Coolside Waste Management Research

Quarterly Report January 1 - March 30, 1996

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Quarterly Progress Report

Report Period January 1, 1996 to March 31, 1996

Summary of Progress

Activities during the quarter centered around preparations to complete the study. Geotechnical work (Subtask 2.2) focused on coring and other tests on the field lysimeters. Work on materials characterization focused on the characteristics of pellets made from dry FGD materials. The data obtained during this reporting period support the conjecture that detrimental swell associated with continued pellet aging upon exposure to humidified air or upon exposure to water is principally a function of calcium sulfate hydration reactions. The main difference between the earlier studied FBC pellets and the spray dryer pellets produced by CONSOL, and used in this investigation, can be summarized as follows: Spray Dryer material has minimal amounts of anhydrite crystals present while anhydrite is a major component in the FBC ash. The differences in mineral components which undergo hydration reactions can be attributed to more or less detrimental swell and pellet decay upon aging. Ten trips to the field site were made during the quarter for sampling purposes (Task 3). Sampling was completed on March 29, 1996. The laboratory leaching study was also completed during the quarter (Task 4) on twenty-two columns which were set up for the study.

Task 2 Materials Characterization

Subtask 2.2 Geotechnical Studies

Active sample collection was scheduled to end at the quarter. The geotechnical characteristics of the materials in the field lysimeters are to be then determined. Lyismeter 1, which was filled with loosely compacted Coolside material, was cored with a press in tube. Samples will be

tested for permeability. These materials are too unconsolidated for strength testing. Lysimeters 2 and 3, the more highly compacted Coolside material, were found to be sufficiently consolidated to produce conventional core samples. The samples produced will be analyzed for both permeability and strength. The strength of the materials will be determined by unconfined compression. Lysimeter 4, filled with PCC fly ash was not sufficiently consolidated for coring. Dutch Cone penetration tests were performed on these cores. The cores will be analyzed over the next quarter and reported on as part of the projects final report.

Task 2 Materials Characterization

Subtask 2.3 Chemical and Mineralogical Analysis

Introduction This study comprises results obtained from an ongoing pelletization work. Our objectives are to determine the importance of different mineral components and their relative abundance in the pellet precursor materials (FBC ash versus spray dryer ash) and to understand the contributions of mineralogical transformations upon hydration and aging on the overall pellet stability.

Anhydrite crystals in the FBC pellets, upon exposure to moisture, undergo a dissolution-reprecipitation reaction that results in the nucleation and growth of gypsum crystals. The mineralogical transformation is associated with a volume increase, leading to detrimental crack and fracture formation in the pelletized FBC materials. The mineralogical transformation is delayed because of the dense crystal structure of the anhydrite grains (see earlier reports on mineralogical transformations in FBC materials) causing earlier formed cementitious bonds to rupture, and overall is leading to poor pellet strength. In contrast, spray dryer materials are lacking "dead burned" anhydrite crystals (the expression "dead burned" being used here to describe the degree of crystallinity of the anhydrite crystals formed at elevated temperatures in a circulating fluidized bed).

The XRD analyses of the two different kinds of ash, FBC ash (Figure 1 and Figure 2) versus spray dryer ash (Figure 3 and Figure 4) used in the pelletization study illustrate the differences in the mineralogical makeup of the pellet precursor materials. Chemical characterization of the FBC

pellets indicates that the main mineral components are anhydrite (CaSO_4), portlandite ($\text{Ca}(\text{OH})_2$), free lime (CaO), minor calcium carbonate (CaCO_3), minor mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$) and, of course, quartz. During early curing the anhydrite did not hydrate to spontaneously form gypsum (Figure 1) but rather resulted in the early hydration products portlandite and ettringite as evidenced by XRD and SEM investigations of the materials (Figure 1). Although ettringite needles form early bonds between mineral grains (SEM in Figure 1), subsequent hydration of anhydrite leads to extremely large gypsum crystals (SEM in Figure 2) that form in voids and fractures, causing the complete disruption of mineral bonds after 160 days curing period.

In the Spray Dryer material, the main mineral components after hydration are: hannebachite, ettringite and calcite, with only minor amounts of gypsum. Mullite, rutile and quartz are present in both the starting and hydrated Spray Dryer pellets (XRD in Figure 3). The XRD peaks for the spray dryer material are typically indicative of the presence of a substantial amount of glassy phase. The glass diffraction "ramp" is centered approximately at $29 - 30^\circ 2\theta$ and is relatively broad, indicative of a high CaO component within the glassy phase. Figure 4 compares the XRD results obtained for the spray dryer ash (SDA-F) with the pelletized material (SDA-P). It is evident from the XRD data that hannebachite ($\text{CaSO}_3 \cdot 0.5\text{H}_2\text{O}$) is the most important mineral participating in the "spray dryer ash" transformation reactions. The aged spray dryer pellets (Figure 4) have abundant hannebachite present as well as ettringite needles, both of which contribute to mineral bonding and early strength gain of the materials. In contrast, gypsum crystals which comprise the bulk of newly formed minerals in the FBC pellets, are only a minor component in the spray dryer pellets, suggesting, that gypsum crystals easily reprecipitate in the FBC material from the Ca and SO_4 supersaturated pore waters, while in the Spray Dryer materials oxidation of SO_3 to SO_4 is the rate limiting step in the reaction forming gypsum. Based on the results of this study it appears that ettringite crystals, which also require the sulfate ion, are more readily formed in a SO_4 starved environment compared to gypsum crystals. One of the prerequisite for the ettringite crystals to form is the presence of Aluminum ions, which, in the pore solutions of the Spray Dryer pellets are most likely supplied by the mullite phase available in the starting material (Figure 3).

In summary the present results suggest that the spray dryer ash constitutes a better precursor material for pelletization work than FBC ash. The results are based on XRD and SEM observations that indicate a lesser effect of mineral transformations and swell causing mineral growth in the Spray Dryer pellets compared to that of the FBC ash pellets.

Task 3. Field Leaching Studies

Subtask 3.2 Field Monitoring

There were 10 trips to the site for sampling during the quarter. Rain was recorded during each sampling interval which totaled 10.38 inches for the quarter. Gas well readings were low during the quarter, reflecting the annual slow down in evapotranspiration. The highest reading recorded was 0.4% (4,000 ppm) CO₂. Which was measured in the L3 lysimeter on March 29, 1996. Over 120 samples were collected during the period. They are currently being analyzed and will be reported in the final project report.

Task 4. Laboratory Leaching Studies

Laboratory leaching studies conducted on twenty-two laboratory columns were terminated in February of 1996 concluding a 12-month investigation. Materials from the four pilot plant runs conducted by Consol in Library, PA, as well as two composite samples from demonstration-plant runs 1 and 3 conducted by Ohio Edison in the Edgewater Power Plant near Loraine, Ohio, were included in the investigation. Variables investigated in the test matrix included solids packing density (49 and 65 lb/ft³), contact with a variable CO₂ atmosphere (0, 2.5, and 5 vol%), the rate and method of water addition (fixed-47 and 94 mL/wk; rain simulation), and the level of prehydration (0, 15, 30, and 45 wt% prehydration water-dry basis).

During the investigation, water additions and withdrawals were made on a weekly basis with water flow realized through 20 of the 22 columns during at least some portion of the study. The only column for which flow was not achieved were two columns in which an excess level of prehydration water was added to the FGD prior to packing the lysimeters. The collected waters from each column were analyzed weekly for Ag, Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg,

Mn, Mo, Na, Ni, P, Pb, Se, Si, Ti, V, Zn, SO_4^{2-} , Cl^- , Br^- , pH, alkalinity, and conductivity. Water additions and withdrawals were also carefully monitored during the test interval. Samples of the solid materials were taken at three levels from each lysimeter for XRD and SEM analysis.

Reduction of the voluminous data set generated from these tests is currently on going and will be discussed in the final report.

Hydration of FBC material

ETTRINGITE HYDRATED LIME

SEM

XRD

Figure 1

Gypsum Formation

160 Day Curing
Submerged in Water

SEM

XRD

Figure 2

Coolside

Pellet Research 1362

Figure 3

SDA-F SDA-P

Spray Dryer Ash Pellets

Figure 4