Coolside Waste Management Research

Quarterly Report October 1 - December 31, 1995

Work Performed Under Contract No.: DE-AC21-91MC28162

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

By
University of Kentucky
Center for Applied Energy Research
3572 Iron Works Pike
Lexington, Kentucky 40511-8433

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Coolside Waste Management Research
Technical Progress Report
Contract No: DE-AC21-91MC28162
Report Period October 1, 1995 to October 30, 1995

Summary of Activity

This study comprises results from an ongoing field testing. Additional data obtained during this reporting period support earlier results indicating that mineralogical transformations continue in the field lysimeters as a function of available moisture, aging and static loading of the Coolside materials. As with earlier results ettringite continues to be the dominant new phase in all lysimeters. Trends in gypsum availability within the lysimeters suggest that gypsum crystals are rapidly leached from the top layers of the lysimeters while some gypsum remains in the deeper lysimeter zones where pore fluids remain saturated with respect to gypsum. Calcium carbonate is a mobile phase and its presence depends strongly on the perk available in the lysimeters. The results are concurrent with mineralogical findings from laboratory-based kinetic studies that suggest that ettringite, calcium carbonate and calcium-alumino-silicate hydrate phases proceed to form within the aging materials, while gypsum may be considered a temporary phase that will be leached out. In specimens with higher degrees of static loading (static loading increases in the order of lysimeter 1 through 3), minerals are forced to grow within available pore space or fractures which leads to less perk causing leaching rates to proceed slower. Leaching rates, in turn, are controlling the dissolution/reprecipitation of minerals in the lysimeter zones.

Task 2 Materials Characterization

Subtask 2.1 Mineralogy of Field Lysimeters

Continuation of Field Lysimeter Tests. This part of study is focusing on the CO₂ uptake and corresponding changes in mineralogy and chemistry of the field lysimeters. Mineralogical changes in the field lysimeters were monitored for lysimeters 1, 2 and 3 samples. Lysimeter 4 is a reference standard. A general material characterization for the field lysimeter samples (including sampling procedures) was presented in an earlier report (Technical Progress Report, Report Period April 1, 1995 to April 30, 1995). Results indicated that differences in packing densities in the field

lysimeters impact the mineralogy of the systems upon aging. Variations in mineral transformations among the lysimeters were mainly attributed to the perk of the systems as increased perk will accelerate the leaching potential and hence the transport of dissolved ions in the lysimeters downwards.

Variable I: Degree of Compaction. Variable II: Lysimeter Depth Changes in mineralogy were monitored as a function of lysimeter depth and compared for lysimeters with different degrees of compaction. Differences are recognized for the relative amounts of ettringite and calcium carbonate in the three lysimeters (Figure 1).

Loose compaction in lysimeter 1 corresponds to an overall increase in ettringite abundance with lysimeter depth (Figure 1A) and calcium carbonate enrichment in the top zone with decreasing abundance in calcium carbonate with increasing lysimeter depth.

A compaction of 41 lb/ft³ in lysimeter 2 corresponds to a minor increase in ettringite abundance with increasing lysimeter depth. A minor decrease in calcium carbonate abundance with lysimeter depth was also observed (Figure 1B).

A compaction of 66lb/ft³ in lysimeter 3 resulted in no detectable variation in ettringite abundance with increasing lysimeter depth. The uppermost layer of lysimeter 3 has calcium carbonate present. Only a relatively small variation in calcium carbonate abundance was observed as a function of increasing lysimeter depth (Figure 1C).

The monitoring of relative mineral abundances in the lysimeters suggests that depletion of ettringite in the upper zone of the least compacted lysimeter (L1) in conjunction with a calcium carbonate enrichment may be caused by:

- rapid leaching and ion migration due to loose compaction and large water / solid contact areas (large void spaces and channel ways). Ion migration causes depletion of the upper lysimeter zone in Al and SO₄. As a result ettringite becomes more soluble.
- ettringite instability and recarbonization due to fluctuations in pH and pCO₂. Fluctuations in pH and pCO₂ are strongly dependent on the migration rates of pore fluids in the upper layers of the loosely packed lysimeter 1.
- calcium carbonate formation due to the disintegration (dissolution) of ettringite.

Because calcium hydroxyhydrate ($\text{Ca}(\text{OH})_2$) is less abundant in the lysimeters and gypsum (CaSO_4) almost entirely absent, ettringite becomes the dominant calcium bearing phase. Therefore, ettringite needles need to be dissolved to provide additional Ca ions for recarbonization of the materials upon interaction with dissolved CO_2 . The observed mineral transformations discussed above would support this mechanism.

Only sparse information is available on what controls ettringite dissolution reactions. In the literature ettringite is discussed to dissolve below its equilibrium pH (11.4). Actual field observations, however, do not indicate a complete decay of ettringite even at pH levels as low as 8. To better understand the mechanisms involved in ettringite precipitation/dissolution reactions, this study compares the release profiles for sulphate and changes in conductivity for the lysimeters with different degrees of compaction (Figure 2,3). Figure 2 indicates that the concentration of sulphate ions in the leachates collected from the loosely compacted lysimeter #1 are relatively high during the first 8 month with corresponding high conductivity values, but both decrease rapidly thereafter to values similar to those observed for the fly ash reference lysimeter.

Sulphate containing mineral phases in the Coolside materials include anhydrite, gypsum and ettringite. Sulphate ions collected in the leachate must have been predominantly derived from dissolving anhydrite/gypsum crystals as those minerals are absent in the aged materials (see XRD investigations illustrated in Figure 1), while ettringite continued to grow in the loosely packed lysimeter 1. The fact that ettringite is more abundant in lower zones within lysimeter 1 (Figure 1A) may simply be the result of infiltrating rainwater that under saturates pore fluids with respect to ettringite near the soil / lysimeter interface. Ettringite crystals that dissolve in the upper lysimeter zone may reprecipitate in lower lysimeter zones where pore fluids are either in equilibrium with, or supersaturated with respect to ettringite. Ettringite crystal formation is a mechanism that helps retain sulphate within the lysimeter that otherwise would be completely lost to the leachate phase.

In contrast to the loosely packed lysimeter 1, lysimeters 2 and 3 show only minor or no increase in ettringite abundance with lysimeter depth Figure 1B,C). The release profiles for the two

compacted lysimeters #2 and #3 with respect to the sulphate release (Figure 2) indicate a significantly slower leaching characteristics than the loosely compacted lysimeter 1. Sulphate uptake from the Coolside material occurs not only at a slower, but also much more steady rate. This is attributed to the slower fluid flow through the compacted lysimeters and longer contact times of the pore fluids with mineral surfaces. The longer residence times of the fluids in voids may lead to local equilibrium conditions and mineral precipitation including that of ettringite needles. The precipitation of minerals further enhances the compaction and density within the lysimeters, thereby reducing the leaching potential of the lysimeters even more. These observations are in agreement with data supported from conductivity release profiles collected for the individual lysimeters (see Figure 3).

The mineral phase that showed the greatest irregularity with respect to where and how much of it occurred in the three differently packed lysimeters is calcium carbonate (Figure 1A-C). As stated above, calcium carbonate is abundantly present in the top zone of the loosely packed lysimeter 1, but less frequently observed in either top zone of the more densely packed lysimeters. All three lysimeters have in common that the abundance of calcium carbonate is greatly reduced downwards in the lysimeters. As can be expected, the decrease is gradual in the loosely packed lysimeter #1, but much more abrupt and pronounced in the compacted lysimeters #2 and #3. There are numerous controlling factors, but two may be more obvious. The most obvious controlling factor seems to be the concentration and migration rate of gas-phase CO_2 in the different lysimeter zones. Gas-phase CO_2 concentrations were measured at varying depths in the field lysimeters and the results are illustrated in Figure 4. The upper zone of the loosely packed lysimeter 1 has the greatest amount of dissolved gas-phase CO_2 with corresponding large quantities of calcium carbonate crystals (compare XRD results in Figure 1A). Deeper zones within this lysimeter #1 have greater values of gas-phase CO_2 when compared to those in the more densely packed lysimeters #2 and #3 which also have less calcium carbonate crystals present as observed in the XRD study of the materials (compare Figure 1B and C). Recarbonization of the lysimeters was found to be controlled by the migration rates of fluids through the lysimeters which are ultimately controlled by the pore fluid flow or degree of compaction within the lysimeters.

Lysimeter #1

(A)

— top 3" --- 6-8" — 18"

Lysimeter #2

(B)

— top 3" --- 6-8" — 16-18"

Figure 1.

Lysimeter #3

(C)

— top 3" --- 6-8" — 16-18"

Lysimeter #4

(D)

— top 3" --- 6-8" — 16-18"

Figure 1.

Figure 2.

Figure 3.

Figure 4. Gas-phase CO₂ concentrations measured at varying depths in the field lysimeters. (L1 to L3-Coolside waste; L4-fly ash).

**Coolside Waste Management Research
Technical Progress Report
Contract No: DE-AC21-91MC28162
Report Period November 1, 1995 to November 30, 1995**

Summary of Activity

This study comprises results from an ongoing laboratory testing. Results presented in this report support earlier data indicating that mineralogical transformations cause swell in the FBC ash samples, which is a function of available moisture, aging and static loading of the materials.

The first part of the report focuses on swell tests of FBC materials. In all, four different types of samples are investigated to differentiate the changes caused by surcharge and age time.

The second part of the report observes changes in the natural clay liner tests which include three clays and two FGD-by-products. The objectives of this part of study focus on long-term changes in permeability of clay liners caused by water leaching through FGD-materials into compacted clay liners.

Phase 1 Task 2 Subtask 2.2

Swell Tests

Monitoring of swell continued on the hydrated and non hydrated FBC ash samples. Both types are still in the primary swell phase. Swell of the hydrated ash has been monitored for 1083 days, while swell of the non-hydrated material has been monitored for 971 days. All samples were remolded near 95% of standard maximum dry density and optimum moisture content. The samples were remolded in CBR molds (6" diameter, 4.584" height) and swell was monitored under the following conditions:

approximately 12.5 lb. surcharge, no age time
approximately 2.5 lb. surcharge, no age time
approximately 12.5 lb. surcharge, 7 days age time
approximately 2.5 lb. surcharge, 7 days age time

Time of aging represents the amount of time before the samples were placed in water. Aged specimens were sealed at room temperature to prevent moisture loss before placement into the water tank. All FBC specimens are still in the primary swell phase. Hydrated specimens have swelled from approximately six to 16 percent of their original volume depending on curing time and surcharge, while non-hydrated samples have swelled from around 20 to 43 percent as shown in Figures 1 and 2.

Phase Task 4 Subtask 4.1

Natural Clay Liner Tests

Natural clay liner tests are continuing with three clays and two FGD by-products. Objectives of the tests are to determine any long-term changes in permeability of clay liners caused by water leaching through FGD materials into compacted clay liners. The long-term permeability of natural clay liners may be affected by materials such as metals, salts, or hydroxides present in FGD leachate. Calcium oxide (CaO) and hydroxide (CaOH₂) are known to react with clays in the presence of water and alter their physical and structural properties. Permeabilities of clay, FGD, and clay-FGD combinations are being monitored in configurations described below. Monitoring of permeabilities began in March 1995. The soils being used are naturally occurring clays which meet most states' criteria for a landfill liner; that is, they have permeabilities less than 10⁻⁷ cm/sec when compacted. The FGD by-products are a FBC from an electrical generating station in Pennsylvania and Coolside material from CONSOL'S pilot plant, run #2. The tests are being performed on compacted soils and FGD by-products. Specimens of these materials were compacted in PVC cylinders that measure 3 inches in diameter and 12 inches in length. The

materials were compacted near 95% of standard maximum density and optimum moisture content. Soil #1 is a residual clay collected from Fayette County, Kentucky; Soil #2 is a glacial till collected at the Franklin County Landfill just south of Columbus, Ohio. Soil #3 is a residual clay collected from a landfill in Kentucky. Three tests consists of water moving through the compacted 12 inch soil specimens. Six tests have water leaching through six inches of compacted FBC and Coolside and six inches of compacted clay. The tests are configured so each clay will be subjected to leachate from each FGD material. Permeabilities of the clays in these six tests will be determined at the end of the leaching period (approximately 1.5 years) and compared to values obtained before leaching. This may show effects of FGD leachate on the permeability of the compacted clay soils. Two tests have 12 inch FBC and Coolside pilot plant #2 specimens. Schematics of the arrangement of samples are shown in Figures 3 and 4.

Water is supplied from a reservoir, mounted above the specimens, through 1/4 inch OD nylon tubing connected to the samples. Silica sand was used to fill the annular space in the end cap between the tubing connection and the sample. Three way valves are located in-line between the reservoir and samples . The valves allow the water supply to be cutoff and the water remaining in the nylon tubing to be vented to atmospheric pressure.

Falling head permeability tests can be performed by measuring the change of water elevation change with increasing time. Permeability measurements are being conducted at various time intervals to determine changes, if any, of the compacted materials. Coefficients of permeability are calculated from Darcy's Law:

$$k = \frac{aL}{At} \ln \frac{h_o}{h_f}$$

where,

k = coefficient of permeability

a = area of standpipe

A = area sample

t = time of test

h_o = time at beginning of test

h_f = time at end of test

In three cases, as shown in Figures 5, 6, and 7, respectively, coefficients of permeability for FGD-soil combinations are lower than individual materials (Coolside -2, Soil #1: FBC, Soil #1, and Coolside -2, Soil #2). For the FBC-Soil #2 and FBC-Soil #3 combinations, the coefficients of permeability are about the same as the coefficients of permeability of soils, Figures 8 and 10. In one case, Figure 9, the coefficient of permeability is greater than the coefficient of permeability of the individual materials. Coefficients of permeability of the clay soils have not changed significantly due to FGD leachate permeating through them. A decrease in permeability did occur in Soil #3 from about 160 to 250 days (Figures 9 and 10) elapsed time for unknown reasons. More definite conclusions cannot be made at this time until the clay specimens are retrieved from the PVC cylinders. At that time, x-ray diffraction and scanning electron microscope tests will be performed on the clay specimens to determine if any physical or chemical changes have occurred in the compacted clays. This data may help to better explain the results of the experiment.

Figure 1. Swell versus time, hydrated FBC ash.

Figure 2. Swell versus time, non-hydrated FBC Ash.

Figure 3. Schematic of System for Monitoring Permeability Changes.

Figure 4. Close up of Compacted FGD and Soil in PVC tube.

Figure 5. Permeability versus time, Coolside-2, Soil #1.

Figure 6. Permeability versus Time, FBC, Soil #1.

Figure 7. Permeability versus Time, Coolside -2, Soil #2.

Figure 8. Permeability versus Time, FBC, Soil #2.

Figure 9. Permeability versus Time, Coolside -2, Soil #3.

Figure 10. Permeability versus Time, FBC, Soil #3.

COOLSIDE WASTE MANAGEMENT RESEARCH
Technical Progress Report
Contract No: DE-AC21-91MC28162
Report Period: December 1, 1995 to December 31, 1995

Statement of Project Objectives

Produce sufficient information on the physical and chemical nature of Coolside waste to design and construct physically stable and environmentally safe landfills.

Summary of Progress for Period.

The following report summarizes results from an ongoing investigation of the capacity of dry FGD wastes to absorb acidic gases. This work is part of a continuing effort to identify and evaluate potential commercial applications for FGD waste materials. Results from an investigation of CO₂ absorption in which waste samples were evaluated in both hydrated-solid and aqueous-slurry forms were previously reported. In that study, emphasis was placed on the removal of CO₂ from multi-component gas streams, particularly, natural-gas streams. The current probe is an expansion of the CO₂ absorption study and includes results from testing of H₂S, SO₂, NO, CH₄, and NO₂ absorption. The relative affinity of the dry FGD wastes for the gases examined thus far was found to be SO₂ > CO₂ > H₂S. CH₄ and NO are not absorbed and NO₂ apparently decomposes on contact with surface water to NO and HNO₃. Either the newly formed HNO₃ or incremental NO₂ passing through the reactor eventually is incorporated into the waste structure to form calcium nitrate following depletion of the excess water of hydration. The role

of particle size and available calcium on absorption capacity as well as mineralogic changes in the wastes resulting from the acid-gas exposure are discussed.

INTRODUCTION.

Utility boilers and tail-gas desulfurization units that utilize limestone-based sorbents to remove sulfur oxides generate ~20 million tons of flue-gas desulfurization (FGD) wastes each year in the U.S.¹ Following SO₂ sorption, a substantial portion of the Ca in these wastes remains unsulfated (as CaO or Ca(OH)₂), particularly in units that produce *dry* wastes such as the Coolside process. When hydrated, these materials exhibit a strong affinity to absorb acid gases at ambient temperature in proportion to their available-calcium content and particle size. Further, such absorption can be both rapid and near complete as shown in previous studies.^{2,3} Such a sorbent may have numerous commercial uses such as for the removal of CO₂ from natural gas (the focus of the prior study). Further, considering that about 95% of the ~20 million tons of flue-gas desulfurization (FGD) wastes generated annually in the US is discarded in landfills or holding ponds, commercial utilization of FGD wastes could stand to benefit from both a plentiful low-cost raw material as well as a significant savings in disposal.

The work reported here is a continuation of previous investigations of CO₂, CH₄, and H₂S absorption that includes more recent studies with NO, NO₂, and SO₂. In addition to waste samples from one of the Coolside demonstration-plant runs⁴ and four Coolside pilot-plant tests,⁵ waste samples generated in four utility/industrial coal-fired boilers were included in the study. With the exception of a utility-derived fly ash that served as a control, all study samples

were dry-FGD materials. Similar to the earlier studies, absorption capacity was examined for both hydrated samples as well as aqueous slurries (except for SO_2 and NO_2) prepared with FGD wastes.

EXPERIMENTAL.

Details for the most recent round of testing with NO , NO_2 , and SO_2 plus a brief description of the reactor system, study samples, and run procedures are presented in this section. Additional details on the reactor and run procedures can be found elsewhere.^{2,3,6,7}

Absorption Reactors. A schematic of the reactor system shown with a pair of 4" x 3/8"-i.d. ss tube reactors as configured for testing hydrated solids is shown on the left of Figure 1. Essentially the same system was used to measure absorption by aqueous waste slurries except that a pair of 250 mL-capacity gas scrubbers were substituted for the tube reactors (Figure 1-right). It should be noted that due to the high solubility of SO_2 in water along with the tendency for NO_2 to decompose on contact with same, only tests with hydrated solids were conducted for these two gases.

Samples. A total of 11 waste samples have been used throughout the investigation.^{2,5} Sample labels along with a very brief description of source as well as the results from 'available calcium' analysis are given in Table 1. Nine of the samples are fly ashes, designated with a -FA suffix. The remaining two, designated with a -BA suffix, are bed ashes. A Class F fly ash (L-FA) from a pulverized-coal-combustion (PCC) utility boiler served as a control and was the only non-FGD

Figure 1. Schematic of the absorption reactors used to measure gas absorption by hydrated-FGD wastes (left) and waste slurries (right).

Table 1. Waste samples examined.

Sample id	FGD Waste	Free CaO (wt%)	Source
L-FA	N	2.7	Utility-Boiler Fly Ash
FU-FA	Y	19.5	Fluidized bed-cyclone/baghouse
FU-BA	Y	26.8	Fluidized bed-bed ash
SD	Y	5.8	Utility spray dryer
CC-FA	Y	8.6	Fluidized bed-cyclone/baghouse
CC-BA	Y	21.2	Fluidized bed-bed ash
PP1	Y	12.9	Coolside pilot-plant waste
PP2	Y	9.1	Coolside pilot-plant waste
PP3	Y	8.5	Coolside pilot-plant waste
PP4	Y	19.9	Coolside pilot-plant waste
CS	Y	6.5	Coolside Demonstration plant

sample examined. The four fluidized-bed combustion wastes (FU-FA/BA and CC-FA/BA) were derived from circulating or entrained flow units operating on high-sulfur bituminous coal. Two types of dry, post-combustion flue-gas scrubber material were also examined, a spray-dryer ash from an industrial boiler in the Midwest, and materials from the Coolside duct-injection technology. The Coolside materials include one sample generated in Ohio Edison's 1990 demonstration of the technology at its Edgewater power plant³ (CS) as well as materials from the CONSOL's Coolside pilot plant in Library, PA (PP1-PP4).⁴ The major differences in the waste samples with respect to absorption appears to be in the particle size (BA > FA) and the proportions of free lime which ranged from <3% in the L-FA control to ~20% or greater in the FU-FA, FU-BA, CC-BA, and PP4 samples. Because the results from absorption studies with CO₂ have been given for all 11 samples in a previous report, tests conducted in this round were limited, for the most part, to the FU-FA and PP4 samples. These correspond to the two fly-ash samples with the highest free-lime content.

Run Procedures. All absorption tests were conducted at ambient temperatures. Hydrated samples were obtained by blending distilled water with dry waste under N₂. All hydrated samples examined in this phase of the study contained ~25 wt% water (dry basis) as this was determined to be near optimum in the previous CO₂ absorption studies. ~0.5-2.0 g of the hydrated sample was packed to the absorbent reactor while 6 g of Ottawa sand was packed to the bypass reactor. For the slurry tests, ~5 g of dry sample were added to 200 mL of distilled water in a 250-mL gas scrubber and stirred continuously during testing. The bypass scrubber contained distilled water only (200 ml).

Gas flow through the reactors was comprised solely of N_2 in the bypass line. Standard-gas blends containing various combinations of CO_2 , H_2S , CH_4 , and Ar were metered through the absorbent line as previously described.^{2,5} Standard-gas blends containing 0.509 vol% NO, 3.82 vol% NO_2 , or 3.81 vol% SO_2 were used in this latest round of tests. These blends were either quantitatively combined with high-purity Ar or with a blend of Ar/ CO_2 / CH_4 (30.3/49.6/20.1 vol%) prior to entering the reactor system.*

The exit streams from both the bypass and sample reactors were combined and continuously sampled with a capillary tube connected to the inlet of a VG-quadrupole mass spectrometer (QMS). The QMS was operated in a selected-ion-monitoring mode in which ion intensities for m/e 15- CH_3^+ (for methane), 18- H_2O^+ , 20- Ar^{2+} , 28- N_2^+ , 30- NO^+ , 34- H_2S^+ , 40- Ar^+ , 44- CO_2^+ , 46- NO_2^+ , and/or 64- SO_2^+ were recorded at approximately 1-second intervals.

For both reactor configurations, data collection was initiated with the switching valve in the bypass position, i.e., the test-gas stream passing through the sand-packed bypass reactor. After a timed interval, the valve was rotated so that the test-gas stream was switched to the absorbent reactor as the N_2 stream was simultaneously switched to the bypass reactor. Following exposure, the valve was returned to the initial position to reestablish the QMS baseline. At the conclusion of a run, the QMS data were exported to a spreadsheet where the molecular-ion signal for each gas of interest was ratioed to the Ar-ion signal. The curves described by these ratios were then numerically integrated over the interval of exposure. By comparison of these integrals to the

* Argon was generally included in all blends as a tracer gas to eliminate potential problems associated with instrumental drift, differential flow rates, and minor reactor leaks.

average test gas/Ar ratio obtained during passage through the bypass bed (before and after valve switch), the fraction of the test gas absorbed could be determined. Since gas flows and sample weights were known, absorption could be converted to and expressed on an absolute basis as standard cubic feet (SCF) absorbed per ton of waste. A similar approach was used for those runs in which more than one test gas was passed through the reactor in the same run.

RESULTS

It was previously shown the absorption of CO_2 required wetting of the dry FGD waste (hydration or slurry formation) without which, absorption proceeded at a prohibitively slow rate.^{2,3,5} This is illustrated in Figure 2 where absorption of CO_2 is observed to increase in a linear manner up to about 25 wt% added water. Further water addition created a mud-like consistency accompanied by a dramatic decline in the apparent absorption capacity. This decline is presumably due to decreased permeability of the hydrated sample preventing gaseous CO_2 from freely entering the sample bed. Though not yet proven, it is assumed that a similar behavior can be expected during absorption of other acid gases.

Absorption curves are shown in Figure 3 for a hydrated sample (top) and an aqueous slurry (bottom) prepared from PP4. This figure shows CH_4 , CO_2 , and H_2S response curves as these gases were simultaneously passed through the absorption reactor. These plots indicate

Figure 2. Absorption of CO_2 as a function of prehydration for samples of FU-FA.

that CH_4 was not absorbed, H_2S was moderately absorbed, and CO_2 was extensively absorbed. Scrutiny of the absorption curves reveals that the H_2S response rose to greater than baseline levels in both runs as H_2S was passed through the sorbent bed. This indicates that some of the H_2S absorbed early in the exposure was displaced by CO_2 as the capacity of the PP4 sample was depleted. Also note that the absorption kinetics were more rapid for the hydrated sample though on an absolute basis, absorption was about twice as great for the aqueous slurry ($\sim 3,800$ SCF/t vs $\sim 1,800$ SCF/t). It was previously shown that CO_2 incorporates into the hydrated waste sample

Figure 3. Absorption curves for CH_4 , CO_2 , and H_2S simultaneously passed through a hydrated sample (top) and aqueous slurry (bottom) of PP4.

to form calcite whereas absorption of CO_2 by the waste slurry resulted in capture as HCO_3^- ions which remain in solution. Thus, each CaO unit in the hydrated solids, following hydration to portlandite ($\text{Ca}(\text{OH})_2$), may capture one CO_2 molecule to form CaCO_3 or in slurry form, capture two CO_2 molecules to form aqueous-phase HCO_3^- ions.

CO_2 absorption by waste slurries is plotted as a function of available-calcium content for the 11 study samples in Figure 4. The majority of the samples plot along a straight line with the exception of the two points on the lower right.

These two outliers represent the two samples of bed ash (FU and CC) whereas the other points

in Figure 4 represent samples of fly ash. This plot emphasizes the dependency of CO_2 absorption on both available calcium and particle size. That is, the significantly larger particle size of the bed-ash samples as well as potential blockage of particle pores by chemisorbed SO_2 likely limits diffusion of CO_2 (and presumably other gases) to the particle interior.

Figure 4. CO_2 absorption as a function of the available calcium. The two points on the bottom right represent samples of bed ash; all others are fly ash samples.

Tests with NO , NO_2 , and SO_2 . Absorption curves for NO , NO_2 , and SO_2 are shown in Figure 5 as these gases were passed through either an aqueous slurry (NO) or a hydrated sample of PP4 (NO_2 and SO_2). For all three runs shown in Figure 5, CO_2 was blended to the test-gas stream prior to routing to the absorption reactor. All hydrated samples examined in this phase of the study contained ~25 wt% water (dry basis) as this was determined to be near optimum in the CO_2 absorption studies.

The top plot shows essentially no absorption of NO . Likewise, no significant absorption of NO was measured when this gas was passed through the slurry without CO_2 (not shown) or when passed through a sample of hydrated PP4 (not shown). Based on these results, it was concluded that the FGD waste materials do not absorb NO in either slurry or hydrated-solid form.

The middle plot in Figure 5 shows simultaneous removal of NO_2 and CO_2 . Both gases were

Figure 5. Test gas/Ar ion ratios for NO (a), NO_2 (b), and SO_2 (c) during exposure to hydrated PP4 (a) and PP4 slurry (b/c). CO_2 absorption shown in all three plots.

extensively absorbed immediately after the valve switch to expose mode. However, ~5 min into the exposure, the response curve for CO_2 exceeded its baseline established during bypass mode (before and after exposure). This suggests that CO_2 initially absorbed was displaced as the run proceeded, i.e., as the absorption capacity of the slurry was depleted. Unlike CO_2 which is chemisorbed by portlandite ($\text{Ca}(\text{OH})_2$) to form CaCO_3 , it is believed that NO_2 is not removed in a like manner (i.e., to form calcium nitrate). Rather, NO_2 appears to decompose on contact with excess hydration water to form HNO_3 and NO . This is supported by the NO and H_2O curves also shown in Figure 5b. Immediately after switching to expose mode, the NO_2 signal is lower than that of NO . However, about 40-45 min into the run, the NO_2 response increases above that of NO concurrent with the depletion of H_2O . This is congruent with a decrease in NO_2 decomposition as the excess hydration water is consumed. The continuing increase in the NO signal in the latter stages of the exposure is due to breakdown of NO_2 molecules as the concentration of this latter molecule increases within the ion source. It appears that either HNO_3 or NO_2 does ultimately react with portlandite to produce H_2O and calcium nitrate hydrate but not until much of the hydration water is depleted. This conclusion is based on results to be discussed in the next section on XRD analyses.

Finally, integration of the CO_2 -response curve revealed a net release of CO_2 of ~150 SCF/t. This net production of CO_2 likely derives from calcite (CaCO_3) inherent to the FGD waste which is attacked by the newly-formed nitric acid. Evidence in support of this supposition will be presented in the section on XRD analyses to follow.

The bottom plot in Figure 5 shows SO_2/CO_2 absorption. As before, CO_2 was initially absorbed

but later displaced, this time by SO_2 , as the run proceeded. Integration of the absorption curves (60 min interval) indicated an average absorption of $\sim 3,800$ SCF/t SO_2 and a net release of ~ 550 SCF/t CO_2 . Again, the net production of CO_2 is attributed to the breakdown of low levels of inherent calcite in the PP4 sample as indicated by XRD (calcite XRD peaks were totally absent in the spectra of wastes following exposure to SO_2). The measured level of SO_2 absorption is essentially the same as the level of CO_2 absorption in the absence of SO_2 . This provides additional evidence that the SO_2 and CO_2 are competing for the same calcium absorption sites and that similar to high-temperature absorption, SO_2 is the more strongly absorbed of the two at ambient temperatures.

Near the end of the 60' exposure, absorption of SO_2 and release of CO_2 is essentially complete. In contrast, during exposure to a blend of NO_2/CO_2 (Figure 5b), NO_2 decomposition and CO_2 displacement is not complete despite the fact that essentially the same volumes of NO_2 and SO_2 were flowed through the reactors during these runs. In a single run with SO_2 and NO_2 (w/o CO_2), SO_2 response began to return to baseline well before NO_2 which again exhibited an inverse relation to water availability. Thus, based on these results, it would appear that SO_2 removal is controlled by the chemistry of the waste sample whereas NO_2 removal seems more dependent on water content. Additional tests are planned to better characterize the parameters that control NO_2 removal.

Changes in mineralogy. X-ray diffraction (XRD) spectra of hydrated-PP4 waste samples are shown in Figure 6. The top plot in Figure 6 is for a hydrated sample that had been simultaneously exposed to CO_2 and H_2S , the middle plot is following exposure to NO_2/CO_2 , and

Figure 6. XRD spectra of PP4; hydrated only-darker lines; exposed sample-lighter shading. c-calcite (CaCO_3); n-calcium nitrate hydrate; g-gypsum ($\text{CaSO}_4 \cdot \text{H}_2\text{O}$); h-hannebachite ($\text{CaSO}_3 \cdot 5\text{H}_2\text{O}$); p-portlandite- $(\text{Ca}(\text{OH})_2)$.

the bottom plot is following exposure to SO_2/CO_2 . A spectrum of a hydrated sample of PP4 that had not been exposed to the test gases is shown in all three plots for comparison (bold lines).

In the top plot, the major mineralogic changes following exposure to the $\text{CO}_2/\text{H}_2\text{S}$ blend was depletion of portlandite ($\text{Ca}(\text{OH})_2$) and formation of calcite (CaCO_3). There is no indication of CaS formation. When H_2S was passed through the sample without CO_2 (not shown), portlandite was again depleted, only this time accompanied by the formation of an unidentified mineral with peaks near 9 and 20 (2-theta). The suspected stoichiometry of the unknown is $\text{Ca}(\text{OH})_{2-x}(\text{HS})_x$ though this structure has not been confirmed. The absence of this unknown in the sample following exposure to $\text{CO}_2/\text{H}_2\text{S}$ is congruent with the QMS data that showed strong absorption of CO_2 (>3,000 SCF/ton) and much lesser absorption of H_2S (~125 SCF/ton) in the presence of CO_2 as discussed earlier.

Again, depletion of portlandite from the parent to the exposed sample can be seen in Figure 6b in which NO_2 and CO_2 were passed through the hydrated sample. Several new peaks appear which were identified as a hydrated form of Calcium nitrate ($\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$). However, for runs that were aborted prior to the depletion of the excess hydration water, the calcium nitrate peaks were not observed in the exposed sample. This suggests that the NO_2 does not initially incorporate directly into the waste matrix. Based on the absence of calcium nitrate peaks in these aborted runs and the fact that NO_2 decomposes on contact with water, it is believed that NO_2 passing through the hydrated sample decomposes to NO and HNO_3 . Since such decomposition would result in the release of NO to the vapor phase (NO was earlier shown not to be absorbed by the waste matrix) and deposition of HNO_3 onto the sample surface, no significant change in

the XRD pattern would be discerned. Thus, the absorbed NO_x species could exist as either HNO_3 or alternately in an amorphous structure without significantly affecting the XRD pattern. Further, at some point during the exposure as the excess water is depleted, either the HNO_3 reacts with portlandite to form H_2O and $\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ or additional NO_2 being fed to the reactor reacts directly with portlandite to generate the same products. Follow-up tests in which the level of hydration water will be varied should provide additional evidence of the mechanism of NO_2 removal.

Depletion of portlandite from the parent to the exposed sample is again evident in the bottom plot of Figure 6 in which a mixture of CO_2/SO_2 was used. Note that the minor calcite peaks that are present in the parent (hydrated) samples are absent in the same sample following exposure. To some extent, the inherent calcite was depleted during exposure to NO_2 but not completely as was the case during exposure to SO_2 . This is again consistent with the greater release of CO_2 observed in the SO_2 runs (~550 SCF/t) compared to analogous NO_2 runs (~150 SCF/t). Returning to the bottom plot of Figure 6, several new peaks appear in the sample following exposure to CO_2/SO_2 which, for the most part, can be attributed to hannebachite ($\text{CaSO}_3 \cdot 0.5\text{H}_2\text{O}$). Thus, it appears that SO_2 is mostly incorporated by substitution for the hydroxyl ions in portlandite with some substitution for CO_2 in the inherent carbonates.

SUMMARY

Hydrated FGD wastes exhibit a strong affinity for CO_2 , H_2S , and SO_2 ranging upwards of 4,000 SCF/t for each of these gases when individually contacted with samples of PP4 and FU-fly ash. In tests conducted with various blends of the study gases, the relative order of affinity at room

temperature appears to be $\text{SO}_2 > \text{CO}_2 > \text{H}_2\text{S}$. In contrast, NO_2 was found to decompose on contact with the hydrated samples to form NO and HNO_3 with the eventual formation of hydrated calcium nitrate following depletion of the excess water of hydration. Little or no absorption of CH_4 or NO was observed. In tests of CO_2 absorption, absorption capacity was found to be directly related to the available-calcium content and inversely to the particle size of the waste. Further, absorption did not proceed at a significant rate without the addition of water to the dry wastes. Though additional tests are required, preliminary indications are that the absorption of H_2S and SO_2 would be dependent on the same factors whereas absorption of NO_2 appears to be more dependent on the amount of excess hydration water. XRD analyses showed that exposure of hydrated FGD wastes to CO_2 , H_2S , and SO_2 resulted in the depletion of portlandite ($\text{Ca}(\text{OH})_2$) in all cases with subsequent formation of calcite (CaCO_3), an unknown mineral, and hannebachite ($\text{CaSO}_3 \cdot \text{H}_2\text{O}$), respectively. Similarly, exposure to NO_2 resulted in the apparent initial formation of either an amorphous nitrate/nitrite mineral or absorbed HNO_3 followed by formation of $\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$.

ACKNOWLEDGEMENT

Our thanks to Mr. Ken Baker of Jefferson Gas Transmission for useful discussions during this phase of the project.

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