

THE EFFECT OF CARBONATION REACTIONS ON THE LONG TERM STABILITY OF PRODUCTS MADE FROM DRY FGD MATERIALS.

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ABSTRACT

Flue gas desulfurization (FGD) technologies such as spray dryers and fluidized bed combustors produce a dry by-product which often has substantial quantities of unreacted lime or hydrated lime. The reactivity of the lime with the other constituents upon hydration, imparts a cementitious property. The major early hydration reactions include: the hydration of calcium sulfate to gypsum, the formation of the cementitious mineral ettringite, a calcium sulfo-aluminate-hydrate and the formation of CAS gels. Weathering is found to decrease the strength and integrity of these materials. Field studies, based on soil gas analysis, indicate that these materials rapidly absorb CO₂. Studies of the mineralogic transformation which take place upon hydration and subsequent weathering indicate that carbonation reactions result in extensive calcium carbonate formation over time. However, carbonate formation takes place at the expense of gypsum, not ettringite as suggested by laboratory studies. Based on field evidence and X-ray data, ettringite appears to be relatively stable.

INTRODUCTION

Dry lime and limestone based flue gas desulfurization methods, such as fluidized bed combustion and spray dryer technologies, produce a dry product which typically contains free lime in a hydrated or unhydrated form. Free lime along with water, the products of sulfation, typically anhydrite CaSO₄, or hemi-hydrate (CASO₄.1/2H₂O), and the decrystallized aluminosilicate mineral matter from the coal readily react to form a hardened mass. Because of this cementitious characterization many uses for these materials have been proposed such as structural fill in mines, road base stabilization, grouts and, in a pelletized form, artificial aggregates for concrete and asphalt application. The use of this material is dependent in most cases on the material's strength, durability and long term stability.

However, the principal cementitious mineral, ettringite, has long been known to be susceptible to attack and degradation from carbonation. Laboratory experiments have determined that ettringite can be readily broken down with high concentrations of CO₂ under hydrous conditions to more fundamental compounds.^{1,2} This results in a loss of strength and material integrity.

STUDY OBJECTIVES, METHODS AND MATERIALS

The objective of this work is to determine how important carbonation reactions are and their effect on the nature of the materials. Studies are being conducted of CO₂ uptake in field lysimeters filled with materials from the U.S. Department of Energy and U.S. the Environmental Protection Agency sponsored demonstration of the Coolside technology at Ohio Edison's Edgewater Power Plant (Coolside #2).³ The Coolside demonstration material was placed in three large (3x3x3.5 m deep) field lysimeter cells. These lysimeters were packed at densities within 5% of 1,100 Kg/m³ (cell L3), 1,040 Kg/m³(L2), and 720 Kg/m³(L1). The cells were monitored for their mineralogical changes after having been exposed for three seasonal cycles. Drill cores were prepared from the upper 0.5 meters of the three lysimeters and the cored material was analyzed for ettringite formation using X-ray diffraction and scanning electron microscopic analyses. Ettringite was observed to have formed in all lysimeters upon reaction of the FGD waste material with the downward penetrating rain water. In April of 1994 the lysimeters were equipped with gas monitoring wells at 20, 40 and 76 cm of depth (Table I). The wells consist of glass tubes, which are open at one end to a given depth and capped with a septum to allow gas to be withdrawn for analysis. In April of 1995, wells at 107 cm of depth were added.

The impact of weathering on the mineralogy of the materials was conducted on samples collected at the Freeman United Coal Company's Crown III Mine, located in central Illinois. The company has pioneered fluidized bed combustion backhaul and disposal methods at this site which was open in 1991. Circulating fluidized bed combustion (CFBC) fly ash is hauled in semi-trailer dump trucks to the mine. The ash is dumped into a hopper and metered out with screw feeders and mixed with water before being pumped to the disposal site. The solids are settled from the slurry and the water returned to the mixer. The solids settle into a mud-like paste that typically hardens within days. In addition to the fly ash materials, coarser bottom ash representing about 20% of the total material received is also handled at the mine. It is disposed of dry in the landfill area and

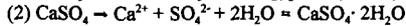
then wetted.

EARLY HYDRATION AND CEMENTITIOUS REACTIONS

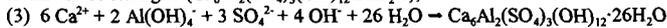
The comparison of the dry fluidized bed combustion materials varies but generally the materials consist of anhydrite (CaSO_4), lime (CaO), quartz (SiO_2), minor calcite (CaCO_3) and glassy silicious ash particles. In spray dryer and duct injection materials the lime and anhydrite may be partially or fully hydrated. The important early hydration reactions consist of the hydration of the lime to portlandite $\text{Ca}(\text{OH})_2$, and its partial dissolution to form a highly alkaline solution, or

$$(1) \text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca}(\text{OH})_2 = \text{Ca}^{2+} + 2\text{OH}^-$$

and the hydration of anhydrite to gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), or



Anhydrite is an orthorhombic mineral and is much denser (2.98 g/cm^3) and more soluble ($K_s = 4.2 \times 10^{-5}$) than monoclinic gypsum (2.32 g/cm^3 and $K_s = 2.4 \times 10^{-5}$). The anhydrite-gypsum transition probably does not occur in the solid state, but rather through a dissolution-precipitation mechanism. Another very important reaction which takes place rapidly upon hydration is the formation of ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$),



The formation of ettringite is a competing reaction to that of gypsum. However, it also requires alumina and hydroxide ions and is typically found on, or near, coal ash particles, its source of alumina.

The ideal form of ettringite is $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$. Stoichiometric ettringite, however, is an artifact of the laboratory, and in nature it is variable in composition. Another important member of the ettringite family is thaumasite, $\text{Ca}_6\text{Si}_2(\text{SO}_4)_3(\text{CO}_3)_2(\text{OH})_{12} \cdot 24\text{H}_2\text{O}$ which contains silica in substitution for some of the alumina and carbonate for some of the sulfate. It is now believed by some that thaumasite and ettringite form a solid solution series.⁴

The structure of ettringite is complex. Work by Moore and Taylor determined that ettringite had a trigonal hexagonal unit cell which consists of columns which have the composition $(\text{Ca}_6[\text{Al}(\text{OH})_6]_2 \cdot 24\text{H}_2\text{O})^{6+}$ which are aligned along the crystallographic c-axis (Al^{3+} ions are octahedral coordinated by $(\text{OH})^-$) and are accompanied by channels of the composition $(\text{SO}_4)_3 \cdot \text{H}_2\text{O})^{6-}$.⁵

CARBONATION REACTIONS

The rapid reaction of carbon dioxide with fresh CFBC material, where ettringite had not yet formed, was measured in our own laboratory experiments and presented previously. We found that the rate of uptake and quantity of gas absorbed was highly dependent upon the degree of hydration.⁶ Dry samples of ettringite also do not react significantly with CO_2 . Hydrated samples of ettringite rapidly reacted with CO_2 and decomposed to form gypsum, aluminum hydroxide and calcite.

The reactivity of CO_2 with synthetic ettringite in the laboratory is not directly relatable to complex mineral assemblages under field conditions. As part of our field study of the leaching potential of the materials generated by the Coolside process, we measured the concentration of CO_2 in both the soil gas and the gas in the Coolside FGD materials. Concentrations of CO_2 , as high as 3% were measured in the soil gases overlying the Coolside materials but were either near the limits of detection or unmeasurable in the gases within the materials themselves or near the soil-FGD material boundary (Table I). Thus, field observations confirmed the absorption of CO_2 by the FGD materials found in the laboratory experiments.

MINERALOGIC TRANSFORMATIONS

The mineralogic transformations which take place during weathering was studied in samples collected from the Freeman United FDG disposal area. A suite of 19 samples were collected, ranging in age from fresh unhydrated materials to severely weathered samples which were approximately 3 years old.

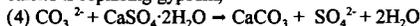
The fresh unhydrated samples were composed of anhydrite, lime and glassy silicious material derived from the coal. Ettringite was found to form rapidly, as it is an important mineral in the 1 day and 1 month old samples and was the dominant mineral phase present in some of the more aluminum rich samples (Figure 1). The total amount of ettringite formed correlated strongly with the amount of alumina in the samples, suggesting that its formation was limited by the availability of this component.

The older samples collected strongly showed the effects of carbonation. They were in general weak and friable compared to the freshly hydrated samples. The amount of calcite present in the older samples was found to be much higher. The hydrated fly ash samples had an average of 6.7% CO₂ versus 16.7% in the fly ash samples older than one year. Thus atmospheric CO₂ is a major reactant in the system.

At very high pHs, i.e. ~12, such as developed by a solution saturated with Ca(OH)₂, CO₂ is readily absorbed, reacts directly with the hydroxide and disassociates to the carbonate ion, (3) CO₂ + OH⁻ = HCO₃⁻ = H⁺ + CO₃²⁻

The carbonate and calcium ions form calcium carbonate, which is highly insoluble at an elevated pH.

The concentration of sulfate in the samples was found to decrease in older samples by about 25%. This was concomitant with the increase in carbonate, which suggests that, in the longer term, calcite is replacing gypsum,



Gypsum all but disappeared in the older samples. This is not unexpected, as calcite has a lower solubility product than gypsum (pK_s ~ 8.4 for calcite vs pK_s ~ 4.6 for gypsum at 25 °C), and is much less soluble under alkaline conditions.

In general the field study indicated that ettringite is highly stable in the weathering environment, as the X-ray diffraction results indicated its presence in abundance in all of the older samples (Figure 1). The most severely weathered sample contained no gypsum and did show some attenuation of the ettringite peaks relative to the other samples, and the ettringite in this sample may have undergone some weathering induced decay. However, in general the ettringite in the samples was found to be highly stable relative to other neoformed hydrous minerals such as gypsum and portlandite.

SUMMARY

The field studies fully confirmed the laboratory measurements indicating the highly reactive nature of the dry FGD materials with respect to CO₂. However, direct carbonation of ettringite was not found. The primary carbonation reaction is the replacement of gypsum by calcite and the presumable loss of sulfate from the system. Only when the gypsum was exhausted was evidence found for the carbonation of ettringite. McCarthy et al. found thaumasite forming in weathered AFBC and LIMBs materials which they studied and noted that the samples lost strength when thaumasite appeared.⁷ No Thaumasite was detected in any of the weathering products for these materials. The loss of competency and strength in these samples appeared to be a function of the breakdown of matrix minerals other than ettringite, such as gypsum and calcite.

ACKNOWLEDGEMENTS

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Lysimeter	Material	Depth	N	Avg %CO ₂	Std Dev	Max	Min
L1-Coolside	Soil	20	39	0.531	0.392	1.9	0.05
	Soil	48	38	0.152	0.100	0.4	dl
	Soil/FGD	76	38	0.008	0.033	0.2	dl
	FGD	107	14	0.002	0.005	0.015	dl
L2-Coolside	Soil	20	39	0.486	0.314	1.4	0.05
	Soil	48	39	0.115	0.114	0.83	dl
	Soil/FGD	76	39	0.013	0.031	0.15	dl
L3-Coolside	FGD	107	14	0.001	0.003	0.01	dl
	Soil	20	30	0.693	0.620	2.8	dl
	Soil	48	29	0.992	0.892	3.2	0.02
L4-PCC FA	Soil/FGD	76	31	0.098	0.351	2	dl
	FGD	107	10	0.007	0.007	0.015	dl
	Soil	20	39	0.218	0.221	0.8	dl
	Soil	46	38	0.084	0.068	0.3	dl
L4-PCC FA	Soil/FA	76	39	0.223	0.214	0.84	dl
	Fly Ash	107	14	0.313	0.280	1	0.04

Table I. CO₂ Concentration Measured in Gas Wells Located Above and in Lysimeter Field Cells Filled with Coolside FGD Materials. Control Cell L4 is Filled with Conventional Fly Ash. CO₂ is in Percent Volume. Atmospheric CO₂ Concentration is Approximately 0.036% (360 ppm) at This Site, Detection Limit (dl) is ~0.0150% (150 ppm).

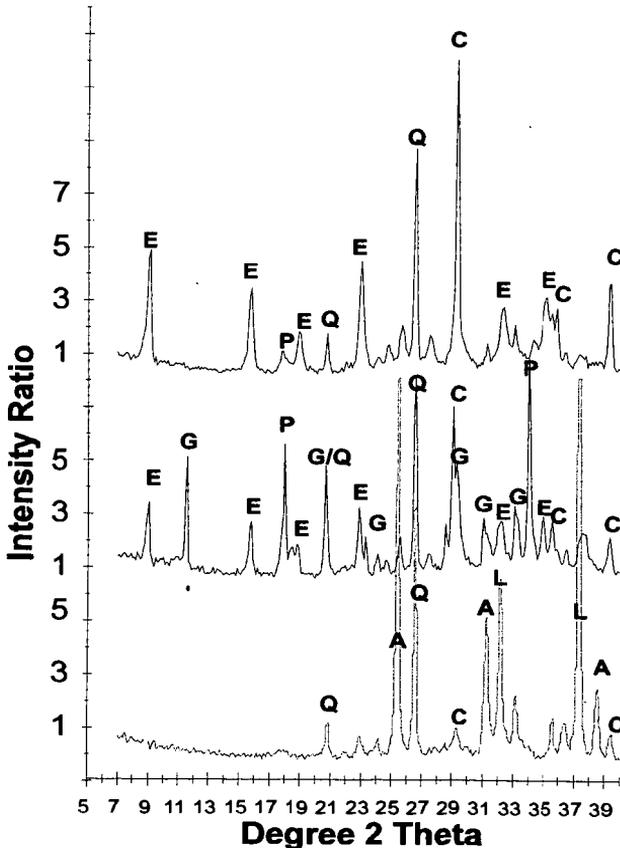


Figure 1. Xray Diffraction Spectra for As-Received dry FGD Material (Lower, Dotted Trace), Recently Hydrated Material (1 Week Old) and Highly Weathered Material (Upper, Approximately 2.2 years Old). Peaks for Calcite (C), Gypsum (G) Anhydrite (A) Ettringite (E), Portlandite (P), Quartz (Q), Lime (L) are Indicated.