scenarios of potential change in water quality and quantity that can occur at a given site based on the above conditions. Serious problems may arise if the mining area covers hundreds to thousands of acres, particularly when this activity takes place in the recharge portion of the hydrologic system. General ramifications include:

- change ground water flow divides that can impact water budgets to contiguous watersheds.
- change location of discharge points for the ground water systems that can impact specific geographic areas.
- concentrate or diminish discharge at original and new geographic areas over time.
- raise or lower the hydraulic head or water table in the ground water system.
- create instability in land masses at and away from the highwall due to concentration of ground water flow at particular discharge areas.
- impact the ground water and, consequentially, the surface water quality in adjacent watersheds.

This last ramification has several general major implications that should be considered prior to implementing a full-scale operation.

These are:

- concentration of ground water flow along the FGD-coal interface may lead to continued chemical weathering and erosion of FGD material, or the sealing of the interface by chemical precipitation of minerals.
- re-routing of ground water flow into previously oxidized but unsaturated areas may create acid-mine drainage through mobilization of products of oxidized pyrite.
- chemical leaching of FGD material could generate increased concentrations of TDS, sulfate, calcium, chloride, and arsenic and selenium if high pH conditions occur in the ground water flow system.

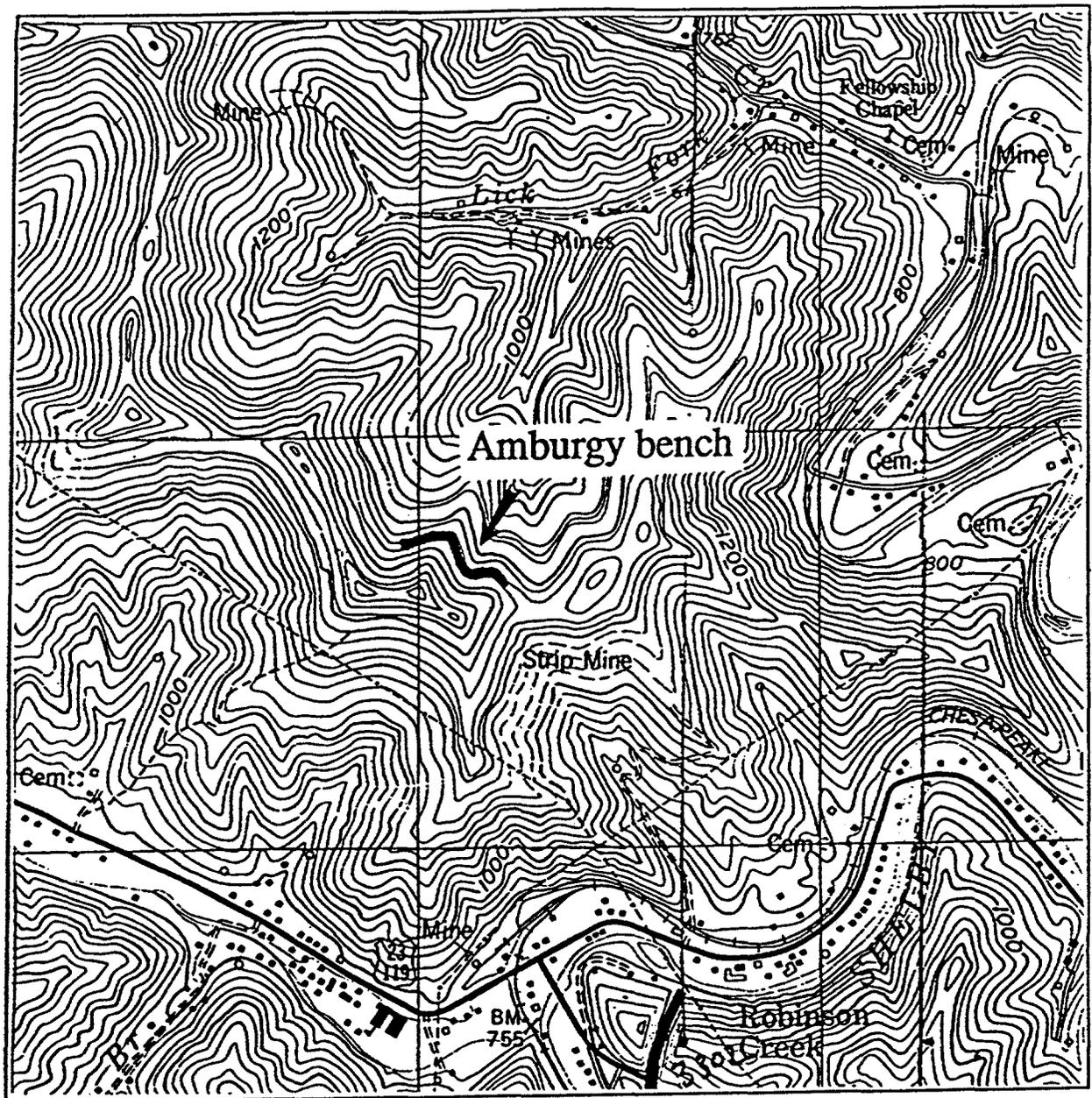


Figure 3. Topographic Map of the Study Area. The Proposed Mine Site is Located on the Pikeville 7.5 Minute U.S.G.S. Quadrangle.

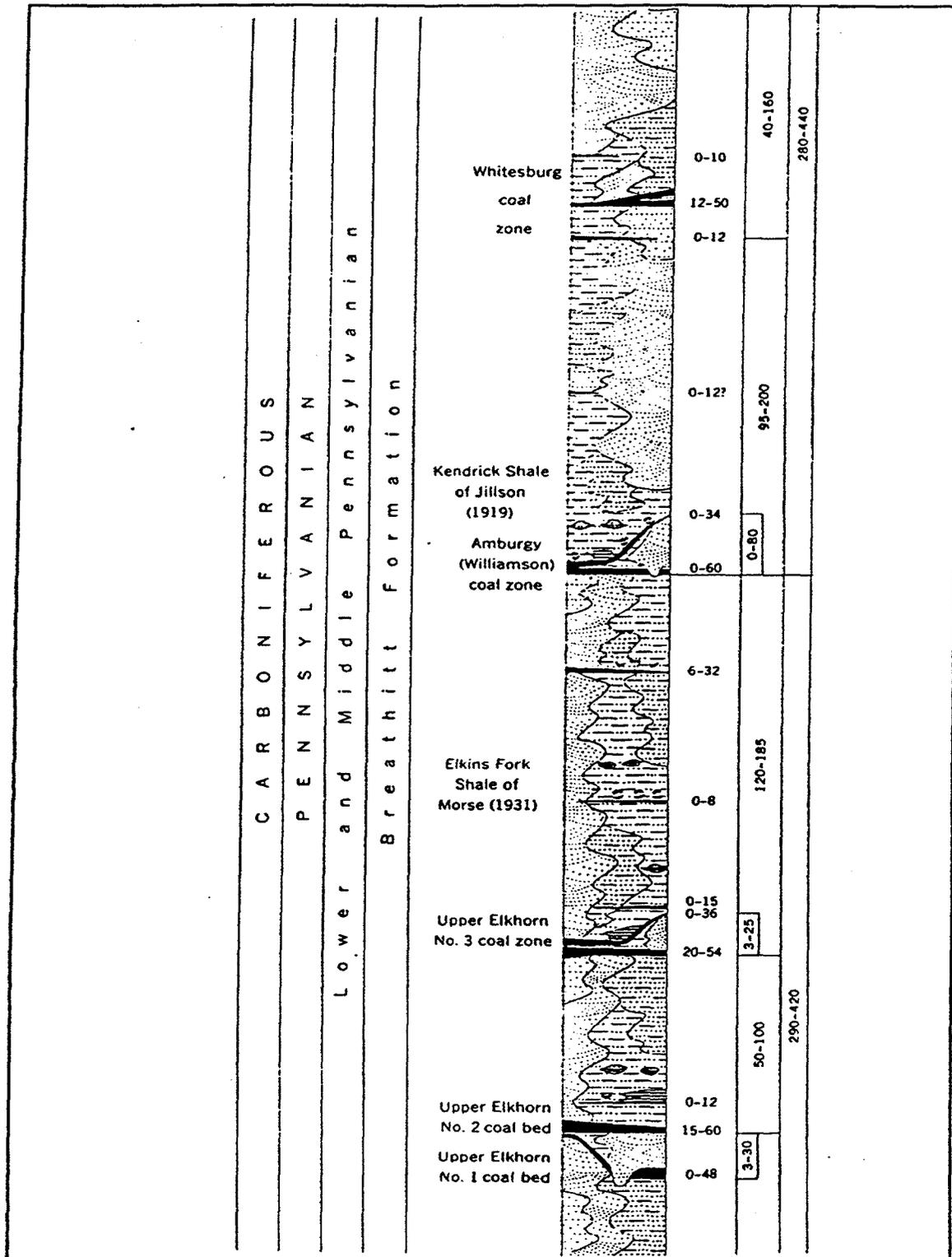


Figure 4. Geologic Section of the Robinston Creek Area. Alvord and Holbrook, 1965, *Geologic Map of the Pikeville Quadrangle, Pike and Floyd Counties, Kentucky*, USGS Map, GQ-480.

- high alkalinity conditions generated by FGD material should not necessarily be considered a solution to acid-mine drainage due to the potential increase in sulfate concentrations in the resulting leachate.

Summary The above issues are general considerations that need specific research to address. This research should be designed to not only characterize short-term effects which may significantly alter the hydrologic system, but it should be continued for a considerable length of time so that long-term effects can be distinguished and their impact on the environment can be analyzed. Determination of this long-term effect is important if the coal and power industries are to continue to economize their operations in a manner that is environmentally acceptable.

Under the current project timetable and field site difficulties there is inadequate time or resources to collect data from a field site to characterize baseline ground water conditions and post-backfill changes that may occur. The feasibility of using geochemical and hydrogeochemical models to assess potential interactions between the FGD material and ambient typical ground water that would be expected in the shallow fracture and coal-bed flow system is currently being investigated.

TASK 4 BACKGROUND FOR PHASE II

Subtask 4.3 Selection and Testing of Transport System

Laboratory Scale Pneumatic Emplacement Test Unit Results

Overview. A laboratory scale transport system has been built at the CAER to evaluate the potential of pneumatic transport for flue gas desulfurization material (FGDM) emplacement and to provide essential data for the mine emplacement demonstration. The system is modeled after shotcreting systems in which water is mixed with cement (FGDM) in a nozzle at the end of the pneumatic pipe. The advantage of a pneumatic system for this application is that the material can be remotely placed without the need for forms. Solids travel approximately 70 ft in the lab-scale system at a rate of up to 6 lb FGDM/minute prior to impingement onto a sample collector. The test program is focusing on determining the pneumatic conditions necessary to maximize the strength of the emplaced FGDM under anticipated mine curing conditions while minimizing dust formation.

System Description. The source of pneumatic air for the emplacement test unit (ETU), Figure 5, 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 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 FGDM 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 pneumatically transferred over a distance of 70 ft within 2-inch schedule-40 steel pipe which is covered by 0.5 inch of foam 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. 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 FGDM shotcrete is evenly distributed over the sample panel. A thermocouple is placed through the bottom of the sample panel at its midpoint 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 inch in diameter) in the pipe.

Experimental Plan. The basic goal of the experimental plan is to evaluate the performance of FGDM as a function of shotcreting parameters so that the requirements for the mine demonstration technology can be specified. Once the important shotcreting parameters are determined for the FGDM, a robotic vehicle based on state-of-the-art mining technology can be fitted with a shotcrete nozzle for remote emplacement. While any new material to be considered for shotcrete emplacement must be experimentally evaluated, the high free lime (CaO) content of most FGDM's makes testing doubly important. Substantial amounts of heat are generated during the hydration of CaO to form $\text{Ca}(\text{OH})_2$, promoting safety concerns. In addition, 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 sample pellets was improved. The experimental 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 FGDM 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 (i.e. less dust liberation). The primary parameters to be evaluated during the test matrix are: 1) Water/Solid/Air Proportions, 2) Use of Pre-wetting Water at Blower Inlet, and 3) State/Composition of Solids (non-prehydrated, prehydrated, fly ash admixtures, etc.).

For each test, a full hopper (0.86 ft³) of FGDM will be used. Complete mass balances will be impossible to achieve because the system is not closed, permitting the escape of dust and mist. However, as discussed later, estimates have been made of mist and dust that remain airborne after impingement of the jet on the surface. 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 analyses.

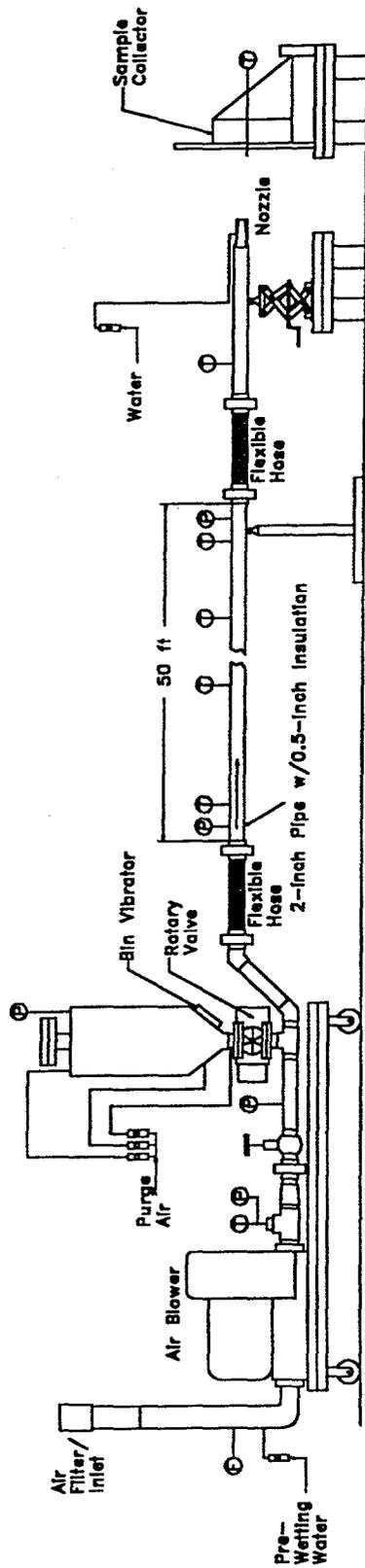


Figure 5. Schematic Diagram of the Pneumatic Laboratory-Scale Emplacement Test Unit (ETU).

Nozzle Optimization. Shotcreting involves the creation of a turbulent jet of air that contains a mixture of solids and water mist. Ideally, the jet impinges on a surface, and particle-free air exits parallel to the surface, leaving the water and solids behind. In reality, however, a significant amount of water and solid particles remain airborne. A study was performed to determine the amount of mist loss as a function of air velocity and distance of the nozzle to the collection surface. While these water-only experiments may not be truly representative of the solid-water mix that remains airborne, it should at least indicate the trends that can be expected for these parameters. During these experiments, water at a rate of 15 gal/hr was injected into the nozzle. The air/water jet then impinged onto a flat plywood surface mounted vertically so that all the water that adhered to the surface would drain into a container. The water collected compared to the amount injected into the air jet was defined as the percentage of water capture, Figure 6. The best results were obtained for the higher velocity runs (362 ft/sec) at a distance of 4 ft. between the collector and the nozzle. These results will be used for the remainder of the study.

Production of FGDM Shotcrete Samples. Several slabs of FGDM shotcrete, up to 3 inches in thickness, have been successfully prepared to date. Prehydrated FGDM was utilized to avoid the complications associated with free lime hydration. The FGDM adhered to the vertically positioned plywood without slumping. The samples exhibited stiffness immediately upon deposition suggesting a consistency that, in larger volumes, would be advantageous for bulk fill applications. The slabs are being cured for chemical and physical analyses.

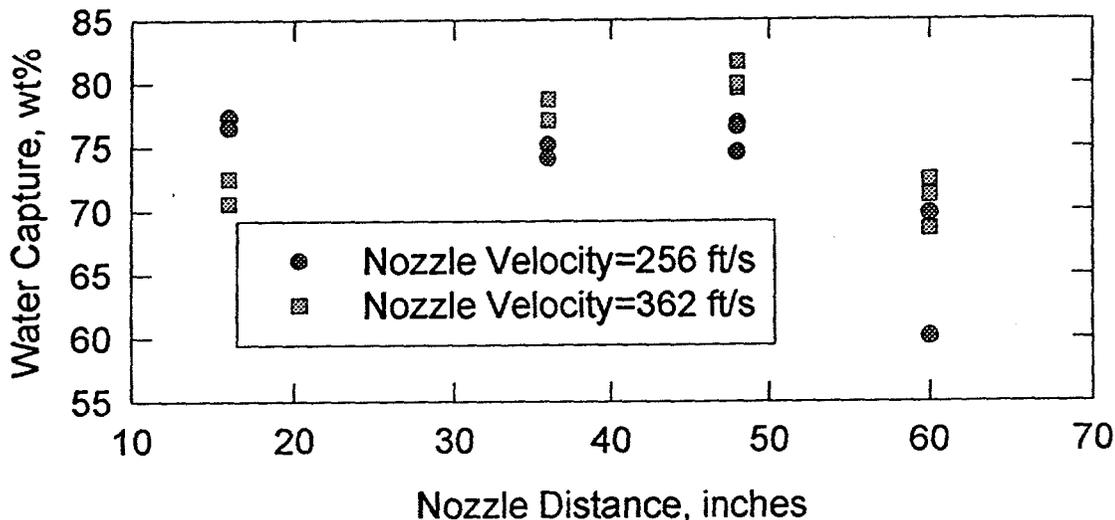


Figure 6. Results of Nozzle Optimization Study Using Water Capture as a Measure of Performance. Water Flow Rate is 15 gal/hr.

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