

## COAL-ASH CORROSION OF MONOLITHIC, SILICON CARBIDE-BASED REFRACTORIES

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### ABSTRACT

Several silicon carbide-based monolithic refractories were subjected to static coal ash corrosion tests to determine corrosion mechanisms and rates. Two castable refractories with 75% and 85% SiC were exposed to two types of coal ash at temperatures from 1090°C to 1430°C. Several plastic refractories were exposed to a high-calcium coal ash at 1430°C for over 100 hours. Optical microscopy and scanning electron microscopy with energy-dispersive x-ray analysis were used to determine the corrosion mechanisms and rates of these materials.

### INTRODUCTION

Silicon carbide-based monolithic refractories are commonly used in coal combustion environments. Their thermal conductivities are superior to conventional materials, such as alumina or chrome-based refractories, so they are useful as replaceable, corrosion-resistant coatings on surfaces through which heat flow is required. Therefore, they are ideal for use as protective coatings on ceramic heat exchangers in advanced coal combustion systems. In these systems, a refractory may be exposed to temperatures above 1400°C, but in conventional fluidized-bed combustors, temperatures are several hundred degrees lower. Therefore, it is important to understand the interactions between SiC (silicon carbide) refractories and coal ashes in a range of temperatures.

Previous corrosion experiments focused on structural ceramics (1, 2) and SiC refractory bricks (3). The corrosion of structural SiC ceramics by acidic coal slags at 1230°C resulted in localized corrosion by iron silicides (1). The corrosion by high-calcium, basic slags at 1240°C was characterized by uniform corrosion by the dissolution of a protective SiO<sub>2</sub> layer by CaO in the slag to form calcium silicate compounds (2). The corrosion of SiC refractory bricks by acidic and basic slags at 1500°C involved the formation of iron silicides, and the basic slag corroded the SiC more rapidly than the acidic slag (3).

Although the literature describes corrosion of SiC ceramics and refractory bricks, little information exists on the corrosion of monolithic SiC refractories by coal ash. To determine slag corrosion mechanisms and rates, five commercially available SiC refractories were subjected to static slag corrosion tests. The materials were tested at three temperatures, 1090°, 1260°, and 1430°C, and with two types of coal ash, a high-calcium Powder River Basin (PRB) coal and a high-iron Illinois No. 6 coal. These coals were chosen because they are frequently used by utility boilers, and utility operators can use the corrosion information to determine the effects of switching from a bituminous eastern coal to a PRB coal. The slag/refractory interfaces were examined after the exposure by scanning electron and optical microscopy to determine the corrosion effects and penetration depths.

## EXPERIMENTAL

These experiments focused on ash corrosion mechanisms and rates for castable and plastic monolithic SiC refractories. Monolithic refractories are nonbrick materials that are usually mixed with water at the application site and develop strength by firing to produce chemical or ceramic bonds. Two common binder materials are phosphoric acid, which produces a chemical bond at 260°C, and calcium aluminate, which develops a ceramic bond above 980°C. The castable materials contained calcium aluminate binders, and the plastics contained phosphoric acid binders. The SiC concentrations in the castables ranged from 75% to 85% and the SiC concentrations in the plastics from 50% to 70%.

The samples were prepared according to manufacturer's instructions, and each sample was formed into a cup shape to hold the coal ash during the exposure. The samples were then prefired, which caused the development of vesicular glass coatings on the plastics, but the calcium aluminate-bonded refractories were not affected, so the vesicular glass formation was attributed to the phosphoric acid binders in the plastic SiC refractories.

The two coal ashes used in the corrosion experiments included a high-calcium PRB coal ash and a high-iron Illinois No. 6 ash (Table 1). Approximately 5 grams of ash was placed into the cup of each sample, then the samples were heated to temperatures of 1090°, 1260°, and 1430°C at a rate of 100°C per hour. The castables were tested with both coal ashes at all exposure temperatures, and the plastics were tested only at 1430°C for 110 hours. All of the samples were quenched in air to determine phases present at temperature, then cross-sectioned and examined.

### LOW-TEMPERATURE EXPOSURE—1090°C FOR 55 HOURS

The two SiC castables, containing 75% and 85% SiC, were exposed to both ashes for 55 hours. After the exposure, the PRB ash was somewhat sintered, but porous and friable, and the Illinois No. 6 ash was well sintered and more dense than the PRB ash. Neither ash adhered well to the SiC refractory substrates, indicating that soot blowing would be an effective means of ash removal at this temperature. X-ray fluorescence of the ashes after the exposure showed that they did not react with the refractory, and there was no infiltration of the ash into the refractory.

### INTERMEDIATE-TEMPERATURE EXPOSURE—1260°C FOR 45 HOURS

A similar test was conducted at 1260°C using the 75% and 85% SiC castable refractories. The samples were held at temperature for 45 hours, then quenched and examined using optical microscopy and scanning electron microscopy with energy-dispersive x-ray analysis (SEM/EDX). Both ashes were liquid at 1260°C and reacted with the SiC refractories.

**Powder River Basin Coal Ash.** Each castable sample contained a 3- to 4-mm layer of dark gray slag, which contained a few small vesicles, approximately 0.5 mm in diameter. The vesicles indicate gas evolution during the exposure. The slag contained a continuous, red reaction layer, 0.5 mm thick, at the undulating, slag/refractory interface. Figure 1 shows several circular, metallic phases, ranging up to 0.25 mm in diameter, at the interface. The circular nature of these phases, which were high in iron, indicates that they were liquid at 1260°C and immiscible with the slag. The maximum depth of penetration of the slag into both refractories was 1 mm.

A few of the high-iron grains at the refractory/slag interface contained mainly Fe (55 wt%) and O<sub>2</sub> (40 wt%), but several other grains contained Fe (60 wt%), Si (up to 10 wt%), and P (up to 20 wt%), which is similar in composition to iron silicides described in other studies (1, 2), although phosphorus is not mentioned. Iron silicides are stable only under reducing conditions and indicate that portions of

the slags had low partial pressures of oxygen during the exposure. The iron oxide in the slag reacts with the SiC to form the iron silicide. This reaction also causes gas evolution of CO or CO<sub>2</sub>, as indicated by vesicles in the slags.

The remaining slags in both sample cups were very similar in composition (Table 2). In comparison with the original ash, the slags contained less calcium oxide and more silica. The decrease in calcium is difficult to explain because no high-calcium phases were identified, but the increase in silica can be explained by the oxidation and dissolution of SiC grains from the refractory into the slag.

**Illinois No. 6 Coal Ash.** The slags remaining in the castable samples ranged from 5 to 6 mm thick and were black in color. Many 0.5- to 2-mm-diameter vesicles were present at the top of the slags, with a few small vesicles (0.5 mm in diameter) present at the slag/refractory boundaries, which were probably formed from CO or CO<sub>2</sub> evolution during the oxidation of the SiC. The samples exposed to the PRB ash contained only a few vesicles, indicating that the refractory reacted less with the PRB ash to produce fewer vesicles or that the PRB slag was less viscous at this temperature, as indicated from the higher base/acid ratio, and allowed vesicles to escape rapidly from the slag.

The maximum depth of corrosion reached 0.25 mm, but corrosion and surface pitting of the refractories were uneven and occurred in isolated areas, unlike the samples exposed to the PRB ash, which caused an even reaction layer. The slag/refractory interfaces contained discontinuous, red reaction layers and circular, iron-rich phases, 0.25 to 0.5 mm in diameter (Figure 2). The iron phases were composed of Fe (75-80 wt%) and Si (15-20 wt%), with little or no O<sub>2</sub> or P.

The resultant slag compositions were similar in both samples and differed only slightly from the original ash composition (Table 2). The slag contained less iron oxide than the ash, but the other major oxides were present in almost equal amounts.

#### HIGH-TEMPERATURE EXPOSURE—1430°C FOR 40 HOURS

Both castable SiC refractories were subjected to a corrosion test with the PRB and Illinois No. 6 ashes at 1430°C for 40 hours. The samples were quenched and analyzed. Reaction between the slags and refractories seemed to be more extensive at this temperature than observed at 1260°C.

**Powder River Basin Coal Ash.** The residual slag layers in the castable SiC refractories ranged from 1 to 3 mm thick. The slags were tan in color and highly vesicular with the vesicles ranging in size from 0.5 to 2 mm in diameter. The slag was able to penetrate 2.5 mm into the refractory materials, and the penetration was aided by dissolution of the refractory binder and the incorporation of SiC grains into the slag. Some of these incorporated SiC grains were coated with red reaction rims that contained high amounts of iron and silicon. These rimmed grains indicate that the iron in the slag can be reduced to elemental iron and react with the SiC to produce iron silicides. Only a few circular, iron-rich grains were present in the slag and ranged from 0.25 to 1.0 mm in diameter. These phases contained 70 wt% Fe, 10 wt% Si, and 10 wt% P.

Chemical analyses of the slag remaining in the SiC refractory samples are given in Table 3. In general, the slag contained less calcium and magnesium and more silica than the original ash composition. The increase in silica content resulted from oxidation and dissolution of SiC grains by the slag.

**Illinois No. 6 Coal Ash.** The castable SiC samples contained layers of residual slag that ranged from 3 to 5 mm thick and the slag/refractory interfaces were undulating. Many vesicles, from 0.25 to 3 mm in diameter, were present along the top surfaces of the slags. Several circular metallic grains were

present at the refractory/slag interfaces and were approximately 0.25 to 0.5 mm in diameter. These grains contained 75 wt% Fe, 20 wt% Si, 5 wt% O<sub>2</sub>, and less than 2 wt% P and were present in isolated areas along the slag/refractory interface. The maximum depth of slag penetration was 0.75 mm.

The castables seemed to react less with the Illinois No. 6 ash than the PRB ash, but some reaction occurred to alter the slag composition (Table 3). The resultant slag contained less iron and more calcium and silica than the original ash. The reduction of iron in the slag resulted from the formation of iron silicides during the dissolution of the SiC refractory.

#### **HIGH-TEMPERATURE EXPOSURE—1430°C FOR 80 HOURS**

**Powder River Basin Coal Ash.** The samples contained residual slag layers 1 to 3 mm thick. The slags were transparent and highly vesicular, with vesicles ranging from 1 to 2 mm in diameter. The slag/refractory interfaces of both samples were marked with a red reaction layer, which contained small (0.25 mm in diameter), iron-rich phases (70 wt% Fe, 10 wt% Si, 8 wt% O<sub>2</sub>, 9 wt% P). The maximum depth of slag penetration was 4 mm.

SEM analysis indicated that the ash reacted with the refractory materials to produce a resultant slag similar in composition to the slag of the 40-hour 1430°C exposure (Table 3). The slags contained more silica and less calcium and magnesium than the original ash. The decreases in calcium and magnesium may be related to the formation of calcium-magnesium phases that were not detected, but other explanations may account for their decreases. The increase in silica was caused by the oxidation and dissolution of SiC grains into the slag.

**Illinois No. 6 Coal Ash.** A 2- to 3-mm layer of slag was present in both of the castable samples after the 80-hour exposure. The gray slags contained a few isolated vesicles (0.25 to 0.5 mm in diameter) at the slag/refractory interfaces. Several, circular iron-rich grains were present at the interfaces and were 0.25 to 1.0 mm in diameter. These high-iron phases contained 70 to 75 wt% Fe, 20 wt% Si, 5 to 10 wt% O<sub>2</sub>, and no P. The occurrences of the iron-rich phases were isolated, which resulted in isolated surface pitting of the refractories, and the maximum depth of slag penetration was 3 mm.

The SEM analyses indicated that the resultant slags were similar in composition to the 40-hour 1430°C exposure and contained more silica and less iron than the original slag (Table 3). The decrease in iron is related to the formation of iron silicides, and the increase in silica is a result of oxidation and dissolution of the SiC grains by the slag.

#### **HIGH-TEMPERATURE EXPOSURE—1430°C FOR 110 HOURS (POWDER RIVER BASIN COAL ASH)**

The 75% SiC castable refractory and three plastic refractories, with SiC compositions ranging from 50% to 70%, were exposed to the PRB ash at 1430°C for 110 hours. After the exposure, the samples were quenched, cross-sectioned, and examined optically.

**Castable SiC Refractory.** The cup of the castable refractory contained a 5- to 6-mm layer of slag intermixed with refractory grains. Several circular metallic grains ranging from 0.5 to 2 mm in diameter were present within the slag and contained high amounts of iron and silicon, similar to the castables exposed to the PRB ash for 80 hours. This slag also was highly vesicular, indicating gas evolution during exposure. The maximum depth of penetration of the slag into the refractory was 3 mm.

**Plastic SiC Refractories.** The plastic samples contained residual slag layers 3 to 4 mm thick. A few small metallic grains were present within the slags, which contained vesicles ranging from 0.5 to 1 mm in diameter. The slag easily penetrated the plastic refractory materials, and penetration depths reached 10 mm in most samples.

## CONCLUSIONS

Table 4 gives the penetration rates for the castable refractories exposed to the PRB and the Illinois No. 6 ashes in the static corrosion tests. The 1090°C exposure showed no ash penetration and was not included in the table, and the plastics were omitted because of their rapid penetration rates. Table 4 also shows the penetration rates relative to a 25-mm (1-in) refractory layer. These penetration rates are derived from static slag corrosion tests and do not take into consideration erosion effects of flowing slag or replenishment of fresh slag in a dynamic system. In a dynamic system, penetration rates are expected to be higher than rates determined from these static tests.

The corrosion of the SiC refractories by the PRB ash was characterized by uniform surface reaction, similar to previous studies (1, 2). Although iron silicides were found, their formation was probably not the main corrosion mechanism for this ash. The CaO in the slag may have dissolved the protective SiO<sub>2</sub> layer on the surface of the SiC to form calcium silicate compounds. The slag also attacked and dissolved the refractory binder and incorporated SiC grains into the slag during the 1430°C exposures.

The Illinois No. 6 ash caused localized surface pitting by the formation of iron silicide compounds. This type of corrosion was not as rapid as penetration by the PRB ash, but was still rapid at the 1430°C exposures. Only the Illinois No. 6 at 1260°C had an acceptable corrosion rate that would require replacement of a 25-mm layer of refractory every 6 months, although this rate is still excessive.

The differences in penetration rates of the two coal ashes may be related to slag viscosity, which is dependent on ash composition and temperature. The base-to-acid ratios indicate that the PRB slag probably had a lower viscosity at all exposure temperatures, which would facilitate the diffusion of corrosive elements (Ca and Fe) to the SiC surface. As temperature increases, viscosity decreases, which would also increase diffusion. The penetration rates also increased when the exposure time was increased from 40 to 80 hours at 1430°C; therefore, the penetration rates are not uniform over long exposure times, and future work should focus on comparisons of short- and long-term slag corrosion experiments.

## REFERENCES

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TABLE 1. Compositions of the Powder River Basin Ash and the Illinois No. 6 Ash Used in the Corrosion Experiments

Oxide	Powder River Basin Ash, wt%	Illinois No. 6 Ash, wt%
Na <sub>2</sub> O	2.52	1.18
MgO	9.44	2.50
Al <sub>2</sub> O <sub>3</sub>	15.93	18.50
SiO <sub>2</sub>	31.08	57.80
P <sub>2</sub> O <sub>5</sub>	1.77	0.00
SO <sub>3</sub>	0.00	0.00
K <sub>2</sub> O	0.30	0.62
CaO	33.00	3.74
TiO <sub>2</sub>	1.03	1.03
FeO	4.40	14.62
Base/Acid*	1.03	0.29

\* Base/Acid = (FeO + CaO + MgO + Na<sub>2</sub>O + K<sub>2</sub>O)/(SiO<sub>2</sub> + Al<sub>2</sub>O<sub>3</sub> + TiO<sub>2</sub>).

TABLE 2. Resultant Slag Compositions for the 1260°C, 45-hour Exposure

Oxide	Powder River Basin Slag, wt%	Illinois No. 6 Slag, wt%
Na <sub>2</sub> O	0.6	0.9
MgO	5.0	0.9
Al <sub>2</sub> O <sub>3</sub>	16.7	20.7
SiO <sub>2</sub>	52.0	62.3
P <sub>2</sub> O <sub>5</sub>	0.0	0.1
SO <sub>3</sub>	0.2	0.1
K <sub>2</sub> O	0.2	1.4
CaO	23.4	5.1
TiO <sub>2</sub>	0.5	0.8
FeO	0.5	7.6
Base/Acid	0.4	0.2

TABLE 3. Resultant Slag Compositions for the 1430°C, 40-hour Test

Oxide	Powder River Basin Slag, wt%	Illinois No. 6 Slag, wt%
Na <sub>2</sub> O	0.9	0.6
MgO	1.7	1.0
Al <sub>2</sub> O <sub>3</sub>	8.9	21.6
SiO <sub>2</sub>	69.4	66.5
P <sub>2</sub> O <sub>5</sub>	0.4	0.0
SO <sub>3</sub>	0.0	0.1
K <sub>2</sub> O	0.1	1.5
CaO	14.5	6.9
TiO <sub>2</sub>	0.8	0.9
FeO	2.9	0.7
Base/Acid	0.3	0.1

TABLE 4. Penetration Rates for Castable Refractories Exposed to Powder River Basin and Illinois No. 6 Ashes

Ash	Temperature, °C	Exposure Time, hours	Penetration Rate, mm/100 hours	Time for Penetration of 25-mm Layer	
				hours	weeks
PRB	1260	45	2.2	1100	6.5
PRB	1430	40	6.3	400	2.4
PRB	1430	80	7.5	300	1.8
Illinois No. 6	1260	45	0.6	4500	26.8
Illinois No. 6	1430	40	1.9	1300	7.7
Illinois No. 6	1430	80	3.8	700	4.2

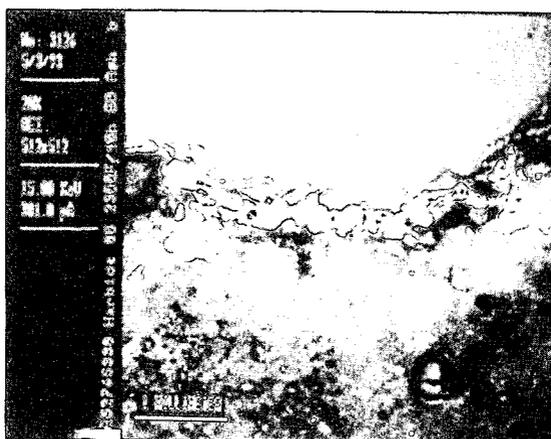


Figure 1. SEM micrograph of the reaction layer between the slag and a SiC castable refractory exposed to a PRB coal ash at 1260°C for 45 hours.

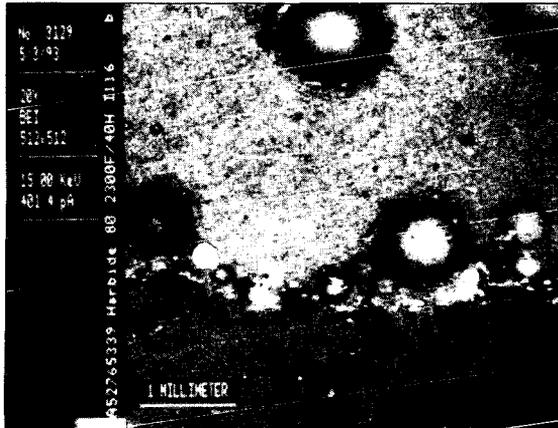


Figure 2. SEM micrograph of the slag/refractory boundary in a sample exposed to an Illinois No. 6 coal ash at 1260°C for 45 hours.