

THE FORM OF OCCURRENCE OF BASIC ELEMENTS IN COAL AND THEIR BEHAVIOUR DURING COMBUSTION

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INTRODUCTION:

The basic elements in coal ash (alkalies, Ca, Fe) exhibit an interesting behaviour during combustion, which is closely related to the form of occurrence of these elements in the parent coal. The objective of this paper is to elucidate their evolution during combustion processes of variable time and temperature. Qualitative determinations are made from the data obtained from Computer Controlled Scanning Electron Microscopy (CCSEM), X-ray Absorption Fine Structure (XAFS) and Mössbauer spectroscopies.

Some of the data and the description of the techniques used in this paper are summarized in several publications (1-8). The main goal of this paper is to discuss some systematic trends in the behaviour of calcium, iron and the alkalies during high temperature coal combustion. It needs to be emphasized that our discussion deals only with high temperature (~1600 to 2000 K) pulverized coal combustion, and is not relevant to fluidized bed combustion.

EXPERIMENTAL PROCEDURES:

The CCSEM method measures the areas of cross-section and the energy-dispersive spectra for at least 1000 different particles in a random, polished section of the coal embedded in epoxy. The data is then reduced to derive the overall mineralogy and semi-quantitative size-distribution of individual mineral categories (9). CCSEM techniques for ash are similar to those for the coal, except that the particles are not embedded in epoxy but are mounted on Nucleopore (0.2 micrometer) filters by a process of filtration in triply-distilled acetone. The amount of material filtered is adjusted to give an optimum density of particles on the filter paper. The data reduction techniques for ash samples are similar to those used for coal minerals analysis (CMA) but the sorting program is based on the intensity of the energy-dispersive X-rays from the three most abundant elements, rather than on specific phases (9).

XAFS is used to examine specific elements and to obtain information on the bonding and structure of that element in the material at dilute concentrations (-0.1 to 1.0%). By comparing with standard materials, the phase in which the element exists is also identified.

Mössbauer spectroscopy complements the CCSEM technique by identifying the form of iron in a coal or ash. With this technique it is possible to measure the relative abundance of the major iron-bearing minerals in complex samples.

Furthermore the Mössbauer technique also provides a direct measure of the pyritic sulfur content.

RESULTS AND DISCUSSIONS:

The set of coals being investigated here are (low-rank coals) Beulah, Eagle Butte and San Miguel, (bituminous coals) Upper Freeport, Kentucky #9, Kentucky #11, Illinois #6 and (Australian brown coal) Loy Yang. These coals were combusted in different scale furnaces at Physical Sciences, Inc., M.I.T. and the University of Arizona (UA). The UA samples were collected on filter from different impactor plates of varying particle diameter.

Mössbauer data show that most of the iron in these coals is in the form of pyrite, except for Upper Freeport, in which 20% of the iron is contained in clay and siderite, and Loy Yang coals and that the pyrite contents of these coals are much higher than that of the bituminous coals. Unlike the U.S. coals, the iron in the Australian coal appeared to be present as iron oxyhydroxide (FeOOH).

If pyrite is contained in a burning coal particle that also contains clay minerals and/or quartz, it is likely to react with these minerals to form an aluminosilicate slag droplet. Isolated pyrite, either liberated or contained in a coal particle transforms into pyrrhotite by devolatilization which then undergoes exothermic oxidation, presumably to a molten Fe-O-S phase (6,7). Iron is found predominantly present as magnetite and as Fe³⁺ in glass in the ash samples of these coals. For these coals, the partitioning between iron oxide and glass appears to be simply related to amount of pyrite in the mineral matter. On this basis one would predict that the amount of iron as oxide should decrease in the order Illinois #6 > Beulah lignite > Kentucky #11 > Upper Freeport > Kentucky #9 > Eagle Butte, which is exactly the order in which iron is partitioned between iron oxide and glass in the ash samples. One would expect that how the pyrite is associated with other minerals would also play a role in determining this order, but for this particular sequence of coals, such association is apparently not an important factor or it is also dependent on the relative amount of pyrite in the sample to a first approximation (Table 1).

XANES spectra of calcium in Beulah lignite and Eagle Butte coals are very similar to the ones measured for other low-rank U.S. coals [10,11] and are characteristic of calcium bound through carboxyl groups to macerals (Fig. 1). XANES of calcium in San Miguel Texas lignite (Fig. 1) also resembles that of the two low rank coals. XANES of calcium in Illinois #6 coal resembles the sum of XANES of calcite and that of a coal with carboxyl-bound calcium.

In the ash samples obtained from low rank coals, the predominant compositional classes are permutations of the three most abundant elements: Ca, Al and Si, except for the finest impactor plate where many Ca and Na sulfate particles are also present. Figures 2 show Ca-Si-Al triangular plots for each of the impactor plates of Beulah ash sample. Here each point represents an ash particle identified by the CCSEM analysis as containing > 80% Ca + Si + Al. The composition of each particle, normalized to three elements, is then plotted on the ternary diagram. The plots show a clear dependency of compositional clustering on size. These trends can be interpreted as indicating a size dependency for the reaction between CaO fume, derived from the carboxyl-bound calcium, and the kaolinite in the coal. The smaller the reactant particle, the

more probable is the formation of a Ca-Al-Si phase, and the less probable is the existence of separate Ca-rich or Al-Si particles. The fine particle compositions indicate the formation of calcium substituted glass phase. The XANES spectra (Fig. 3) are quite similar to that attributed to calcium in aluminosilicate glass [5] and indicate that the amount of CaO or CaSO₄ in ash is relatively minor (<10 vol%). Hence, the broader range in the Ca-Al-Si cluster observed for the coarser particles must represent the compositional range of Ca-Al-Si glass rather than mixed CaO-Al-Si particles. It should also be noted that there is a tendency for Ca enrichment near particle surfaces.

The principal alkali species in lignite is Na, believed to be molecularly dispersed through the maceral and bonded to the carboxyl group, like calcium. Sodium may also be present as hydrated Na⁺ ions in the moisture associated with low-rank coals and this is probably the case with Loy Yang coal, even though appreciable NaCl was noted in the CCSEM analysis for the dried sample of this coal. Potassium is significant only for the four bituminous coals and San Miguel lignite. K in these coals is almost entirely present as illitic clays. Some KCl was noted in the CCSEM analysis of Loy Yang coal.

The behaviour of alkalis during combustion is strongly dependent on their form of occurrence in the parent coal. K, which is present as illite, is likely to remain with the aluminosilicate particle and form a molten slag droplet. Confirmed by potassium XANES (Fig.4) obtained from various ash samples, partial melting occurs because of eutectic regions in the K-Si-Al phase diagram [8,12]. The aluminosilicate glass produced by melting illite yields precisely this type of potassium XANES spectrum [8,13]. The composition of these molten particles is similar to that of the parent illite, as illustrated in Figure 5. Figure 4 shows the comparison of potassium XANES spectra of ash samples from different coals and all appear characteristic of potassium in glass. The subtle difference between the Eagle Butte spectra and the other spectra most likely reflects either its different bulk ash composition (richer in Ca, poorer in Fe) or a different mode of occurrence for potassium in the original coal.

The CCSEM analysis of Beulah lignite ash shows an abundance of sodium-aluminosilicate particles (Fig. 6). In contrast to the similar plot for calcium rich particles, the Na-rich particles cluster in the center of the Na-Al-Si ternary plot. The composition of this cluster of points corresponds to the phase nepheline (NaAlSi₃O₈). This phase must have been formed by reaction between kaolinite and Na cations volatilized in the combustion of the coal. This is an example of the efficiency of aluminosilicates derived from clays for the fixation of alkali elements in coal ash. This refutes the suggestion that alkali elements can be readily volatilized from clays or other aluminosilicates during combustion, at least to 1500 K under oxidizing conditions.

SUMMARY:

Iron (pyrite) either reacts with clay minerals to form aluminosilicate slag or devolatilizes and undergoes oxidation to form oxides and sulfides, depending on whether it is associated with clay and quartz or isolated. Calcium is molecularly dispersed in coals and is bonded to carboxyl groups in the macerals. On combustion it forms CaO which may further react with clays to form aluminosilicate glass. Potassium in bituminous coals is contained in illite which melts and forms aluminosilicate glass. Finally, sodium which is believed to be molecularly dispersed in the macerals, volatilizes and reacts with clays

to form aluminosilicate glass with compositions corresponding to that of nepheline.

REFERENCES:

1. F. E. Huggins, N. Shah, G. P. Huffman, R. G. Jenkins, F. W. Lytle, and R. B. Greegor, *Fuel*, 67, 938-942 (1988).
2. G. P. Huffman, F. E. Huggins, and N. Shah, "EXAFS Spectroscopy: A New Technique for Investigating Impurity Elements in Coal that Control Slagging and Fouling Behaviour", Engineering Foundation Conference on Mineral Matter and Ash in Coal, Santa Barbara, CA, 1988, Eds., K. S. Vorres and R. W. Bryers, to be published by Elsevier.
3. F. E. Huggins, G. P. Huffman, and A. A. Levasseur, "Ash Deposits from Raw and Washed Coals", *ibid.*
4. F. E. Huggins, G. P. Huffman, A. A. Levasseur, ACS Division of Fuel Chemistry Preprints, Vol. 33, No. 2, 73-80 (1988).
5. G. P. Huffman, F. E. Huggins, A. A. Levasseur, F. W. Lytle, R. B. Greegor, and A. Mehta, *Fuel*, 68, 238-242 (1989).
6. G. P. Huffman, F. E. Huggins, A. A. Levasseur, O. Chow, and S. Srinivasachar, *Fuel*, 68, 485-490 (1989).
7. S. Srinivasachar and A. Boni, *Fuel*, 68, 829 (1989).
8. G. P. Huffman, F. E. Huggins, R. W. Shoenberger, J. S. Walker, F. W. Lytle, and R. B. Greegor, *Fuel*, 65, 621-632 (1986).
9. G. P. Huffman, F. E. Huggins, N. Shah, and A. Shah, "Behaviour of Basic Elements During Coal Combustion", to be published in *Progress in Energy and Combustion Science*.
10. F. E. Huggins, G. P. Huffman, F. W. Lytle, and R. B. Greegor, "An EXAFS Investigation of Calcium in Coal", Proceedings of International Conference on Coal Science (Pittsburgh, PA), 679-682 (1983).
11. G. P. Huffman, and F. E. Huggins, "Analysis of the Inorganic Constituents in low-rank Coals", ACS Division of Fuel Chemistry, Preprints, Vol. 264, 159-174 (1984).
12. E. M. Levin, H. F. McMurdie and H. P. Hall, *Phase Diagrams for Ceramists*, Amer. Ceramic Soc., Inc., Columbus, Ohio, 1964.
13. C. Spiro, J. Wong, F. W. Lytle, R. B. Greegor, D. H. Maylotte, S. Samson, and B. Glover, *Fuel*, 65, 327 (1986).

TABLE 1. - Mössbauer data for ash samples from University of Arizona combustor

Coal	%Fe Distribution of Iron among Phases			
	Hematite	Magnetite	Ferric glass	Ferrous glass
Illinois #6	-	84	16	-
Beulah Lignite	-	71	24	5
Eagle Butte	-	46	54	-
Kentucky #11	8	67	12	14
Upper Freeport	3	67	18	13

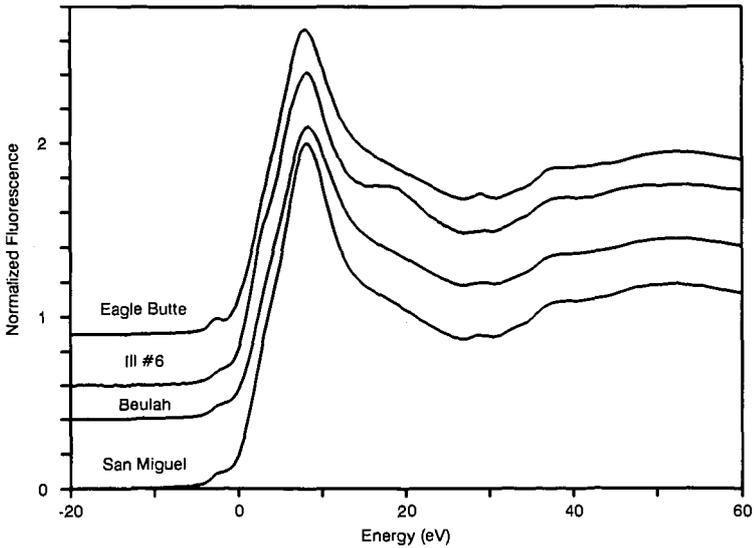


Figure 1. Ca XANES of high calcium PSI coals.

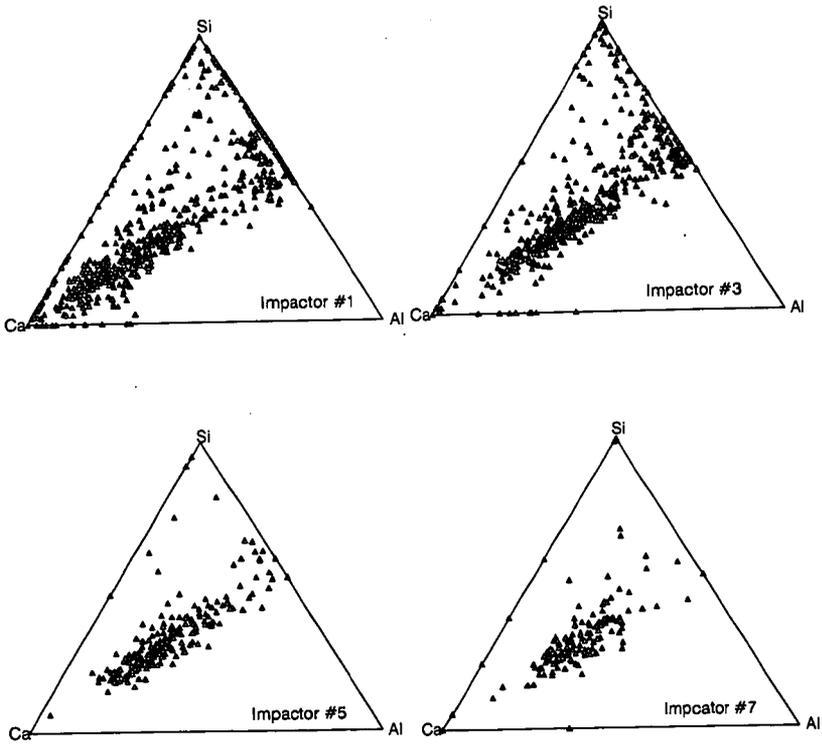


Figure 2. Ca-Al-Si triangular plots for Beulah lignite ash on different impactors in UA combustor. All particles contain Al+Si+Ca > 80%.

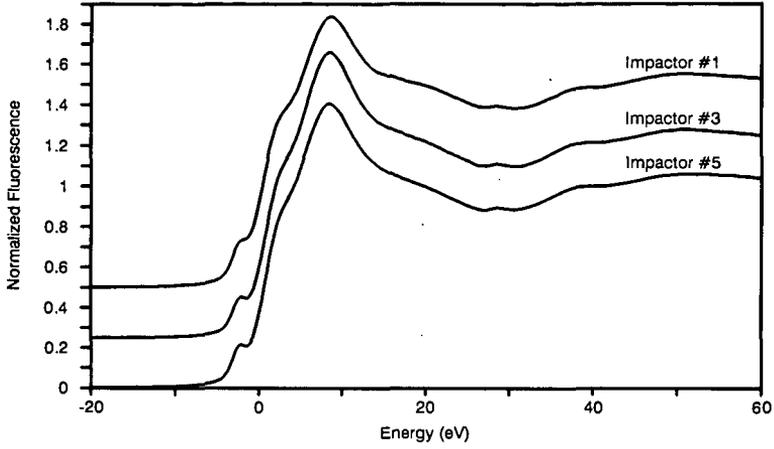


Figure 3. Ca XANES for Beulah ash from size segregated impactors of UA combustor

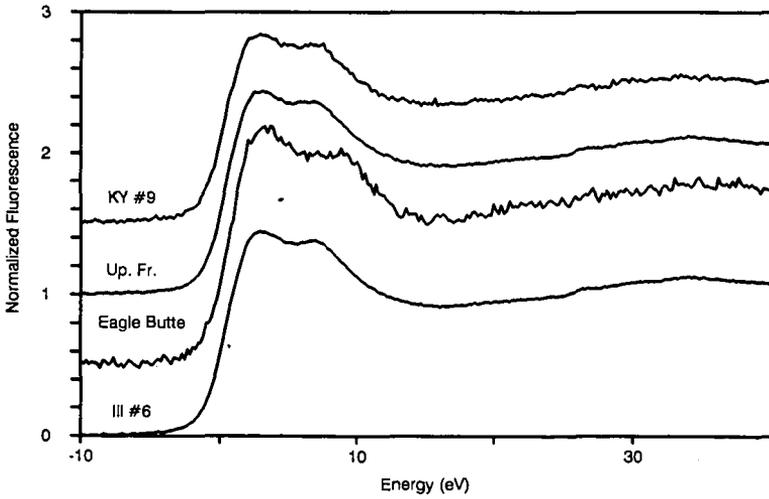


Figure 4. Potassium XANES of ash samples from MIT combustor.

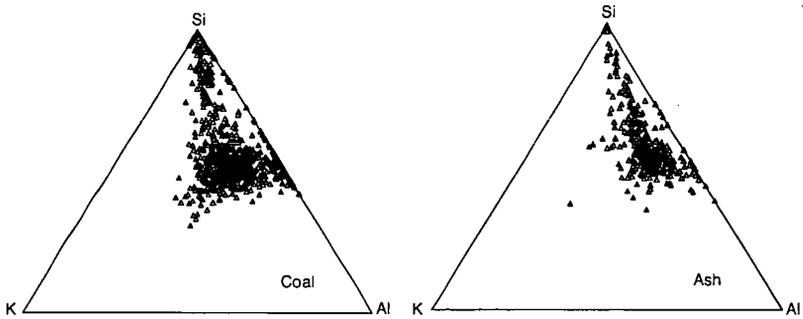


Figure 5. K-Si-Al triangular plots for Upper Freeport coal and ash

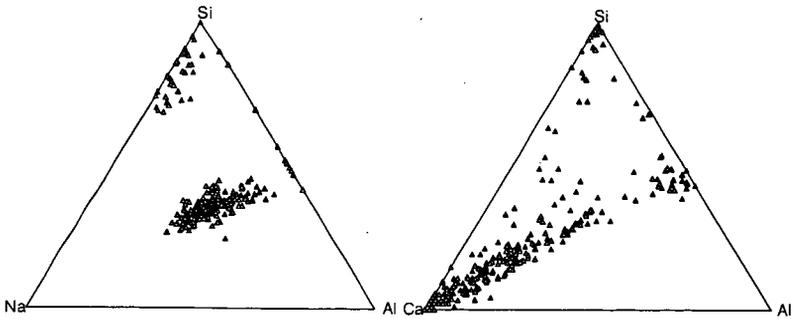


Figure 6. Triangular plots for Beulah ash from PSI drop tube furnace.
All particles contained $Al+Si+Na/Ca > 80\%$.