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Dispersed Volcanic Ash in Feed Coal and Its Influence on Coal Combustion Products

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INTRODUCTION

The U. S. Geological Survey (USGS) and the University of Kentucky Center for Applied Energy Research are collaborating with an Indiana power plant to determine the chemical and mineralogical properties of feed coal and coal combustion products (CCPs). A major part of the study is to determine the abundance, mode of occurrence, and temporal variability of these properties (Affolter and others, 1997; Brownfield and others, 1997; Brownfield and others, 1999). To accomplish this, more than 220 samples of feed coal and CCPs were collected and analyzed by chemical and mineralogical methods. This part of the study focuses on the mineralogy and modes of occurrence of trace elements in the feed coal and CCPs.

METHODS

The Indiana power plant utilizes a low-sulfur (0.23 to 0.47 weight % S) and low ash (5.3 to 6.9 weight % ash) subbituminous coal from the Wyodak-Anderson bed in the Tongue River Member (Paleocene) of the Fort Union Formation, Powder River Basin, Wyoming. In order to evaluate sample variability, three intervals were tested. The samples were first collected on a daily (15 samples), then on a weekly (14 samples), and finally on a monthly basis (9 samples). Feed coal and two fly ash samples (old and new samplers) were collected using automated sampling devices while the economizer and truck fly ash and the bottom ash was collected manually by the power plant personnel. For each sampling, fly ash was collected at four sites in the power plant: one from the economizer (closest to the furnace); two from automated fly ash collectors; and a truck silo sample. Because of plant problems, some individual samples could not be collected during the study.

Ash yields and analysis of major-, minor-, and trace-element contents of feed coal, fly ash, and bottom ash were determined by the USGS. Coal samples were ashed prior to analysis at 525°C and reported on an ash basis. Most elements were determined using inductively coupled plasma-atomic emission spectrometry (ICP-AES), inductively coupled plasma-mass spectrometry (ICP-MS). Mercury was done by cold vapor atomic absorption spectroscopy (CV-AAS) using unashed coal and reported on a whole-coal basis. Coal ash for mineralogical studies was derived by two methods: 1) by a low-temperature gas plasma ashing unit (LTA) using compressed oxygen at temperatures below 150° C and 2) by treating the coal with aqueous sodium hypochlorite. Mineralogy of the coal ash, fly ash, and bottom ash samples were determined using X-ray diffraction (XRD) methods. Polished samples were prepared and examined using microprobe and scanning electron microscope (SEM) methods, supporting the mineralogical identifications. Magnetic separations (Cathcart and others, 1997) were conducted on some fly and bottom ash samples and the separates were later analyzed by XRD methods. Relative abundance of minerals was determined using reference intensity methods.

FEED COAL

About 40 samples of feed coal were collected and analyzed from the coal-fired plant. XRD analyses of Wyodak-Anderson coal LTA reveal a predominance of well-crystallized kaolinite and quartz (table 1). SEM and XRD analysis of coal and coal ash revealed minor amounts of), hydrated alumino-phosphate minerals containing Ba, Ca, and Sr (fig. 1) and trace amounts of beta-form quartz (fig. 2), apatite, and zircon. Previous investigators (Brownfield and others, 1987; Tripplehorn and others, 1991; Crowley and others, 1993) have attributed these minerals to air-fall and reworked volcanic ash deposited in the peat forming mires. Other minerals identified in the feed coal include detrital quartz, kaolinite, calcite, biotite/muscovite, anatase, barite, and pyrite (cleat filling and framboid). Two mineral suites were identified in the Wyodak-Anderson feed coal. A primary suite (not authigenic) consisting of quartz (detrital and volcanic beta-form grains), biotite, apatite, and zircon and a secondary authigenic mineral suite consisting of calcite, kaolinite, alumino-phosphates (crandallite and gorceixite), quartz, anatase, barite, and pyrite. Feldspars, pyroxenes, and amphiboles, which are common in volcanic air-fall ash, may have been present in the original ash. Dissolution and alteration of these minerals most likely occurred either in the early diagenetic peat-forming stage (strong leaching environment) or possibly also during the coalification/late diagenetic stage and contributed to the authigenic mineral suite (kaolinite, calcite, anatase, crandallite, gorceixite, barite).

Table 1. X-ray diffraction, SEM, and Microprobe results of feed coal, fly ash, and bottom ash, includes magnetic fraction. Listed in order of relative abundance. Ma=Major (> 10 percent); Mi=Minor (5 to 10 Percent); T=Trace (less than 5 percent)

Feed Coal	Fly Ash	Bottom Ash
Quartz-SiO_2-alpha form-Ma	Glass-Ma	Glass-Ma
Kaolinite-$Al_2Si_2O_5(OH)_4$-Ma	Perovskite-$CaTiO_3$-Ma	Quartz-Ma
Carbonates-calcite-$CaCO_3$-Mi	Lime-CaO-Ma	Anorthite-$CaAl_2Si_2O_8$-Ma
Biotite/Muscovite-Mi	Gehlenite-$Ca_2Al(Al,Si)O_7$-Ma	Augite-$(Ca,Na)(Mg,Fe,Al,Ti)(Si,Al)_2O_6$-Ma
Crandallite Group-Mi	Quartz-Mi	Fassaite-Fe-Al diopside or augite-Mi
Quartz-SiO_2-beta form-T	Apatite-$Ca_5(PO_4)_3F$-Mi	Rhodonite-$(Mn,Fe,Mg,Ca)SiO_3$-Mi
Anatase-TiO_2-T	Periclase-MgO-Mi	Akermanite-$Ca_2MgSi_2O_7$-T
Barite-$BaSO_4$-T	Mullite-$Al_6Si_2O_{13}$-Mi	Melilite-$(Ca,Na)_2(Al,Mg)(Si,Al)_2O_7$-T
Pyrite-FeS_2-T	Melilite-$(Ca,Na)_2(Al,Mg)(Si, Al)_2O_7$-Mi	Pyrite-T
Zircon-$ZrSiO_4$-T	Magnesioferrite-$MgFe_2O_4$-Mi	Anhydrite-T
Apatite-$Ca_5(PO_4)_3F$-T	Hematite-a-Fe_2O_3-Mi	Zircon-T
Plagioclase-T	Whitlockite-$Ca_9(Mg, Fe)(PO_4)_6(PO_3,OH)$-T	
	Merrillite-a-$Ca_3(PO_4)_2$-T	
	Magnetite-$FeFe_2O_4$-T	
	Anhydrite-$CaSO_4$-T	

Major- and minor-oxides and selected trace element contents are shown in tables 2 and 3 for the Wyodak-Anderson feed coal. The feed coal displayed little variation in element content during the sampling period. The small variation is attributed to the coal coming from one bed (single source). This was not true in previous studies where the feed coal supply was from several sources (Affolter and others, 1997). Even though the feed coal is from a single source, there can be minor trace element variation within the thick Wyodak-Anderson coal bed (up to 140 ft thick) resulting from both vertical and lateral changes in mineral content and the amount of individual mineral phases within the analyzed sample. These variations can be seen in figures 3 and 4, which show the mean contents of Ba and P (crandallite group) for all the sample types during the first 15 samples. The feed coal contains more Ba, Ca, Mg, Mn, Na, Sr, P, Th, and U when compared to analyzed eastern feed coals (Brownfield and others, 1999). These elements are associated with the minerals crandallite (Ba, Ca, P, and Sr), gorceixite (Ba, Ca, P, and Sr), biotite (Ba, Ca, and Mg), calcite (Ba, Ca, Mg, Mn, and Sr), zircon (Th and U), and clay minerals (Ca and Mg). Feed coal element associations are indicative of coals influenced by volcanic ash (Brownfield and Affolter, 1988; Affolter and others, 1997).

In low-rank coals major amounts of Ca, Mg, and Na are often associated with the organic matter through cation exchange. Additionally, detrital mineral input and the epigenetic ground-water flow may have affected the geochemistry of the feed coal.

COAL COMBUSTION PRODUCTS

More than 150 fly ash samples were collected and analyzed for this study. XRD analysis of the Ca/Mg rich fly ash samples revealed a predominance of glass, perovskite, lime, gehlenite, and periclase with minor and trace amounts of quartz, apatite, anhydrite, hematite, and spinel group minerals (table 1). Periclase and lime occur in all fly ash samples except the economizer fly ash (fig. 5). Microprobe and SEM analysis of fly ash samples revealed quartz, zircon, monazite, euhedral laths of corundum with merrillite, hematite, dendritic spinels/ferrites, and rounded grains of wollastonite with periclase. Among fly ash samples gehlenite was more abundant in the economizer ash while perovskite was more abundant in the fly ash. The anhydrite in the fly ash occurs as thin coatings on the fly ash grains. A small percentage of fly ash grains (< 5 percent) are composed of cryptocrystalline phosphorus phases with whitlockite ($Ca_9(Mg, Fe)(PO_4)_6[PO_3(OH)]$) and its anhydrous analogue merrillite, or a-$Ca_3(PO_4)_2$ as the most likely minerals (O'Connor and Meeker, 1999). Petrographic analysis of fly ash also revealed minor amounts of mullite, quartz, and spinel/ferrite with trace amounts of coke and inertinite (James Hower, 1998, written commun.).

Magnetic minerals in fly ash have been described by previous workers as magnetite, ferrites, and hematite (Lauf and others, 1982; Brownfield and others, 1997; Cathcart and others, 1997). The magnetic fraction recovered from fly ash samples in this study ranges from 1.0 to 2.0 percent and consists of dendritic magnetite and magnesioferrite and euhedral hematite. The small percentage of magnetic minerals here is the result of the low pyrite content of the feed coal when compared to Appalachian and Illinois Basin coals (Brownfield and others, 1997).

XRD analysis of more than 35 samples of the bottom ash revealed quartz, plagioclase (anorthite), and pyroxene (augite and fassaite) with minor and trace amounts of rhodonite, and akermanite (Table 1). All the samples contained varying amounts of amorphous aluminum silicate glasses and char (unburned coal). Lesser amounts of quartz, pyrite, sulfate minerals, and illite and/or muscovite were found. SEM analysis of samples revealed detrital grains of quartz and zircon and high-Al pyroxene (fassaite) laths with anorthite.

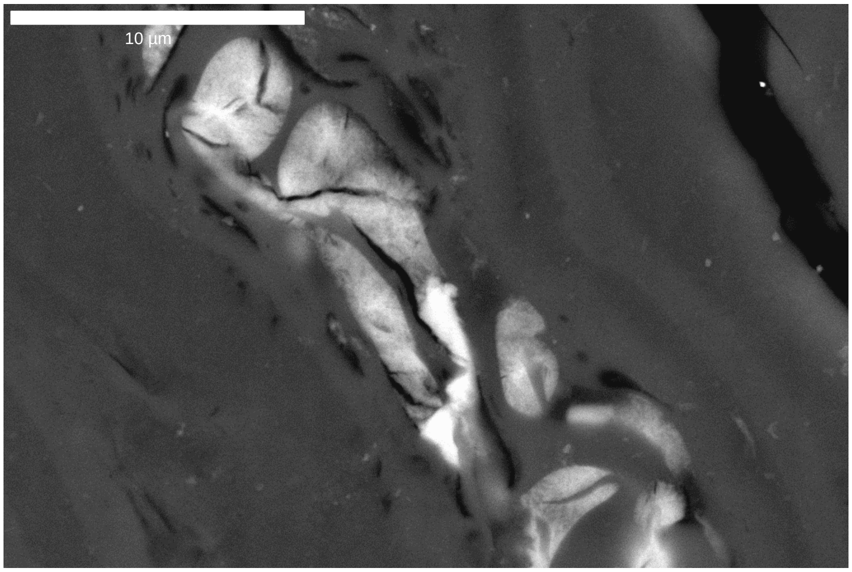

Figure 1. SEM photomicrograph of hydrated alumino-phosphate (crandallite) from the Wyodak-Anderson feed coal, Powder River Basin, Wyoming.

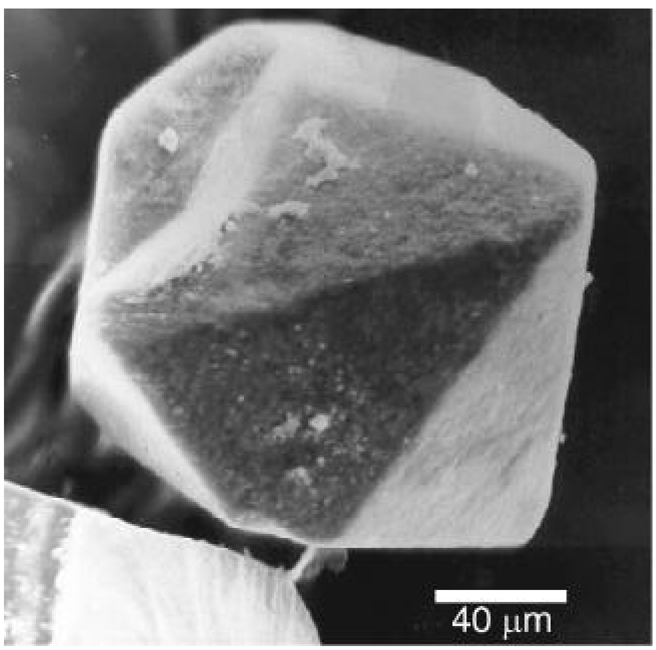

Figure 2. SEM photomicrograph of a euhedral crystal of beta-form quartz from the Wyodak-Anderson feed coal, Powder River, Wyoming.

Table 2. Mean, range, standard deviation (Std. Dev.) for ash and major- and minor-oxide contents in the laboratory ash for the first sampling period (n=15) of feed coal. (All values are in percent and on an ash basis)

		Range		
	Mean	Min	Max	Std. Dev.
Ash	6.2	5.3	6.9	.42
SiO_2	30	28	33	1.4
Al_2O_3	15	14	17	.83
CaO	23	22	27	1.2
MgO	5.1	4.2	5.8	.45
Na_2O	2.0	1.7	2.7	.26
K_2O	.29	.24	.36	.04
Fe_2O_3	5.2	4.7	6.1	.34
TiO_2	1.3	1.2	1.5	.09
P_2O_5	.96	.74	1.1	.11

Table 3. Mean, range, and standard deviation (Std. Dev.) of selected element contents from the feed coal for the first sampling period (n=15). (Values are in parts per million and on an ash basis. Hg content on a whole coal basis)

		Range		
	Mean	Min	Max	Std. Dev.
As	17	10	30	7.2
Ba	5700	5100	6500	330
Be	4.3	4.0	5.0	.46
Cd	1.1	.9	2.0	.26
Co	27	23	32	2.7
Cr	90	71	220	37
Hg	.07	.04	.26	.06
Mn	200	140	300	43
Ni	56	39	100	14
Pb	19	10	40	7.0
Sb	1.4	1.0	3.0	.63
Sr	4000	3700	4800	300
Th	22	20	25	1.3
U	8.9	7.2	15	1.8

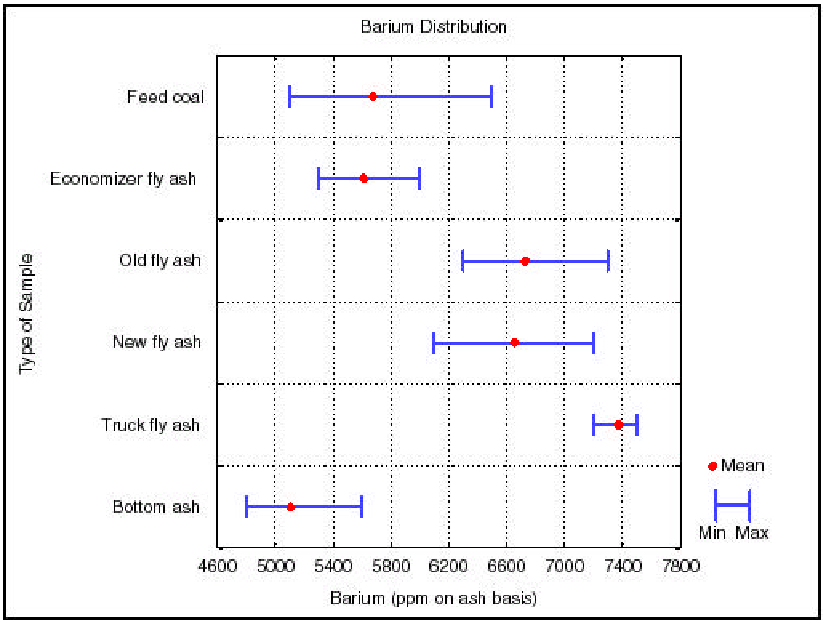

Figure 3. The variation of barium content during the first sampling period. Range plot showing the mean, minimum, and maximum values from the feed coal (n=15), economizer fly ash (n=15), old fly ash sampler (n=11), new fly ash sampler (n=9), truck fly ash (n=11), and bottom ash (n=15).

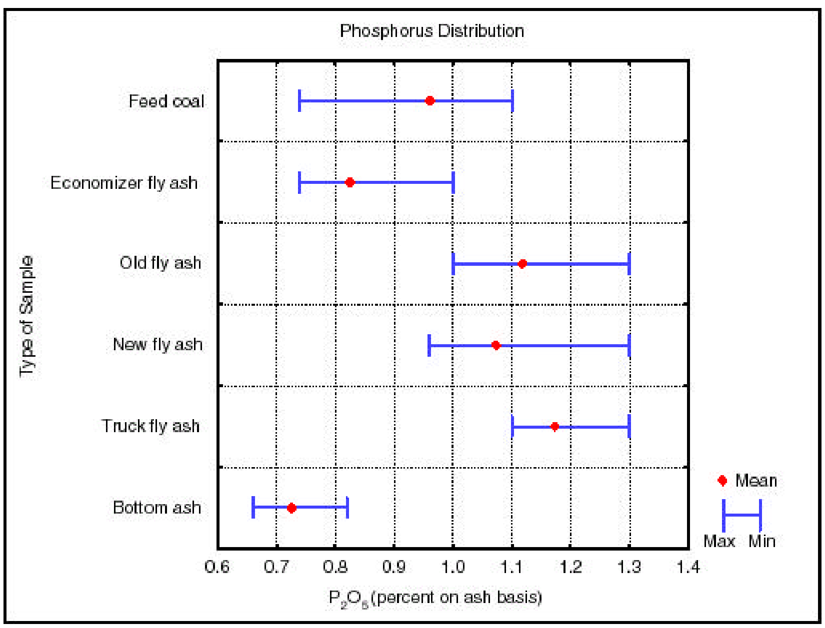

Figure 4. The variation of phosphorus content during the first sampling period. Range plot showing the mean, minimum, and maximum values from the feed coal (n=15), economizer fly ash (n=15), old fly ash sampler (n=11), new fly ash sampler (n=9), truck fly ash (n=11), and bottom ash (n=15).

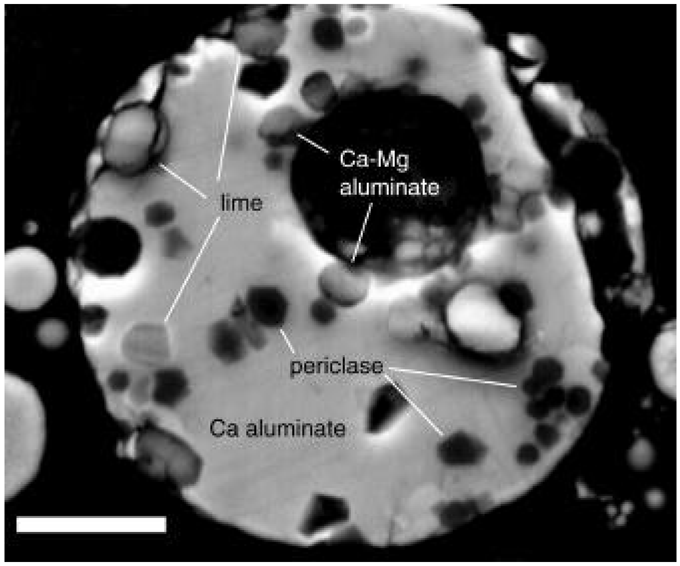

Figure 5. SEM photomicrograph of a fly ash grain with euhedral light gray lime and dark gray periclase crystals with subhedral Ca-Mg aluminate crystals in a Ca aluminate matrix.

SUMMARY

Wyodak-Anderson feed coals contain higher amounts of Ba, Ca, Mg, Na, Sr, and P when compared to previously analyzed eastern feed coals. In the coal these elements are associated with hydrated alumino-phosphate (crandallite and gorceixite) and clay minerals as well as biotite, calcite, apatite, and barite. Feldspars, pyroxenes, and amphiboles, which are common in volcanic air-fall ash, were also likely present in the original volcanic ash. The element and mineral associations in the feed coal are indicative of coals influenced by volcanic ash. Dissolution and alteration of the original volcanic minerals occurred in the early diagentic peat forming stage and/or during the coalification/late diagenetic stage and contributed to the observed authigenic mineral suite (kaolinite, calcite, anatase, crandallite, gorceixite, and, barite).

The abundant Ca-Mg- and less abundant P-mineral phases (gehlenite, lime, perovskite, periclase, whitlockite, and merrillite) in the fly ash and bottom ash can be related to the presence of carbonate, clay, phosphate, and biotite minerals in the feed coal. Therefore, the Ca- and Mg-rich mineral phases in the CCPs can be attributed to the volcanic minerals deposited in the peat-forming mire and the resulting authigenic mineral suite.

In low-rank coals major amounts of Ca, Mg, and Na are often associated with the organic matter through cation exchange. Additionally, detrital mineral input and the epigenetic ground-water flow may have affected the geochemistry of the feed coal.

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