

# The Effect of Chlorine and Sulfur on the Composition of Ash Deposits in a Fluidized Bed Combustion System

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The major advantage of fluidized bed combustion (FBC) of fuels is the ability to absorb  $\text{SO}_2$  and HCl when limestone is used in the combustor. The combustion of high chlorine coal does generate some concerns about the possibility of chlorine-related corrosion of boiler components at high temperatures. It is believed that molten alkali salts may cause severe corrosion when they deposit on the surfaces of heat exchange tubes in a boiler. A better understanding of the effect of temperature on the deposition of alkali chloride will help find a way to convert them to harmless salts before they condense on the components of an FBC system. Furthermore, the knowledge of the distribution of sulfur and chlorine in ash under different conditions is necessary not only to understand the principle and efficiency of desulfurization by limestone, but also to evaluate the role of limestone in the capture of HCl. In this study three different fuels with different chlorine, sulfur, and alkali contents were burned in a 0.1 MWth bench scale FBC system. The effects of coal types, temperature, position, and exposure time on the composition of ash deposits were investigated by ICP-AES and XRD spectroscopy. The major compound in the ash deposits is  $\text{CaSO}_4$ . The experimental results show that the operating temperature has a major effect on the condensation of alkali chloride. The absorption of HCl is favored at the lower temperatures.

## Introduction

For the next century, coal is likely to remain the most important fuel for electricity generation in many countries, especially in the U.S.A., U.K., Germany, and China. With the development of combustion technology for fossil fuels, the load capacity and thermal efficiency of single units has been increased remarkably in the past several decades. For instance, generating units have grown from 6 MWe with low operational parameters to a supercritical parameter 600 MWe unit. The thermal efficiency of systems has also increased from 20% to 47%. However, there are many boiler operational problems associated with the mineral impurities in coals. The more notable among these are corrosion and erosion of boiler heat exchange tubes, and fireside deposits on tubes in high-temperature regions including vaporization tubes and superheater tubes.

Since the 1970s there has been interest in the use of solid waste as low-cost fuel, which includes municipal solid waste (MSW), wood waste, straw, etc., to replace some of the coal or oil now being burned in large power plants. This trend toward the burning of waste in water-wall combustors with heat recovery and steam generation using standard boiler furnace design has also resulted in concern about corrosion and deposits that occur under these circumstances.

The fireside deposits on heat transfer surfaces of boilers has been found both in the combustion chamber

where the wall and screen tubes are subjected to radiant heat transfer and in the tube tanks of the convective passes. The material consists mainly of ash derivatives bound together by complicated chemical and/or mineralogical compounds of widely different composition. Their nature is thought to be strongly dependent on the temperature/time history of the fly ash particles, as well as on the local composition of the solids/fuel gas suspension. The deposits lead not only to a significant reduction in heat transfer to the tubes but also diminish the gas flow area in the convective part of the boilers, sometimes to the point of complete blockage and even destruction of the boiler. The partial or complete blockage increases the flue gas velocities. The consequence is increased erosion and corrosion of tubes, increased fan power requirements and ultimately a complete shutdown of the plants for cleaning.<sup>1</sup> It has been estimated that the fireside problems collectively cost the electrical generating industry \$4 billion per year.

The fireside problems are very complex phenomena depending upon the transformation of the inorganic components found in the impurities in fuels upon heating and cooling; the chemical reaction between gas, liquid, and solid phase in motion and at rest; the existence of non-equilibrium conditions usually associated with supercooling; and the attachment of impurities to surfaces and the detachment of deposited liquids

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and solids.<sup>2,3</sup> In the past 2 decades, Ca-based sulfur sorbents (limestone, CaO, etc.) have been more commonly used in the flue gas desulfurization systems of coal-fired boiler, especially with the development of fluidized bed combustion technology.<sup>4</sup> Unfortunately, more ash deposits were formed in this case compared to the case without sulfur sorbent. This formation can be a result of a sintering process in which the CaO reacts with components in the flue gas after adhering to a heat exchange surface. The heaviest sintering was measured when CO was present in the gas phase.<sup>5</sup> The study of the mechanism of ash deposits indicated that the accumulation of ash particles on metal surfaces depends on the ability of the particles to form strong bonds with the heat exchange surface. This layer depends on the characteristics of the reacted layers on the steel surface, the temperature of the steel surface, the melting performance of the ash particle, and the thermal and chemical compatibility of the deposit and ash particle. Once a strongly bonded surface layer has accumulated, the temperature of the surface can increase, producing a liquid phase that should act as a collector of impacting ash particles. In addition, the ash deposits can react with inorganic species such as SO<sub>2</sub>.

It is generally accepted that alkali chloride products may play important roles in ash deposit formation, especially in FBC systems, due to their low melting temperatures. It is likely that the sodium, potassium and calcium initially deposited as oxides or possibly chlorides and then react with metal components to form strong bonds with the heat transfer surface. Then, in the presence of SO<sub>2</sub> in the flue gas, alkali chlorides may be converted to sulfates by reaction with SO<sub>2</sub> and oxygen during the exposure period, with the release of HCl from the deposits.<sup>6</sup>



Between 1992 and 1993, TVA's Shawnee Plant observed that the boiler tubes in the primary superheater region of the 160 MWe FBC system had heavy ash deposits and wastage/corrosion problems. The unit had been firing Illinois Basin coal with a relatively high chlorine content.<sup>7</sup> The study of ash deposits in straw-fired boilers also indicated the chloride and alkali contents in the fuels were key factors to influence the ash deposits on heat transfer surfaces. The deposits were dominated by high contents of potassium and chloride.<sup>8</sup>

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**Table 1. Analytical Values<sup>a</sup> for the Coals and PVC Used in the Study**

|                             | Coal 95011 | Coal 95031 | PVC   | KY limestone |
|-----------------------------|------------|------------|-------|--------------|
| % moisture                  | 10.07      | 8.32       | 0.00  | 0.19         |
| % ash                       | 9.37       | 10.78      | 0.36  | 57.93        |
| % volatile matter           | 43.34      | 37.21      | 99.64 | 18.90        |
| % fixed carbon              | 47.29      | 52.02      | 0.00  | 22.98        |
| % carbon                    | 74.08      | 72.16      | 38.71 | 11.18        |
| % hydrogen                  | 5.08       | 4.82       | 4.20  | 0.16         |
| % nitrogen                  | 1.54       | 1.54       | 0.07  | 0.00         |
| % sulfur                    | 3.20       | 2.38       | 0.22  | 0.00         |
| % oxygen<br>(by difference) | 6.72       | 7.57       | 0.00  | 30.73        |
| % chlorine                  | 0.012      | 0.31       | 56.45 | 36           |
| BTU/pound                   | 13203      | 12842      | 8556  | n/a          |

<sup>a</sup> Moisture is as-received; all other values are reported on a dry basis.

In this study three different fuels with different chlorine, sulfur and alkali contents were burned in a 0.1 MWth bench scale FBC system. The effects of coal types, temperature, position, and exposure time on the composition of ash deposits were investigated using ICP-AES and XRD spectroscopy.

### Experimental Section

All experimental work was conducted with a 0.1MWth bench FBC system at Western Kentucky University (WKU), which has a 0.3-m i.d., a 4.0-meter effective height, and uses limestone as the bed material. A full description of the FBC system has been presented by Xie and co-workers,<sup>9</sup> so only a brief description is given here. In this study, an under-bed continuous fuel/limestone feeding system was installed 0.1 m above the distributor in the FBC system. Six moveable heat exchange tubes in the bed area were added to the FBC system. Typical operation involves setting the correct coal/limestone feeds and air flows and then using the moveable tubes to adjust the bed temperature to the desired setting. Another 66 gas heat-exchange tubes are in fixed positions which are located approximately a half-meter from the top of the combustor to protect the wet cyclone. The hot gases from the combustor are allowed to enter a wet cyclone scrubber where they are met with a wall of water, which subsequently takes almost all the solids out of the cyclone into a holding tank. The operating parameters (air/water flow, coal/lime feed, bunker weight, temperatures, and pressure) are controlled and logged to file with a Zenith 350 MHz computer utilizing the LABTECH software version 3.0. During the combustion runs any needed changes in the parameters could easily be entered into the computer, by accessing the correct control screen and making the necessary corrections on line.

Three fuels were used in this study, including a low-chlorine (0.012% Cl, 3.0% S, and 4.72% alkali (in ash)) western Kentucky # 9 coal (WKU 95011), a high-chlorine (0.28% Cl, 2.4% S, and 6.93% alkali in ash) Illinois # 6 coal (WKU 95031), and a blend of coal 95031 with 3.3 wt % of PVC. Analytical data for the three fuels used in this study are presented in Table 1. The analytical data for the coal ash are presented in Table 2.<sup>10</sup>

The major operating parameters for the experiments were as follows: excess air level, around 1.3; Ca/S ratio, approximately 3; the bed temperature controlled between 1140 and 1160 K; and the fluidizing velocity was 1.25 m/s. The samples of ash deposits were collected from four different

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(10) Pan, W.-P.; Riley, J. T. Behavior of Chlorine during Coal Combustion in FBC Systems. Final Report, W09002-13; April, 1997; p 78.

**Table 2. Analytical Values for Ashes from the Coals and Limestone Used in the Study**

| Metal Oxides                   | 95011 | 95031 | KY limestone |
|--------------------------------|-------|-------|--------------|
| SiO <sub>2</sub>               | 49.22 | 47.32 | 2.93         |
| P <sub>2</sub> O <sub>5</sub>  | 3.36  | 4.46  | 2.79         |
| CaO                            | 1.86  | 1.62  | 75.60        |
| K <sub>2</sub> O               | 4.14  | 5.03  | 0.37         |
| TiO <sub>2</sub>               | 1.11  | 1.14  | 0.20         |
| Fe <sub>2</sub> O <sub>3</sub> | 19.90 | 17.04 | 0.27         |
| Na <sub>2</sub> O              | 0.58  | 1.90  | 0.18         |
| MgO                            | 0.70  | 0.80  | 3.73         |
| Al <sub>2</sub> O <sub>3</sub> | 17.12 | 18.18 | 11.41        |
| MnO <sub>2</sub>               | 0.02  | 0.02  |              |

regions in the FBC system. The temperatures and positions at the deposits formation sites are as follows:

(i) Moveable heat-exchange tube in the fluidized bed zone is placed 0.3–0.7 m from the distributor. The temperature of the flue gas is 850 °C; the tube surface is about 90 °C.

(ii) Transition region between the fluidized bed zone and the freeboard is placed 1.5 m above the distributor. The temperature of the flue gas is in the range of 700–820 °C, and the temperature on the deposit surface is around 600 °C.

(iii) Corrosion test coupon is placed 3.5 m above the distributor. The temperature of the flue gas and coupon surface is 570–650 °C.

(iv) Convective region is 3.75 m above the distributor. The inlet temperature of the flue gas is 560–640 °C, the outlet temperature is 200–300 °C, and the tube surface is 70 °C.

Inorganic elemental analysis of the ash deposits was carried out with a LECO Plasmarray ICP-AES system and a JEOL JSM-5400 scanning electron microscope (SEM) system with attached KEVEX Sigma energy dispersive X-ray system (EDX). The sulfur contents were determined with a LECO SC-432 sulfur analyzer following ASTM Method D 5016. Chloride contents were measured by bomb decomposition followed by determination of chloride with an ion selective electrode following ASTM Method D 4208. A Phillips X-pert X-ray diffraction system equipped with CuK $\alpha$  radiation was used to determine the compounds present in the ash deposits. The XRD patterns were identified using a compound database of over 80,000 inorganic compounds.

## Results and Discussion

The results of this study are being reported in two major parts. One is a focus on the composition in the ash product layer on metal surfaces which was produced from the reaction between ash deposits and the metal surface. These deposits have high densities, stick tightly to the metal surfaces, and can only be removed by chemical methods. This portion of the study was conducted with the SEM-EDX system. The second major part of the paper focuses on the composition of the porous ash deposits which cause fouling and collect on metal surfaces from particulates in the flue gas. The stress between this ash deposit layer and the metal surface is very small. It can be cleaned through physical methods. This portion of study was investigated using ICP-AES, sulfur and chloride analysis, and the XRD system.

**Ash Products Layer on the Metal Surfaces.** *The Effect of Exposure Time.* Two kinds of coal (95011 and 95031) were burned in two 1000-h test runs. The effect of exposure time in the combustor on the ash products layer as well as the composition of this layer was investigated. The elements in the ash products layer on each coupon were determined after every 250 h during each 1000 test run. The color of the deposits on the coupons is generally tan. No chloride was detected in

the ash products layer of all coupons. This may indicate that the alkali chlorides that may have formed initially were converted to alkali sulfates and released HCl through the reaction with SO<sub>2</sub> and oxygen at high temperatures, as illustrated in eq 1.

Figure 1 shows the results of the sulfur contents in the ash products layer from tests with coals 95011 and 95031. The figure indicates that the sulfur content in this layer increases with an increase in the exposure time in the combustor. In the case of alloy 347, the sulfur content in the ash products layer increases very fast in the first 500 h and then decreases to a lower value. This indicates spallation from the metal surface may have increased after 500 h. This conclusion is also supported by the significant change in the thickness of the test specimen, as shown in Figure 2. In the case of alloy 309, the amount of sulfur content increases gradually for the entire test run. This may be due to the higher chromium and nickel content in the alloy 309 to produce protective layers.

Examination of the effects of coal on the ash products layer show mixed results. The high chlorine, low sulfur, and high alkali content coal produced more sulfur content in the layer in the case of 347. However, contradictory results were observed in the case of alloy 309. This behavior may indicate that the composition of the metal is a more important factor for the formation of the ash products layer and even ash deposits. Higher chromium and nickel contents will prevent the reaction between sulfur and the metal itself. Higher chlorine and alkali content coals can produce more alkali chloride vapor in the flue gas at high temperatures, and initially form more strong bonds with the metal surface to support more ash deposits than coals with lower chlorine and alkali contents. Another explanation is the sulfur in the deposit can react with chromium to form chromium sulfide in the ash products layer, destroying the original structure of the alloy which leads to break down and spallation. This is then followed by reformation of deposits and ash products layer as illustrated in Figure 1. For Alloy 309 the higher chromium and nickel concentration inhibits corrosion and spallation of the outside layer of the coupon surface. Thus, the high sulfur and low chlorine content coal shows more sulfur content in the ash products layer.

The effect of exposure time on the alkali (K+Na) contents in the ash products layer is shown in Figure 3. Alkali contents in the ash products layer formed from burning high alkali content coal is much higher than those from low alkali content coal for all test coupons. The curves of alkali contents showed the same trend as the sulfur content profiles, as shown in Figure 1. However, upon comparison to other elemental contents in the ash products layer, the alkali contents increase very slowly during the first 250 h of the test run, then rise significantly in the second 250 h period. This may be due to the characteristics of the metal surface. It is known that the condensation of alkali-based compounds on metal surfaces is the first step in the build up of ash deposits or to produce an ash products layer. At the beginning, the surface is very smooth and it is difficult for materials to adhere to the surface. After 250 h, some corrosion will have occurred on the metal surface and the surface becomes rough. The thickness of the ash

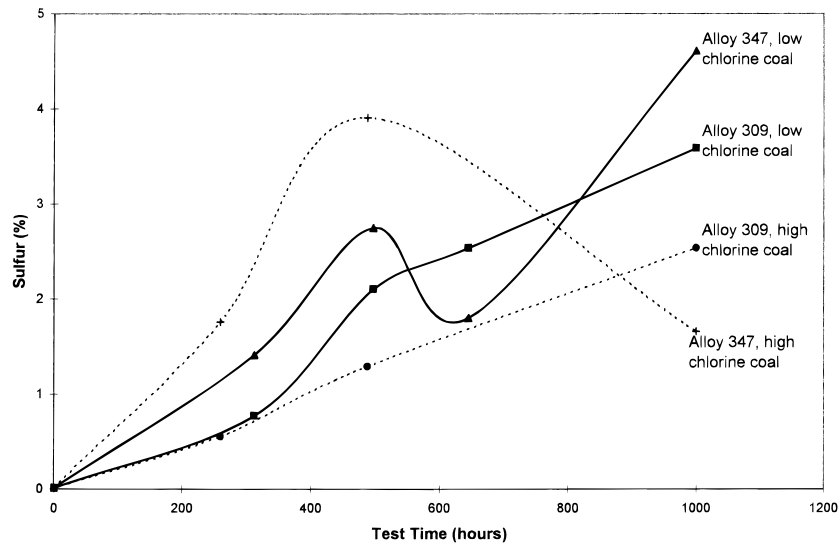


Figure 1. The effect of exposure time on sulfur contents in the ash deposits on coupon surfaces.

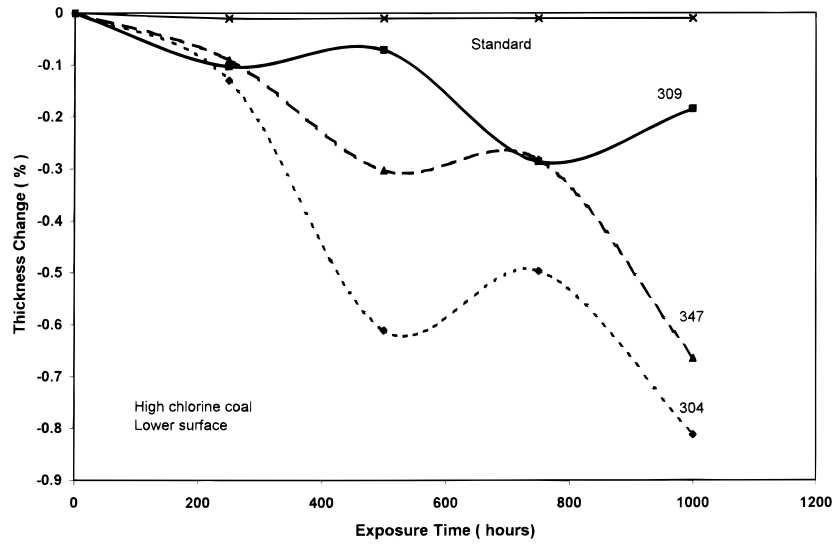


Figure 2. The effect of exposure time on the thickness changes of the test coupons.

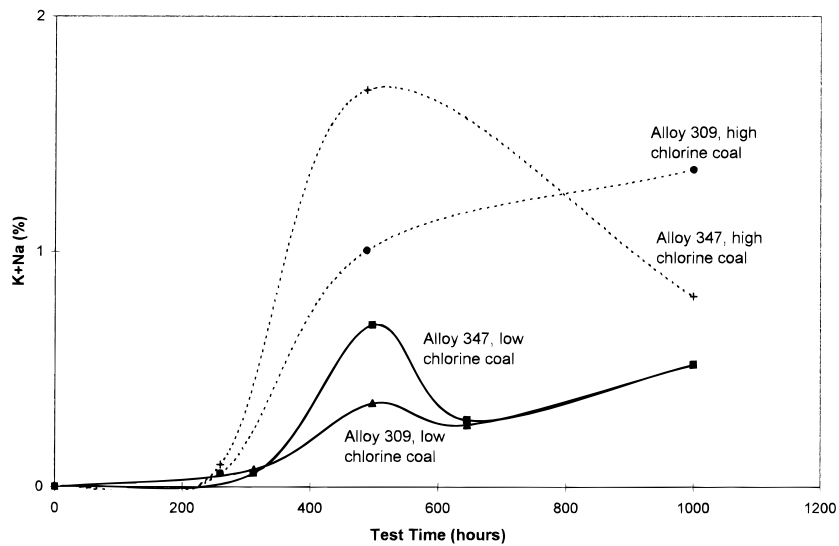
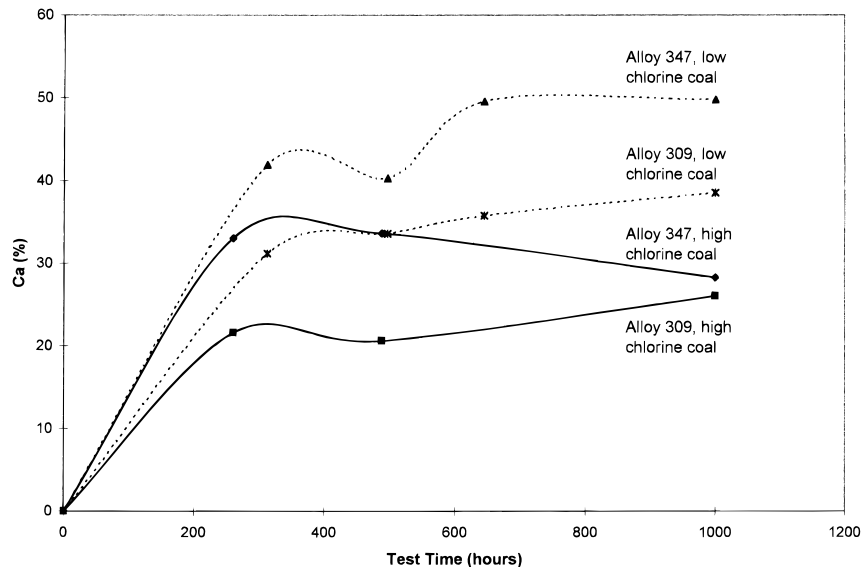


Figure 3. The effect of exposure time on alkali contents (K+Na) in the ash deposits on metal surfaces.

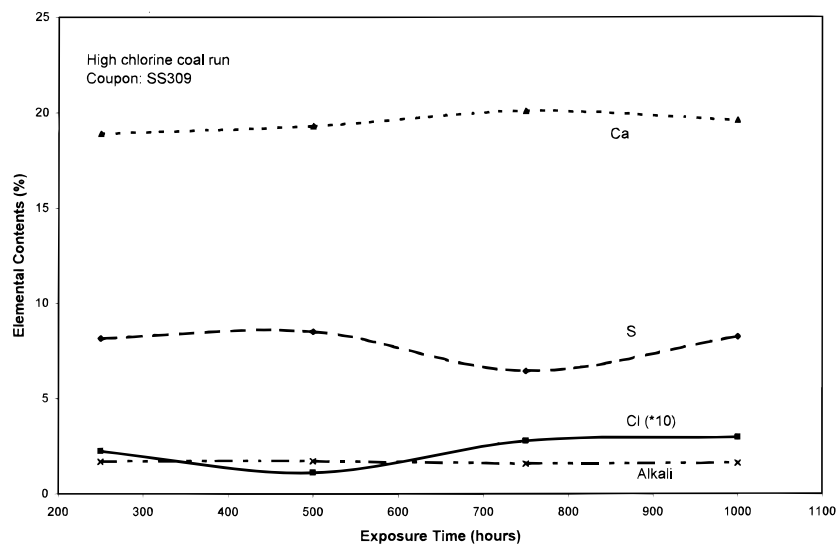
products layer determined by SEM also provides interesting evidence. The thickness of the ash products layer ( $0.5 \mu\text{m}$ ) at the first 250 h point is much thinner than

that obtained at the 500 h point ( $4 \mu\text{m}$ ). Consequently, alkali chlorides can easily deposit on the metal surface.

When the low chlorine coal (95011) was burned both



**Figure 4.** The effect of exposure time on the calcium contents in ash deposits on coupon surfaces.



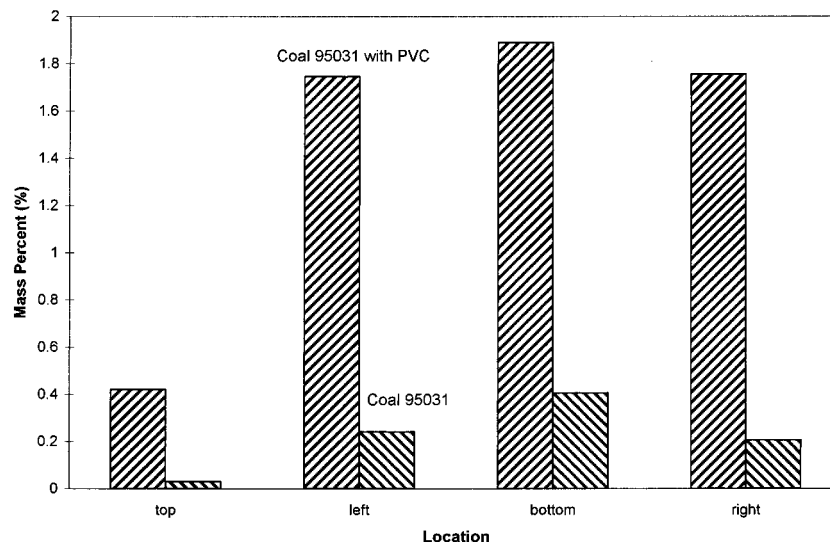
**Figure 5.** The effect of the exposure time on elemental content profiles in the ash deposit on alloy coupon SS309.

alloys showed the same behavior with regard to the alkali content in the ash products layer. Comparing the two alloys, alloy 347 can more easily capture alkali compounds and form a heavier layer of deposits than alloy 309. The analytical data for the calcium content in the ash products layer shows the same trend, as shown in Figure 4. The major element in the ash products layer from the FBC system was calcium, and the major compounds are calcium products including  $\text{CaO}$ ,  $\text{CaCO}_3$ , and  $\text{CaSO}_4$ . The calcium content in this reacted layer were not necessarily dependent on exposure time, since after 250 h, the calcium contents were fairly constant. The results illustrated in Figure 4 indicate that calcium-based compounds are the predominant materials forming deposits on the metal surfaces.

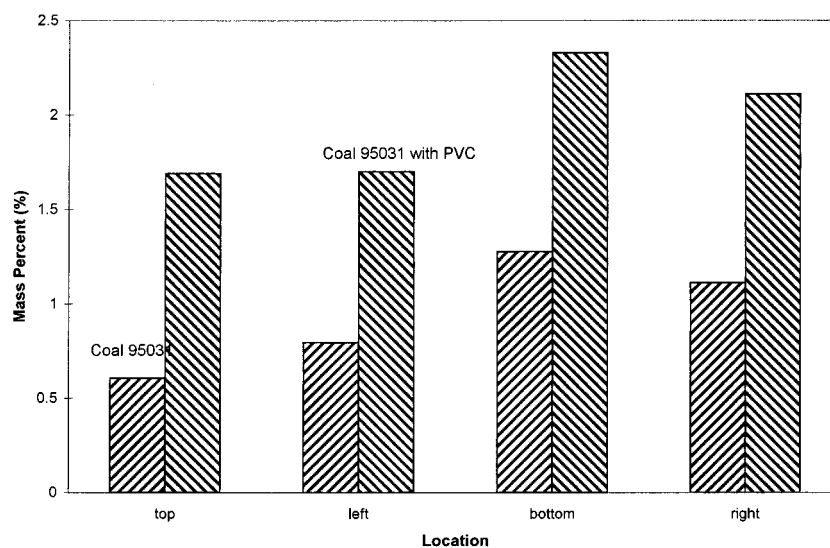
**Ash Deposits. Elemental Distribution in the Ash Deposits on Coupon Surface.** Ash deposits were only observed on the top of the coupons for the high chlorine and alkali coal test run. However, ash deposits were formed only on the bottom part of the coupons that faced the flow direction for another coal. The particle size is less than  $75 \mu\text{m}$ . The carbon content in the ash deposit

is in the range from 0.2% to 0.5%. The effect of the exposure time on elemental content profiles in the ash deposit on alloy coupon SS309 is shown in Figure 5. It is clearly indicated that the elemental (Ca, Alkali, Cl, and S) contents in the ash deposit are independent of the exposure time. After the first 250 h, no significant changes are observed for all four element concentrations in the ash deposit during the continuous 1000-h test run. For example, the sulfur content is in the range of 6.5%–8.2%, Ca ranges from 18.9% to 20.1%, the alkali ranges from 1.6% to 1.7%, and with Cl 0.13%–0.27%. The major compounds in the ash deposits are calcium-based products in the FBC system. However, one phenomenon that is observed is that the chloride content in the ash deposit can influence the sulfur content in the deposit. The chloride content decreased when the sulfur content in the deposit increased within the 1,000-h tests. For instance, the sulfur content in the ash deposit reaches a maximum of 8.53%, while the chloride content reaches a minimum of 0.13% at the 500 h point.

**The Effect of Chlorine Content in Fuels on Ash Deposits on Convective Region Tubes.** The major focus of this section is to compare the effect of the chlorine



**Figure 6.** The chlorine contents in deposits at different locations of the convective pass tube bank in tests with two fuels.



**Figure 7.** The sulfur contents in deposits at different locations of the convective pass tube bank in tests with two fuels.

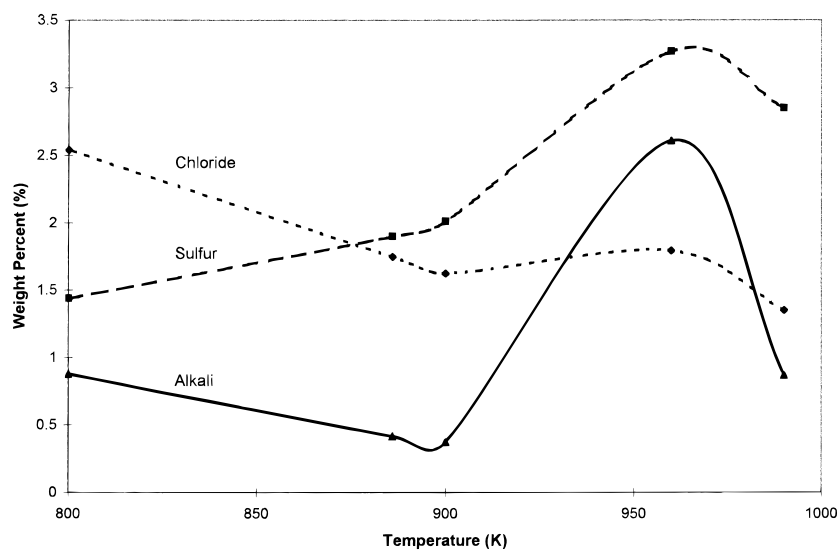
content in the fuel on ash deposit composition. To examine the effect of the chlorine content in fuel on deposit formation, an additional 150-h test firing a mixed fuel (2.08% chlorine, coal 95031 blended with 3.3% PVC) was conducted in this study. Since the PVC/coal ratio used was very low (3.3 wt %), the elemental analysis values for the coal and the PVC/coal blend can be considered to be nearly the same, with the exception of the chlorine content. The ash deposits on the convective pass heat exchange tube bank were collected at different locations (such as the bottom, top, right, and left tubes) during the test burns with the two fuels. A serious ash deposit on heat exchange tubes was observed after 150 h burning the blend of coal with PVC. The chlorine and sulfur distribution in the deposits on the heat exchange tubes for different fuels are shown in Figures 6 and 7, respectively. Both higher chlorine and sulfur contents were present in the ash deposits after burning the blend with a very high chlorine content. Most of the chlorine was retained on the high temperature tubes (bottom and both sides) for both fuels. This may indicate that the tubes in the direct path of the flue gas flow are more easily attacked by chloride than tubes somewhat sheltered from the gas flow. Sulfur

was more evenly distributed on the tubes. The results may indicate that the chlorine content in the fuel may enhance the formation of ash deposits on the metal surface.

A total of 14 samples were collected from the convective heat exchange tube bank, the transition region from the fluidized dense zone to the freeboard of the FBC furnace and the moveable heat exchange tubes to investigate further the effect of chlorine content in the fuel on the possible chloride- and calcium-related components of the ash deposits other than the Al-, Si-, and Mg-based compounds. All samples were gathered after the combustor was cooled from 850 °C to room temperature. X-ray diffraction spectroscopy was used to determine the possible compounds at a 95% confidence level. The analytical data from the XRD analysis is listed in Table 3. Alkali chlorides (KCl and/or NaCl) were only found in the ash deposits on the moveable heat exchange tube surfaces, where the flue gas temperature is around 850 °C and the metal surface temperature is only about 90 °C. The amount of alkali chloride in the deposits decreased with an increase in the height above the fuel distributor (lower temperature). Comparing the ash deposit data from the above-bed heat exchange tubes

**Table 3. Alkali Chloride Contents Compared to CaCO<sub>3</sub> in Ash Deposits as Determined by XRD Spectroscopy**

| deposit position            | relative (%)<br>KCl/CaCO <sub>3</sub> | CaSO <sub>4</sub> | comments<br>about NaCl | color      |
|-----------------------------|---------------------------------------|-------------------|------------------------|------------|
| convective region           | 3.5                                   | minor             | No NaCl                | tan        |
|                             | 4.9                                   | minor             | No NaCl                | tan        |
|                             | 1.5                                   | minor             | No NaCl                | gray       |
|                             | 5.7                                   | minor             | No NaCl                | dark gray  |
|                             | 10.8                                  | minor             | No NaCl                | dark gray  |
| transition region           | 9.9                                   | minor plus        | No NaCl                | dark gray  |
|                             | 9.0                                   | minor plus        | No NaCl                | dark gray  |
|                             | 8.2                                   | minor plus        | No NaCl                | dark gray  |
| top                         | 12.1                                  | minor             | No NaCl                | dark gray  |
|                             | 13.5                                  | near major        | No NaCl                | dark gray  |
| moveable heat-exchange tube | 68.5                                  | major             | possible               | white/gray |
|                             | 75.1                                  | minor             | possible               | white/gray |
|                             | 61.5                                  | major             | possible               | mixture    |
| bottom                      | 120.0                                 | minor plus        | possible               | white/gray |

**Figure 8.** The effect of temperature on chlorine, sulfur and alkali retention in the ash deposits.

with that from the in-bed heat exchange tubes, the higher temperatures at the metal surface are more favorable for the reaction between alkali chlorides in the deposits and SO<sub>2</sub> in the flue gas to form alkali sulfates. The XRD results also show strong evidence for the existence of CaO, Ca(OH)<sub>2</sub>, CaCO<sub>3</sub> and CaSO<sub>4</sub> in the deposits. Unfortunately, the presence of CaCl<sub>2</sub> cannot be confirmed from the XRD data, because the major XRD line of CaCl<sub>2</sub> overlaps with lines from CaCO<sub>3</sub>.

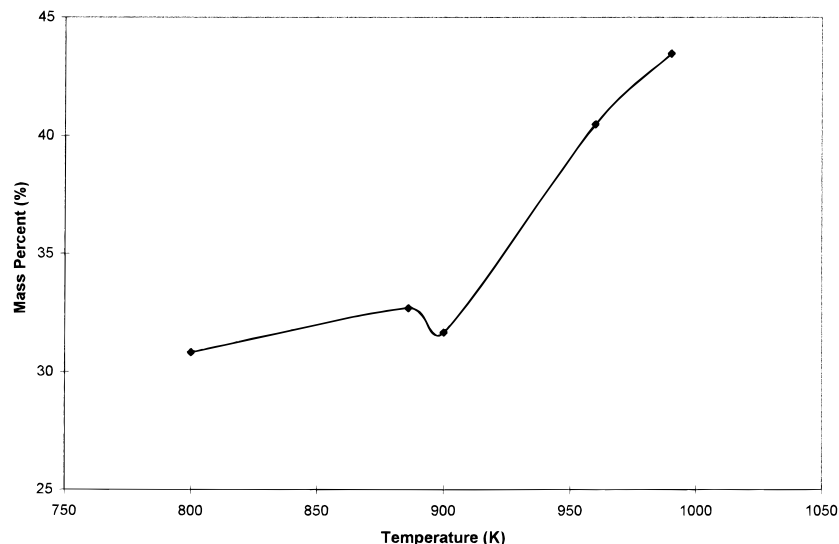
*The Effect of Surrounding Temperature.* The effect of temperature on the components in the ash deposits is illustrated in Figure 8. Samples were collected at five positions after the second 1,000-hour run. Higher chloride contents in the deposits were observed at the lower temperatures. Most alkali products condensed on the metal surfaces around their melting point. The capture of HCl by limestone is more difficult than the capture of SO<sub>2</sub>, especially at the high temperatures in the fluidized bed of the combustor. However, the reaction between HCl and CaO is more favorable at the lower temperatures in the freeboard area. This information on the distribution of sulfur and chloride in ash will be useful in efforts to minimize corrosion of heat exchange tubes.

The effect of temperature on calcium contents in the ash deposits is shown in Figure 9. The figure illustrates that calcium compounds become the major compounds

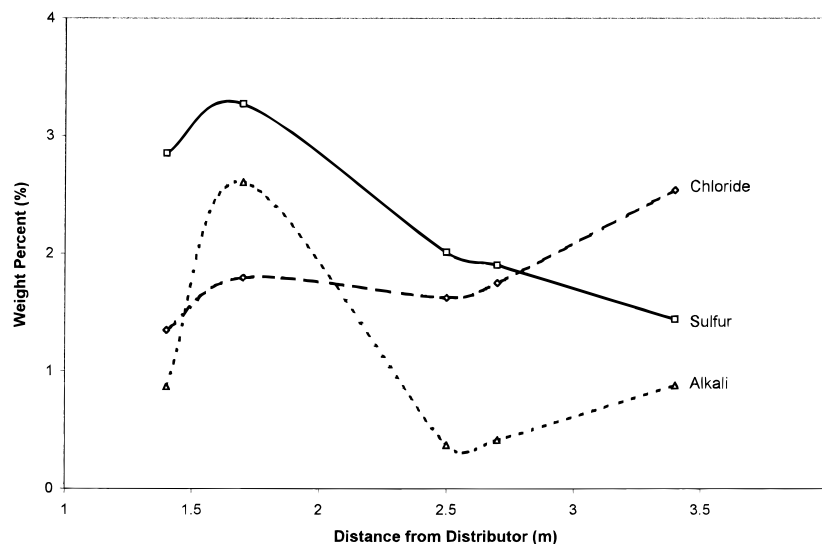
as the temperature is increased. At the same time, sulfur contents also increase with an increase in the temperature. This may be attributed to more calcium sulfate being formed on the metal surfaces at high temperatures.

*The Effect of Combustor Position.* The profiles of sulfur, chloride, and alkali contents in deposits along the height of the furnace are shown in Figure 10. The highest concentrations of alkali compounds in the deposits occurs at 1.7 m above the distributor. The local temperature in this region is 650–700 °C, while only small alkali contents were obtained in the other locations. The alkali contents in deposits decreased very quickly from 2.5% to 0.4% within the furnace as the height increased from 1.7 to 2.5 m. After 2.5 m, the alkali contents leveled off. At lower positions (below 1.2–1.3 m) is the fluidized zone, which is the major combustion zone for the fuel.

The combustion temperature in the FBC system was controlled between 850 and 900 °C, where all alkali compounds should be in the vapor phase except for complex substances formed from alkalis and metasilicates. The chloride contents in the deposits increased with an increase in the height of the furnace, while the sulfur contents in the deposits decreased. Perhaps this may be caused by one or more of the following two factors: (1) different reaction temperatures favoring SO<sub>x</sub> reacting with CaO or HCl with CaO and (2) favorable



**Figure 9.** The effect of temperature on calcium contents in the ash deposits.



**Figure 10.** The elemental profiles of sulfur, chlorine and alkali as a function of furnace height.

reaction temperatures needed between chloride compounds and  $\text{SO}_x$  in the deposit layers. Our results indicated that the  $\text{SO}_x$  concentration in the flue gas was reduced gradually along the height of the furnace. The reaction between chloride compounds and  $\text{SO}_x$  also is favored at relatively high temperatures. Thus, the chloride contents in the deposits increased with an increase in the height. At high positions (lower temperature and lower  $\text{SO}_x$  concentration), the major chloride compounds may be calcium chloride due to the very low alkali contents (Na and K) in the deposits. This would be caused by the reaction between HCl and CaO under relatively low temperatures, which is also shown in the figure illustrating the Ca content profile.

The elemental profiles in the circumference of the combustor are illustrated in Figures 11 and 12. These samples were collected from the convective pass heat exchange tube bank after burning high chlorine coal for 1,000 hours. Zero degrees represents the position facing the flue gas flow (the bottom location) and 180 degrees represents the position opposite the flow (the top location). The direction order referred to is counterclockwise.

As shown in Figure 11, the profile of alkali content was almost uniform in the circumference and only a slightly higher value was obtained at the 180 degree location. The interesting profiles are those of sulfur and chloride, which have different trends. The baseline of both elements is very close, in the range of 1.7% to 1.9%. However, in the space with the angle from 105 to 225 °C, the sulfur profile had a positive curve while chloride had a negative profile. At 180 °C, the sulfur content in deposits had reached a maximum and the chloride content was at a minimum. The reason for this behavior may be that more adhesion stress for forming deposits is needed at the bottom (0 °C) of the tubes to withstand the erosion from the flow of the particles. On the other hand, more chloride compounds condensed on the surface and more adhesion force was supplied.

As shown in Figure 12, the profile of calcium is in normal distribution, the maximum was found at the top position (180 degrees). The result indicated that the major compounds in deposits at opposite positions is calcium-based compounds.

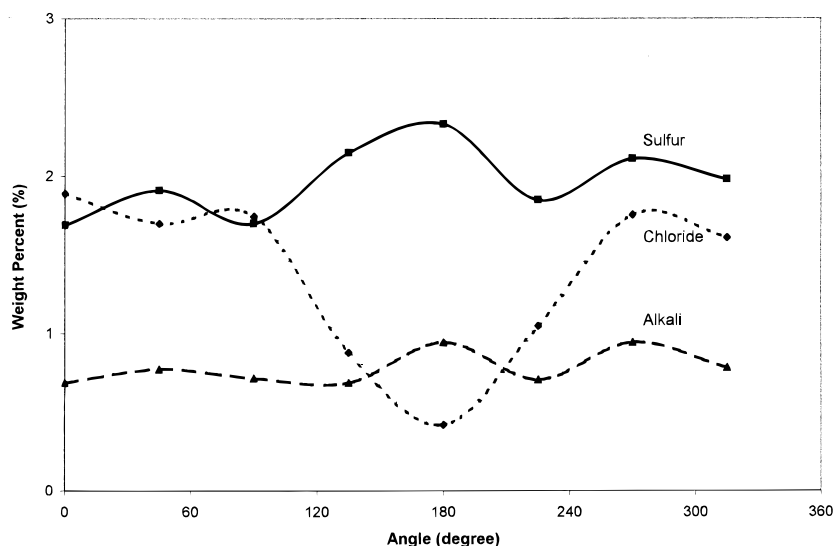


Figure 11. The elemental profiles of sulfur, chlorine and alkali in the circumference.

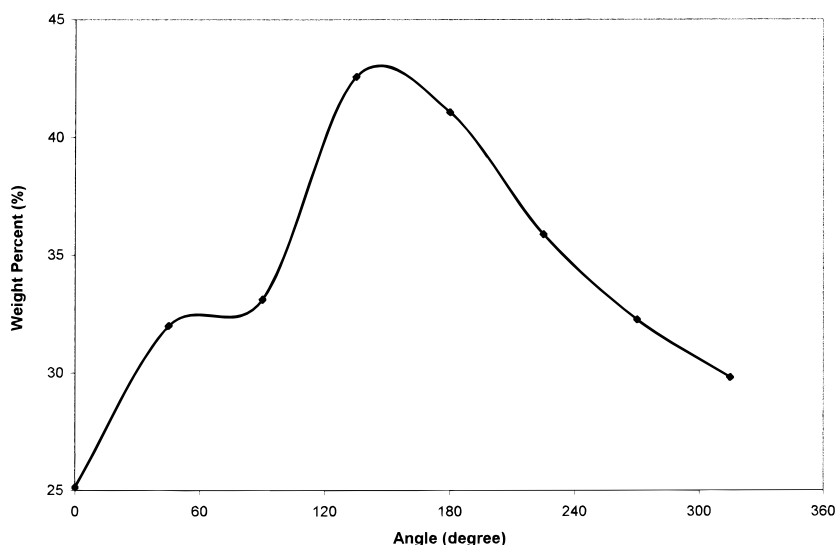


Figure 12. The profile of calcium in the circumference.

Table 4. Typical ICP-AES Analytical Data for Ashes Collected from the FBC Combustor

| metal oxides                   | fly ash | bed ash | ash deposit |
|--------------------------------|---------|---------|-------------|
| SiO <sub>2</sub>               | 17.66   | 10.56   | 18.92       |
| P <sub>2</sub> O <sub>5</sub>  | 1.35    | 0.45    | 2.04        |
| CaO                            | 23.41   | 42.51   | 28.31       |
| K <sub>2</sub> O               | 0.90    | 0.32    | 1.42        |
| TiO <sub>2</sub>               | 0.41    | 0.31    | 0.42        |
| Fe <sub>2</sub> O <sub>3</sub> | 12.30   | 8.51    | 4.25        |
| Na <sub>2</sub> O              | 0.45    | 0.31    | 0.60        |
| MgO                            | 3.24    | 2.31    | 5.11        |
| Al <sub>2</sub> O <sub>3</sub> | 6.46    | 4.52    | 7.71        |
| MnO <sub>2</sub>               | 0.02    | 0.01    | 0.02        |

### Discussion

A typical metal analysis of the fly ashes and bed ashes of the FBC system is given in Table 4. The major compounds in the ashes are calcium compounds, especially for bed ashes. In the WKU-FBC system, the average particle size of bed ash is 1.24 mm with a range from 0 to 3.5 mm. The carbon content in the bed ash is less than 0.70%. The average particle size of the fly ash is 0.23 mm with a range from 0 to 0.56 mm, in which the carbon content is in the range from 5% to 15%.

However, the particle size of the ash deposits is less than 0.075 mm, and the carbon content is around 0.35%.

On the basis of elemental analysis of the deposits the five chlorides that are the most likely to be present in these deposits are CaCl<sub>2</sub>, KCl, NaCl, MgCl<sub>2</sub>, and FeCl<sub>3</sub>.<sup>11</sup> Since both NaCl and KCl have appreciable vapor pressures (0.4 and 0.7 kPa, respectively, at 1173 K) at the fluidized-bed combustion temperature range, their vapors are expected to be in the FBC flue gas. In the case where there is a relatively high concentration of chlorine in the fuel, alkali chlorides are likely the compounds governing deposit formation. Many researchers have suggested that as the vapor of the alkali chloride reaches the heat recovery surface (normally below 600 °C), the vapor will directly condense and provide a sticky layer (the first layer, ash products layer) on the tube surface for the future adhesion of ash particles in the flue gas. Once the liquid binder is formed, inorganic particles (including coal ash and absorbents, calcium compounds) all will be captured and

(11) Xie, W.; Xie, Y.; Pan, W.-P.; Riga, A. Characterization of the Ash Deposits from FBC System Using Thermal Techniques. *Thermochim. Acta* **1999**. In press.

adhere to this layer to form a second layer (ash deposit layer), which is a solid layer when the fine particles (fly ashes or bed ashes) pass over the tubes. The thickness of the first layer is very thin, or on the order of a few microns. The thickness of the second layer is typically a millimeter or more thick. With an increase in the amount of ash deposits on the tube surface, the conductive heat exchange through the tube is decreased. Thus, the temperature of the deposit layer reaches a higher value gradually while the boiler load remains constant. On the other hand, the higher temperature of the metal surface is more favorable for the reaction between alkali chlorides in the deposits and SO<sub>2</sub> in the flue gas to form alkali sulfates and release chloride as HCl during the long-term combustion run, which have higher melting points and stronger adhesion to the rest of the deposits than alkali chlorides. As a consequence, more ash deposits are formed.

On the basis of the chemistry involved, the pure calcium compounds have relatively high melting points, which are higher than the operating temperatures of commercial FBC systems (850–900 °C). However, when a mixture of these compounds are heated, the behavior of the mixture is far different from that of the pure substances. For example, the theoretical decomposition temperature for pure CaSO<sub>4</sub> is around 1350 °C. When CaSO<sub>4</sub> is blended with a little of CaS, the decomposition temperature of the mixture shifts to a very low value (830 °C).<sup>12</sup> The reason may be that a solid–solid reaction takes place as illustrated by the following equations:



CaS can be produced under local O<sub>2</sub> lean conditions and in the presence of CO as follows:



Reaction 2 also causes the formation of a melt in the calcium sulfide/calcium sulfate system. This low-melting eutectic bonds fly ash particles to each other on the tube surface, and increases deposit formation. This may be the reason more ash deposits are formed in FBC systems compared to systems not using sulfur sorbents. After particles (from fly ash or bed ash) were captured by the liquid “glue” layer, the particle may continue to burn out or break down during the particle combustion to reduce the size to a very small value.

### Conclusions

On basis of this study, the chlorine and sulfur contents in fuels are key factors in affecting ash deposition on heat exchange tubes in FBC systems. More ash deposits are observed with high chlorine content fuels. Different alloys have significantly different deposition behavior. High chromium alloys have slight deposits with low rates of deposit formation. Although alkali chlorides can react with SO<sub>2</sub> to form alkali sulfates and release HCl, the reaction rate is very slow at the low temperatures of metal surfaces of heat exchange tubes.

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(12) Xie, Y.; Xie, W.; Pan, W.-P.; Riga, A.; Anderson, K. A Study of Ash Deposits on the Exchange Tubes Using SDT/MS and XRD Techniques. *Thermochimica Acta* **1998**, *324*, 123–133.