ROLE OF CALCIUM DURING COAL COMBUSTION REVISITED

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ABSTRACT

Calcium is one of the most abundant elements found in low rank coals and plays a major role in ash fouling and slagging processes that result in reduced boiler efficiency during combustion of such coals. The form of occurrence of calcium in the parent coal and its interaction with other mineral matter in coal and with gaseous components during pulverized coal combustion govern the fundamental mechanisms in ash formation and ash characteristics. Several lignite and bituminous coals and their combustion products have been analyzed using Computer Controlled Scanning Electron Microscopy (CCSEM). Comparison of combustion tests carried out in different size furnaces indicate minor differences in the calcium behavior implying that the form of occurrence of calcium in the coal is more important than the scale of test facilities in determining the fate of calcium and other elements. Hence comparative combustion experiments carried out in small scale test facilities can accurately reflect the behavior of coal in utility boilers. Depending on its occurrence, calcium may react with clays to form molten Ca-aluminosilicate slag or may react with SO_2 and volatile Na to form Ca-Na sulfates.

INTRODUCTION

In low rank coals, calcium is predominantly dispersed in the macerals and is bound to carboxyl groups, whereas in bituminous coals, it is present as the discrete mineral, calcite (1). This difference in the form of occurrence plays a major role in the behavior of calcium during combustion. Past work indicates that both forms of calcium eventually react with clay minerals to form a molten glassy phase (1,2). The extent to which glass formation takes place depends on the mineral types, size and amounts in the original coals.

This paper investigates by means of the computer controlled scanning electron microscopy (CCSEM) technique, several reactions of calcium that occur during combustion, including their reactions with clays. In our research of the behavior of different elements during coal combustion, we have examined several low rank and bituminous coals and their combustion products from different test facilities of varying scale (2). The calcium behavior in ash from several bituminous and low rank coals is discussed in order to relate the form of occurrence in coal to ash formation processes. Comparative CCSEM analyses on Beulah lignite ash from several test facilities are also presented to emphasize that the size of the test facilities is of

secondary importance.

EXPERIMENTAL

Combustion experiments at three very different size test facilities were carried out at comparable temperatures. At University of Arizona (UA), a 1.8-5.0 kg/hr utility grind combustor was used to conduct the combustion tests and the samples were collected in size-segregated Anderson impactor plates. At the State Electricity Commission of Victoria (SECV), Australia, a 35 kg/hr pilot scale combustion test facility was used and the samples were collected at different locations in the facility. At PSI Technology Co. (PSI) and at MIT, combustion tests were carried out in a drop tube furnace (DTF). More specific information can be found in reference 2. Details on the CCSEM technique, sample preparations, and analyses are described elsewhere (3,4,5).

RESULTS AND DISCUSSIONS

Forms of occurrence of calcium in different coals : The four different coals compared to illustrate the effect of the form of occurrence of calcium on its interactions during combustion are an Illinois #6 bituminous coal, an Eagle Butte sub-bituminous coal, a San Miguel lignite, and a Beulah lignite. The forms of calcium in these coals were established in previous papers using CCSEM and XAFS techniques (1,2). To summarize briefly, calcite is the dominant Ca-bearing mineral in Illinois #6 coal and occurs either in close contact with other minerals or as discrete particles. Carboxyl bound calcium and a minor phase containing Ca-Sr-Al-P, possibly crandallite, are the major Ca-rich forms in Eagle Butte coal. In San Miguel lignite, calcium exists in two dominant forms: as a carboxyl bound, dispersed through the macerals and as a zeolite mineral. In Beulah lignite, calcium is primarily carboxyl bound in the macerals.

Calcium behavior during combustion in different coals : The four coals were combusted in DTFs at MIT and at PSI under similar conditions (7% O_2, approx. 1750K). The CCSEM analyses of the ash indicate varying degrees of interactions between calcium and clays as shown in the volume percentage-ternary diagrams in Figure 1. These diagrams show the volume distribution of all the ash particles identified by the CCSEM as containing > 80% Ca+Si+Al.

There is comparatively little interaction between discrete calcite and silicate minerals found in Illinois #6 coal during combustion. Some of the calcite remains as CaO particles in the ash.

In the Eagle Butte ash, numerous particles are identified by the CCSEM as Ca-rich, which are principally CaO derived from the carboxyl-bound calcium present in the coal. Calcium also interacts strongly with the clays and quartz forming Ca-aluminosilicate glass and calcium silicate phases (figure 1b). The glass phases may also form due to reaction of crandallite minerals and the clays. The crandallite mineral in the coal, which is a mixture of Ca, Sr, P and Al, probably plays a role in

the formation of an unusual Ca-rich calcium aluminate phase seen in the volume percentage-ternary diagram.

The Ca-Si-Al phase in the San Miguel lignite is richer in Si-Al. This is due to the presence of the Si-Al rich zeolite mineral in the coal. Any dispersed carboxyl-bound calcium must react with clay minerals and adds to the Ca-Si-Al glass phase. The majority of the Ca-Si-Al phase is directly formed from decomposition of the zeolite mineral.

Beulah lignite ash shows a narrow band of composition extending from the Ca-rich apex to the Si-Al border at ~Si/Al=1. The calcium that is molecularly dispersed in the macerals bound to the carboxyl group, apparently coalesces to form CaO. Some of the CaO fumes may react with clays to form Ca-Si-Al phase.

There is little formation of calcium sulfate observed in any of the DTF ash samples. The particle sizes of the Ca-Si-Al phase are comparable.

Comparison of calcium behavior in Beulah coals combusted in different size combustors : The UA impactor samples and the SECV ash samples of Beulah lignite show a similar calcium behavior to that observed in the DTF samples. Several combustion tests were carried out in the UA combustion facility. The CCSEM analysis on the size segregated ash samples collected from these tests show Ca-aluminosilicate glass as one of the dominant calcium phases. With the decrease in the particle size of the UA impactor samples, there is a reduction in the Ca-rich (CaO) particles. The Ca-aluminosilicate glass phase is more concentrated near the center of the volume percentage-ternary diagram for the finer ash fraction (figure 2).

The Ca-aluminosilicate phase in the SECV ash samples shows similar characteristics. The electrostatic precipitator (ESP) ash sample which consists of finer particles than the combustion chamber sample, show a tendency to form a phase shifted towards the center of the Ca-Si-Al plot. This shift in the composition is due to the fact that the smaller particles yield a more homogeneous glass phase. There is also a reduction in the CaO particles in the ESP as observed in the finer UA samples.

The UA and SECV samples also contain a substantial Ca-S-Na phase which is not present in the DTF samples. Figure 3 presents the volume percentage-ternary diagrams for these samples. The calcium sulfate phase is formed due to the reaction between CaO fumes and the SO_2 that is present in the gas phase during combustion. Sodium with a much lower volatilization temperature, undergoes sulfation in the vapor state to form Na_2SO_4. The two sulfates form a Ca-S-Na solid solution on rapid cooling.

The sulfate phase is dominant only in the finer ash samples. This is again attributed to the occurrence of calcium in Beulah coal and also to the fact that the sulfate phase arises from the fumes and the vapor phase. The varied compositional range in different samples is expected due to slightly different operating temperatures and due

to different sample collection methods. It appears that the combination of the size-segregated UA ash samples would cover the entire range of composition found in the plot of Ca-S-Na in the SECV samples (figure 3).

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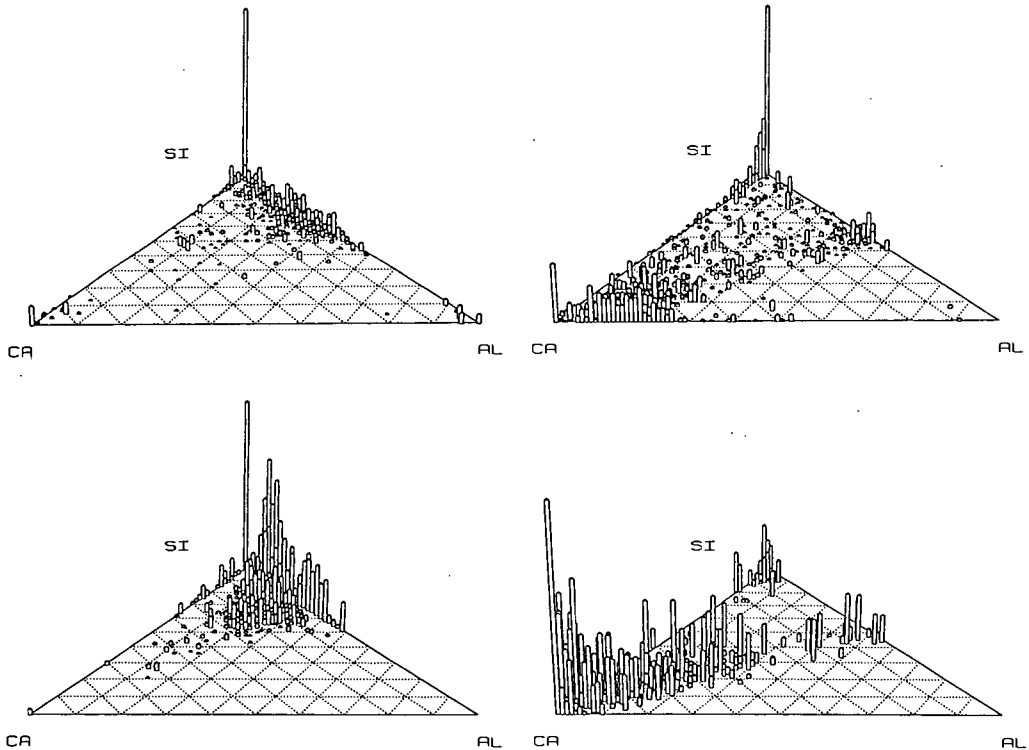

Figure 1. Ca-Si-Al volume percentage-ternary diagrams for the DTF ash samples of a)Illinois #6, b)Eagle Butte, c)San Miguel, and d)Beulah lignite. Combustion conditions 7% O_2, approx. 1750K.

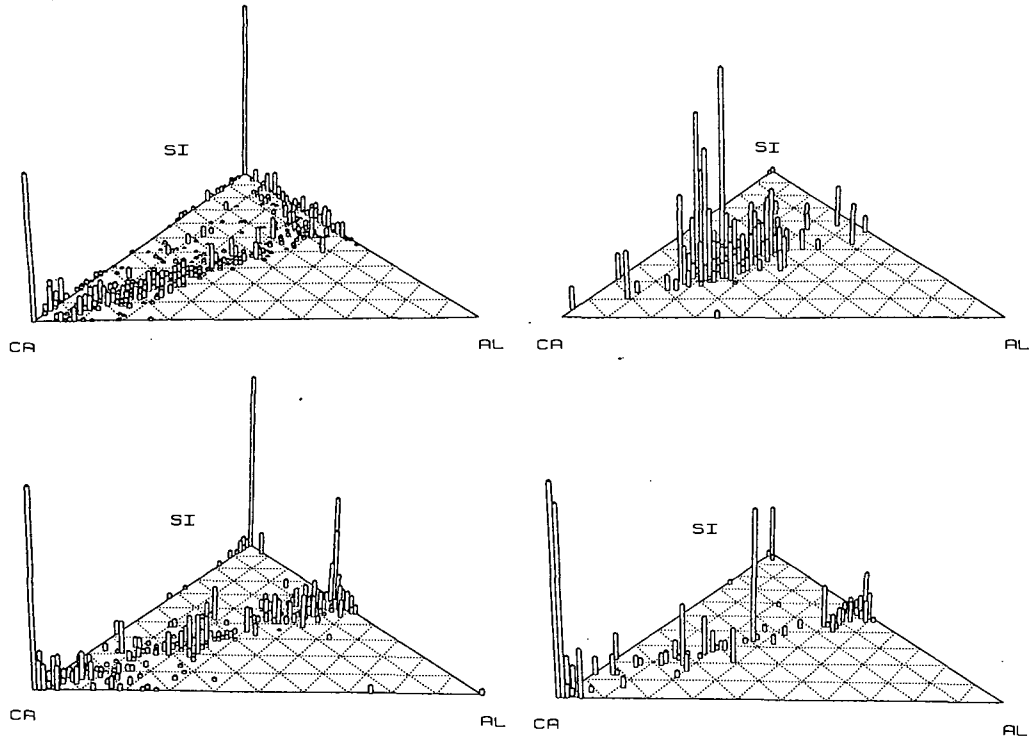

Figure 2. Ca-Si-Al volume percentage-ternary diagrams of Beulah lignite ash from a)UA combustor, impactor 1, b)UA combustor, impactor 7, c)SECV combustor, combustion chamber, and d)SECV combustor, electrostatic precipitator.

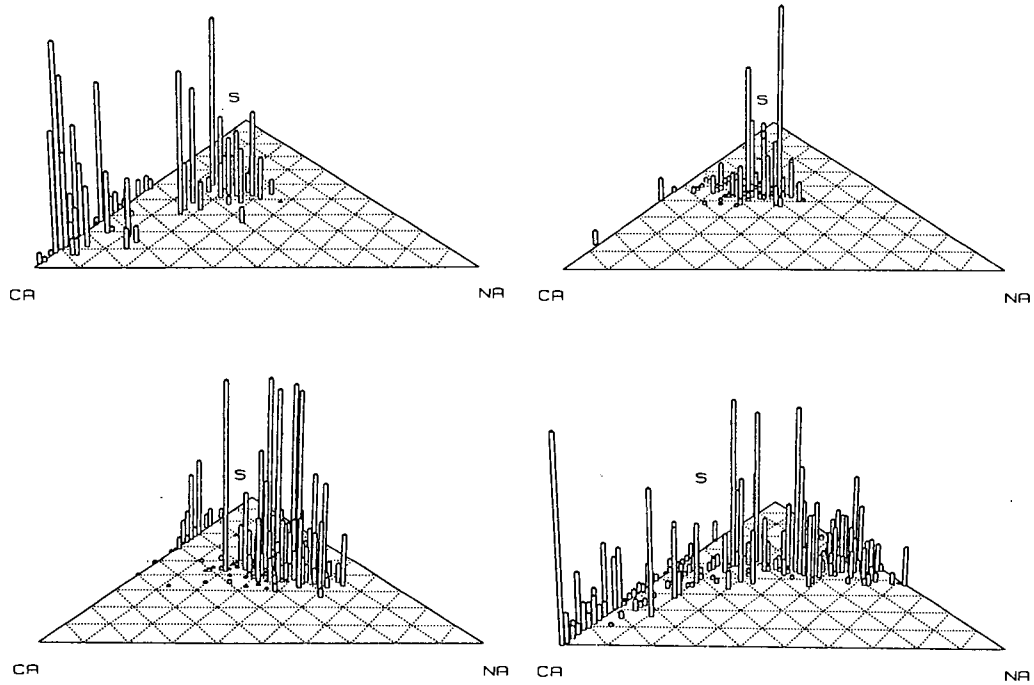

Figure 3. Ca-S-Na volume percentage-ternary diagram for Beulah lignite ash from a)UA combustor, impactors 1+cup, b)UA combustor, impactors 2+3+4, c)UA combustor, impactors 5+6+7+8+AF, and d)SECV combustor, electrostatic precipitator.