

BEHAVIOR OF BASIC ELEMENTS DURING COAL COMBUSTION

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ABSTRACT

X-ray absorption fine structure (XAFS) spectroscopy, Mossbauer spectroscopy, and computer-controlled scanning electron microscopy (CCSEM) have been used to investigate the reactions of Ca, Fe, and alkalis in combustion systems. Ca may either transform to a CaO fume that reacts with SO_2 to form CaSO_4 , or may react with clays, quartz, and other minerals to form slag droplets, or flyash. Similarly, pyrite may devolatilize and oxidize exothermically to form molten or partially molten iron sulfide-iron oxide mixtures, or may react with other minerals to become part of the slag. Alkalies in lignites (principally Na) volatilize and may react with either SO_2 to form sulfates or with clay minerals (principally kaolinite) to form aluminosilicate slag droplets. K in bituminous coal is contained in illite which melts and becomes part of the slag phase. The calcium and alkali sulfates and the iron-rich species are observed to be concentrated in the initial layers of deposits, while the complex aluminosilicate slag droplets collect to form an outer glassy layer.

INTRODUCTION

The basic elements in coal ash (alkalies, Ca, Fe) exhibit an interesting dual behavior during combustion. Not surprisingly, this dual behavior is closely related to the way in which these elements are contained in the coal being burned. In this paper, some recent experimental results on the behavior of basic elements in combustion systems are reviewed and qualitative models of their combustion reactions are discussed.

EXPERIMENTAL PROCEDURES

Much of the data on which the current paper is based is summarized in detail in several recent and forthcoming publications.⁽¹⁻⁷⁾ Bituminous coals and lignites and a variety of combustion products obtained from both pilot scale combustion rigs and drop-tube furnaces have been investigated. The principal characterization techniques used were XAFS spectroscopy, Mossbauer spectroscopy, and computer-controlled scanning electron microscopy (CCSEM).

EXPERIMENTAL RESULTS

The principal experimental observations for the dominant basic elements are summarized below.

Calcium - In lignite, calcium is molecularly dispersed in the coal macerals and is bonded to the oxygen anions in carboxyl groups, while in bituminous coal it is predominantly contained in the discrete mineral, calcite. A systematic change from carboxyl-bound calcium to calcite is observed with increasing rank.⁽⁸⁾ During pyrolysis and gasification reactions the molecularly dispersed calcium in lignite is observed to agglomerate and, eventually, form CaO.⁽¹⁾

A recent XAFS study of the combustion products of a lignite and a bituminous coal detected two forms of Ca, Ca incorporated in aluminosilicate glass and CaSO₄.⁽⁵⁾ Solids rapidly extracted from within and above the flame contained all Ca in glass. In both superheater and waterwall deposits, glass was the dominant Ca-bearing phase in the outer (fireside) deposits, while CaSO₄ was dominant in the inner or initial deposits. In work currently underway, the forms of Ca in samples produced by combustion of Beulah lignite and other coals in drop-tube furnace studies are being investigated by CCSEM and XAFS spectroscopy. Typical results are shown by the ternary diagram in Figure 1. 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. It is seen that there are a substantial number of Ca-rich (principally CaO) particles, and aluminosilicate glass particles with a fairly broad range of Ca contents.

Iron - Pyrite and its oxidation products are the dominant iron-bearing phases in both low and high rank coals, although bituminous coals frequently contain substantial amounts of iron in clays and siderite.⁽⁹⁾ 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. Mossbauer spectroscopy has demonstrated that most of the iron in flyash samples quenched from within or above the flame of a pilot scale combustor, and most of the iron in the outer layers of deposits, is contained in aluminosilicate glass.^(3,4)

Pyrite particles that are isolated within a coal particle or that are liberated behave much differently. Recently, Mossbauer spectroscopy and CCSEM measurements were conducted to determine the transformation products formed from pyrite removed from coal in drop tube furnace tests at gas temperatures of 1311 to 1727 K and residence times from 0.07 to 1.2 seconds in a 95% N₂ - 5% O₂ atmosphere.⁽⁶⁾ Magnetite was the dominant oxide formed, while pyrrhotite (Fe_{1-x}S) was the dominant sulfide. CCSEM results show evidence of extensive melting, even at the lowest gas temperature. This is consistent with a thermodynamic model⁽¹⁰⁾ which yields particle temperatures significantly in excess of the gas temperature because of the exothermic oxidation of pyrrhotite. These results are also consistent with the observation of iron-rich initial layers observed in deposits^(3,4) that appear to have been formed from the impaction of highly viscous liquid droplets. The inner layer is

transformed to hematite over a period of time at the lower temperatures within the deposit near the waterwall or the superheater tubes.

Alkalies - The principal alkali species in lignite is Na, believed to be molecularly dispersed through the macerals and bonded to the oxygen anions in carboxyl groups. K is low in abundance but can be inserted into carboxyl bound sites in the coal macerals by cation exchange. In bituminous coals, K is the dominant alkali and it is contained almost exclusively in the clay mineral illite. Illite has a strikingly different XAFS spectrum from that of cation-exchanged K in lignite.⁽²⁾ Na in bituminous coals is usually contained as NaCl, frequently in solution in moisture adsorbed in coal pores and capillaries.⁽¹¹⁾

The behavior of alkalies during combustion is strongly dependent on their form in the coal. Carboxyl bound alkalies or alkalies in solution volatilize. Several volatile species are possible, but NaOH is the most likely for lignite.⁽¹²⁾ K in illite is likely to remain with the aluminosilicate particle and form a molten slag droplet. Partial melting occurs at 900-1000°C because of eutectic regions in the $K_2O - SiO_2 - Al_2O_3$ phase diagram.^(13,7) Volatile alkalies have a strong tendency to be absorbed by the aluminosilicates derived from clays^(7,12) and significantly lower the melting point of the resulting slag. This is illustrated by Figure 2 which shows the ternary Na - Si - Al diagram generated from CCSEM data on ash particles collected during combustion of Beulah lignite in a drop-tube furnace. Each data point indicates the normalized three-element composition of a particle identified in the CCSEM analysis as containing $\geq 80\%$ Na + Si + Al. The Ca - Si - Al diagram of Figure 1 is from the same sample. It is seen that the $NaO_2 - SiO_2 - Al_2O_3$ slag particles fall into a relatively small range of compositions.

When volatile alkalies reach the upper regions of the furnace they react with SO_2 to form molten alkali sulfates that react strongly with metal superheater tubes.⁽¹⁴⁾ In a limited set of experiments, we have used XAFS and CCSEM to determine that superheater deposits from a boiler firing North Dakota lignite contained a mixture of alkali sulfate and alkali-containing glass.⁽¹⁵⁾

SUMMARY AND DISCUSSION

On the basis of the results summarized above, qualitative models of the behavior of the major basic elements during combustion can be deduced. These models are indicated in the schematic diagrams of Figure 3.

Calcium in lignite is molecularly dispersed and bonded to carboxyl groups in the macerals. It rapidly agglomerates into Ca - O clusters and CaO, while the calcite in bituminous coal devolatilizes to form CaO. The CaO may be given off from the burning coal particles as a CaO fume or may remain with the particles and react with the clay, quartz or other minerals to form a molten aluminosilicate slag. The CaO fume apparently reacts with SO_2 to form $CaSO_4$ which is part of the initial, presumably sticky, layer in both superheater and waterwall deposits⁽⁵⁾.

Pyrite that is liberated or isolated alone in a coal particle devolatilizes to form pyrrhotite which undergoes exothermic oxidation that raises the particle temperature sufficiently far above the gas temperature to exceed the melting point of magnetite.^(6,10) The molten iron-rich particles impinging on the walls and tubes may be iron sulfide-iron oxide mixtures or magnetite, depending on residence time and temperature. Because of the high momentum of these particles, they readily impinge on the walls and tubes, forming a major part of the initial sticky layer for pyrite-rich coals. Those pyrite particles that are contained in coal particles containing clay, quartz and other minerals react to form molten aluminosilicate slag or flyash droplets which stick on top of the initial iron-rich, layer.

There is less good experimental data on alkalis in combustion systems. Nevertheless, some speculations can be made. It appears that Na is bound to carboxyl groups in lignite and readily volatilizes, presumably to NaOH, although other volatile species are certainly possible. Sodium reacts strongly with clay (mainly kaolinite in lignite) and quartz, both within the burning coal particle and in the vapor phase to form aluminosilicate slag droplets or flyash. The volatile NaOH also reacts with SO₂ to form NaSO₄ which has a low melting point (884°C) and becomes part of the initial sticky layer.

Finally, K in bituminous coal is contained in illite which melts and becomes part of the slag or flyash component of the ash stream.

While the simple diagrams of Figure 3 are consistent with the general trend of slagging and fouling behavior observed in coal combustion systems, it is clear that we have ignored many reactions and made a number of speculations for which there is no firm experimental proof. The current "model", therefore, should really be considered as a point of departure for future discussion and experimentation.

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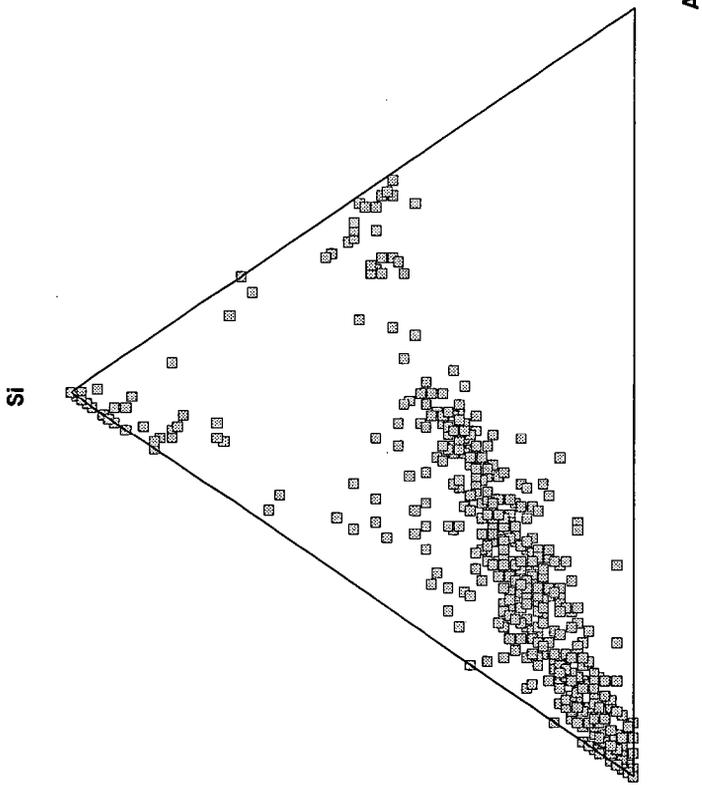


Figure 1. Ca - Si - Al diagram derived from CCSEM data for Beulah ash particles from a drop tube furnace combustion experiment.

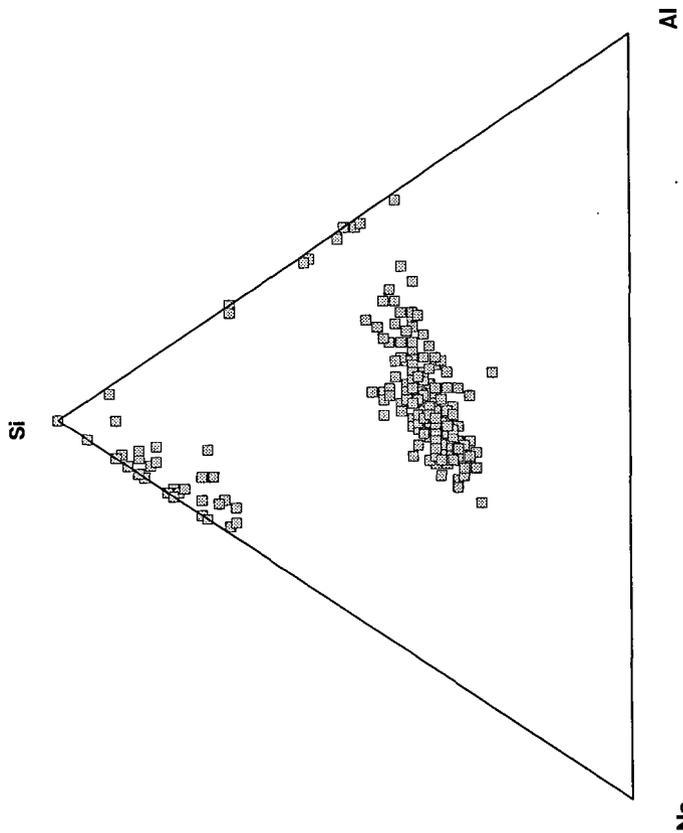


Figure 2. Na - Si - Al diagram derived from CCSEM data for Beulah ash particles from a drop tube furnace combustion experiment.

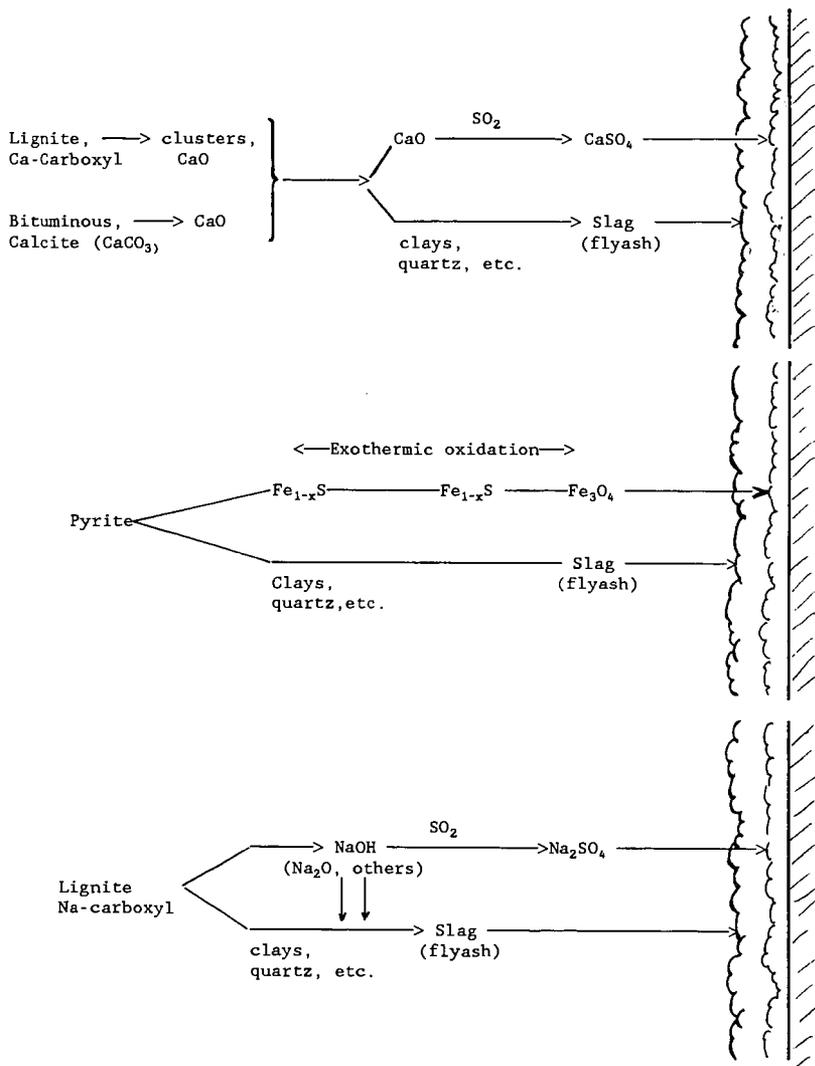


Figure 3. - Schematic diagram indicating the behavior of basic elements in combustion systems.