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

Phase 2: Field Investigations

**Quarterly Report
January 1 - March 31, 1998**

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

Phase II: Field Demonstrations

Cooperative Agreement No.: DE-FC21-93MC30251

Quarterly Report for the Period January 1 to March 31, 1998

Summary of Activity for the Quarter

The factors that control the strength of FBC ash grout were the focus of work during this quarter. As was discussed in previous reports, laboratory experiments have been conducted to further elucidate the influence of water content and curing temperature on compressive strength. The values of these parameters have been selected to approximate field conditions.

Samples were prepared at different water contents and placed into cylindrical PVC molds. The specimens were then cured in an atmosphere of approximately 100% humidity, at three different temperatures. During specimen preparation, geotechnical properties including water:solid ratio, initial void ratio, quantity of bleed water accumulated in one (1) hour, and observed swell or shrinkage were recorded. At specified curing intervals, the grout cylinders were subjected to unconfined compressive strength testing as per procedures described in previous reports. Chemical, mineralogical, and microscopical analyses were also conducted on the samples.

It was found that higher curing temperatures significantly increase the strength gain rate of the FBC ash grout, in agreement with earlier results. As expected, water content also exerts a strong influence on the strength of the grout. The compressive strength data obtained for the laboratory-prepared samples are in excellent agreement with strength data obtained on grout placed in auger holes during the field demonstrations. The data also indicate that the field samples suffered negligible deterioration over the course of the curing period in the auger holes.

Analysis of the laboratory prepared grout samples using XRD revealed a mineralogy similar to the field samples. A correspondence between ettringite abundance and compressive strength was observed only during grout curing. The formation of minerals such as ettringite is apparently a good indication that curing reactions are progressing and that the grout strength is increasing, but mineral distribution by itself does not explain or predict final strength.

The microscopy data, in combination with geotechnical and XRD data, suggest that the strength of the grout is largely a function of the density of an amorphous (or finely crystalline) material that comprises the majority of the cured grout. Therefore, an increase in density of this material results in an increase in grout strength.

Phase II. Field Investigations

Task 2. Data Analysis

Analysis of the variables which exert the greatest control on strength of FBC ash grout has been the focus of work during this quarter. Laboratory experiments have been conducted to further study the kinetics of compressive strength development as a function of curing temperature, at several different water contents. This is important because the rate of strength gain, in addition to the final strength, will determine the curing time required for mining of the "shut-in" coal behind the auger-mined highwall. The experiments were designed to replicate as accurately as possible the water contents of the grout produced during the field demonstration, and the curing conditions within the auger holes, but in a controlled, laboratory setting. The laboratory data were then compared with the field data; close agreement between the sets of data imparts a more fundamental understanding of the variables controlling strength development of grout injected into auger holes.

Experimental

FBC fly ash was obtained from the Lodestar Energy Inc. railway load-out facility in Ivel, Kentucky. A representative fraction of the dry ash was sieved through a #4 (4.75 mm) sieve, and the mass obtained. Distilled deionized water was added to the ash to produce grout with four different water:solid (w:s) ratios: 0.62, 0.67, 0.72, and 0.77. During preparation of the grout samples, no significant temperature gain was noted for most specimens, although several specimens became slightly warm. After mixing, the grout specimens were placed into sections of Schedule 40 PVC pipe (100 mm in length, 51 mm inside diameter). Each of these samples was capped at the bottom and sealed using a waterproof sealant. At least three grout samples were prepared at each w:s ratio. The specimens were then cured in an enclosed water bath at a fixed temperature. The open top of each specimen was above the water line in the bath such that curing occurred in an atmosphere of approximately 100% humidity. Curing temperatures selected were 50°C, 30°C, and room temperature (approximately 21°C). During specimen preparation the water:solid ratio, initial void ratio, quantity of bleed water accumulated in one (1) hour, and observed swell or settlement, were recorded.

After curing for a predetermined time period, each of the specimens were analyzed for density, moisture content, void ratio, and unconfined compressive strength; these procedures are described in the October 1 to December 31, 1977 report. Any visible evidence of axial swell or settlement was also noted. Selected samples of the broken specimens were then subjected to x-ray diffraction (XRD) analysis and optical microscopy.

Samples were prepared for XRD analysis on the day following compressive strength testing. Preparation procedures and analysis parameters have been described previously (October 1 to December 31, 1997 report). Transmitted-light optical microscopy of the laboratory grout samples was conducted using thin sections prepared at a commercial laboratory. These sections were prepared by cutting a small block from the grout sample, mounting it on a glass slide using a cold setting resin, and grinding this section to a thickness of 30µm. A thin cover slip was then

glued to the top (exposed) surface of the grout thin section. During the preparation procedure, exposure of the grout samples to the atmosphere was minimized, and water was not used as a lubricant/coolant during the grinding procedures.

Results: Geotechnical Testing

The effect of water content on the unconfined compressive strength of the FBC fly ash (FA) grouts is evident in Figures 1-3. Increasing the water:solid ratio results in a significant decrease in strength at each curing temperature. This is an expected result based not only on similar behavior in commercial grout/cement materials, but also on earlier results of this project (April 1 through June 30, 1996 report). The water content affects the final density of the grout and the quantity of bleed water that is expelled prior to setting, in such a manner that a high water content will result in excessive bleeding from the mix and a high degree of porosity in the hardened grout. Although bleeding reduces porosity, the bleed channels can also introduce inherent weaknesses into the cement structure that ultimately lower the compressive strength. Moreover, loss of water through bleeding increases the wet grout viscosity and decreases its ability to flow during emplacement.

The effects of curing temperature on grout strength also are evident in Figures 1-3, and are presented in Figures 4-6. At each water content the rate of strength gain is considerably increased as the curing temperature increases. The maximum strength is achieved in less than 10 days for the 50°C samples and approximately 25 days when cured at 30°C, whereas the grout cured at the low temperature appears to slowly continue to gain strength even after 100 days curing. This is supported by previous work which also indicated that higher curing temperature significantly increased the curing kinetics (April 1 through June 30, 1996 report). However, the increase in curing temperature also causes a slight decrease in strength after the maximum strength is achieved; at 50°C, maximum strength occurs at approximately 10 days and decreases slightly thereafter (Figure 3). Although there are less data for the 30°C curing conditions, a similar trend occurs (Figure 2). Conversely, curing at 21°C results in continued strength gain after 100 days, (Figure 1; Figures 4-6). These data are consistent with those reported in studies on the effects of curing temperature on concrete strength. In general, these studies have found that although higher curing temperature increases the early strength of concrete, it often adversely affects the longer-term strength, possibly because the higher temperature results in greater porosity and more poorly developed physical structure (Neville, 1996).

Based on the laboratory data it is evident that, even at a high moisture content of 43.5% (0.77 w:s), grout can be produced with sufficient strength for a mine support application. The high curing temperature within the auger hole, resulting from the large volume of grout being insulated within the hole, should result in adequate strengths being achieved within several days of curing. However, this assumes that the FBC ash produces a significant heat of hydration during mixing and emplacement; if not, then longer curing times are necessary, perhaps on the order of several months if the curing temperature were to remain at ambient conditions (~16°C) over the course of curing.

Despite the rapid strength gain and high compressive strengths obtained, the decrease in longer-term compressive strength of the grout samples cured at elevated temperatures in the laboratory is a cause for some concern. In practice, re-mining of shut-in coal may not occur soon after the grouting operation, making it necessary for the grout to have adequate long-term durability. As is discussed above, a long curing time is advantageous for low temperature curing, but may not be advantageous when higher temperatures are experienced, such as those recorded during the field demonstration (July 1 to September 30, 1997 report). Comparison of field data with laboratory data (Figure 7) reveals that the range of compressive strengths is very similar for the two data sets. This indicates that the laboratory grout mix proportions and curing conditions were ostensibly similar to the field conditions and that, more importantly, an insignificant loss of grout compressive strength has occurred over the course of curing within the auger holes.

X-Ray Diffraction (XRD)

Analysis of the laboratory prepared grout samples using XRD revealed a mineralogy similar to the field samples. Crystalline phases identified include ettringite, portlandite, calcite, quartz, and gehlenite. The effect of curing time on grout mineralogy is shown in Figures 8 and 9 for the low- and medium-temperature samples. Over the course of curing there was a loss of portlandite and an increase in ettringite and calcite abundance; the remaining phases remain more-or-less unchanged. The formation of ettringite has been associated with increased strength of FBC fly ash grouts in previous studies (Graham et al., 1995; July 1 to September 30, 1995 report). However, a correspondence between ettringite abundance and compressive strength was observed in the present study only as the grout samples cured and hardened. Once the final strength was achieved, mineral distribution no longer related to differences in strength between samples prepared at different water contents (Figures 10-12). The XRD spectra show that after curing for long periods of time, the distribution of crystalline phases such as ettringite was unaffected by water content, whereas the compressive strength was strongly influenced by this property. Therefore, the formation of ettringite is probably a necessary curing reaction for the development of grout strength, but the abundance of this mineral alone does not explain or predict final strength.

The effects of temperature, at a single curing time, on mineralogy is similar to the effects of curing time at a single temperature. Higher temperatures accelerate the grout curing rate and thus accelerate the rate of ettringite and, to a lesser degree, calcite formation, whilst increasing the rate of decline in portlandite abundance (Figure 13). After the final strength was achieved, curing temperature had no significant effect on mineralogy of the grout samples (Figure 14).

Optical Microscopy

In thin section, the majority of the FBC grout appeared brownish colored and amorphous on the scale of the optical microscope, with small crystals interspersed (Figure 15). The amorphous material probably comprises a poorly crystalline calcium-aluminum-silicate-hydrate gel, as in concrete "paste", and/or very small, sub-micron size crystals. In fact, although ettringite is a dominant phase in XRD data, it was rarely observed optically because of the small size of the crystals. This observation is consistent with that from optical microscopy of concrete and cement

(Jakobsen et al., 1997). Gehlenite crystals were also not definitively identified in any of the sections, suggesting that they also were too small for optical observation. Quartz crystals were clearly observed, as was calcite; the latter is particularly evident at the edge of the thin section where carbonation occurred during sample handling (Figure 16). In fact, an unexpectedly large amount of calcite was observed in most of the samples, compared with the XRD data, indicating that the samples carbonated rapidly during preparation of the thin sections, despite the minimal exposure to the atmosphere.

The optical microscopy observations suggest that the strength of the grout is largely a function of the density of the amorphous or finely crystalline paste component that comprises the majority of the cured grout. More specifically, similar to concrete and cement, an increase in density (with concomitant decrease in porosity) of this material results in an increase of grout compressive strength. Increasing the water content causes an increase in porosity and decrease in the density of the paste material, with a reduction in compressive strength. In contrast, increasing the curing temperature merely increases the rate of the curing reactions but exerts much less of an influence on the final density and strength of the paste.

References

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Figure 1. Unconfined compressive strength of laboratory grout samples cured at 21°C.

Figure 2. Unconfined compressive strength of laboratory grout samples cured at 30°C.

Figure 3. Unconfined compressive strength of laboratory grout samples cured at 50°C.

Figure 4. Unconfined compressive strength of laboratory grout samples prepared at a water:solids ratio=0.62

Figure 5. Unconfined compressive strength of laboratory grout samples prepared at a water:solids ratio=0.67

Figure 6. Unconfined compressive strength of laboratory grout samples prepared at a water:solids ratio=0.72

Figure 7. Unconfined compressive strength of laboratory grouts (cured at 50°C) compared with strength of field grout samples

Figure 8. XRD spectra of grout samples cured at 21°C for 11 and 44 days

Figure 9. XRD spectra of grout samples cured at 30°C for 5 and 40 days

Figure 10. XRD spectra of grouts prepared at four w:s ratios and cured for 44 days at 21°C

Figure 11. XRD spectra of grouts prepared at four w:s ratios and cured for 40 days at 30°C

Figure 12. XRD spectra of grouts prepared at four w:s ratios and cured for 51 days at 50°C

Figure 13. Averaged XRD spectra of grouts cured for 11 days at 21° and 50°C

Figure 14. Averaged XRD spectra of grouts cured for ~50days at 21° and 50°C

Figure 15. Transmitted light optical photomicrograph of FBC grout thin-section, under cross-polarized illumination. Width of photo equals 1mm. Gray material is amorphous and/or finely crystalline "paste", whilst light areas are crystalline material such as calcite and quartz. Black regions are mainly pores and particles of carbon.

Figure 16. Transmitted light optical photomicrograph of FBC grout thin-section, under cross-polarized illumination. Width of photo equals 1mm. Bright regions and "pin-points" of light are mainly calcite (calcium carbonate) from carbonation of thin-section upon exposure to atmosphere during preparation.