Effects of calcium in ash on the corrosion performance of Ni-based alloys in simulated oxy-fuel environment

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Abstract

Increasing the efficiency of coal power plants requires raising the operating temperature above 650°C. However, coal ash can severely attack alloy materials at high temperature. For example, the corrosion rates of commercial Fe- and Ni-based alloys are generally greater than 2 mm/year at 750°C in the gas environment of oxy-fuel combustion. Thus, a critical study is needed to determine the effect of the constituents in the ash on corrosion and find an approach to reduce the corrosion rates in an ash-laden environment at high temperature.

The role of CaO in the ash (typical of U.S. Western coal ash) has been investigated in laboratory exposure environments with various structural alloys. Detailed results are presented on weight change, scale thickness, internal penetration, microstructural characteristics of corrosion products, and the cracking of scales for the alloys after exposure at 750°C. The thermal stability of $K_3Al(SO_4)_3$ under the environment of oxy-fuel combustion was determined by thermogravimetric analysis and differential thermal analysis. The reaction of this low melting temperature salt with the CaO-containing ash is discussed. In addition, we performed synchrotron nanobeam X-ray analysis to study the phase and chemical composition of the oxide layers on the alloy surface. Results from these studies are used to address the role of CaO in ash in the long-term corrosion performance of alloys.

Key words: Ash corrosion, Oxy-fuel, CaO, Ni-based alloys.

1.0 Introduction

Energy production, particularly electricity generation, is expected to continue to increase globally due to population growth and a per capita increase in energy consumption. To meet the energy needs, fossil fuels (coal, oil, and gas) will play a major part in energy production, even with a projected increase in alternative renewable sources. However, to minimize greenhouse gas emissions, the current power plant systems emphasize the capture of carbon dioxide and subsequent sequestration. Oxy-fuel combustion systems (without the diluent nitrogen gas) would enable recycling of the carbon dioxide to the compressor, use of novel gas turbines, and advanced reuse of CO₂. The U.S. Department of Energy/Office of Fossil Energy is supporting the development of combustion systems that replace air with nearly pure oxygen, with the goal of achieving a coal-based power system with near zero emissions. For this purpose, turbines and combustor technologies that use pure oxygen in fuel combustion are being developed. The major advantage of combustion under pure oxygen is the potential for the separation and capture of CO₂ and for power system efficiencies in the range of 50% to 60%.

The presence of H₂O/CO₂ and trace constituents such as sulfur and chlorine in the gas environment and coal ash deposits, including alkalis at the operating temperatures and pressures, can have adverse effects on the corrosion and mechanical properties of the structural alloys in these plants [1]. The concentrations of CO₂, SO₂, and H₂O in oxy-fuel environments are higher than those under air combustion conditions, because of the absence of airborne N₂. Various investigators have studied the alloy corrosion behavior of steel materials in H₂O and CO₂ environments. Increasing steam content can lead to breakaway oxidation [2]. Carburization was observed when stainless steels were exposed to CO₂ at elevated temperature [3,4]. High CO₂ and H₂O

concentrations also assisted in partially oxidizing SO_2 to SO_3 [5]. The concentration of SO_3 in the oxy-fuel environment is typically three or more times higher than that under the air combustion condition. This SO_3 can react with steam to form sulfuric acid. Subsequently, higher SO_3 and H_2O concentrations can lead to higher concentrations of corrosive H_2SO_4 under oxy-fuel conditions. Thus, the response of structural and turbine materials in simulated oxy-fuel environments needs to be evaluated to select materials that have adequate high-temperature mechanical properties and long-term environmental performance.

Sulfur can also be transported through oxide scales on alloys and increase their oxidation rates in coal plants. Radiometric analysis has indicated that the inward transport of sulfur is primarily due to the SO_2/S_2 molecular transport. Sulfides were observed in the inner scale layer [6]. However, the effect of sulfur on corrosion in an oxy-fuel system has scarcely been studied [7]. Coal ash can also lead to severe corrosion at high temperature [8-20].

The corrosion of alloys in the oxy-fuel and ash environments has been little studied [21-24].

While coal power plants are designed to be operated for a long time, recent studies usually report only short-term test results regarding alloy performance. If the oxidation follows a parabolic law, short-term test results can provide useful information. However, if the oxide scale on the alloy breaks down after the incubation period, the corrosion rate can dramatically increase. Then, short-term test results below the incubation time will not be sufficient to establish the alloy performance. This paper is the result of a study of the long-term corrosion performance of alloy materials in oxy-fuel environments.

Ash corrosion is more severe than other types of corrosion in the environment of coal power plants, especially if the operating temperature is increased to improve the efficiency. Ash corrosion is also more complicated than other types of corrosion since it involves solid, liquid, and

gas phases. In addition, it involves multiple corrosive gases: O_2 , SO_2 , SO_3 , CO_2 , H_2O , HCl , and Cl_2 . Ash corrosion could also be localized, and this localization dramatically increases the uncertainty in determining the corrosion rate. Therefore, it is a great challenge to adequately characterize and explain the ash corrosion. In our previous studies [18, 21-23], we performed corrosion tests to evaluate the performance of structural alloys in the presence of simulated U.S. Eastern coal ash, consisting of alumina, silica, and iron oxide along with sodium and potassium sulfates. Detailed results were presented on weight change, scale thickness, internal penetration, microstructural characteristics of the corrosion products, and cracking of scales after exposure of the alloys at $750^\circ C$. Tests were also conducted in environments with and without steam in oxy-fuel gas atmospheres. Results from these tests were also used to address the role of steam in the long-term corrosion performance of alloys.

The U.S. Eastern coal is rich in iron oxide, while U.S. Western coal is rich in calcium oxide. The calcium content in ash is an important parameter that affects alloy corrosion. Typically, the calcium oxide contents in the ash of U.S. Western coal from the Powder River Basin (PRB) and Beulah-Zap coal zone are much higher than those in the ash of U.S. Eastern coal. It is thus necessary to understand the effect of the calcium content on ash corrosion. Moreover, $CaCO_3$ is also added to furnaces in coal plants to absorb SO_2 and reduce SO_2 emissions. It is also necessary to understand the reactions of CaO and $CaCO_3$ with alloy materials. For this paper, we investigated the effect of calcium on Ni-based alloy corrosion in ash with and without calcium oxide. The effect of calcium on Fe-based alloy corrosion in ash will be reported in another paper.

2.0 Experimental Procedure

2.1 Alloy Composition

The compositions of the alloys selected for the study are listed in Table 1. High-Ni alloys (333, 617, 625, 602CA, 230, 693, 740, and 718) were included in the study, especially for application in superheaters at temperatures above 700°C. Apart from fire-side and steam-side corrosion resistance, the alloys selected for applications in steam superheaters and reheaters should possess adequate strength at elevated temperatures for the duration of service.

Table 1. Nominal composition (in wt. %) of alloys selected for corrosion study

Material	C	Cr	Ni	Mn	Si	Mo	Fe	Other
333	0.05	25.0	45.0	-	1.0	3.0	18.0	Co 3.0, W 3.0
617	0.08	21.6	53.6	0.1	0.1	9.5	0.9	Co 12.5, Al 1.2, Ti 0.3
625	0.05	21.5	Bal	0.3	0.3	9.0	2.5	Nb 3.7, Al 0.2, Ti 0.2
602CA	0.19	25.1	62.6	0.1	0.1	-	9.3	Al 2.3, Ti 0.13, Zr 0.19, Y 0.09
230	0.11	21.7	60.4	0.5	0.4	1.4	1.2	W 14, Al 0.3, La 0.015
693	0.02	28.8	Bal	0.2	0.04	0.13	5.8	Al 3.3, Nb 0.67, Ti 0.4, Zr 0.03
740	0.07	25.0	Bal	0.3	0.5	0.5	1.0	Co 20.0, Ti 2.0, Al 0.8, Nb+Ta 2.0
718	-	19.0	52.0	-	-	3.0	19.0	Nb 5.0, Al 0.5, Ti 0.9, B 0.002
WASP	0.02	20	Bal	0.5	0.75	4.3	2.0	Co 12-15, Ti 2.6-3.25, Al 1.0-1.5, Zr 0.1

2.2 Gas Composition

In oxy-fuel combustion, since the concentration of the diluent nitrogen gas is very low, the SO_2 concentration in the flue gas is generally three to four times higher than that in the flue gas of air combustion. This result is supported by both computer simulation and actual measurements from recent pilot-scale work [25-27]. The effect of a high SO_2 concentration on the alloy corrosion in oxy-fuel combustion systems has been studied by several groups [8-20]. The SO_2 concentrations in these studies varied from 0.32 to 1.5% [24, 28], depending on the design of the oxy-fuel systems and the types of coal targeted for combustion. We selected an SO_2 concentration of 0.99% consistent with U.S. Eastern coal with a high sulfur content, based on the premise that if the corrosion problems in a severe condition can be understood, then those in an environment with a low SO_2 content can be more easily solved.

To evaluate the effect of gas composition on alloy corrosion, we previously exposed alloys to six different gas mixtures in several corrosion tests. The results from these exposures were reported at earlier conference papers [21-23] and in a journal paper [18]. In the current paper, we used two gas mixtures (designated A and B) whose compositions are listed in Table 2. These gas mixtures contain the same concentrations of O₂ and SO₂, but A contains steam and B does not. Reference reported that the conversion rates from SO₂ to SO₃ are different with and without water since water can act as a catalyst for the conversion [5]. However, in our experiment, the test alloys were buried in ash containing Fe₂O₃, which acts as a catalyst for the conversion of SO₂ to SO₃ [29]. Since the diffusion rate of gas in and out of ash is slow, it is reasonable to assume that the conversion has reached equilibrium when the gas reached to the surface of alloys. For the following two reactions:

p_{O2} is the same in Gas A and B, and P_{SO2} is also the same in Gas A and B. Since the p_{H2SO4} is very small (only 1.85x10⁻⁶ atm), we assumed that the concentration of SO₂ and SO₃ for both reactions are very similar when reactions 1 and 2 reach equilibrium. At equilibrium condition, the partial pressure of SO₂ and SO₃ for both Gas A and B are 0.078 and 0.021 atm, respectively, at 750°C since part of SO₂ will be converted to SO₃.

Table 2. Gas compositions for experiments

Gas #	CO ₂ (%)	H ₂ O (%)	O ₂ (%)	SO ₂ (%)
A	68.14	26.9	3.97	0.99
B	95.04	0	3.97	0.99

2.3 Coal-Ash Composition

Corrosion tests were performed with ash prepared simulating both U.S. Eastern and Western coals. The U.S. Eastern coal is rich in sulfur but contains a low concentration of CaO. In

contrast, the calcium content in the U.S. Western coal is high, but its sulfur concentration is low. It has been reported that alloy corrosion rates are affected by the SO_2 content. Our previous study on the ash corrosion of U.S. Eastern coal was performed in a gas environment with 0.99% SO_2 [21-23]. If a study of high calcium ash on the alloy corrosion is performed in an environment with a low SO_2 concentration, the primary effect may be due to the difference of gas composition. To understand the effect of calcium on ash corrosion, we therefore used the same gas compositions for tests of alloy performance in ash with high calcium concentration and ash without calcium.

The synthetic coal-ash deposit that simulates ash from U.S. Eastern coal consisted of a mixture of reagent-grade SiO_2 , Al_2O_3 , and Fe_2O_3 in a ratio of 1:1:1 according to weight. The alkali sulfate mixture consisted of Na_2SO_4 and K_2SO_4 in the ratio of 1:1 according to weight.

The synthetic coal-ash deposit that simulates ash from U.S. Western coal consisted of a mixture of reagent-grade 36% SiO_2 , 16% Al_2O_3 , 9% Fe_2O_3 , 29% CaO , 5% Na_2SO_4 , and 5% K_2SO_4 . Since coal ash generally forms at high temperature after combustion at temperatures greater than 1100°C, these oxides can react with each other at high temperature. We also sintered these oxides at 1100°C in air, so that they form phases similar to what is observed in ash deposits in plants. The alkali sulfate mixture consisted of Na_2SO_4 and K_2SO_4 at a 1:1 ratio according to weight. The ash contained 90% sintered oxides and 10% sulfates (5% Na_2SO_4 + 5% K_2SO_4).

2.4 Test temperature

In 1970's and 80's the coal plants operated at steam temperatures around 500°C and the superheater tubes were rarely exposed above 600°C. However, currently DOE-Fossil Energy is interested in improving the efficiency of boilers and also cut the CO₂ emissions. As result, the projected steam temperatures of 700°C calls for superheater tubes to operate at 750°C or higher. Therefore, the corrosion studies were conducted at 750°C.

It was reported that alloy corrosion in a certain ash composition follows a bell shaped dependence of corrosion rate on temperature. The maximum rate should appear at 650° to 700°C when alloys were exposed to alkali iron trisulfate [30]. The low melting temperature K₃Fe(SO₄)₃ decompose below 680°C. No melting salt would appear at 750°C in the above test. Therefore, the corrosion rates dropped and form a bell-shaped rate behavior. However, there is also aluminum oxide in a real coal ash beside iron oxide. K₃Al(SO₄)₃ was also found in coal ash. Alkali iron sulfates decompose below 680°C, but K₃Al(SO₄)₃ may not. Reference reported that K₃Al(SO₄)₃ is more stable than potassium iron sulfates. To better understand the stability of K₃Al(SO₄)₃ in oxy-fuel gas environment, X-ray diffraction and thermal analysis were performed on K₃Al(SO₄)₃ in oxy-fuel gas environment. Bell-shaped theory is right for a simple “ash” of iron based sulfates. However, coal ash is not so simple. Some sulfates decomposed below 750°C, but other sulfates in ash may not decompose. The peak temperature could move higher or may not have a peak if there are serious sulfates with various decomposing temperatures in a coal ash with complex compositions. This study provides our simulated ash composition is close to the real coal ash composition.

2.5 Experimental Method

The thickness of coal ash deposition on superheater tubes can be as large as or greater than 1 mm, and in some cases is over 15mm. At the trailing edge heat transfer tube, the alloy material is actually buried in ash, and enhanced corrosion occurred at this location. At the other side of the tube, ash deposition is thin, and corrosion is minimal.

Therefore, in coal power industry, although most heat exchanger tubes are covered by thin ash deposition, these locations may not be attacked by ash corrosion. In contrast, the problem locations are usually covered with heavy ash deposition, which is where we need to study.

Meanwhile, low melting temperature salt can vaporize at high temperature. A thin coating of ash on alloy surface may not have enough salt for long term test and may lead to reactant starvation. Therefore, instead of coating with a thin ash layer on alloy surface, the alloy specimens were buried in the ash, which was contained in an alumina boat.

Recently, coal power industry and US Department of Energy are interested on raising operating temperature to 750°C to increase the efficiency of coal power plants. Therefore, corrosion tests were performed at 750°C for up to 3600 h. The experiments were generally stopped approximately every 300 h. A soft bristle brush was used to remove loose ash particles after the specimens were cooled to room temperature, and we paid attention not to use force to remove the ash and reaction products that stick to the alloy surface. An adherent oxide scale would not be removed by a soft brush. When the soft brush was used on the alloy surface with regular oxide scale, no weight loss was observed. Therefore, our experimental results have indicated that the soft brush in our experiment does not remove regular oxide scale.

Specimen re-exposures were then continued with a fresh supply of the ash mixture. The specimen temperature was controlled to within $\approx 3^\circ\text{C}$.

2.6 Characterization Methods

Upon completion of the corrosion kinetics experiments, the alloy specimens were examined by optical metallography and scanning electron microscopy (SEM) combined with energy-dispersive X-ray (EDX) analysis. In some cases, the deposit materials and the scales (which developed on the alloy specimens) were analyzed by X-ray diffraction (XRD). Optical examination of cross sections of exposed specimens and analyses with the SEM were used to identify the morphological features of the corrosion-product phases in the scale layers and to establish the thickness of the scales and depth of intergranular penetration, if any, in the alloys. The original thickness of alloy plates were measured and recorded. For localized ash corrosion, when the original surfaces are still present after exposure, the original surface was used as reference point. For some samples, the original surfaces were lost after heavy corrosion. In these cases, the thicknesses of the alloys at the location with the deepest corrosion depth were measured. The maximum corrosion depths were obtained by following equation:

$$d = (t_o - t_{rm})/2 \quad (3)$$

d is the maximum corrosion depth, t_{rm} is the minimum remaining metal thickness, and t_o is the original metal thickness measured before test.

Synchrotron nano-beam X-ray analysis was performed at the 2ID-D beamline of the Advanced Photon Source (APS) at Argonne National Laboratory. Using a Si(001) double-crystal monochromator and zone plate optics, the X-ray nanoprobe in the experimental station produces a monochromatic X-ray beam of size 200 x 300 nm with a photon flux of 5×10^9 photons/s with an X-ray energy bandwidth (dE/E) of 0.01%. The focal plane of the zone plate optics was adjusted so that the minimum spot size was obtained at the surface of the specimen. The beam energy was 8.5 keV for the XRD experiment. The position of the oxide-metal interface was determined by monitoring the iron-fluorescence counts as the sample was translated across the beam.

3.0 Results and Discussion

3.1. Incubation Period of Ash Corrosion and Localized Corrosion

Corrosion experiments in the presence of high-calcium ash with alkali sulfates were conducted at 750°C using both Gas A and B with a total exposure time of 3600 h. Specimens were retrieved and weighed periodically, and the ash was replenished after every 300 h of exposure. Figure 1 shows weight loss data for all alloys tested in the presence of high-calcium ash in Gas A (with steam) and B (no steam) at 750°C. Since there are different elements in the alloys, the reaction of these alloy constituents with ash is also different. Most alloys lost weight after exposure to the ash and oxy-fuel gas at 750°C. However, Alloy 718 gained weight initially because the reaction products adhered to the samples. Several alloys showed low weight loss during the testing period (Figure 1), and many exhibited an incubation period during which the corrosion rate was low. Upon exceeding the incubation period, the corrosion accelerated, and the

corrosion process did not follow the parabolic rate law. It seems that the ash corrosion rate follows linear kinetics after incubation period, as we have discussed in our previous paper [18]. The weight change trends in Figure 1 may not be very clear, since data are presented for several alloys to minimize the number of figures for publication in a reasonable form. The detail weight change data for individual alloys in the following 18 figures are presented in supplementary figure S1. Most figures show linear corrosion behavior, and none of these alloys follows the parabolic rate law in the 18 figures.

As shown in Figure 2, the incubation time ranged widely in the tests conducted with and without steam. No clear trend for the effect of steam on incubation time was discernable. In general, the incubation times for high Cr alloys such as 333, 693 and 740 are long. The incubation times of alloys with large amount of W and Mo are short. The addition of aluminum does not benefit in ash corrosion.

The corrosion of some alloys, such as Alloy 602CA, is localized in the ash environment. The localized attack on Alloy 602CA initiated at the edge, and then the corroded products grew outward. Although the weight loss may be low for such alloy samples, the local penetration rate can be very high. For coal power plants, penetration rates are more important than weight loss rates in evaluating long-term performance of alloys in an ash corrosion environment.

Generally, the incubation time for localized corrosion is strongly related to surface condition. Figure 3 (left) shows the effect of surface preparation on ash corrosion. The left specimen of Alloy 602CA was polished by 400 grit polishing paper before exposure. The right specimen of the same alloy was not so polished. After 300-h exposure to Eastern ash and Gas A at 750°C, the surface of the polished specimen was still smooth, as shown in Figure 3 (right). In contrast, corrosion has started at the edge on the unpolished specimen.

When compared to the lifetime of a coal power plant, an incubation period of several hundred to several thousand hours is a short period. Since alloy materials have to be used for years in coal power plants, data on the long-term corrosion rate are important for use in practical application. Figure 2 indicates that many alloys showed an incubation period of over 1000 hours. For long-term application, a 1000-h incubation time is only a short period. Since the important parameter is the rate after the incubation time, the best methodology for analyzing the ash corrosion data is to use the following equation:

$$r = \frac{d}{t - IT} \quad (4)$$

where r is the long-term corrosion rate (mm/year), d is the corrosion depth (mm), t is the total exposure time, and IT is the incubation time.

Figure 3 indicates that the incubation time is strongly dependent on surface condition. To obtain the same surface condition, we polished all of our coupon specimens with 400 grit paper, so that the incubation times of different alloys are comparable. However, for an industrial process, the alloy surface can be affected by many factors, which lead to different surface conditions and different incubation times. If incubation times are not subtracted when the corrosion rates are calculated, the data will not be reliable. In contrast, the effect of incubation is removed if the rate is calculated according to equation (3). Therefore, to obtain long-term ash corrosion rates that are reliable, it is necessary to test alloy materials long enough and to obtain data after the incubation period.

3.2. Effect of Alloy and Gas Composition on Ash Corrosion Rate

Figure 4 shows the rate of corrosion penetration for alloys in the presence of high-calcium ash (simulating U.S. Western coal) and gases A and B at 750°C. The penetration rates of alloys after exposure to ash are much higher than those after exposure to the gas environment without ash [22]. In general, the linear penetration rates for the alloys ranged between 0.84 and 8.04 mm/y. Alloy 740 had the lowest penetration rate of 0.84 mm/y, and Alloy 602CA had the highest rate. The corrosion rates of WASP, 617, 718, 625, and 230 are lower in the gas environment with than without steam. The effects of gas composition on corrosion rates are complicated because of the many different reactions of the alloying elements with ash and gas.

The performance of Alloy 740 was the best among the Ni-based alloys. Localized corrosion was observed on this alloy. In the non-protective region, deep corrosion with a thick oxide layer was observed. In contrast, the thickness of the oxide scale at the protective region is generally thin. Elemental mapping by EDX analysis of Alloy 740 revealed a SiO₂ layer with thickness of 10 to 20 μm on the outer layer of the oxide scale in the protective region (Figure 5, center image). Nanobeam X-ray analysis indicates that silicon oxide is hexagonal phase. This thick SiO₂ layer should not have developed from the diffusion of Si in Alloy 740, since the Si concentration was very low (0.5 wt%). The thickness of the SiO₂ layer should not have exceeded 9 μm if all Si in the Alloy 740 plate with thickness of 1.1 mm had diffused to the surface. Therefore, some of this SiO₂ layer apparently formed from the ash due to a long-term diffusion process.

Ash particles hardly stuck on alloy surfaces. When samples were cut to examine in cross section, loose ash particles spalled. Therefore, there is not regular ash particle in the cross section sample for the EDX analysis in Figure 5 and 6. Reaction products and oxide scales from alloying elements do not contain calcium. Only silicon oxide from ash bonded to alloy surface scale.

Calcium diffuses away from the silicon oxide layer as we stated. The driving force that Ca^{2+} to diffuse out is that SO_2 comes from gas environment, and SO_4^{2-} formed at the out-layer of ash. Ca^{2+} diffuses out to combine with SO_4^{2-} to form a chemically stable compound CaSO_4 . Therefore, the calcium content in both oxide scale and silicon oxide layer is very low. EDX analysis results indicate that the calcium contents in both layers are below 1%, which is the limit for reliable EDX analysis. Such a thick silica layer has not been observed at exposure times less than 1200 h. It may need further study to evaluate how a continuous silica layer form on alloy surface. The diffusion process may be driven by sulfur oxide gradient and charge transfer in alloy oxidation process. A possible mechanism for the formation of this SiO_2 layer is proposed as following. SO_2 and O_2 diffuse into ash from surface to the bottom and Fe_2O_3 acts as a catalyst to convert SO_2 to SO_3 . Electrons diffuse out from alloys in the process of alloy oxidation. Oxygen obtains electrons and form O^{2-} . Ca^{2+} diffuse out to form stable CaSO_4 , and SiO_2 left on alloy surface. Al^{3+} , Fe^{3+} in ash also diffuse out to form $\text{K}_3(\text{Al,Fe})(\text{SO}_4)_3$, SiO_2 left on alloy surface and form a SiO_2 again. Alloying elements such as Cr^{3+} , Co^{2+} , Ni^{2+} and electrons also diffuse out through the SiO_2 layer, and SiO_2 layer bonds to oxide scale on alloy surface in the diffusion process. After a long diffusion time, a dense protective SiO_2 layer will form and stick on surface of oxide scales.

The key is that calcium, aluminum, iron, chromium, nickel and cobalt can form sulfates, but silicon cannot. Therefore, when there is a small sulfur oxide gradient in ash layer and a charge gradient due to the alloying elements lose electrons at the bottom and oxygen obtains electrons at surface, a driving force will lead positive cations of Ca^{2+} , Al^{3+} and Fe^{3+} diffuse up. Sodium and potassium may help silicon oxide to stick to the surface of oxide scale since $\text{K}_2\text{O-SiO}_2$ and $\text{Na}_2\text{O-SiO}_2$ are low melting temperature materials, which can assist the diffusion of silicon to form a bonding between the SiO_2 layer and oxide scale.

In the non-protective region, where the sulfur concentration is obviously higher than that in the protective region, the SiO_2 layer is not continuous (Figure 6, center image). The non-protective and protective regions have several layers. Although their average chemical compositions can be analyzed by EDX, the phase compositions cannot be identified by this method. Also,

conventional XRD techniques are inadequate to determine the phases and the compositions and structures of each submicron-thick sublayer, since regular X-ray beam sizes are too large (> 2 mm). However, the nano-probe at the Argonne APS has the capability to evaluate the local phase composition in the oxide scale. The synchrotron X-ray nano-beam (beam size of $200\text{ nm} \times 300\text{ nm}$) was scanned across the cross section of the protective and non-protective regions.

X-ray nanobeam fluorescence analysis indicates four layers in the cross section of the protective and non-protective regions in Alloy 740 (Figure 7). The outside layer of the protective region primarily consists of SiO_2 , as shown on the EDX map (Figure 5). The inner layer labeled II in the X-ray fluorescence plots in Figure 7 indicates the presence of Ni, Co, and Cr. The chemical shifts from the X-ray fluorescence analysis indicate that the oxidation number of Ni is +2 (Figure 8A), and the oxidation number of Co is +2 to +3 (Figure 8C). The X-ray nanobeam diffraction patterns in Figure 9 indicate that layer II consists of spinel $(\text{Ni, Co})\text{Cr}_2\text{O}_4$ and Cr_2O_3 ; layer III primarily consists of Cr_2O_3 ; and in layer IV, chromium is deeply depleted near the surface of the alloy. As shown in Figure 7, chromium is depleted by $\sim 44\%$ in the protective region and $\sim 78\%$ in the non-protective region. The severe depletion of Cr dramatically reduces the capability of the alloys to form a protective oxide scale to resist corrosion. The concentrations of Ni, Co and Cr return to normal in the inner alloy layer, labelled “V”.

A Cr_2O_3 layer is also observed in the cross section of the non-protective region on Alloy 740 (Figure 6). The outer oxide layer in this region is a mixture of Cr_2O_3 and $(\text{Ni,Co})\text{Cr}_2\text{O}_4$ spinel. In contrast to the protective region, layer II does not contain the spinel. Usually, a Cr_2O_3 layer without spinel resists inward diffusion of oxygen and is, therefore, protective against high

temperature corrosion [4, 31]. However, this Cr_2O_3 layer in the non-protective region is not a pure Cr_2O_3 layer, although other phases were not clearly observed by the synchrotron nano-beam XRD diffraction. The EDX analysis results in Figure 6 indicates that this Cr_2O_3 layer contains sulfur. Experimental results by others indicate that the solubility of sulfur in Cr_2O_3 is 16-93 ppm at 1000°C, depending on the combined effect of the partial pressure of O_2 and S_2 [32]. Our EDX analysis at the oxide layer in the non-protective region indicates that the overall concentration of sulfur is 0.52 wt%. However, the oxide layer in the non-protective region is not uniform, and at the dark inclusion spots, the sulfur concentration is over 1.5 wt%. Therefore, the sulfur concentration in the Cr_2O_3 layer is over the reported solubility, indicating the presence of sulfide inclusions. The EDX analysis also indicates that the dark spots contain more sulfur-potassium and less oxygen than the other areas. In contrast, the Cr_2O_3 layer in the protective region contains little sulfur. The sulfide inclusions in the oxide layer of the non-protective region may cause the Cr_2O_3 layer to lose its capability to resist continued oxidation.

Figure 7 indicates that layer III in the non-protective region is a mixture of Ni, Co, and Cr_2O_3 . The X-ray fluorescence analysis confirmed that the chemical shifts of Ni and Co in this region are close to those of metallic Ni and Co (Figures 8B and 8D, respectively). The XRD analysis indicates that there are metal particles in layer III (Figure 9, right). Alloy 740 is austenitic with a lattice parameter of 3.571 Å. At the non-protective region, chromium was severely depleted, and the lattice parameter drops to 3.545 Å in Layer IV. At the protective region, Cr also depleted, but not as severe as at the nonprotective region. The lattice parameter drops to 3.555 Å in Layer IV.

3.3. Mechanistic Understanding of Ash-Alloy Reactions

3.3.1 Possible Reactions with Sulfate in Ash

A high Cr concentration (over 25 wt%) in alloys is necessary to resist ash corrosion at 750°C. However, a high Cr concentration does not guarantee a low corrosion rate. For example, the corrosion rate of 602CA, which has 25.1 wt% Cr, is much higher than that of Alloy 617, which has 21.6 wt% Cr. This discrepancy shows that ash corrosion is much more complicated than corrosion without ash because of the multiple reactions among the ash, alloy constituents, and gas species. There are various elements in the alloys that we investigated. For example, Alloys 740, 617, and WASP contain over 3 wt% Co; Alloys 625, 617, WASP, 718, and 333 contain 3 wt% or higher Mo; Alloys 230 and 333 contain over 3 wt% or higher W. Alloys 718 and 625 contain over 3 wt% Nb. Alloys 693 and 602CA contain over 3 wt% Al. These different elements can react in different ways with ash and gas. These reactions can also combine to affect the corrosion rate. If compounds with low melting temperature are formed, the corrosion rate of the alloy will increase. It was reported that sulfates with low melting temperature (Table 3) can affect the corrosion rate. The following possible reactions between the alloys and ash lead to low-melting-temperature sulfates:

Table 3. Melting temperature of sulfates that could affect ash corrosion

Compounds	Melting point (°C)
$\text{Al}_2(\text{SO}_4)_3$	770
$\text{K}_3\text{Al}(\text{SO}_4)_3$	654
$\text{Na}_3\text{Al}(\text{SO}_4)_3$	646
$\text{K}_3\text{Fe}(\text{SO}_4)_2$	618
$\text{Na}_3\text{Fe}(\text{SO}_4)_3$	624
$\text{KFe}(\text{SO}_4)_2$	694
$\text{NaFe}(\text{SO}_4)_2$	690
CoSO_4	735
$\text{NiSO}_4\text{-Na}_2\text{SO}_4$	671

At 750°C in an oxy-fuel gas environment, the sulfates CoSO_4 and NiSO_4 are stable when they dissolve into $\text{CoSO}_4\text{-Na}_2\text{SO}_4$ or $\text{NiSO}_4\text{-Na}_2\text{SO}_4$ molten salts. However, $\text{NaFe}(\text{SO}_4)_2$, $\text{NaAl}(\text{SO}_4)_2$, $\text{KFe}(\text{SO}_4)_2$, $\text{Na}_3\text{Fe}(\text{SO}_4)_3$, and $\text{Na}_3\text{Al}(\text{SO}_4)_3$ are not stable. The stability of $\text{K}_3\text{Fe}(\text{SO}_4)_3$ depends on the gas composition. It has been reported that $\text{K}_3\text{Fe}(\text{SO}_4)_3$ and $\text{KAl}(\text{SO}_4)_2$ are responsible for high-temperature ash corrosion up to 760°C [33, 34]. However, the stability of $\text{K}_3\text{Al}(\text{SO}_4)_3$ is higher than that of $\text{KAl}(\text{SO}_4)_2$ [35, 36]. The former has also been identified by XRD as a constituent of corrosive ash deposit [37].

Figure 10 shows thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) results for $\text{K}_3\text{Al}(\text{SO}_4)_3$ in air. The endothermic effect at 380°C is assigned to a polymorphic transformation of $\text{K}_3\text{Al}(\text{SO}_4)_3$. The weight of $\text{K}_3\text{Al}(\text{SO}_4)_3$ does not change at this temperature. Weight loss of $\text{K}_3\text{Al}(\text{SO}_4)_3$ initiates at 650°C , followed by the second endothermic effect at 680°C , which is also assigned to the melting temperature of $\text{K}_3\text{Al}(\text{SO}_4)_3$. If $\text{K}_3\text{Al}(\text{SO}_4)_3$ had totally decomposed, the compound would have lost 27.8% of its weight. However, the weight loss of $\text{K}_3\text{Al}(\text{SO}_4)_3$ is only 2.8% at 800°C .

Figure 11 shows the TGA and DTA results for $\text{K}_3\text{Al}(\text{SO}_4)_3$ and $\text{KAl}(\text{SO}_4)_2$ in air. When the temperature increases, $\text{KAl}(\text{SO}_4)_2$ forms from $\text{K}_3\text{Al}(\text{SO}_4)_3$ by the following reaction:

Since $\text{KAl}(\text{SO}_4)_2$ is less stable than $\text{K}_3\text{Al}(\text{SO}_4)_3$, the decomposition of $\text{KAl}(\text{SO}_4)_2$ starts at a lower temperature, 650°C (Figure 11), according to the reaction:

In $\text{KAl}(\text{SO}_4)_2$ - $\text{K}_3\text{Al}(\text{SO}_4)_3$ solution, the decomposition temperature increases with decreasing concentration $\text{KAl}(\text{SO}_4)_2$. At 760°C , the TGA curve is flat, which indicates that all the $\text{KAl}(\text{SO}_4)_2$ has almost fully decomposed. In Figure 10, the weight loss of 2.8% after $\text{KAl}(\text{SO}_4)_2$ decomposition indicates that the molar fraction of $\text{KAl}(\text{SO}_4)_2$ in the mixture is ~10%. Above 915°C , the sample starts to lose more weight. It seems that $\text{K}_3\text{Al}(\text{SO}_4)_3$ is

stable up to 915°C in air. If $K_3Al(SO_4)_3$ totally decomposed, the weight loss should be 27.8%. However, the weight loss has not finished at 1020°C.

Most TGA and DSC analyses on $K_3Al(SO_4)_3$ have been done in air. To understand the stability of $K_3Al(SO_4)_3$ in the oxy-fuel gas environment, a mixture of $K_2(SO_4)$, Al_2O_3 , Fe_2O_3 , and SiO_2 with molar ratio of 3:1:1:1 was reacted with Gas A at 750°C for 24 h, then quenched to room temperature to avoid phase formation at low temperature in the cooling process. X-ray diffraction confirmed that $K_3Al(SO_4)_3$ can form at 750°C in an oxy-fuel gas environment (Figure 12). When the temperature was increased to 870°C, the $K_3Al(SO_4)_3$ still formed. Therefore, liquid $K_3Al(SO_4)_3$ phase can form at 750°C in the oxy-fuel gas environment. Generally, the molar content of Al_2O_3 is greater than that of Fe_2O_3 in coal ash. Therefore, $K_3Al(SO_4)_3$ plays an important role in alloy corrosion due to ash at 750°C. Note that the local concentration of SO_3 at the boundary of the ash to the oxide scale on the alloy surface can be much higher than that in the gas because of the local catalytic action of Fe_2O_3 in the ash [38-39].

3.3.2 Possible Reactions with Calcium in Ash

To understand the effect of calcium in ash on alloy corrosion, we compared the alloy performance in the same oxy-fuel environment with different ash mixtures. Figure 13 (left) shows that the incubation times of Alloy WASP, 740, RA333, 718, and 602CA in Gas A are higher in tests using ash with a high calcium content compared to ash without calcium. In contrast, the incubation time of Alloy 693 significantly decreased and the incubation times of Alloys 625 reduced somewhat for exposure to ash with high calcium content.

Figure 14 shows that the long-term corrosion rates of most alloys in Gases A and B were lower after exposure to the ash with a high calcium content than without calcium. Therefore, high calcium content in ash can reduce long-term corrosion rates. For example, the corrosion rate of Alloy 740 decreased from 1.2 mm/y for the ash without calcium to 0.84 mm/year for high-calcium ash.

Since the gas composition and other furnace parameters were the same in these test series, the lower corrosion rates of alloys should be due only to the effect of the calcium in the ash. The reactions of the calcium compounds in ash and other corrosion products may affect the corrosion rate. The ashes with and without calcium were analyzed by XRD after 300-h exposure to Gas A at 750°C. As evident in Figure 15, $K_3Al(SO_4)_3$, Al_2O_3 , Fe_2O_3 , and SiO_2 were identified in the ash without calcium. Also, $Al_3Fe_5O_{12}$ may be present as a minor phase. In contrast, for the high-calcium ash, there was no $K_3Al(SO_4)_3$ phase. Since $K_3Al(SO_4)_3$ melts at 654°C, oxide scales could have dissolved into the molten salt and led to rapid corrosion. Figure 15 also indicates that, after a reaction with SO_2 and oxygen in Gas A, most of the calcium in ash was converted to $CaSO_4$, and $K_2Ca_2(SO_4)_3$ formed from the combination of K_2SO_4 and $CaSO_4$. Sodium may be substituted for potassium in $K_2Ca_2(SO_4)_3$ to form a solid solution of $(K, Na)_2Ca_2(SO_4)_3$. A small amount of $CaSiO_3$ phase was still observed in the high-calcium ash. This compound can react with $K_3Al(SO_4)_3$, $CoSO_4$, and $NiSO_4$ to form the following;

The melting temperature of CoSO_4 is 735°C , and NiSO_4 can also form a low-melting-temperature mixture with Na_2SO_4 (see Table 3). The formation of these low-melting-temperature phases was considered to lead to fast corrosion. However, they cannot form if CaSiO_3 is in the ash. Therefore, calcium silicates and calcium aluminosilicates in ash can retard the formation of some base metal low-melting sulfates that can lead to rapid corrosion.

In coal combustion, the oxides in the ash are sintered at high temperatures before deposition on the superheater metal surfaces. However, limestone (CaCO_3) is also used as an additive in coal power plants to reduce the SO_2 concentrations in the fuel gas. Since CaCO_3 can decompose to CaO at high temperatures, we conducted corrosion tests to understand the effect of CaO on the incubation time of the alloys in test environments with sintered and unsintered ash. The ash without sintering contained free CaO , Al_2O_3 , Fe_2O_3 , and SiO_2 . The experimental results indicated that the alloys react with the ash that has not been sintered. The surfaces of Alloy 718, WASP, and 602CA were obviously attacked. Figure 16 shows the effect of the attack on Alloy 693 after exposure to this ash for only 300 h in gas B. In contrast, the incubation time for Alloy 693 was longer than 3900 h. Since the incubation time is sensitive to the surface condition, basic CaO can react with the oxide scale to initiate localized corrosion. Reactions of calcium oxide and sulfate were reported in references [40-43]. The attack of CaO on oxide scales were also observed [43-44]. Thermochemical calculations also indicated that CaCO_3 and CaSO_3 can react with Cr_2O_3 in the oxide scale. However, if CaO reacts with SiO_2 to form calcium silicates in the sintering process, then calcium silicates cannot react with Cr_2O_3 in the oxide scale. The free

energies of the reactions between the various calcium oxides and Cr_2O_3 are given below.

Equation 16 shows that only the free energy of the reaction with $\text{Ca}_3\text{Si}_2\text{O}_7$ is positive.

X-ray diffraction indicated that CaSiO_3 , $\text{Ca}_3\text{Si}_2\text{O}_7$, and other calcium aluminosilicates form after sintering oxides (CaO , Al_2O_3 , Fe_2O_3 , and SiO_2) at 1100°C for 24 h. These silicates are stable at 750°C . The reactions of the test alloys with the sintered ash are much less corrosive than those with the unsintered ash, as shown in Figure 16B. After sintering, CaO reacts with SiO_2 and other oxides in the ash, and the attack of CaO on the alloy surface is minimized. Figure 13 shows that the incubation times of alloys such as 740, RA333, and 602CA that were exposed to the sintered ash with high calcium content were longer than the incubation times of alloys exposed to ash without calcium. This experiment indicates that the methods used to introduce limestone or other calcium additives into a coal combustion facility can affect the incubation time in the corrosion of structural alloys.

3.3.3 Possible Reactions with SO_2 in Flue Gas

Figure 14 indicates that the penetration depths of alloys such as Alloy 740 are lower in an environment with high calcium ash simulating U.S. Western coal ash than in an environment with ash without calcium simulating U.S. Eastern coal ash, even though the corrosion tests were performed in the same gas composition. The sulfur content in U.S. Western coal is much less

than that in U.S. Eastern coal. Therefore, the SO_2 content in flue gas from the combustion of U.S. Western coal will be less than in the flue gas from the combustion of U.S. Eastern coal. Others have reported that the corrosion rates of alloys in the gas environment with a low SO_2 concentration are lower than those in the gas with a high SO_2 concentration [45]. Therefore, it is expected that the corrosion rate will be further lowered, if the alloys are exposed to high-calcium Western ash and a low SO_2 concentration in the flue gas. Addition of calcium oxide to coal has two effects. First, it reduces the concentration of SO_2 in gas environment, thereby, reduce alloy corrosion rates. Second, calcium oxide inhibits the formation of low melting temperature sulfates in ash mixture.

It has been reported that a high SO_2 concentration in oxy-fuel combustion increases the efficiency of in-furnace desulfurization and leads to a higher conversion of SO_2 to other sulfur species because the decomposition of CaSO_4 is retarded by a high SO_2 concentration in furnaces [7, 46]. The absolute amount of SO_2 in exhaust gas is much smaller than that in conventional coal combustion even though the SO_2 concentration in a furnace is higher. This condition is considered to be an advantage of oxy-fuel combustion. However, higher concentrations of SO_2 can lead to increased ash corrosion. If an off-furnace SO_2 removal process has to be used to decrease the SO_2 concentration in a furnace to avoid ash corrosion in a high SO_2 gas environment, not only is the advantage of in-furnace desulfurization using the high SO_2 concentration from oxy-fuel combustion lost, but also it turns into a corrosion problem. This study reveals that the corrosion rates of alloys that are exposed to ash and high SO_2 gas environments can be reduced by using additives to change the chemical composition of the ash. Our results indicate an alternative approach to reducing the alloy corrosion rate in high

concentrations of SO_2 in oxy-fuel combustion besides SO_2 removal, so that the high efficiency of in-furnace desulfurization for oxy-fuel combustion can be retained.

4. Summary

We have conducted a detailed study to evaluate the corrosion performance of structural alloys at 750°C in simulated oxy-fuel environments in the presence of synthetic ash and sulfur-containing gaseous environments. Ash with a high calcium content (simulating U.S. Western coal ash) and ash without calcium (simulating U.S. Eastern coal ash) were used in this study. The performance of the alloys that were exposed to the two ashes were compared. Ash-induced corrosion can be localized and have an incubation period. Sulfide inclusions in the Cr_2O_3 layer indicated that the alloys cannot form a uniform and dense oxide scale to resist the oxygen inward diffusion, thereby leading to a high corrosion rate.

Calcium in the ash can affect both the incubation time and the long-term corrosion rate of alloys. Adding CaO to ash without sintering can reduce the incubation times of the alloys because CaO or CaCO_3 can react with the oxide scale to initiate localized corrosion. After sintering, CaO reacts with SiO_2 and other oxides in the ash to form stable calcium silicates or aluminosilicates, and the attack of CaO on the alloy surface is minimized. On the other hand, calcium silicates or aluminosilicates can retard the formation of some low-melting-point base metal sulfates, which can lead to accelerated corrosion. Experimental results indicate that the long-term corrosion rate of alloys that are exposed to oxy-fuel gas and high-calcium ash at 750°C is lower than that exposed to the same gas and temperature but using ash without calcium. The long-term corrosion rate of Alloy 740 with ash is reduced to <1 mm/yr upon increasing the calcium content in the ash. The test results indicate the ash corrosion problem in the oxy-fuel gas environment

might be mitigated by alloy selection. It is also possible to form a dense and continuous silicon oxide protective layer above the oxide scale on the alloy surface to further reduce the corrosion rate.

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Figure Captions

Figure 1. Weight loss for alloys after exposure to high-calcium ash and Gas A (with steam) and Gas B (without steam) at 750°C.

Figure 2. Incubation times for Ni-based alloys after exposure to high-calcium ash in Gas A (with steam) and Gas B (without steam) at 750°C.

Figure 3. Photograph and weight loss graph of polished and unpolished alloys after exposure to the ash without calcium in Gas A at 750°C for 300 h.

Figure 4. Corrosion rate data (after subtraction of incubation time) for alloys after exposure to high-calcium ash in Gas A (with steam) and Gas B (without steam) at 750°C.

Figure 5. Energy-dispersive X-ray spectroscopy of cross section of Alloy 740 at protective region. The alloy was exposed to high-calcium ash in Gas A (with steam) at 750°C for 3600 h. An SEM image of region shown in center.

Figure 6. Energy-dispersive X-ray spectroscopy of cross section of Alloy 740 at non-protective region. The alloy was exposed to high-calcium ash in Gas A (with steam) at 750°C for 3600 h. An SEM image of region shown in center.

Figure 7 X-ray fluorescence of Alloy 740 after exposure to high-calcium ash in Gas A (with steam) at 750°C for 3600 h.

Figure 8. X-ray fluorescence of Ni and Co at various locations from surface in the cross section of protective and non-protective region of Alloy 740 after exposure to high-calcium ash in Gas A (with steam) at 750°C for 3600 h.

Figure 9 X-ray diffraction at various locations from surface on cross section of protective region (left) and non-protective region (right) of Alloy 740 after exposure to high-calcium ash in Gas A (with steam) at 750°C for 3600 h.

Figure 10. Weight and temperature change determined from TGA and DTA of $K_3Al(SO_4)_3$.

Figure 11. Weight change determined from TGA and DTA of $K_3Al(SO_4)_3$, $KAl(SO_4)_2$, and mixtures of $K_3Al(SO_4)_3$ - $KAl(SO_4)_2$.

Figure 12. X-ray diffraction of reaction product of mixture of $K_2(SO_4)$, Al_2O_3 , Fe_2O_3 , and SiO_2 with molar ratio of 3:1:1:1 with Gas A at 750°C (top) and 870°C (bottom) for 24 h. The standard $K_3Al(SO_4)_3$ diffraction lines (PDF card # 00-027-1337) match the major diffraction peaks of the reaction product. The rest of the peaks in the XRD pattern belong to $Fe_2O_3(\Delta)$ and $SiO_2 (+)$. Al_2O_3 diffraction peaks disappear after reaction.

Figure 13. Incubation times of alloys after exposure at 750°C to high-calcium ash and ash without calcium and to Gas A (left) and Gas B (right).

Figure 14. Long-term corrosion rates (after incubation times subtracted) of alloys after exposure to high-calcium ash and ash without calcium at 750°C to (A) gas with steam and (B) gas without steam.

Figure 15. X-ray diffraction of high-calcium ash and ash without calcium after exposure to Gas A at 750°C for 300h. ♥: $CaSO_4$; ♠: $K_3Al(SO_4)_3$; *: SiO_2 ; °: $K_2Ca_2(SO_4)_3$; ∇: Fe_2O_3 ; ◇: Al_2O_3 . ♦: $CaSiO_3$.

Figure 16. SEM cross section image of Alloy 693 after (A) 300-h exposure at 750°C in Gas B to ash in which the oxides (CaO , Al_2O_3 , Fe_2O_3 , and SiO_2) were not sintered before exposure to alloys and (B) 600-h exposure at 750°C to Gas B to ash without calcium oxide.

Figure S1. Weight loss for alloys after exposure to Gas A and ash without calcium (left) and ash with calcium at 750°C.

Table 1. Nominal composition (in wt.%) of alloys selected for corrosion study

Material	C	Cr	Ni	Mn	Si	Mo	Fe	Other
333	0.05	25.0	45.0	-	1.0	3.0	18.0	Co 3.0, W 3.0
617	0.08	21.6	53.6	0.1	0.1	9.5	0.9	Co 12.5, Al 1.2, Ti 0.3
625	0.05	21.5	Bal	0.3	0.3	9.0	2.5	Nb 3.7, Al 0.2, Ti 0.2
602CA	0.19	25.1	62.6	0.1	0.1	-	9.3	Al 2.3, Ti 0.13, Zr 0.19, Y 0.09
230	0.11	21.7	60.4	0.5	0.4	1.4	1.2	W 14, Al 0.3, La 0.015
693	0.02	28.8	Bal	0.2	0.04	0.13	5.8	Al 3.3, Nb 0.67, Ti 0.4, Zr 0.03
740	0.07	25.0	Bal	0.3	0.5	0.5	1.0	Co 20.0, Ti 2.0, Al 0.8, Nb+Ta 2.0
718	-	19.0	52.0	-	-	3.0	19.0	Nb 5.0, Al 0.5, Ti 0.9, B 0.002
WASP	0.02	20	Bal	0.5	0.75	4.3	2.0	Co 12-15, Ti 2.6-3.25, Al 1.0-1.5, Zr 0.1

Table 2

Table 2. Gas compositions for experiments

Gas #	CO ₂ (%)	H ₂ O (%)	O ₂ (%)	SO ₂ (%)
A	68.14	26.9	3.97	0.99
B	95.04	0	3.97	0.99

Table 3. Melting temperature of sulfates that could affect ash corrosion

Compounds	Melting points(°C)
$\text{Al}_2(\text{SO}_4)_3$	770
$\text{K}_3\text{Al}(\text{SO}_4)_3$	654
$\text{Na}_3\text{Al}(\text{SO}_4)_3$	646
$\text{K}_3\text{Fe}(\text{SO}_4)_2$	618
$\text{Na}_3\text{Fe}(\text{SO}_4)_3$	624
$\text{KFe}(\text{SO}_4)_2$	694
$\text{NaFe}(\text{SO}_4)_2$	690
CoSO_4	735
$\text{NiSO}_4\text{-Na}_2\text{SO}_4$	671

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

In protective region

In non-protective region

Figure 10

Figure 11

Figure 12

Figure 13

Figure 14

Figure 15

Figure 16