CHARACTERISTICS OF PNEUMATICALLY-EMPLACED DRY FLUE GAS DESULFURIZATION MATERIALS

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ABSTRACT

The University of Kentucky in collaboration with the Department of Energy, Addington, Inc. and Costain Coal is currently developing a commercial concept for the haul back of dry flue gas desulfurization materials (FGDM) into highwall mine adits. The University's Center for Applied Energy Research (CAER) is investigating emplacement systems for a mine demonstration which is planned for the third quarter of 1996. A laboratory-scale transport system has been built at the CAER to evaluate the potential of pneumatic transport for FGDM emplacement. 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. 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. Prehydrated FGDM from a circulating fluidized bed combustor has been successfully emplaced onto vertically positioned sample surfaces without excessive dust liberation. The test program is focussed on determining the pneumatic conditions necessary to maximize the strength of the emplaced FGDM under anticipated mine curing conditions while minimizing dust formation. The mineralogy and strength of a pneumatically created sample are described following curing for 60 days.

INTRODUCTION

An important potential advantage of the FGDM haul-back concept for a highwall mining company is that 100% coal recovery is possible. Current highwall techniques must leave behind a structural web of coal, recovering approximately 65 to 75% of the resource. By leaving coal webs equivalent to the width of the mining head, it is possible with the haul-back scheme to fill the empty adits with FGDM and then mine the remaining coal web by using the hardened FGDM for structural support. This concept requires that the emplaced FGDM be sufficiently strong to provide support during the second phase of coal mining. The overall strength of the emplaced FGDM depends not only on its physical properties but also on the efficiency of emplacement. A relatively strong material is useless in this application if only, say, 75% of the adit is filled. Therefore, an essential characteristic of the emplacement technology for this haul-back concept is high fill efficiency. Another essential feature is that the material must be emplaced remotely because no worker should ever be required to enter a highwall mine with an unbolted roof. It is almost certain that roof bolting, accompanied by some amount of manual emplacement, would not be economically feasible.

A pneumatically-based system was chosen for initial consideration in this project because of the potential of shotcrete technology to completely fill the mine adit without forms. Hydraulic backfill of highwall adits is difficult because the adits are normally horizontal and slump prevents fill to the ceiling. With pneumatically-based (shotcrete) technology, however, concrete can be applied to vertical and even overhead surfaces, making it ideal for underground tunnel support. A prime example is its use in portions of the Metro subway system in Washington, D.C. For underground mining environments, Krantz found that shotcreting was successful in sealing, preventing spalling, and providing roof stability.[1] The ability to remotely line tunnels and shafts using shotcrete technology has also been demonstrated.[2,3] A disadvantage of shotcrete technology is that its production rates are relatively low compared to hydraulic concrete emplacement methods. Shotcreting has been primarily used for lining applications and not for bulk filling. However, it has been reported that a hybrid shotcreting system, the "Blastmixer," is capable of placing 50 tons of concrete per hour using large volumes of low-pressure air.[4]

EXPERIMENTAL

<u>System Description.</u> The source of pneumatic air for the emplacement test unit (ETU), Figure 1, is a vortex blower with a capacity of 220 ft^3/min @ 0 psig and 50 ft^3/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 tstream of the blower. The temperature and pressure are mea 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 ft^3 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 inches 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 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.

Testing Objectives. The basic goal of the experimental plan is to evaluate the performance of FGDM as a function 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 many types of FGDM makes testing doubly important. Substantial amounts of heat are generated during the hydration of CaO to form $Ca(OH)_2$, promoting concerns about ignition of the coal seam and about possible steam explosions during emplacement. In addition, hydration of FGDM containing free lime in excess water has been shown to decrease the strength of sample pellets.[5] By prehydrating the FGD material with only enough water to hydrate the CaO, the strength of sample pellets following subsequent hydration was increased. 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). For this paper, the FGDM was prehydrated prior to pneumatic transport. While a fundamental goal of this effort is to optimize the workability of the material during emplacement, another important objective is to characterize the establishment of strength as a function of time. This paper examines the chemical and physical characteristics of a shotcrete sample produced from prehydrated FGDM after curing for 60 days.

X-Ray Diffraction Analyses. X-ray diffraction (XRD) analyses were performed on the prehydrated feedstock and on three samples of the cured FGDM slab 60 days after emplacement. Cu Kα radiation from 7° to 40° (63° for the feedstock) 2θ at 0.1° increments was utilized. Crystalline phases were identified using the JCPDS file on CD-rom. Samples were ground with a mortar and pestle prior to analysis.

Material Studied. Fly ash from the Archer Daniel Midland (ADM) co-generation plant in Decatur, Il. was used in this study. The plant utilizes circulating fluidized bed combustion (CFBC). Freeman United Mining Co. disposes of the FGDM at its Crown III facility in Farmersville, Il. The sample was collected in air-tight plastic drums upon arrival at the Freeman United facility. The FGDM was prehydrated at a weight ratio of 1 part water to 10 parts FGDM. This ratio was determined from previous work to slake the free lime without initiating cementitious reactions. The following minerals comprised the majority of the crystalline phases of the prehydrated FGDM as determined by XRD: anhydrite ($CaSO_4$), portlandite ($Ca(OH)_2$), quartz (SiO_2), hematite (Fe_2O_3), magnetite (Fe_3O_4), calcite ($CaCO_3$), periclase (MgO), and lime. In addition to these major minerals, ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$) and gypsum ($CaSO_4\cdot 2H_2O$) were identified in minor amounts.

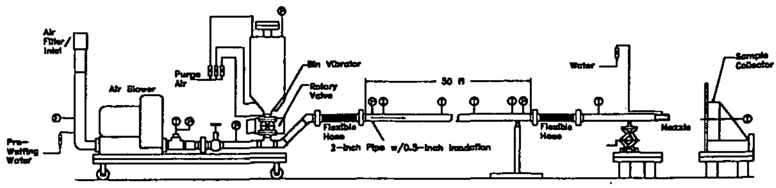

Figure 1. Schematic diagram of the pneumatic laboratory-scale emplacement test unit (ETU).

From this analysis it was determined that the free lime was almost completely converted and that cementitious reactions had not occurred to a significant degree. Therefore, it was confirmed that an optimal quantity of prehydrating water had been utilized.

RESULTS AND DISCUSSION

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 and could be measured. The best results, approximately 80% retention efficiency, were obtained for the higher air velocity runs (362 ft/sec) at a distance of 4 ft between the collector and the nozzle. These conditions were used for the production of the shotcrete sample studied in this paper.

Production of FGDM Shotcrete Samples. For each test, a full hopper (0.86 ft^3) of dry FGDM is used. Complete mass balances are impossible to achieve because the system is not closed, permitting the escape of dust and mist. However, as discussed previously, it is estimated that 80% of the particles and droplets in the air jet are retained on the sample collector under the conditions of this study. Several slabs of FGDM shotcrete, approximately 3 inches in thickness and 1 foot in diameter, have been successfully prepared to-date. The pneumatically emplaced FGDM adhered to the vertically positioned plywood without slumping. The FGDM/water mixture exhibited stiffness immediately upon deposition suggesting a consistency that, in larger volumes, would be advantageous for bulk fill applications without the need for forms. For the FGDM shotcrete sample that is the focus of this paper, a water/FGDM ratio of 0.45 was utilized. This ratio was chosen because it was shown during previous tests to provide the best emplacement results. A relatively high water addition rate is beneficial because it reduces dust formation and it gives the material good workability for even deposition. Excessive water is squeezed out of the sample because of the force of the impingement. Therefore, the moisture content of the sample immediately after emplacement was likely lower than the 0.45 water/FGDM ratio that was produced in the nozzle. Moreover, the water content of freshly deposited shotcrete is not a highly variable parameter because the water content tends to be self regulating for the range of water addition rates that produce good shotcrete consistency.

Immediately after formation, the sample slab was covered with damp cloth and then with plastic to prevent moisture evaporation without providing excessive water. For strength tests, 2-inch-long 1.4-inch-diameter cores were produced using a carbide-steel-tipped hole saw. The cores were then kept moist prior to testing.

Strength Development During Curing. Unconfined compression tests were performed on core samples at 20 and 50 days following emplacement. The 20 day strength was 200 psi, and the apparent density of the core sample was determined to be 1.47 g/cm^3. The strength at 50 days was determined to be greater than 650 psi. A more precise measure of the compressive strength at 50 days was not obtained because the testing apparatus was not set up for stresses greater than 1000 lb to be placed on the sample. An uncompressive strength of at least 500 psi will be necessary for the emplaced FGDM to prevent subsidence when the structural web of coal is removed during the second phase of mining. Previous work has shown that compressive strengths greater than 1000 psi are possible with these materials when the samples are formed and cured within a rigid container.[5] The present study has now confirmed that pneumatically emplaced FGDM will be able to develop sufficient strength for this backhaul concept.

Mineralogy of Cured FGD Shotcrete. A highwall coal mine adit can contain essentially no water, or it can be completely filled with water. Therefore, the amount of excess water that is available to the emplaced FGDM during curing can be quite variable. Curing of the slab of shotcrete was performed under conditions most closely related to a dry mine environment. This sample will be subsequently referred to as 'dry-cured' for simplicity, even though it was stored with some moisture present. A subsample of the main slab was removed after 7 days and completely immersed in water to simulate a water-saturated mine. Samples of the dry-cured and the water-immersed shotcrete were analyzed by XRD 60 days after pneumatic emplacement. To observe the change in mineral forms as a result of the hydration of the feedstock and the different curing environments, selected mineral peaks were standardized to the quartz {101} peak (Figure 2). By doing so, it is assumed that quartz remained unaffected by the curing condition and that quartz was not selectively eliminated or concentrated in the shotcrete during emplacement.

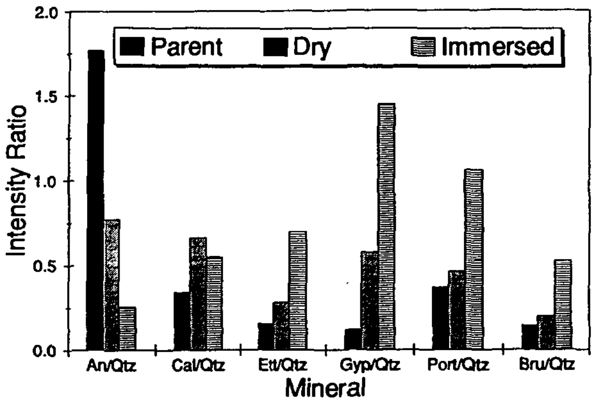

Figure 2. Comparison of major XRD peak intensities, normalized by quartz {101}, for the feedstock, dry-cured shotcrete, and water-immersed shotcrete samples.

The decreased abundance of anhydrite and corresponding increase in gypsum for the dry-cured sample compared to the feedstock (Figure 2) illustrates a major hydration reaction for this material. Other hydration reactions include the additional formation of ettringite, portlandite, and brucite ($Mg(OH)_2$). The formation of ettringite and gypsum are responsible for the strength that was shown to develop for the dry-cured slab. The amount of calcite was highest for the dry-cured sample because of contact with atmospheric CO_2. Continued hydration reactions were observed for immersed sample as illustrated by increased quantities of ettringite, gypsum, portlandite, and brucite. While the formation of additional ettringite can promote extra strength, the continued formation of gypsum from anhydrite by reaction with water that is diffusing back into the solid can reduce strength. Ettringite needles tend to fill pores which increase the density and strength of the FGDM cement. Gypsum also fills pores, but it can swell sufficiently to create cracks and decrease the strength of the solid. While no strength tests were performed for the immersed sample, it was obvious during sample preparation for XRD that the strength of the sample was diminished compared to the dry-cured sample. The formation of additional gypsum in the immersed sample may have been responsible for its reduced strength.

SUMMARY

Prehydrated FGDM from a CFBC was successfully emplaced onto a vertical surface by shotcrete technology. The strength developed by the dry-cured sample after 50 days was determined to be greater than 650 psi which is sufficient to support the mine roof during mining of the structural web of coal. The levels of ettringite and gypsum in the dry-cured sample were consistent with the strength which had developed. It appears that some decrease in strength can be expected for these materials if subjected to excess water during curing in an unconfined environment.

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