

# PHASE RELATIONSHIPS IN COAL ASH CORROSION PRODUCTS

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## **ABSTRACT**

The corrosion of heat transfer surfaces in coal-fired utility boilers is a major concern to the efficient operation of these units. Despite the importance of the corrosion there has been limited research on the relationship between the ash components on the tube surface and the interactions and reactions between the various components and the steel surface. Mechanisms such as molten phase corrosion, sulfidation, and high temperature oxidation have been identified as leading to extensive wastage of tube metal. However, while the corrosion process can be identified using techniques such as metallography and x-ray diffraction there is limited insight into the role of the coal mineralogy and ash deposits on the surface in the corrosion process.

This paper describes research into the formation of molten or semimolten phases within ash deposits which are associated with corrosion of superheater and reheater fireside surfaces. For example, the phases potassium pyrosulfate ( $K_2S_2O_7$ ) and potassium aluminum sulfate ( $K_2Al_2SO_7$ ) have been determined by x-ray diffraction to be present in deposits where fireside corrosion has occurred. However, both these phases are not directly derived from coal minerals or the common matrix observed in ash deposits. The examination of the reactions and interactions within deposits which result in the formation of these and other phases associated with corrosion will be discussed in the paper.

## **INTRODUCTION**

The high temperature corrosion of pressure parts in utility boilers is a major aspect of the design and operation of the system. The ideal design of heat transfer surfaces would be a material which would be resistant to creep damage and exhibit no corrosion. In reality the economics of boiler design requires the use of steels which are not only susceptible to creep damage (at temperatures above 650° C and pressures above 14 MPa) but also susceptible to corrosion. The corrosion is important as the reduction in wall thickness caused by the wastage results in reduced capacity to contain steam pressures, increased hoop stresses within the tube, and in reduced creep life. Therefore, it is very important that the corrosion process occurring on the fireside surface of heat transfer surfaces be understood and thereby reduced by either fuel choice or change in design/operating conditions.

The high temperature corrosion of heat transfer surfaces is usually observed in coal fired systems and confined to superheater and reheater components. In many cases the corrosion is localized to the tubing with the highest metal temperatures within the component such as the outlet portion. The metal temperatures in this location are either known or measured and are functions of unit design and operation. However, a knowledge of the metal temperatures is only a part of the issue with respect to the corrosion process. A major aspect is the reactions and interactions of the phases within the ash deposit and the relationship between these phases and corrosion processes.

The most aggressive form of fireside corrosion occurs with a molten phase. The mechanism is referred to as molten ash corrosion or liquid ash corrosion. Wastage rates of up to 0.5 mm per year for tubes 10-20 mm thick are not uncommon and can result in rapid reduction of component planned life expectancy. Despite the importance of the corrosion process there has been limited research to date with respect to the relationship between the coal ash properties (coal mineralogy), the ash deposit formed on the fireside

surface and the presence of molten ash corrosive phases. In recent years, however, significant efforts have been placed on the understanding of ash deposition processes. From this research methods to characterize and predict ash behavior on heat transfer surfaces have been developed. In addition to understanding the growth of deposits, itself important to the design and operation of utility boiler systems, these techniques and models have now been applied to understanding the relationships between the deposit and the tube metal surface.

When considering the corrosion process it is important to understand the nature of the tube metal surface. The type of metal used can be a ferritic alloy such as SA213-T22 (iron based alloy with a nominal 2.25 wt% chromium and 1.0 wt.% molybdenum) or an austenitic alloy such as SA213-304 (type 304 stainless steel). In both cases, resistance to high temperature oxidation and corrosion is due to the presence of an intact adherent external protective scale. In the case of the ferritic alloy this scale is predominantly magnetite ( $\text{Fe}_3\text{O}_4$ ). For austenitic alloys, the protective scale is chromium oxide. Phases within the deposit which affect the integrity of this scale will result in wastage of the tubing. It is the molten phases formed during the liquid phase corrosion mechanism which are most aggressive towards the protective scale. Under these conditions the high mobility of corrosive ions and the removal of corrosion products including the protective scale results in increased wastage.

Therefore, it is important to understand the phase relationships within deposits and how these phases contribute to the corrosion process. This requires a description of ash deposits and the techniques used to characterize the interactions and reaction with respect to the corrosion interface.

#### **CHARACTERIZATION OF ASH DEPOSITS**

Ash deposits are formed from the coal minerals present in the fuel. The common minerals observed in coal are listed in Table 1 along with the nominal chemistry. As the minerals are geological in nature some minerals are poorly defined chemically. The minerals are not distributed uniformly throughout the coal and may be associated with the coal maceral (inherent) or excluded from the coal matrix (extraneous). Furthermore, there is a great variation in size of the mineral grains between different coal sources. The variation of the mineralogy results in a variation in the nature of the ash produced. However, while the ash may be different the bulk chemical composition may show less variation. This difference makes it very difficult to relate the chemical composition of the ash to the behavior of the ash in a combustion system. The mineralogical transformations of the minerals during combustion are complex and do not lend themselves to simplistic correlations. The coal mineralogy is established using a technique called computer controlled scanning electron microscopy (CCSEM). This technique determines the size and chemistry of the various minerals observed in coals. Specifically, CCSEM analysis establishes the size distribution of mineral species in the sample.

Knowing the mineralogy of the coal is the first step in understanding the deposits and their relation to corrosion. It is important to establish the mineralogy of the ash produced in the combustion system. This is performed by again using CCSEM analysis on ash which has passed through the system (fly ash). The comparison of the mineralogy of the coal and the mineralogy of the fly ash allows determination of the complex phase transformations of the minerals. Furthermore, by establishing the mineralogy of the ash it is possible to identify precursors to deposition and potential corrosive molten phase formation within the deposit.

The second stage is to examine and understand the phase relationships within the deposits present on a corroded tube. This analysis is in addition to the forensic analysis of failed or corroded superheater and reheater tubes. Normally, the tube sample is subjected to visual and metallurgical analysis. In cases where fireside corrosion is suspected, the ash deposit is sometimes subjected to x-ray diffraction and chemical analysis. It is from the powder x-ray diffraction analysis of the ash on the tube that the basis of the phase relationship within the deposits and the corrosion was postulated. Table 2 lists some of

the phases associated with high temperature corrosion and the melting point of these phases.

All the phases listed in Table 2 have melting points around the metal skin temperature of the tube. There are a number of issues to discuss with respect to the phases listed. First, the detection of these phases is performed by x-ray diffraction analysis. This analysis only detects crystalline phases and therefore, does not identify "molten" or amorphous phases. The second issue is the application of melting point data for complex salt mixtures. Mixtures of salts such as those found in these deposits will have eutectic and liquidus temperatures below that of the melting point of the pure end members. Therefore some knowledge of the mixture is necessary in order to assess the impact of the phase on melting. This data is obtained by performing an analysis called scanning electron microscopy point count (SEMPC) at and around the corrosion interface. SEMPC was developed to determine the phase assemblage of coal ash deposits. The technique involves the analysis of over 200 random points using scanning electron microprobe analysis methodologies. The chemical analysis of each point is then processed through a normative computer program which establishes if the point can be classified as a given phase. For example, a point is classified as quartz when the chemical analysis contains essentially pure silicon and oxygen (oxygen is determined by difference). More complex phases such as mullite ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) are classified based on the presence of essentially silicon, aluminum, and oxygen with the silicon and aluminum at the correct molar ratio (within a reasonable tolerance). The analysis involves the identification of crystalline and amorphous phases. The results are used to determine the type of bonding in an ash deposit and the role of the various phases in deposit growth and development of strength. This involves the application of models of ash transformations and viscosity. Furthermore, the ability to identify and quantify the various amorphous or molten phases allows determination of key characteristics which are related to the chemical composition. These characteristics include the eutectic temperature of a selected region or phase and the potential for reaction with another phase. The eutectic temperature is obtained from phase equilibria.

The potential for reaction is obtained by looking at the base to acid ratio of the individual points classified as amorphous in the SEMPC analysis. Highly basic phases will tend to be more reactive towards acidic phases than other basic phases. Thus it can be seen that SEMPC analysis can have great value in establishing the characteristics of corrosion interfaces. The technique can identify the various phases which are present including the amorphous phases. The eutectic and melting characteristics can be obtained from suitable phase equilibria data and models. Mass transfer of corrosion products and corrodents can be determined using a model of viscosity. Corrosion potential is determined by examining the propensity for interaction between the different amorphous phases (acidic or basic) with the basic or amphoteric oxides of the protective scale. Another advantage of the application of the SEMPC technique to the study of ash corrosion is the ability to determine the relationship between key components within the deposit. For example, while it is difficult to identify the presence of a potassium pyrosulfate phase by x-ray diffraction it is possible to identify phases rich in potassium and sulfur with molar ratios corresponding closely to that of pyrosulfate (i.e.  $K/S = 1.0$  while potassium sulfate has a molar ratio of  $K/S = 2$ ). Furthermore, the presence of iron with this and similar "corrosive" phases indicates the role of this phase in the corrosion process. Another area where the SEMPC analysis can be used is to establish the change in chemistry and phase within the deposit. As noted above, a phase commonly associated with high temperature corrosion is that of potassium aluminosulfate. This phase is of particular interest as there is no direct precursor to this phase from the coal mineralogy. In most coals all the aluminum is observed with clay species such as kaolinite and illite. Furthermore, the potassium is also mainly associated with the illite clay in coals. A simplistic reaction pathway for this phase would be:



The melt phase would be a mixture of potassium aluminosulfates, the composition of which would be dependent on the original mineral chemistry and the amount of

potassium aluminosulfate formed. Clearly, significant disassociation of the aluminosilicates is necessary to facilitate the reaction of the aluminum and potassium from the reactants. This is not observed in most coal ash deposits where the Si/Al molar ratio (a defining parameter for most clay species) tends to remain constant. The SEMPC technique not only allows one to detect and quantify the amount of potassium aluminosulfate, amongst other phases, but can give valuable insight into the nature of the melt phase. In relation to corrosion the following question is postulated: is the potassium aluminosulfate the corroding phase or is the amorphous phase associated with the potassium aluminosulfate which causes the corrosion.

An example of SEMPC data is given below. The deposit was from a superheater tube where corrosion had been noted based on ultrasonic thickness measurements. The deposit was scraped off and submitted for SEMPC analysis. The phase assemblage is listed in Table 3. The phases include iron oxide, mullite, calcium silicate, calcium sulfate, ferric sulfate, pyrrhotite (FeS), pyrite, aluminosilicate (resembling kaolinite clay) and unclassified phases. The unclassifieds represent the amorphous phases. As part of the SEMPC analysis the points are averaged to obtain a "bulk" chemical composition. This chemical composition corresponds to the average chemistry of the region selected for the analysis and represents the region where the corrosion occurs. The ability to separate the different phases, and thus the corresponding chemistry, allows a determination of the average composition of the amorphous phases. Both these chemical compositions are listed in Table 4. The data shows that the bulk composition of the deposit was enriched in iron oxide, sodium oxide, and sulfur trioxide compared to the original coal ash (12% Fe<sub>2</sub>O<sub>3</sub>, 1% Na<sub>2</sub>O, 3% SO<sub>3</sub>). The amorphous phase was further enriched in SO<sub>3</sub>, Na<sub>2</sub>O, and K<sub>2</sub>O and depleted in CaO and Fe<sub>2</sub>O<sub>3</sub>. This data shows that the corrosion was due to the presence of a corrosive alkali sulfate phase. However, further analysis can be performed on the SEMPC results. For example, Figure 1 shows a ternary molar plot of Fe, S, and Na for all the points rich in iron, sulfur, and sodium. The graph shows that sulfur is only associated with the points with 5-10 mole % sodium. However, no definitive phase can be ascertained confirming the amorphous nature of the corroding phases. Similar graphs can be produced to establish the relationships between selected components in order to develop a more accurate assessment of the effect of ash chemistry and mineralogy. Furthermore, from this data methods to predict the corrosive potential of a given coal ash with gas and metal temperatures can be developed.

## CONCLUSION

The phase relationships in coal ash deposits and their effects on high temperature corrosion have been introduced. The complex nature of deposition and corrosion can be studied by the application of advanced analytical techniques such as computer controlled scanning electron microscopy (CCSEM) and scanning electron microscopy point count (SEMPC). The valuable data from these techniques combined with design and operating conditions can be used to develop methods to control coal ash corrosion.

Table 1  
Common Minerals Observed in Coal

Mineral name	Nominal Chemistry
Quartz	SiO <sub>2</sub>
Pyrite	FeS <sub>2</sub>
Kaolinite	Al <sub>2</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub>
Illite	K <sub>1-1.5</sub> Al <sub>4</sub> Si <sub>7-8.5</sub> Al <sub>1-1.5</sub> O <sub>20</sub> (OH) <sub>4</sub>
Calcite	CaCO <sub>3</sub>

Table 2  
Melting Point of selected phases observed in ash deposits

Compound	Melting Point/°C
K <sub>2</sub> Fe(SO <sub>4</sub> ) <sub>3</sub>	618
K <sub>3</sub> Al(SO <sub>4</sub> ) <sub>3</sub>	654
Na <sub>3</sub> Fe(SO <sub>4</sub> ) <sub>3</sub>	624
Na <sub>3</sub> Al(SO <sub>4</sub> ) <sub>3</sub>	646
KFe(SO <sub>4</sub> ) <sub>2</sub>	694
NaFe(SO <sub>4</sub> ) <sub>2</sub>	690

**Table 3**  
Phase Assemblage of Deposit as Determined by SEMPC

PHASE	VOLUME %
MULLITE ( $3Al_2O_3 \cdot 2SiO_2$ )	0.5
CALCIUM SILICATE ( $CaSiO_3$ )	0.5
IRON OXIDE	18.6
ANHYDRITE ( $CaSO_4$ )	1.0
FERRIC SULFATE ( $Fe_2(SO_4)_3$ )	4.0
PYRRHOTITE ( $FeS$ )	2.0
PYRITE ( $FeS_2$ )	1.0
ALUMINOSILICATE (KAOLINITE)	1.0
UNCLASSIFIEDS	71.4

**Table 4**  
Chemical Composition of Ash Deposit

OXIDE	BULK	AMORPHOUS
SILICA	18.1	21.5
ALUMINA	10.3	12.0
IRON OXIDE	36.2	24.7
TITANIUM DIOXIDE	0.5	0.5
PHOSPHOROUS PENTOXIDE	0.3	0.4
CALCIUM OXIDE	1.2	0.6
MAGNESIUM OXIDE	1.0	1.1
SODIUM OXIDE	3.4	4.1
POTASSIUM OXIDE	1.9	2.5
SULFUR TRIOXIDE	26.8	32.1

**Figure 1**  
Ternary plot of sodium, sulfur and iron.

