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

**Quarterly Report
April 1 - June 30, 1996**

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

Phase I: Laboratory Investigations

Cooperative Agreement No.: DE-FC21-93MC30251

Quarterly Report for the Period April 1, 1996 to June 30, 1996

Summary of Activity for the Quarter

The target for the project has been shifted from filling highwall mine adits to filling auger holes with FGD material to provide a stable highwall for automated highwall mining. As reported previously, this shift in emphasis is economically desirable and practical, as the filling operation is safer and permits access to "locked in" high quality coal behind existing auger holes. As also reported previously, the fill material was shifted from dry FGD materials to a Fluidized Bed Combustion fly ash from the Archer Daniel Midland No. 6 facility in Illinois. Previous reports have summarized the characterization of this material for the project. However, due mostly to economic concerns with prehydration and transport of the Archer Daniel Midland (ADM6) material, several new desulfurization by-products stored at the Costain facility in Allen, Kentucky were considered during this quarter.

At this stage of the project, the change in fill material required rapid assessment in much the same way an applied working project would demand quick evaluation. This change thus provided an opportunity to demonstrate a rapid assessment of material suitability. The results described below were obtained in a short time frame, and with the exception of characterizing the long term swell and durability of the products, the rapid assessment was a success. No rapid assessment methodology for long term behavior has been developed at this time.

The mineralogical characteristics of the two Costain materials will not be summarized in detail here. Unlike the ADM6 ash, the spray dryer and FBC materials currently under review do not include the large percentages of free lime (CaO) that was shown to cause high mixing temperatures in the nonprehydrated ADM6 product. This absence of free lime in the raw by-products is immediately evident when mixing with water, as no significant heating of the mixture is observed.

TASK 2. LABORATORY STUDIES

SUBTASK 2.3 Geotechnical Characterization

Environmental Conditions and Development of Strength and Swelling Response

Work by other researchers has shown that curing of the mixtures is accelerated at higher temperatures. This is logical, since reaction kinetics for crystal formation suggest typically higher reaction rates at higher temperatures. However, during curing, several mineral formation processes are occurring, and the rate at which minerals of a certain kind are formed can affect the geomechanical behavior of the resulting mixture. For example, it is well recognized that increased swelling typically corresponds to reduced strength. When swelling stresses exceed the bond strength in the matrix, the bonds are broken, leading to reduced strength. Conversely, if sufficient bond strength is present to resist swelling pressures, then little swelling occurs and increased strength is the result. This was demonstrated in the early stages of this project when it was shown that the strength and swell characteristics of a specific mixture could be dramatically altered by curing under different moisture conditions (submerged versus 80% relative humidity).

The presence or lack of moisture during curing affects reaction chemistry, while temperature affects reaction kinetics. If the kinetics of all significant mineral formation processes were similarly dependent on temperature, then higher curing temperatures can be used to accelerate curing, and rapid assessment of mix designs is possible after the effect of temperature on reaction kinetics is determined. Application of mine filling with by-products will depend on the rapid assessment of mix suitability, so increased curing temperature is a potentially powerful tool for this evaluation. However, if for example swelling kinetics are linearly proportional to curing temperature, while bonding kinetics are proportional to temperature to some power greater than one, then higher curing temperatures would result in higher early strengths and less swelling. The resulting mix design would predict higher strengths than are likely at lower temperatures. Further, some mineral formation kinetics may be adversely affected by higher temperature.

Ettringite growth in the curing product is a case in point. This group has theorized that early ettringite formation leads to strength enhancement due to crystal interlocking, but long term strength gain is reduced due to excessive ettringite formation that causes swell. Early swelling is also due to gypsum formation in the matrix. The processes leading to strength gain and swelling are likely dominated by these or other minerals and thus independent or perhaps interdependent crystal formation kinetics. Ettringite formation is impeded by high temperatures, so early strength gain due to ettringite formation is reduced, while long-term strength gain is enhanced, due to reduced ettringite growth at high temperatures. Of course, other mineral and gel formation kinetics also figure in both the strength gain and swelling. The resulting material properties will be a function of all these interacting kinetics.

In addition to temperature, particle size, matrix permeability, and reactant stability will affect the rate of formation of important crystals and gels. Water is a critical reactant in all

of the processes to provide both elements in the mineral formation and as a solvent to promote mineral changes. An understanding of the mineral kinetics provides a basis for controlling material properties to meet specific criteria for materials manufactured from FGD by-products. Similarly, careful selection or control of in situ placement conditions (such as winter versus summer curing) could favor certain desirable material properties. Essentially, if the crystal formation environment can be altered in some way to favor one process over the other, then the resulting material will have geomechanical properties reflecting the formation of the dominant mineral. Clearly, an understanding of the mineral processes that dominate certain material behavior, and the kinetics and chemistry of these processes, will greatly facilitate economic utilization of FGD by-products.

Assessment of Costain Spray Dryer Ash

One of the ash products stored at the Costain mine in Allen, Kentucky is a spray dryer ash. This ash is low in free lime and sulfates, with most of the sulfur being present as sulfite (SO_3) rather than sulfate (SO_4). The sulfite is less reactive in the formation of gypsum and ettringite, and thus swelling is reduced in the short term. There remains some question as to whether long term swelling is a significant risk with sulfite. The strength gain in some spray dryer materials has been reported to progress slowly at lower curing temperatures, as compared to other desulfurization by-products, but long term strength even at low temperatures is reported to be acceptable. The low free lime content eliminates a strong exothermic reaction upon water addition, thus avoiding the need for a prehydration step before final mixing. The potential for reduced swelling with moderate strength gain and no prehydration resulted in the selection of the Costain spray dryer material for assessment in the field study.

Effect of Curing Temperature on Costain Spray Dryer Strength. Consideration of the potentially differing mineral formation kinetics led to a brief study of the effects of curing temperature on the strength gain and swelling of the Costain spray dryer by-product. This could also potentially lead to an accelerated curing methodology to promote faster material assessment methods.

Twelve approximately 50 mm diameter by 100 mm tall cylindrical specimens were prepared in PVC molds for preliminary assessment of the Costain spray dryer by-product. Mixing water content was selected based on achieving a qualitative workability similar to that developed for the ADM6 by-product. The resulting mixture consisted of 32% water with 68% solids, by weight. Six of the specimens were submerged in a water bath at 13°C (55°F), while the other six were submerged in a water bath at 38°C (100°F).

For strength evaluation, consolidated undrained triaxial compression was selected at this stage. This was due to the ability to assess the pore pressure response in undrained compression and to provide confinement to potentially soft specimens in the early stages of curing. The test methodology was the same as that followed for undrained triaxial testing of the ADM6 material. During specimen preparation, back pressure saturation was used until B-value measurements exceeded 0.95. The specimens were then isotropically

consolidated to effective stresses of approximately 35 and 275 kPa (5 and 40 psi) to permit assessment of both friction and cohesion in the curing product. During shearing to failure, the specimens were maintained in an undrained state, so that volume change was not possible. The resulting pore pressure response to undrained shear thus caused changes in the effective confining pressure. Failure of each specimen was defined as being the point of maximum principal stress ratio, σ_1'/σ_3' .

Specimens from each curing temperature were tested in undrained triaxial compression as soon as visual and tactile inspection indicated they were sufficiently strong to survive removal of the PVC mold and mounting in a triaxial testing device. Two 38°C specimens were tested after 4 days and found to have an undrained triaxial deviator stress at failure (comparable to unconfined compressive strength) of approximately 480 kPa (~70 psi). The specimens cured at 13°C had not hardened sufficiently for triaxial compression testing until 24 days after mixing, and even then the undrained triaxial deviator stress at failure ranged only from 150 to 345 kPa (22 to 50 psi). This provides a clear indication of the acceleration of strength gain under higher temperatures for the Costain spray dryer ash. The results of the consolidated undrained triaxial compression tests on these specimens are provided in Figure 1. The data show that the strength gain rate (psi/day) at 38°C was on the order of 50 times the rate at 13°C.

All specimens tested showed strongly contractive behavior, resulting in high increases in pore pressure during shear and approximately zero confining stress upon failure. Thus, assessment of individual contributions of cohesion (interparticle bonds) and intergranular friction to the measured strength was not possible. Typical behavior of the specimens during shear are shown in Figure 2.

In the course of performing the strength testing, a series of vertical swell tests was also conducted on the material at 13°C and 38°C curing temperature. Over a 30 day period, none of the specimens exhibited significant swell.

Despite the rapid strength gain observed at 38°C, the very poor strength gain at 13°C, which is more representative of in situ temperatures, led to removal of the Costain spray dryer ash for filling in the field study.

Assessment of Costain FBC Fly Ash

In addition to the spray dryer ash, Costain is also handling FBC fly ash (FA) and bed ash (BA) at the field site. Both materials are offloaded from rail cars, and are often mixed in the same car even if they were independently loaded. The bed ash has a relatively free lime content. The heat and steam generation caused by this free lime has caused some difficulty with storing the material at the Costain facility, so a prehydration stage is used at the Costain mine to eliminate the majority of the free lime from the bed ash.

Representatives at the Costain facility have reported no significant heating has been observed upon wetting of the FBC fly ash. Samples of these ashes were collected for

Figure 1. Effect of curing temperature on deviator stress at failure for Costain Spray Dryer ash.

Figure 2. Typical consolidated undrained triaxial compression results for Costain spray dryer ash

assessment after elimination of the spray dryer ash from consideration. The samples were collected to assure separation of the fly ash and bed ash for independent evaluation.

Upon wetting in the laboratory, the reports from Costain field personnel were validated, as the fly ash showed no significant heating, while the bed ash generated excessive heat and steam upon water addition. Based on previous experience with the ADM6 bed ash, and upon concerns about the economics of adding a prehydration step into the placement process, the investigation focused on the Costain FBC FA. Discussions with field personnel indicated the ash loading sequence generally consists of partially filling the rail cars with bed ash, then covering the bed ash with the less reactive fly ash for transport. Thus, by careful unloading, it is possible to keep the BA and FA separate when preparing a mixture in a concrete truck.

Mix Optimization of Costain FBC FA. Following the testing sequence used for the Costain spray dryer ash, multiple specimens of the Costain FBC FA were prepared in PVC molds and cured at 13°C and 38°C. Strength testing was performed on these specimens when visual and tactile inspection indicated suitable strength to survive mold removal and test setup. The planned testing matrix would require testing 4 or more specimens in a single day to allow completion of the study on short notice. Only one or two triaxial compression tests can be set up and performed per day, while many unconfined compression tests are possible in a single day. Further, earlier studies had shown that most of the specimens of spray dryer and ADM6 materials tested in triaxial compression are strongly contractive, causing the pore pressure to dramatically increase during undrained shear so that the effective confining pressure upon failure is not much greater than zero, and usually very similar regardless of initial effective confining stress. It was thus decided to assess the strength of the FBC FA specimens using unconfined compression testing with careful measurement of the stress-strain response to permit accurate assessment of both strength and modulus. The unconfined compression results for specimens cured at 13°C (55°F) are shown on Figure 3. These findings indicate that for mixtures consisting of 32 to 35% water and 68 to 65% Costain FBC FA, 28 day unconfined compressive strengths on the order of 2760 to 3450 kPa (400 to 500 psi) can be achieved in the laboratory. Earlier in this project, a correlation was developed between unconfined compressive strength and modulus for ADM6 ash. Based on this correlation, and on the findings of a finite element study on Addcar Highwall Mine adits filled with ADM6 ash, an unconfined compressive strength on the order of 300 to 500 psi was considered necessary. Thus, the findings of these tests appeared promising for mixtures with low mixing water percentages. Increasing mixing water percentages resulted in marked decrease in strength, as shown in Figure 3.

In the hope of increasing flowability of low water content mixes, and also providing enhanced strength, mixtures comprised of Costain FBC FA, conventional class F fly ash (PFA), and water were also investigated. The solids portion of these mixes were prepared consisting of 10% and 15% PFA with Costain FBC FA being the remainder. These solids portions were then combined with water at mixing percentages ranging from 34% to 40%, placed in PVC molds, and cured at 13°C and 38°C for unconfined compression testing.

Figure 3. Effect of water content on strength of Costain FBC FA (55F)

Figure 4. Effect of class F PFA on unconfined compressive strength of Costain FBC FA

The results of these tests are shown in Figure 4. Comparison of Figure 4 with Figure 3 shows the addition of PFA had no significant effect on the strength gain over the first 28 days of curing.

Young's modulus of the specimens was also determined. Since accurate low strain measurement of modulus was not possible with the equipment available, and since the modulus was to be compared with that found in conventional coal testing, the modulus was determined using standard rock mechanics guidelines. The secant modulus, E_{25-75} , is determined as the slope of a line on the deviator stress versus axial strain plot extending from 25% to 75% of the ultimate strength. For this study, it was found the modulus varied from about 60 to 100 times the unconfined compressive strength at low mixing water percentages (see Figure 5a). As the water content increased, the modulus decreased more rapidly than the unconfined compressive strength, so that at high water contents, the modulus was found to be on the order of 20 to 40 times the unconfined compressive strength (Figure 5b). Modulus is likely the most significant factor in the performance of the fill during mining, so the addition of high mixing water appears to be a less than desirable method for improving placement in the auger holes.

Effect of Curing Temperature on Costain FBC FA Strength. As with the spray dryer testing described above, the effect of curing temperature on the strength gain and swell of the Costain FBC FA was investigated. The results of the testing on specimens cured at 13°C (55°F) and 38°C (100°F) are shown on Figure 6. The strength gain rate at 100°C was on the order of 6 times the strength gain rate at 13°C. Clearly, the kinetics of strength gain is different for the FBC FA as compared to the Costain Spray Dryer ash, where the strength gain rate at 38°C was on the order of 50 times the strength gain rate at 13°C.

Development of Field Quality Control Procedures

In the laboratory, it is easy to assure mixing percentages for the materials being studied. However, under field conditions, preparation of batches with the desired mix ratios is much more difficult to achieve. A simple field test is necessary to determine whether the approximate desired water ratio has been achieved. In Portland cement concrete technology, one of the most common tests is the slump cone, wherein a cone of the mixture is formed in a mold, the mold is removed, and the height change of the mix (slump) from its original height in the cone is measured. For high flow grouts, a similar test consists of placing the grout in an open ended cylinder standing on end, then removing the cylinder and measuring the lateral spread of the grout on a flat surface.

For this project, the use of a cylinder or cone with a simple measure of flow, such as that described above, was judged to be the most applicable for quality control. Due to the quantity of material that could be easily mixed in the lab, a full size concrete flow cone required an excessive amount of mix, so a half size flow cone was fabricated for both lab and field use. Open ended cylinders 2 inches in diameter and 4 to 6 inches long were also considered for flow and water content assessment.

Figure 5a. Modulus versus mixing water for Costain FBC FA w/PFA

Figure 5b. Effect of mix water on normalized modulus for Costain FBC FA w/PFA

Figure 7. Mini-slump cone measurements versus water content for various mixes

The open ended cylinder method was not found to be productive for the FBC grouts studied herein. In the case of a low water content mix, the cylinder of grout would topple over upon mold removal, rather than slump along its axis. At high water contents, the amount of slump did not correlate well with the mixing water percentage in multiple tests. Consequently, the flow cylinder method was abandoned for this portion of the project.

Use of a half size slump cone was more productive than the flow cylinder. The results of some of the testing are shown on Figure 7. The findings showed a slight improvement in flowability with the addition of fly ash to the mixture, but not to an extent sufficient to justify the additional cost. Testing with the addition of a plasticizer at the manufacturer's recommended minimum plasticizer to cement ratio was more productive. The slump improved significantly with the addition of plasticizer. Since the liquid plasticizer comprised a small percentage of the total mix, its addition had little effect on liquid to solids ratio, though the flow was much improved. Unfortunately, plasticizer is a moderately expensive additive that may not be economical for large volume use of this methodology. However, it is recommended the addition of a plasticizer to the mix be considered in this study as one option to using only FBC FA with water. The addition of the plasticizer should improve pumpability and flow during the field demonstration, provide a basis for economic assessment of the additive's use, and increase the likelihood of a successful field demonstration.

Recommendations

In summary, the evaluation of the desulfurization by-products available at the Costain facility showed that the FBC fly ash has the most potential for use as fill in the field demonstration. Low mixing water contents are an important criteria for these materials, but low water ratios result in less flowable mixtures, so that pumping of these materials presents a challenge. The addition of a plasticizer to improve pumpability while retaining a low water content is recommended as an alternative procedure, although the cost of plasticizer addition makes this option less economically feasible. Batch mixing of the field mixtures should be as accurate as possible on the basis of weighing the mixing trucks before and after addition of each component, and mini slump tests should be performed on each batch as a means of increase confidence in the planned water percentage. Multiple test cylinders of each mix should be obtained to permit lab validation of the field observations.