

Coal Combustion By-Product Diagenesis II

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INTRODUCTION

Class C fly ash, some flue gas desulfurization (FGD) residues, and by-products of many clean coal technologies are cementitious, which indicates a potential for high-volume utilization in civil engineering. As described in the 1995 and 1997 Symposia,¹ the established 18-hour, 7-day, or 28-day regulatory or engineering tests of chemical and physical properties may not be representative of the long-term behavior of these materials when exposed to the environment. Studies of the behavior of disposed CCBs, however, can provide insights into the long-term stability of these materials in natural utilization settings.

The goal of this project is to learn more about the phenomenon of coal conversion by-product (CCB) diagenesis, first described by our group and co-workers at UND EERC seven years ago. CCB diagenesis is a change over time in the mineralogy that occurs after some CCBs are disposed in a landfill or utilized for a civil engineering application. This change in mineralogy is typically accompanied by a gain, loss or redistribution of major, minor and trace elements, and alteration of physical properties²⁻⁴. To attain this goal, two objectives were defined. The first is to develop improved methodology for quantitating mineralogy of these complex crystalline phase assemblages, using a modern quantitative X-ray Diffraction (QXRD) technique which has significant advantages over existing, often inadequate techniques. The Rietveld QXRD method has been successfully implemented in quantitative characterization of CCB mineralogy. The second objective is to investigate the phenomenon of CCB diagenesis further by studying additional materials recovered from disposal landfills or civil engineering works. Over 300 feet of core material has been recovered and quantitatively characterized from eight boreholes at four sites representing a range of CCB types.

MATERIALS AND METHODS

Core material was recovered from four sites. CCBs derived from a clean coal combustion technique (Circulating Fluidized Bed Combustion, CFBC), dry-process flue gas desulfurization (FGD), and Class F and C fly ashes in long-term disposal settings have been studied. Three of these sites were disposal landfills adjacent to the power plants that produced the CCBs, and the fourth site (CFBC material) was a road embankment.

Crystalline phase assemblages were identified using X-ray diffraction. The diffractograms presented here were obtained on instruments utilizing CuK α radiation, and equipped with theta-compensating variable divergence slits and graphite diffracted beam monochromators. Detailed discussions of XRD characterization⁵ and CCB mineralogy⁶ have been presented previously. Quantification of crystalline phases identified by XRD was performed by Rietveld analysis, using GSAS software.

RESULTS AND DISCUSSION

Rietveld QXRD analysis. Hydrated CCBs are chemically and mineralogically complex, which makes quantitative mineralogy determination by conventional X-ray diffraction unusable or unreliable. The whole-pattern Rietveld quantitative X-ray diffraction (RQXRD) method, however, can overcome many of the problems and seems well suited to improve reliability.

CCB materials typically contain a large number of crystalline phases, with many present in minor quantities. Many of these phases exhibit solid solution behavior and polymorphism, as well as varying degrees of crystalline order. Additionally, a significant amorphous or glassy content is typically present, further reducing crystalline signals. Many of the phases present contain large numbers of diffraction peaks which overlap with those of other phases. These factors make conventional semi-quantitative XRD analysis, which utilizes small numbers (often only one) of analyte peaks, and which depends on the availability of representative reference materials, unreliable for precise and accurate quantitative determinations.⁵ Reference materials used in conventional semi-quantitative XRD are often difficult to obtain and are typically not representative of the actual CCB phases, which, as noted above, are subject to solid solution behavior, polymorphism, variable degrees of crystallinity, and severe peak overlap.

Rietveld analysis, originally developed for refinement of known crystal structures, has recently progressed to include fully quantitative multiphase analytical capabilities. This method uses the full XRD profile to simultaneously refine the crystal structures of all constituent crystalline phases, and can model structural parameters sensitive to chemical variation (e.g., site chemical compositions), specimen texture effects (i.e., preferred orientation), and parameters indicative of crystalline order (crystallite size and strain, stacking fault defects).⁷

Successful implementation of Rietveld analysis requires a sophisticated understanding of X-ray crystallography, qualitative and quantitative XRD analysis, and CCB crystal chemistry and phase behavior. Based on full characterization of a wide variety of disposed CCBs, including thorough testing of the applicability of Rietveld analysis to CCBs, this study provides the coal ash community with not only a generic understanding of long-term behavior of CCBs exposed to the natural environment, but also a structured set of protocols to follow in use of the Rietveld QXRD method for many CCBs. General recommendations and procedures have been developed and are provided for the method overall, along with specific protocols for the freely available public domain package, GSAS, developed at Los Alamos National Labs.⁸ These recommendations may be viewed at [<http://qxrd.chem.ndsu.nodak.edu/ccbs>].

The first step in utilizing the Rietveld method is selection of crystal structure data for each crystalline phase in a mixture. Review of the literature and crystallographic databases for the most reliable structures, and testing with the DOE code GSAS were completed in 1997. The downloadable GSAS input data sets are available for use by other analysts at our website [<http://qxrd.chem.ndsu.nodak.edu/ccbs/>]. Several other Rietveld codes were evaluated for CCB analysis, but GSAS was found to be the most robust and applicable software for this application. A GSAS-based RQXRD protocol has been developed, and analytical sensitivity, precision and accuracy have been determined using standard mixtures of NIST Standard Reference Materials (SRMs) and other CCB phases. Relative error determined from the standard mixtures is typically in the ± 10 -15 wt% range (Table 3). The protocols are in use now for characterization of CCB samples obtained for this project. The protocol has also been applied to a group of NIST SRM Fly Ashes as well as the core material in this project.

Recovered core material from the four sites has been successfully modeled using the Rietveld QXRD method. Three to eight crystalline components, plus an internal standard added for crystalline content normalization, were analyzed, as shown in Figure 1. Multiphase peak overlap was easily accounted for, and peak broadening and preferred orientation were modeled for each of the phases present, as necessary.

CCB Diagenesis. Detailed discussions of earlier studies of emplaced CCBs have been previously presented^{1-4, 9-13}. Briefly, three of the five materials, at three of the four sites studied experienced significant by-product diagenesis, including mineralogical alteration coincident with dramatic change in physical properties. This includes disposed materials from two advanced combustion techniques and dry process flue gas desulfurization. The predominant new compound generated in the three sites during diagenesis, and associated with undesirable engineering properties, was the mineral thaumasite (see Table 2 for nominal compositions of cited minerals). The appearance of thaumasite in two of the test cell core samples was accompanied by loss of much of the initial strength.^{2,12} If thaumasite formation is not a major cause of strength loss, it is certainly associated with it.

Diagenesis was not observed in two of the five CCBs studied. In the case of fluidized bed combustion disposed under arid conditions, no significant alteration beyond initial hydration was observed. This has been attributed to insufficient moisture infiltration. The other case in which no diagenesis occurred involved a disposed material composed of a blend of AFBC by-products and fly ash¹⁰. The absence of significant by-product diagenesis in this second case may be due to the additional, less-reactive, C-S-H in the cementitious matrix, or simply to insufficient moisture infiltration to continue hydration reactions and transport leached constituents within the materials¹².

Of the four disposal sites characterized in the present study, two have shown indications of long-term diagenetic alteration. One of these involves Class F fly ash and other conventional boiler by-products from a disposal site in Kentucky, which contains material emplaced for up to 19 years. The material contains predominantly unaltered Class F fly ash components (quartz, mullite, magnetite, hematite, and low calcium aluminosilicate glass) as predicted. However, samples from each of the two boreholes indicate a zone enriched in ettringite, a common

component of high calcium CCBs. Occurrence of this phase in this Class F fly ash pond is curious. The chemical components calcium and sulfur, as well as the extreme (high) pH conditions typically required for formation are not expected in this setting. Representative quantitative results for the materials studied are given in Table 4.

Samples from the Indiana road embankment, which contains a mixture of Stoker ash and CFBC by-products appear to be in the process of alteration seen in previous studies of emplaced FBC materials. This is indicated by the presence of thaumasite in a few of the samples in addition to the typical hydration mineralogy of CFBC materials.

Core samples from the Midwestern FGD site show little change from predicted initial hydration mineralogy. Assemblages characterized show typical nonreactive high-Ca fly ash phases, and unreacted (portlandite) and reacted (bassanite, gypsum, and hannebachite) scrubber residues. Phases formed by later hydration or carbonation include ettringite, calcite, and gypsum. The only long-term alteration observed in the core samples studied to date involves continued hydration of bassanite to gypsum in many of the near-surface samples, as well as leaching of gypsum near the surface of the landfill. No evidence of thaumasite has been found in these samples.

The Class C fly ash materials sampled from the backhaul site in central North Dakota also show little change from predicted initial hydration mineralogy. Typical (unreactive) Class C fly ash components (quartz, merwinite, periclase, hematite, high calcium aluminosilicate glass) were found. Minor amounts of ettringite (<10 wt%) were present in addition to occasional occurrence of the hydration phases monosulfoaluminate and strätlingite. XRD results from two of the boreholes from the older site (up to 19 yrs emplacement) sampled at this location also indicate significant FGD residue codisposed with the Class C fly ash. The scrubber phase, hannebachite, is present in major quantities (up to 50 wt%). In many cases where hannebachite is present, the ettringite phase identified shows significant deviation in diffraction peak position, potentially indicating sulfite substitution in the channels typically occupied by sulfate oxyanions.

IMPLICATIONS FOR COAL COMBUSTION BY-PRODUCT UTILIZATION

The initial behavior one observes on hydrating the cementitious CCB materials discussed here is similar to that of a low-strength concrete. However, by-product diagenesis associated with many of these CCBs has been observed to reduce strength by up to 90%, and increased permeability by two orders of magnitude, after just a few years in the natural environment²⁻⁴. The characteristics of the altered byproducts resemble those of soils more than concrete. These results should be noted by those working on utilization of this class of by-products for civil engineering and construction applications, manufacturing of aggregates, etc. Initially promising 7-day or 28-day laboratory tests of strength and permeability may not be characteristic of these materials on exposure to the environment. Blending of CCBs with fly ash to increase the proportion of cementitious C-S-H, and controlling subsequent moisture additions could minimize deleterious by-product diagenesis. Alternatively, for some applications, it might be desirable to design a system where by-product diagenesis is allowed to develop naturally.¹⁰

The Rietveld whole-pattern quantitative X-ray diffraction technique has been shown useful in determining mineralogical abundances of crystalline CCB phases (as well as noncrystalline phases, by difference). While not straightforward in many cases, especially in the presence of hannebachite, the Rietveld technique has been successfully employed with four distinctly different CCB assemblages. This technique has significant advantages over conventional semi-quantitative methods such as RIR. The applicability of the method to CCBs has been rigorously tested, allowing for the development of suggested estimated standard deviations for the phases most commonly encountered in CCBs.

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Table 1. Sites and materials involved in this study.

Code	CCB Type	Coal Type	Landfill Site	Climate	Core Age
Midwest FGD	Dry-Process Flue Gas Desulfurization Residue	MT Sub-bituminous	Midwestern US	Humid	Up to 5 yrs
IN CFBC	Circulating Fluidized Bed Combustion, Stoker Ash	IN Bituminous	Indiana	Humid	Up to 3 yrs
ND C	Class C fly ash, FGD residue	ND Lignite	North Dakota	Semi-arid	Up to 17 yrs
KY F	Class F fly ash, bottom ash, slag, etc.	KY Bituminous	Kentucky	Humid	Up to 19 yrs

Table 2

Selected Mineral Names and Nominal Compositions

Mineral Name	Nominal Chemical Composition
Quartz (Qz)	SiO ₂
Mullite (Mu)	Al ₆ Si ₂ O ₁₃
Hematite (Hm)	Fe ₂ O ₃
Magnetite (Ma)	FeO*Fe ₂ O ₃
Merwinite (Mw)	Ca ₃ Mg(SiO ₄) ₂
Periclase (Pc)	MgO
Calcite (Cc)*	CaCO ₃
Hannebachite (Hb)	CaSO ₃ • 1/2H ₂ O
Bassanite (Bs)	CaSO ₄ • 1/2H ₂ O
Gypsum (Gp)	CaSO ₄ • 2H ₂ O
Ettringite (Et)	Ca ₆ Al ₂ (SO ₄) ₃ (OH) ₁₂ • 26H ₂ O
Thaumasite (Tm)	Ca ₆ Si ₂ (SO ₄) ₂ (CO ₃) ₂ (OH) ₁₂ • 24H ₂ O
Monosulfoaluminate	Ca ₄ Al ₂ (SO ₄)(OH) ₁₂ • 10H ₂ O
Strätlingite	Ca ₂ Al(Si,Al) ₂ O ₇ • 8H ₂ O

Table 3. Suggested estimated standard errors associated with CCB phases analyzed by RQXRD.

ese ^a at given abundance level			Minerals
<1 wt%	1-5 wt%	>5 wt%	
25%	15%	10%	anhydrite, calcite, ettringite, gypsum, hannebachite, lime, magnetite, mullite
15%	15%	10%	quartz, hematite
30%	25%	15%	Brownmillerite, "C ₃ A", melilite, merwinite, periclase, ye'elinite

^aese = estimated standard error

Table 4. Selected results from the sites involved in this study.

KY Class F Fly Ash			
Typical		Zone containing ettringite	
Phase	wt%	Phase	wt%
Quartz	10.8(1.1)	Quartz	7.1(7)
Mullite	26.0(2.6)	Mullite	13.3(1.3)
Magnetite	2.1(3)	Magnetite	7.0(7)
Amorphous	61.1	Calcite	0.5(1)
		Hematite	4.1(6)
		Ettringite	3.5(5)
		Amorphous	64.5

ND Class C Fly Ash			
Phase	wt%	Phase	wt%
Ettringite	7.8(8)	Magnetite	2.5(4)
Quartz	6.0(6)	Merwinite	2.1(5)
Calcite	5.7(6)	Periclase	1.1(3)
		Amorphous	74.8

IN CFBC By-product + Stoker Ash			
Phase	wt%	Phase	wt%
Quartz	4.4(6)	Gypsum	21.1(2.1)
Calcite	5.5(6)	Ettringite	31.4(3.1)
Hematite	4.0(6)	Thaumasite	6.5
		Amorphous	27.2

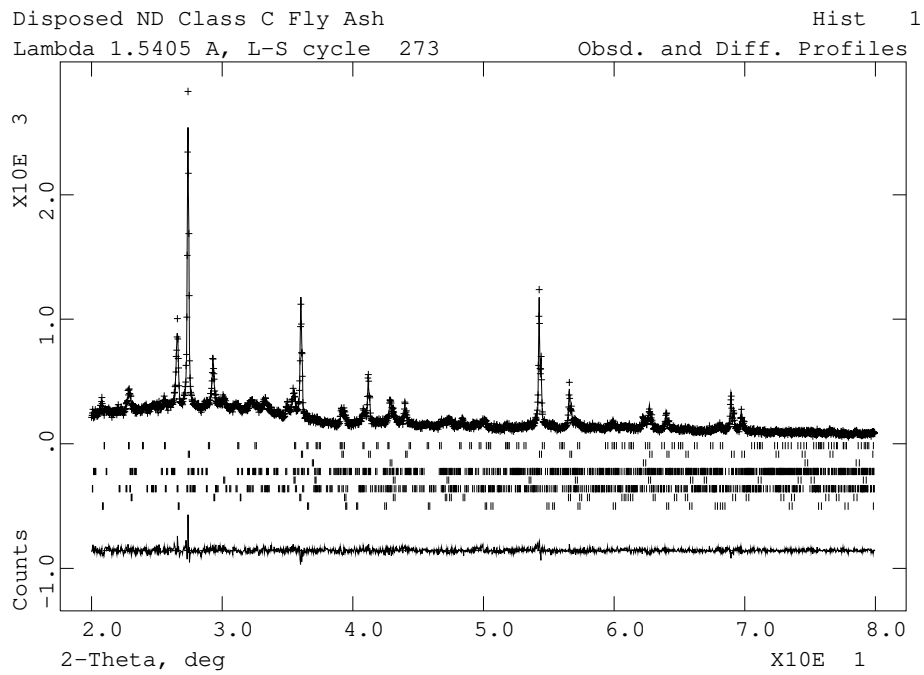
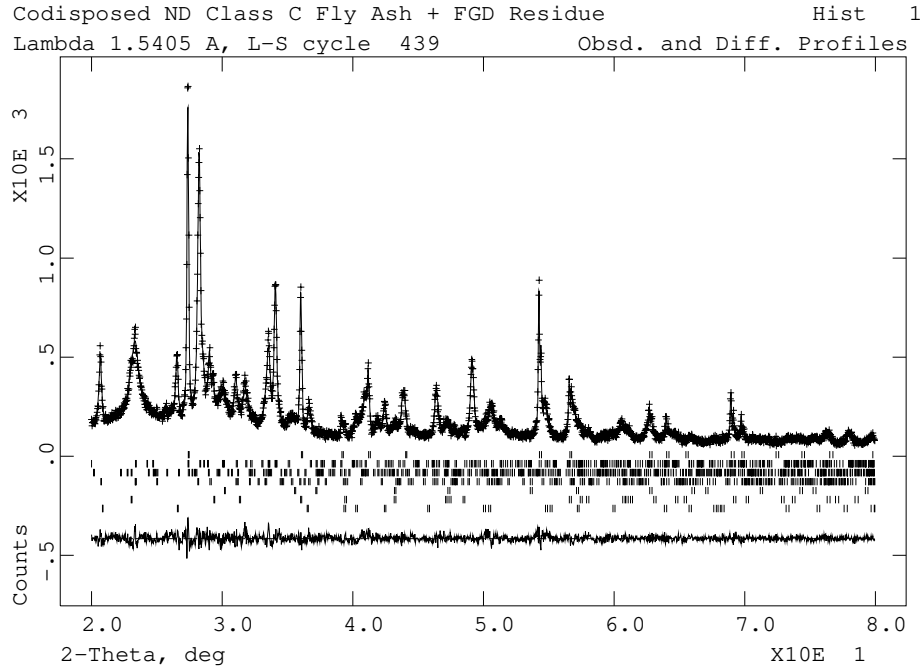


Figure 1. Rietveld refinements of two selected CCB materials. “Pluses” are observed data, continuous line is calculated, hashes indicate possible diffraction peak positions for each phase modeled, and lower curve shows the residual between observed and calculated.