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Project Title: **A STUDY OF CHLORINE IN HIGH TEMPERATURE CORROSION
OF ALLOYS IN AN FBC SYSTEM**

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ABSTRACT

The major purposes of this research project are to help the Illinois coal industry and TVA's FBC operators at the Shawnee Power Station understand whether the previously experienced corrosion and ash deposit problems with evaporating tubes in the FBC system may or may not be associated with the chlorine content in coals. Seven 1,000-hour combustion tests firing seven different coals were conducted in a 0.1 MW_{th} FBC facility at WKU with the operating conditions simulating to Shawnee Power Station's parameters. Seven coals were selected with various sulfur (S) and chlorine (Cl) contents from high S (4.48%) and high Cl (0.47%) to low S (0.97%) and low Cl (0.012%). For comparison, the coals selected consist of high S & low Cl; high S & high Cl; low S & high Cl; and low S & low Cl. Among them, the low sulfur and low chlorine coal was used as the baseline of erosion investigation. The calcium/sulfur ratio was held at 3 for all tests except the erosion baseline test which was controlled at 9 as a rate equivalent to that used for a 3% sulfur content and assuming a Ca/S ratio was being used. Three types of uncooled coupons (304SS, 309SS, and 347SS) were prepared and installed, based on the advice of TVA, to simulating the tubes in the superheater region [1,020-1,100°F (550-600°C)]. An air-cooled A210-C evaporating tube was adapted to simulate conditions of a 663-697°F (340-370°C) surface temperature in an 1500°F (815°C) surrounding flue gas environment. Metal wastage of each coupon was obtained by measuring the thickness before and after each combustion test. No Cl was found in the corrosion scale or on the metal surface. Alkali metals, K and Na, were only observed on the surface of the alloys. High S contents were found in the outer part of the deposits, and appeared to be associated with calcium and magnesium, suggesting that the fly ash may react further after being deposited on the surface of the metal. Locations of high S concentrations correlated well with the high chromium content of the inner layers of the corrosion scale of the samples, indicating that corrosion involved sulfidation attack. Sulfur is the major factor causing the corrosion of the metal. However, based on the 304SS coupon testing results, there was no significant corrosion found for all seven 1,000-hour tests in the pilot FBC units by extrapolating the data in terms of metal lost per year. This indicates that the calcium sorbent in the FBC system can capture not only the sulfur but also the chloride effectively. This effect helps bring the gas phase chloride concentration in the system below the level of less than 60 ppm. This reduction in Cl species in the gas phase has possible implications for decreased corrosion problems not only in the freeboard, but also in the cold end of the boiler.

EXECUTIVE SUMMARY

At least half the known economically minable coal reserves in Illinois have a chlorine content around 0.3%, which has been a concern for potential end users of these coals. Between 1992 and 1993, TVA's Shawnee Plant observed that the boiler tubes in the primary superheater region of the atmospheric fluidized bed combustion (FBC) system had

wastage/corrosion problems. The system had been firing some Illinois coal and in 1993 TVA declined to renew an Illinois Basin coal (0.4% Cl) contract for approximately 4 million tons per year. The decision was made solely on the chlorine content of the coal. This concern is reflected in the suggested coal chlorine limits used by boiler manufacturers and in the application of coal chlorine content limitations in coal contracts.

It is known that FBC systems can absorb sulfur oxides with limestone in the combustor with high sulfur retention efficiency. Limestone can also capture hydrogen chloride at relatively low temperatures in the freeboard region of the FBC system. The scope of this project is to study the behavior of chlorine during coal combustion in an FBC system. The results from this research project could help reduce the fuel costs for the 160 MWe FBC unit at the Shawnee Steam Plant near Paducah, KY, if raising the specification limit for chlorine content is possible after completion of the study. A successful project demonstrating the utilization of high chlorine coals may open new markets for Illinois high chlorine coals. It will also reduce the risk of serious damage to commercial units using high chlorine coal, if power plant operators know the limits for utilization of such coals.

A three-phase investigation was carried out in order to study the fate of chlorine during coal combustion in an FBC system and to study the susceptibility of boiler components to corrode in the combustion gases containing hydrogen chloride. In Phase 0 (1995-1997), a preliminary stage, two 1,000-hour burns were conducted with a western Kentucky #9 coal (3.2% S and 0.012% Cl) and an Illinois #6 coal (2.38% S and 0.31% Cl) which was requested by TVA. In Phase I (1997-1999), three Illinois high chlorine coals (0.21, 0.47 and 0.42%) were burned for a total of 3,000 hours to determine the threshold limitation of chlorine in the coal which will cause severe metal wastage (if any is due to the chlorine). In order to study which element (sulfur or chlorine) is the major element influencing metal corrosion and erosion blank in the FBC system, two coals [one Kentucky coal (0.97% S and 0.026% Cl) and one blend (4.48% S and 0.41% Cl) of Illinois high chlorine coal with pyrite] were chosen and tested in Phase II in 1999. The major contribution in this report was focused on the results obtained from Phase I and II.

In order to honor the requests of TVA for corrosion tests under conditions simulating those of the 160 MWe FBC system at the Paducah Shawnee Plant, three types of uncooled coupons (304SS, 309SS and 347SS) were installed at the top of the freeboard to simulate the tube performance in the superheater region [1,020-1,100°F (550-600°C) surface temperature] for the three phases. An air-cooling method was adapted for a A210-C test evaporating tube to match the conditions of 663-697°F (340-370°C) surface temperature on the tube, in an 1500°F (815°C) surrounding flue gas temperature during phase 1 and 2. During the past four years, seven 1,000-hour runs were conducted in the 0.1 MW_{th} FBC facility at WKU using seven different coals with chlorine contents ranging from 0.012% ppm to 0.47% and sulfur contents ranging from 0.97% to 4.4%, including one corrosion blank test firing low chlorine (0.026%) and low sulfur (0.97%) coal. During the corrosion blank test (6th 1,000-hour run), the limestone feeding ratio was kept the same as that used for a 3% sulfur content coal, making the Ca/S ratio around 9. The thickness changes of the test boiler tube (A210-C) and the uncooled steel coupons should correspond to the erosion caused by particles in the flue gas. In the Phase I and II study, five samples of cooled-boiler tubes (A210-C) were examined after 5,000 hours of testing in the FBC system. A parallel test was run with a boiler tube in an electrically heated furnace with the intent of obtaining information on the corrosion rate caused by sulfur and/or chloride in the FBC system and metal wastage rate caused by oxidation only during Phase I. Sixty-six test coupons (22 each of 304SS, 309SS and 347SS alloys) were analyzed after corrosion tests in the FBC system. The major operating parameters were as follows: combustion temperature -- 1450-1550°F (788-843°C); Ca/S ratio -- about 3.5; fluidizing velocity -- ~1.25 m/s; excess air ratio -- ~1.25; bed height -- ~1.1 m; surface temperature on the cooled test tube (A210-C) -- ~700°F

(371°C); surrounding temperature of test tube -- ~1480°F (805°C); temperature of uncooled test coupons -- ~1000°F (538°C).

A 1,000-hour corrosion blank test with a boiler tube (A210-C) heated in an electric furnace under a simulated flue gas atmosphere (without SO_x and HCl) was completed. The tube was designed for two different experimental conditions by having two separate parts divided by an inner plate. One side was heated under a nitrogen atmosphere. The other side was heated in a flue gas atmosphere (15% CO₂, 5% O₂, and 1% CO in nitrogen). The purposes of this test were to (1) study the deterioration rate (temperature effect) of the A210-C tube in an inert atmosphere (N₂) at 700°F (371°C), and (2) study the corrosion rate (flue gas effect) of the A210-C tube in a flue gas atmosphere (without SO_x and HCl) at 700°F (371°C). By comparing the data from the two parts of the tube heated in the same furnace at the same temperature, the corrosion rate of the tube in a flue gas atmosphere (without SO_x and HCl) can be determined. The temperature conditions were: 725°F (385°C) in the electric furnace, with a temperature of 650°F (343°C) to 760°F (404°C) at the surface of the boiler tube.

A total of 140 cross-section species were prepared from the 70 coupons, and 80 cross-section samples were prepared from the five cooled A210-C tubes. The analysis of the corrosion products included examination with a Scanning Electron Microscope (SEM) system with an Energy Dispersive X-ray (EDX) spectrometer. In the work, corrosion of the two sections from each coupon was selected for investigation. One was the bottom section facing the gas and particle flow (6 o'clock placement), and the other is the top section (12 o'clock). In Phase I and II, for the stainless steel test coupons, samples were taken after 250, 500, 750 and 1,000 hours of exposure in the FBC hot flue gas stream system resulting from the firing of coal with various sulfur and chlorine contents. The A210-C tube was only removed from the combustor after the entire 1,000-hour test.

No significant corrosion was found for all seven 1,000-hour runs in the 0.1 MW_{th} WKU-FBC facility. The maximum metal loss for stainless steel and A210-C was 3.62 mils/year (10.5 μm/1000hours) and 28.3 mils/year (82 μm/1000hours) at the requested surface temperature, respectively. Upon comparison of the results obtained from coals 98011 and 99426 (with almost the same sulfur content, ~1.0%), the worst metal loss only increases by 0.97 mils/year (2.8 μm/1000hours) for 304SS, 0.86 mils/year (2.5 μm/1000hours) for 347SS and 0.28 mils/year (0.8 μm/1000hours) for 309SS after tests with coals having chlorine contents from 0.026% to 0.47%. At the same time the worst metal loss increased from 0.66 mils/year (1.9 μm/1000hours) to 2.62 mils/year (7.6 μm/1000hours) for 304SS, from 0.55 mils/year (1.6 μm/1000hours) to 2.03 mils/year (5.9 μm/1000hours) for 347SS, and from 0.31 mils/year (0.90 μm/1000hours) to 0.86 mils/year (2.5 μm/1000hours) for 309SS, respectively, when the sulfur content increased from 0.97% to 3.2% by comparing results obtained from runs firing coals 95011 and 99426. No chlorine was found in the corrosion scale or on the metal surface of the alloy samples. The alkalis (K, Na) were only observed on the surface of the alloys. In the outer layer of the corrosion scale, high sulfur contents were associated with calcium, silicon and magnesium, which indicates that the fly ash must react further after being deposited on the metal surface. There was a good correlation between the high sulfur concentrations and the formation of high Cr-containing inner layers in the corrosion scale. Ash deposits and erosion were the two major factors accelerating metal corrosion in the FBC system.

In order to study the relationship between metal corrosion and ash deposits, a total of 170 ash deposits were collected from the test coupon surfaces during phase I and II and analyzed. The analysis included determination of metal concentrations by ICP-AES spectroscopy, determination of sulfur content with a LECO SC-432, and determination of chloride by bomb decomposition (LECO AC-350) and ion chromatography (Dionex DX-120). The major components in the deposits were calcium-based compounds, with sulfur content

around 10-15%, and chloride content around 0.5-5%. It was concluded that the calcium sorbent in the FBC system can capture not only the sulfur but also the chloride effectively, and as a result decreases the gas phase chloride concentration in the FBC system down to a level of less than 60 ppm. The concentration is unlikely that it contributes much to corrosion of the metal in the FBC system.

As to future research on high temperature corrosion in an FBC system firing high chlorine and sulfur coal, we are proposing a project to determine what is the optimal (critical) operating conditions to not cause corrosion problems when high chlorine coals are used. We believe this can be accomplished by controlling the Ca/(S+Cl) ratio and flue gas velocity in the combustor. It is well known that the desired temperature for capturing SO₂ by calcium-based sorbents is around 1562°F (850°C) and less than 1202°F (650°C) for capturing HCl. In an FBC system, the sorbent reacts with SO₂ first in the dense fluidizing zone. If the limestone feeding rate is chosen only based on the sulfur content when firing a high chlorine coal, the amount of limestone used will be too low to capture HCl effectively in the freeboard. Consequently, high HCl concentrations will remain in the flue gas. For the proposed project, one or two high chlorine coals can be selected. The study can be carried out by making a change in test conditions such that feeding the coal and limestone with three different Ca/(S+Cl) molar ratios and with three flue gas velocities. The results from the proposed project will help us determine the critical operating conditions to minimize corrosion when high chlorine coals are used in FBC systems.

OBJECTIVES

The major purposes of this research project are to help the coal industry solve corrosion problems on evaporating tubes in the FBC bed associated with the utilization of high chlorine coal, and to provide technical support for the operation of the 160 MWe atmospheric fluidized bed combustion (FBC) system at TVA's Shawnee Steam Plant near Paducah, KY. A successful project demonstrating the utilization of high chlorine coals may open new markets for some Illinois coals. It will also reduce the risk of serious damage to commercial units using high chlorine coal, if power plant operators know the limits for utilization of such coals. Seven coals with different chlorine contents (0.012%, 0.026%, 0.2%, 0.31%, 0.41%, 0.42%, and 0.47%), and ash contents around 10% were burned in seven 1,000-hour experimental runs. The scope of this project is to study the behavior of chlorine and sulfur during coal combustion in an FBC system. The project includes three major tasks for burning three coals with different chlorine contents and similar alkali metal contents, which were:

- A. Studies of chloride and sulfur emissions during coal combustion in an FBC system;
- B. Studies of fly ash and ash deposits from different regions in an FBC system;
- C. Studies of the effects of coal chloride and sulfur contents on corrosion of steel alloy coupons and evaporating heat exchange tubes in the FBC bed at high temperatures in an FBC system.

INTRODUCTION AND BACKGROUND

For the next century coal is likely to remain the most important fuel for electricity generation in many countries, especially in the USA, UK, Germany and China.¹ With the development of combustion technologies for fossil fuels, the load capacity and thermal efficiency of single units have been increased remarkably during the past several decades, for example, from a 6 MWe unit with low operational parameters to a supercritical parameter 600 MWe unit. The thermal efficiency of systems has also increased from 20% to 47%.

There are many boiler operational problems associated with the mineral impurities in coals. The more notable among these is corrosion and erosion of boiler heat exchange tubes, and fireside deposits on tubes in high temperature regions, including vaporization tubes and superheater tubes. The fireside problem has been estimated to collectively cost the electrical generating industry \$4 billion per year.² It is generally accepted that sulfur, chlorine and molten alkali chlorides from coal may play roles in this corrosion and in the formation of ash deposits. Some studies have indicated that the corrosion rate of boiler tubes increased proportionally with increasing chloride concentration in the flue gases. Based on these studies, many United States boiler manufacturers set their recommended chloride levels at less than 0.3% for burning U.S. coals. Such limitations apparently are rooted in the history of problems presented by the Central Electricity Generating Board in Great Britain and have been extrapolated to the probable corrosion behavior of U.S. coals.³ However, in a recent survey conducted through a joint effort of the Electric Power Research Institute and the Illinois Clean Coal Institute, as well as a study by the Kerr-McGee Coal Corporation,⁴ it was reported that many midwestern United States utilities have decades of experience burning high-chlorine Illinois coal in a large variety of boilers with no reported chlorine-related fireside corrosion problems. This suggests that the effect of chlorine in coal on corrosion of boiler components is not only directly related to the content in the coal, but to how and in which form it occurs during combustion. Now the majority view is that, at least for superheater boiler tube corrosion, the alkali content of the coal plays a more significant role in the corrosion, and that the chloride acts on corrosion indirectly by facilitating the release

of alkali metals.

The chloride content in Illinois coals has been a concern for potential end users of these coals. This concern, regardless of whether or not chlorine in coal causes corrosion, has had a great impact on the coal market. In 1993, TVA declined to renew an Illinois Basin coal (with 0.4% Cl) contract (approximately 4 million tons per year) for its FBC unit, due to unexplained wastage/corrosion problems in the primary superheater region between 1992 and 1993. A need to open new markets, or recover previous markets, for Illinois coals is a challenge faced by the Illinois Department of Commerce and Community Affairs/Office of Coal Development and Marketing (DCCA/OCDM).

The chloride content of coal varies from just a few parts-per-million (ppm) to hundreds ppm. Emissions of chloride from coal-fired plants can range from 50 to several thousand ppm by volume, depending on the original concentration in the coal, the type of combustor, and any pollution control equipment installed. It has been estimated that 94% of the chloride in coal is volatile, and during combustion processes it generally is emitted as gaseous HCl in the 572-1112°F (300-600°C) temperature range.⁵ Some of the HCl reacts with gaseous alkali metal atoms and ions to form alkali chlorides.

It is known that FBC systems can absorb sulfur oxides with high sulfur retention efficiency when limestone is used as the bed material in the combustor. The addition of limestone may also help reduce chloride emissions, since it is possible that limestone degenerates to CaO, and CaO reacts with HCl to produce CaCl₂. A study by Liang and others⁶ showed that the capture efficiency of chloride by limestone in the combustor depends on the surrounding temperature and the ratio of calcium-to-sulfur. Their data indicated that chloride capture shows a large variation with temperature, moving from a low of 18% gaseous HCl at 1292°F (700°C) to 99% HCl at 1742°F (950°C). The resulting product is almost entirely in the form of liquid CaCl₂. Munzner and Schilling⁷ studied the effect of limestone in a bench-scale FBC system. The results showed that a greater recapture of chloride occurred with larger excesses of limestone, or when the Ca/S ratio was greater than 2. Pan and co-workers⁸ used a tube furnace to study the behavior of HCl at high temperatures under oxygen-rich conditions while investigating the effect of chloride on SO_x emissions under simulated FBC conditions. It is possible that chloride might also affect the detailed chemistry of sulfur capture in FBC systems. Xie⁹ concluded that more than 90% of the gaseous HCl was captured by limestone in an FBC system when the Ca/S ratio = 3. Only 250 vol ppm HCl was measured in the flue gas when a blend fuel with 3.3% PVC (by weight percent) was fired in an FBC system.

One of the main goals of this project is to evaluate the critical point of coal chlorine content which may cause initial corrosion. The chlorine content of most coals burned in U.S. coal-fired boilers has generally been limited to less than about 0.3% by weight to avoid aggravation of the potential for fireside corrosion. However, no formal report has been published to prove it, although there have been several examinations conducted in the United Kingdom which indicated that aggressive fireside corrosion can be correlated with the use of high-chlorine British coals.¹⁰

This study was conducted to predict the performance of high chlorine coals in various combustion systems, to better understand the combustion behavior of chlorine during coal combustion in an FBC system, and to evaluate the critical point of coal chlorine content which may cause initial corrosion. The project focused on the effect of coal chlorine and sulfur contents on ash deposits on the boiler components, the relationship between ash deposits and corrosion, and on the high temperature corrosion performances of different

metals in fluidized bed combustors during coal combustion.

EXPERIMENTAL PROCEDURES

The bench-sized 0.1 MW_{th} fluidized bed combustor (FBC) at Western Kentucky University (WKU), with a 0.3 m I.D. and 3.5 m height, was designed to serve as a flexible research and development facility to evaluate combustion performance and estimate the effects of flue gas emissions. The FBC system has been configured to simulate the operating and combustion conditions of the 160 MWe FBC system at TVA's Shawnee Power Plant.

In order to honor the request of TVA for corrosion testing of the surrounding components in the FBC system and to attain the goals of this project, the 0.1 MW_{th} FBC facility at WKU was extensively modified including the combustor, the electrical system, the gas and solid sampling systems and the cooling system. The schematic diagram¹¹ of the modified system is shown in Figure 1 (Figures and Tables are given in the Appendix). After the 1997 runs, the FBC combustor was modified by installing two sets of secondary air nozzles, and a new secondary air forced draft fan. The goal of this modification was to utilize staged combustion technology, which can improve combustion and reduce pollutant emissions. The oxygen concentration in the flue gas, temperature, and the utilization coefficient for fine particles in the combustor can be adjusted by changing the primary/secondary air ratio. A Shimadzu GC-8A gas chromatograph was used to continuously monitor the concentration of oxygen, carbon monoxide and carbon dioxide in the flue gas during the 1000-hour runs. The results were used directly to adjust the coal and limestone feeding rates and combustion air flow rate. For the local atmosphere of the test coupons and A210-C tube, a photoacoustic multi-gas analyzer (INNOVA 1312), which is based on the absorption of IR radiation, was chosen to measure carbon dioxide, moisture and hydrogen chloride concentrations in the flue gas, while an IMR 7000 multi-gas analyzer, which is based on an electrochemical principal of measurement, determined carbon monoxide, oxygen and sulfur dioxide concentration at same time during Phase I and II. The measurement errors are: 0.1 ppm for SO₂, HCl; 1 ppm for CO; 0.1% for H₂O, CO₂, and O₂. These three instruments were calibrated with standard gases twice each day.

In order to honor the requests of TVA for corrosion tests under conditions simulating those of the 160 MWe FBC system at the TVA Shawnee Plant, three types of uncooled stainless steel coupons (304SS, 309SS and 347SS, with compositions listed in Table 1) were installed at the top of the freeboard to simulate the tube performance in the superheater region [1022-1122 °F (550-600°C) surface temperature] for seven 1,000-hour runs. In Phase I and II an air-cooling method was adapted for the A210-C test boiler tube to match the conditions of evaporating tubes [644-700°F (340-370°C) surface temperature] and 1499°F (815°C) surrounding flue gas temperature. The A210-C is currently used as evaporator tubes in the bed area at the TVA plant.

A set of metal coupons (maximum eight coupons used at one time) was placed 3.5 m above the air distributor, which is 10 cm below the convective pass heat exchange tubes. The coupons were held in place by a machined tungsten rod (powder metallurgically prepared) and separated by ceramic mounts. The procedure for cleaning the specimen was to blow off any deposits using compressed nitrogen until the weight of the specimen remained constant. An A210-C cooled tube to be used for corrosion testing was placed at 1.45 meter above the air distributor. This position is about 0.3 meter above the fluidized bed surface and 0.2 meter below the first set of secondary air nozzles. The effect of erosion from bed material and from secondary air flow was minimized in this position.

A total of 70 tons of coals and 11 tons of Kentucky limestone was bought, transferred, air dried, crushed to -4 mesh, analyzed, and stored in a trailer for the seven 1,000-hour burns. The analytical data for the seven test coals are given in Tables 2 and 3. During combustion runs, limestone and coal were auger-fed into the combustor under positive pressure at a port 0.2-meter above the air distributor; the feed rate of coal and limestone were controlled separately. The conditions for mounting the test specimens and A210-C tube are shown in Table 4.

The goal of the seventh test burn was to study the effect of high chlorine (around 0.4%) and high sulfur (above 4%) coal on corrosion of boiler components. It was very difficult to obtain such a coal at any currently operating mines. Either high sulfur with low chlorine or high chlorine with low sulfur coal were the choices. Thus, the next step was to blend a high chlorine coal with the high pyrite refuse from a coal-fired power plant. The criteria for the blend coal were (1) the blend coal must have a very similar ash content (around 9-13%); (2) the sulfur behavior in the blend is similar to that in naturally occurring coals. In order to meet these requirements, the sulfur content in refuse had to be around 25%. With the full support of Steve Smith, Gale Miarecki, Alan Finke, and Greg Barbee at TVA, several refuse samples at different locations in the Paradise Coal Preparation Plant in Kentucky were obtained and analyzed. Unfortunately, the analytical results showed this kind of refuse did not meet our needs since the sulfur content was around 10-12%. Following this, samples from several pyrite boxes in the Widows Creek Power Plant in Alabama were also collected and analyzed. The analytical data for two of these refuse samples gave 27-30% sulfur content. Consequently, a total of 25,000 lbs of an Illinois high chlorine coal and 2,500 lbs of pyrite (Widows Creek Power Plant, AL), were acquired, air dried, blended, and crushed to -4 mesh (4.8 mm). The final blend had 90% of the high chlorine coal and 10% of the Widows Creek pyrite refuse.

Five cooled tubes (A210-C steel) were tested in the FBC system to determine the corrosion rates due to chloride in flue gases during Phase I and II. Another tube was tested in an electric furnace to determine metal oxidation and wastage under different temperatures and gas conditions (15% CO₂, 5% O₂, and 1% CO in nitrogen) but without HCl and SO₂ gases. The difference between the metal wastage of the A210-C tube in the FBC system and that in the electric furnace can be determined. The difference will only be due to erosion or due to corrosion caused by alkali, sulfur, or chloride compounds. In order to obtain more corrosion information, thickness measurements on three longitudinal cross-sections of the tubes and one end cover were made with four-point measurements on each section. In each section, two thermocouples were installed to measure the local corrosion temperature.

RESULTS AND DISCUSSION

1. Preliminary Study (Phase 0)

In the Phase 0 (1995-1997) period, two 1,000-hour burns were conducted with 0.1 MW_{th} WKU FBC system. The first 1,000-hour burn was done with a low-chlorine and high-sulfur (0.012% Cl and 3.2% S) western Kentucky #9 coal (coal 95011), which is the same type of coal as that supplied to TVA plant during 1993. The second 1,000-hour burn was conducted with a middle-chlorine and middle sulfur (0.31% Cl and 2.38% S) Illinois #6 coal (coal 95031). Proximate and ultimate analyses of both coals are very close except for the chlorine and sulfur contents. The ash compositions for both coals are also very similar. The purpose of the tests was to evaluate combustion performance, the extent of hydrochloric acid formation during the combustion, and the effect of combustion conditions (limestone

addition) on HCl emission.

Four different metal alloys [carbon steel C1020 (0.18% C and 0.05% Cr), 304SS, 309SS and 347SS] were exposed uncooled in the freeboard at the entrance to the convective pass heat exchange tubes, where the metal temperature was approximated 1112°F (600°C). The carbon steel samples were essentially destroyed. A small amount of scale spallation was observed on the other three samples in both test runs. No severe corrosion was observed during both test runs. The worst metal loss for each type metal after 1,000 hours exposure time is presented in Table 5. The major component of the outer layer in the scale of the coupons is hematite. Internal precipitates in the metal just below the metal-oxide interface, and sometimes in alloy grain boundaries, had a globular appearance like chromium sulfide, but were not identified during this study. Based on the SEM-EDX mapping results, there was no localized chloride distribution observed on the surface of the coupons, neither in the scale spallation area nor on the rest of the metal part. Some trace amount of chloride was found, but evenly distributed on the surface of the coupons. There was no concentration of chloride on the spot of scale spallation.

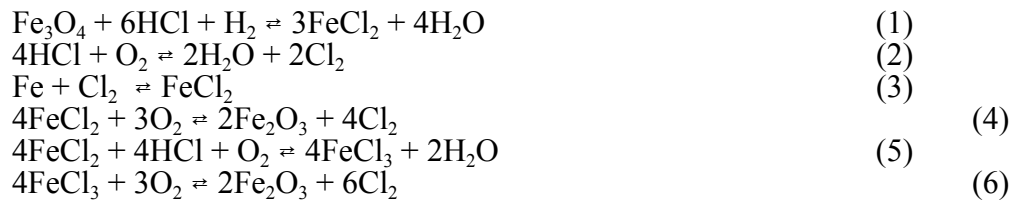
In a study of the FBC ashes, the major compound in the bed ash was CaSO_4 and the predominant minor compound was CaO in both test runs in Phase 0. The average chlorine content in the bed ash from the high chlorine coal was approximately 650 ppm. CaCl_2 was not identified using XRD spectroscopy. One special phenomena was that during the combustion of the high chlorine coal more sulfur was captured in the bed ash than was captured during combustion of the low chlorine coal. Similar results were found in the ash deposits on the metal coupons installed in the combustor during the test.

It should be noted that the highest coal chlorine content in Phase 0 was only 0.31% (coal 95031). In order to extend the range of Illinois high chlorine coals studied (to around 0.4%) and to determine a safe limit of chlorine content for power plant operators, the Electric Power Research Institute and the Illinois Clean Coal Institute decided in 1997 to continue supporting Western Kentucky University in the study of chlorine in high temperature corrosion of alloys in FBC system, noted as Phase I and Phase II. In Phase I, the major tasks were (1) to find the threshold chlorine content which will cause severe corrosion (if any is due to chlorine) and (2) to study the effect of sulfur on metal corrosion while keeping the coal chlorine relatively constant. The major tasks in Phase II were (1) to run an erosion blank in the FBC system and (2) to observe the effects on metal corrosion when high sulfur and high chlorine (4.48% S and 0.41% Cl) coal is burned in the FBC system. Several benefits can be achieved through co-firing high sulfur and high chlorine coals, including lower organic emissions and high utilization efficiency of limestone. This report focuses on the results from Phase I and II.

2. Corrosion Tests

Several studies¹²⁻¹⁴ have shown that the corrosion rate of boiler tubes increased proportionally with increasing chloride concentration in the flue gases of pulverized coal (PC) boilers. Based on these studies, many United States boiler manufacturers set recommended chloride levels at less than 0.3% for burning U.S. coals. Reviews on the effect of chloride on metal corrosion conducted by James¹⁵, Bakker¹⁶ and Sorell¹⁷ proposed the rate of metal loss depends on the metal temperature, local gaseous environment and heat fluxes. Unacceptable rates of fireside corrosion (>100 nm/h) only happens when exposed simultaneously to substoichiometric (reducing) gaseous environments and high radiant heat fluxes. Where these conditions persist, increase in the weighted mean coal chlorine content (beyond the perceived 0.2% threshold), will exacerbate the rate of metal loss according to

an empirical relationship derived in the early 1980s, although the thresholds below which chlorine exerted no influence on corrosion was specific to each research. Above the threshold, which is in the 100-300 vol ppm range, the presence of HCl will affect mixed oxidant corrosion of most stainless steels. The model and mechanism by which chloride permeates a previously “protective” scale remains speculative. Most investigators currently favor HCl as the dominant species, accessing the metal scale interface or by passing along naturally occurring micro-cracks and pores present in the oxide scale, to form ferrous chloride (FeCl_2) in the presence of H_2 or O_2 through the reactions represented by the following equations:



The release of HCl, and particularly Cl_2 , has been conjectured to take place directly adjacent to the metal surface, and therefore play a critical role in the corrosion mechanism. In that connection, it is noted that Cl_2 is far more corrosive than HCl. Otherwise, the chlorination of iron by highly corrosive elemental chlorine is self-perpetuating, since fresh Cl_2 continues to be generated by the corrosion process.

In a recent survey conducted through a joint effort of the Electric Power Research Institute and the Illinois Clean Coal Institute, as well as a study by the Kerr-McGee Coal Institute¹⁸, it was reported that many midwestern United States utilities have decades of experience burning high-chlorine Illinois coal in a large variety of boilers with no reported chlorine-related fireside corrosion problem. If this experience relates to the burning of high-chlorine coal as the only fuel, and not as part of a blend, it would suggest that the effect of chlorine on corrosion of boiler components is not simply related to its content in the coal, but to how and in which form it occurs during combustion.

In a simulated flue gas environment (PC system) maintained at 1940°F (1060°C) containing up to 2% by volume hydrogen chloride, the influence of hydrogen chloride on the corrosion behavior of boiler tubes was investigated in detail by Mayer¹⁹ at metal temperatures of 1004 (540), 1292(700), 1832(1000), and 1940°F(1060°C). Three distinct layers were identified for each specimen using SEM techniques: an inner wustite layer, an intermediate magnetite layer and an outer hematite layer. Chloride was found to accumulate in the outer part of scales, while sulfur accumulated in the magnetite and wustite at the metal-oxide interface in the form of FeS. Nevertheless, the calculations of wastage were approximately equal to that reported for the oxidation of iron in air at similar temperatures. Data from Cutler²⁰ also showed that the corrosion rate was increased by the addition of 500 ppm of HCl to the combustion gas, and that the HCl in the gas caused alkali (especially K) to be leached from the refractory brick in the test apparatus. Based on this observation, Wright and coworkers²¹ suggested that the effect of chlorine on superheater and waterwall corrosion in PC boilers may not be directly related to the chlorine content itself, but to its effectiveness in releasing the alkali metals, sodium and potassium, from the coal and its ash. This action may possibly lead to the formation of complex alkali sulfate deposits with lower melting temperatures than sodium-based sulfates alone.

In the FBC system the calcium sorbent can capture not only the sulfur but also the chloride effectively. This can help bring the gas phase chloride concentration in the freeboard of the

FBC system down to a level of less than 60 ppm even when firing high chlorine coal (0.47%). The 60 ppm level, as shown in Table 4, is not likely to contribute much to corrosion of metal in the FBC system. As a consequence, the major causes of corrosion in this project are from oxidation and sulfurization.

During Phase I and II, test coupon samples were examined after 250, 500, 750 and 1,000 hours of exposure in the FBC hot flue gas stream resulting from the firing of coals with various chlorine contents. No significant corrosion was found for all seven 1,000-hour runs in the 0.1 MW_{th} WKU-FBC facility. The maximum metal loss for stainless steel and A210-C was 3.62 mils/year (10.5 μm/1000hours) and 28.28x10⁻³ inch/year (82 μm/1000hours), respectively. No chlorine was found in the corrosion scale or on the metal surfaces of the alloy samples. The alkalis (K, Na) were only observed on the surfaces of the alloys. In the outer layer of the corrosion scale, high sulfur contents were associated with calcium and magnesium which indicate that the fly ash may react further after being deposited on the metal surface. The high sulfur concentration in the coals also correlates well with the high chromium content of the inner layers of the corrosion scale. Ash deposit and erosion are two serious factors to accelerate metal corrosion in the FBC system. Comparing the performance of the three of alloys under the same experimental conditions, type 304 stainless steel had the thickest corrosion scale, followed by alloy 347, with alloy 309 showing the thinnest oxide scale on the surface. The degree of spallation, which was mainly determined by the weight change of each metal was in the following order: 304>347>309.

2.1. Weight Changes of Alloy Coupons

Weight changes of test coupons is one of the current effective methods to evaluate the corrosion behavior of metals in a corrosive atmosphere. In the syngas system, the weight gain is due to oxidation of the metal, and the weight loss is due to the scale oxide spallation or the evaporation of low boiling point components. In a gas-solid multi-phase system, ash deposits and erosion from mineral particles will also promote weight gain and weight loss of the test specimens. As a consequence, in the FBC system fired with fossil fuels, the weight gain is due to both the oxidation of metal and ash deposit, and the weight loss is due to both the oxide spallation and particle erosion. The two reactions compete with each other. The spallation might be due to the cooling effect, thermal stress, as well as sulfur and chlorine attack. Figure 2-(a-e) shows the weight changes vs. exposure time in FBC combustion gases resulting from five 1,000-hour runs during Phase I and II. The type 304 specimen showed the heaviest weight changes among the three samples in all five 1,000-hour runs. For example, from 0.042% weight gain for coal 97025 to 0.43% weight loss for coal 98011, followed by type 347, and finally type 309. SEM/EDX analytical results indicate the high calcium content (weight percent) on the specimen surface is generally accompanied with the weight gain of the specimen. It appears that ash deposits are the major sources causing test coupon weight gains. Only a slight weight gain (<0.01%) was found for all three metal alloys during the erosion blank test run (coal 99426). This indicates a mass balance can be calculated between ash deposits and erosion of the coupon surfaces during the erosion blank test run.

2.2. Thickness Changes of Alloy Specimens

Thickness changes of boiler tubes is always a major concern for power plants, for safety reasons. An ultrasonic thickness gauge was used to determine the thickness changes of test coupons and the A210-C tubes at several marked positions during the 1,000-hour test periods during Phase I and II. Only one point, the final metal loss, was also measured after the 1,000-hour test in Phase 0. The thickness of each coupon decreased for all test specimens

during the seven 1,000-hour runs. The effect of chlorine and sulfur content in coal on stainless steel metal loss after 1,000-hour exposed to WKU-FBC facility is presented in Figure 3-(a-b). A plot of coupon thickness change versus exposure time (corrosion history) during Phase I and II is shown in Figure 4-(a-c). Comparing the performance of the three types of alloys, type 304 stainless steel showed the formation of the thickest oxide scale on the surface, followed by alloy 347, with alloy 309 showing the thinnest oxide scale. The degree of spallation, which was mainly determined by the thickness change of each metal, was in the order: 304>347>309. In order to eliminate the erosion influence on thickness changes, only the measurement data from the upper point of the coupons (12 o'clock position), which is opposite to the flue gas flow direction and protected by the tungsten rod used for supporting coupons inside the combustor, is given in the figure. During the 1,000-hour test run, the decrease in thickness is mainly due to the spallation of corrosion scale and/or ash deposit (reacting with metal) layer. The increase of thickness is due to the depth oxidation of base metal and/or more ash deposits on the coupon surface. As presented in Table 5, by comparing the results obtained from coal 98011 and coal 99426 (almost the same sulfur content), the worst metal loss only increased by 2.8 μm (0.97 mils/year) for 304SS, 2.5 μm (0.86 mils/year) for 347SS and 0.8 μm (0.28 mils/year) for 309SS after the 1000-hour tests with the coal chlorine content ranging from 0.026% to 0.47%. By comparing the results from runs for coals 95011 and 99426, the worst metal loss increased from 1.9 μm (0.66 mils/year) to 7.6 μm (2.62 mils/year) for 304SS, from 1.6 μm (0.55 mils/year) to 5.9 μm (2.03 mils/year) for 347SS, and from 0.9 μm (0.31 mils/year) to 2.5 μm (0.86 mils/year) for 309SS with the coal sulfur content ranging from 0.97% to 3.2%. More evidence is also provided in Figures 3-(a) and 3-(b). The results from coals 95011, 95031 and 97025 show only slight metal wastage as a function of coal chlorine content. However, as shown in Figure 3-(b), two or three times the metal loss was observed when the sulfur content increased from 1.09 to 4.48 %. The most significant finding from Figure 4 is the maximum thickness change being somewhat related to the sulfur content in the coal [Coal 99626 (sulfur content = 4.48%)>95011 (3.20%)>97025 (3.06%)>95031 (2.38%)>98111 (1.68%)>98011(1.09%) > 99426 (0.97%)]. The maximum thickness change increased from 0.074 mils (1.87 μm) to 0.411 mils (10.44 μm) for 304SS, 0.066 mils (1.67 μm) to 0.414 mils (10.52 μm) for 347SS, and 0.0354 mils (0.90 μm) to 0.237 mils (6.01 μm) for 309SS. The significant thickness loss from type 304 occurred at an exposure time between 400 and 600 hours, as shown in Figure 4-(a). The fly ash on the surface of alloy 304 started to build up (or react with the metal) after 600 hours. The significant thickness loss from type 347 was observed between 700 and 900 hours, as plotted in Figure 4-(b). The thickness change of type 309 was almost constant after 250 hours except coal 99626 as shown in Figure 4-(c). The only difference between the coals is the wave (maximum) point occurred in the early stage between 100 and 300 hours. The wave of the thickness change was not observed in the case of 99426.

During coal combustion, the major compound from alkali and chloride in the coal are alkali chloride products, which have low melting temperatures and easily condense on the coupon surfaces, and then undergo a chemical reaction with the elements from the coupon surface to form ash deposits. With an increase in the exposure time in FBC systems, the chemical-reaction-induced deposit layer increases. In this case, the drag stress in the deposit layers, resulting from flue gas and moving particles, also increases. This, as a consequence, leads to spallation of the corrosion scale and formation of new corrosion products. The fresh corrosion products will possibly exfoliate again when the new deposits build up to a critical thickness. This may be a reason for spallation of the corrosion scale, as occurred in several test runs, as illustrated in Figure 4-(a, b, and c).

2.3. SEM/EDX Analysis of Alloy Coupons

2.3.1. Elemental Profiles on the Coupon Surfaces

The surface corrosion scales on a total of 270 spots on the 66 coupon samples were analyzed using a Scanning Electron Microscopy (SEM) system with Energy Dispersive X-ray (EDX) analysis. During each experiment, four points (12'O, 3'O, 6'O and 9'O position) for each specimen were chosen and marked to provide the same point to measure after every 250-hour test. From the EDX results, the content of (Mg+Al+Si+Ca) represents the amount of ash products from fly ash reacted with metal on the outer layer of the surface of each coupon. The analytical data of element content (by weight percent) in the surface corrosion scales on the three test alloys *vs.* exposure time during the seventh 1,000-hour run is presented in Figure 5-(a-c).

The oxygen content on the surface increased with burning time for the three alloys. The results for iron are opposite to the results for oxygen. In the first 250 hours, the oxygen content for the three alloys is very close (around 9-11% by weight) with even distribution on the surface, less ash products (the content of Mg+Al+Si+Ca is around 1.0-1.5% by weight) and low sulfur content (<1.0% by weight). No significant depletion of Cr, Ni, Mn and Fe can be detected for all three alloys. The content of these four elements approaches their value in the original base metal. However, no chloride and alkali were found. These results may indicate that the major corrosion of metal is oxidation of the base metal during the initial period.

At the 250-hour point, a higher oxygen content was observed at the 12'O location than that of the other three locations for the three alloys, which also corresponded to higher sulfur and (Mg+Al+Si+Ca) contents. No chloride could be identified on the surfaces of the three alloys during the remaining 750 hours of testing. However, the alkali metal, K, was detected on the alloy surface, especially for type 304 alloy. A small alkali content (<1.0%) existed on the surface of the type 304 alloy during the last 750 hours. It should also be pointed out that high sulfur contents were also found at the locations where the alkalis were present.

Generally speaking, sulfur and (Mg+Al+Si+Ca) concentrations in the scale increased with exposure time. At the 12'O position, the content of S and (Mg+Al+Si+Ca) both increased with the increase of exposure time for 309SS and for 347SS. For 304SS there is a small decrease in both the contents after 500 hours of exposure. At the 6'O position for all three materials, the content of S and (Mg+Al+Si+Ca) mixture in the corrosion scale increased only within the first 500 hours, and then decreased to a low value after 750 hours, and increased again to a high level after 1000 hours. Moreover, a high content of sulfur and calcium appeared at the 12'O position as compared to that of the elements at 6'O position. However, the (Mg+Al+Si+Ca)/S ratio by weight at the 12'O position is far lower than that at 6'O position of the coupon, while the Ca/S percentage at the 12'O position is a little higher than that at 6'O position of the coupon. The difference may be related to the difference in the conditions for depositing. It was determined that at the 6'O position there is a much thicker ash deposit layer formed during the test. The deposit layer can play a blocking barrier role in separating the sample from SO₂ in the corrosive atmosphere. In the absence of the deposit layer, SO₂ readily contacts the sample and makes the following reaction easier,



giving rise to the introduction of M₂SO₄ into the surface corrosion scale. The low alkali

content in the surface corrosion scale supports this hypothesis. Therefore, the high content of S at the 12'O position is believed to result from M_2SO_4 from the reaction. The S and (Mg+Al+Si+Ca) content distribution and their relationship to the surface corrosion scale indicated that the majority (more than 80%) of the compounds in ash product is $CaSO_4$ at the 12'O position, while the major source (more 60%) for ash product comes from the coal ash at the 6'O position. The effect of exposure time on Cr and Ni distribution in the scales formed on the coupons is illustrated in Figure 5. Alloy 309 always keeps Cr at a high concentration at the surface to depress the corrosion among the three samples using our experimental conditions. The Cr concentrations in alloys 304 and 347 gradually decreased after 500 hours during the test. The nickel concentration decreased sharply with time of exposure in the combustor. There are very interesting results for the element of Mn in the coupons. Generally, the concentration of Mn remains constant in the all three alloys during the test runs. This behavior may indicate that the element Mn can endure attack of sulfur during combustion. The relationship between S, and Cr or Ni was established during the five test runs. A higher sulfur concentration on the surface of coupons is observed when the concentrations of Cr and Ni are lower. It is understood that S can react with Cr to form chromium sulfide, which can prevent the alloy from forming (or reforming) a continuous layer of protective oxide scale.

Similar phenomena were observed for the coupons exposed to the flue gases from coals 95011, 95031, 97025, 98011, and 98111. This is illustrated by the variation of the contents of S, alkali and (Mg+Al+Si+Ca) in the corrosion scale. High sulfur contents in the coal will increase the wastage of the materials and the appearance of peak maxima for thickness changes will occur in the early stages of the combustion tests.

2.3.2. Cross-Sections of the Coupons

In order to investigate the effects of sulfur and chlorine from coal on corrosion scale, two small parts from each specimen, a total 6 pieces (samples) from 3 coupons during Phase 0, and 24 pieces (samples) from 12 coupons during Phase I and II, were removed from the combustor after each 1,000-hour test, cut, mounted, polished, coated and analyzed by SEM/EDX. Five locations (6'O surface, 6'O edge, 12'O surface, 12'O edge and inner edge) for each coupon were examined using SEM/EDX. The location of the inner edge is only exposed to flue gas without any attack by flue particles. This is due to the protection of the tungsten rod mount and the ceramic spacer.

The average thicknesses of corrosion scales (excluding ash deposit layers) formed in the seven 1,000-hour test runs at the 6'O position are shown in Figure 6-(a). SEM cross-sections of the corrosion scale during Phase I and II are illustrated in Figure 7. The corresponding EDX analytical data for alloys 304, 309 and 347 during the coal 99626 test are shown in Figure 5-(d-f). The alloy 309 exhibits the best corrosion resistance among the three alloys tested, as shown in Figure 6-(a). It was also determined that there is no difference in the effects of coal chlorine, in the range of 0.012-0.47%, on the corrosion of alloy 309. The thickness of the corrosion scale formed is within the range of 8-13 μm for the seven test runs. The corrosion scale is much higher than that formed [0.0394-0.0787 mils (1-2 μm)] in the erosion blank test (6th run -- lower sulfur and chlorine coal).

Figure 7-(a-d) shows the corrosion scale on alloy 309 as being double-layered. The outer thin dense layer (see white arrow sign) is formed by the reaction between melting ash and metal. The high content of sulfur (over 4.0%, maximum 13.6% for the coal 98011 run) and (Mg+Al+Si+Ca) (more than 3.6%) was observed in this layer. The inner porous layer (indicated by ②) is mainly comprised of chromium (as high as 55.0 wt% at some locations),

iron, and manganese. In this porous layer, the iron concentration is gradually reduced toward the substrate. The concentration of Cr is in the opposite direction. One of the reasons that 309 has the best corrosion resistance is presumed to be related to the presence of the outer layer (white arrow) with the mixture of (Mg+Al+Si+Ca) on the top of the corrosion scale. This can make the scale avoid erosion from particle attack directly. When the outer layer covers the corrosion scale, it may also reduce the partial pressure of oxygen, sulfur and chlorine and penetration into this porous layer. Under these conditions, the formation of a protective Cr₂O₃-rich layer is also more favorable.

The 304 alloy exhibits the worst corrosion resistance among the three alloys, as is illustrated in Figure 6-(a). The thickness of the corrosion scale is around 2.165 mils (55 μm), almost a factor of 5 times thicker than that formed on alloy 309. With an increase in sulfur content in the coals (coals 98011, 98111 and 99626), the corrosion rate increases dramatically, from 0.630 mils (16 μm) in the coal 98011 test, to 2.165 mils (55 μm) in the coal 99626 test. No common relationship between corrosion scale and chlorine content can be found in this Figure. These results may indicate that sulfur is the major factor influencing metal corrosion in the FBC system.

The ash product layer can not be detected on the corrosion scale of alloy 304. The corrosion scale on 304 is also double-layered, as is illustrated in Figure 7-(e). The outer layer is rich in iron oxide and has a porous structure (position 1). The inner layer is more dense and rich in Cr (position 2). Lower amounts of Ni and Mn could be detected in the corrosion scale. The thickness of the corrosion scale formed is also related to the sulfur content of coal. Among the three similar chlorine content (0.4%) coals, the thickness and porosity of the outer layer (position 1) of 304 is increased with an increase in the sulfur content of the coal. For instance, the high concentration of S can be measured in the corrosion scale (both layers) of 304 in the case of the 98111 and 99626 tests. Upon comparison with the morphology of cross sections of alloy 304, 347 exhibited a generally lower corrosion rate. The corrosion scale formed on alloy 347 also has a double-layer structure similar to that on 304, as shown in Figure 7-(f). However, it appears to have a lower porosity in the outer layer of corrosion scale than that of 304.

The average thicknesses of corrosion scales formed under different conditions (excluding ash product layer) at the 12'O position are given in Figure 6-(b). It should be noted that the average value of the corrosion scale is very close for each of the six coals (coal 95011, 95031, 97025, 98011, 98111 and 99426). Within the same 1,000-hour test, both erosion and formation of ash deposits (did not react with metal) on the metal surface are different between the 12'O position and 6'O positions on the coupon. During Phase I and II, ash deposits were only found on the top (12'O) of the coupons in the case of the coal 97025 test run. However, ash deposits built up on the bottom part of the coupons that faced the flow direction in the case of the tests for coals 98011, 98111, 99426 and 98626. Compared to the average thickness of corrosion scale at the 6'O position, lower corrosion rates occurred at the 12'O position in the case of the tests for coals 98011, 98111, 99426 and 99626 tests. However, the heavier corrosion scale was found at the 12'O position in the case of the coal 97025 test. This is due to the ash deposit formation on the coupon surfaces. Therefore, these results may also indicate that ash deposits on the coupon surface can accelerate the growing rate of corrosion products in the FBC system. Among the three alloys, 309 [0.315-0.394 mils (8-10 μm) scale] still has the best corrosion protection performance at the 6'O position, followed by alloy 347 [0.512-0.591 mils (13-15 μm) scale], and finally 304. The worst corrosion of 304 happened in the first 1,000-hour run with coal 97025 with a high sulfur and middle chlorine content (0.21%). The thickness of the corrosion scale at the 12'O position with heavy ash deposit reaches 1.575 mils (40 μm).

SEM results indicate that the corrosion scale on alloy 309 at the 12'O position presents a single dense layer (in contrast to double-layers at 6'O position) comprised of the corrosion products of iron and chromium. However, a double-layer corrosion scale was found in both positions in the case of 304 and 347. Thus, the porosity of the corrosion scale is not only dependent on the sulfur and chlorine contents in the coal, but also depends on the amount of ash fouling on the surface. Whenever the ash deposits cause fouling on the coupon surface, the density of porous layer in the corrosion scale increases dramatically. These results again indicate that ash deposit fouling of the coupon surface is one of the important factors affecting metal corrosion at high temperatures.

2.3.3. The Effect of Erosion and Deposits

The effect of erosion and ash deposits on average thicknesses of metal corrosion scale resulting from the 7th 1,000-hour run is presented in Figure 6-(c). Among five locations on the coupon in the combustor listed in Figure 6-(c), the possibility for the occurrence of erosion is in the order of: the outer edge of 6'O position, surface of 6'O position, surface of 12'O position, outer edge of 12'O position and inner edge of coupon (erosion blank). The degree of ash deposits on the coupon in the combustor is in the following order: the outer edge of 12'O position, surface of 6'O position and 12'O position, outer edge of 6'O position and inner edge of coupon (no any ash deposits). From these results, alloy 309 exhibits a good corrosion inhibiting performance for all outside surfaces. No significant influence on the corrosion scale was caused by erosion and ash deposits. For the other two alloys, 304 and 347, there is a similar trend on profiles of corrosion scale. Severe corrosion scale appears on the surface of 6'O position, followed by that on the surface of the 12'O position, then that on the outer edge of the 6'O position, Figure 6-(c). The corrosion scale on the outer edge of the 12'O position shows the lowest corrosion rate among four outside surface samples. The inner edge (without any ash deposits and erosion) of the coupon shows the thinnest scale. This confirms that ash deposits and erosion will increase the corrosion rate. A thin and dense layer was observed in the inner edge of the coupon, as illustrated in Figure 8-(a-c). EDX results, as illustrated in Figure 8-(d-f), indicate that this layer was comprised of a very higher concentration of Cr. It is almost 3 to 4 times that of the substrate. For instance, the Cr content for alloy 309 reaches 95.29% in this scale. Another significant difference among the three alloys is the thickness of this scale. Alloy 309 has the thickest scale [0.217 mils (5.5 μm)], followed by alloy 347 [0.126 mils (3.2 μm)] and 304 shows the thinnest scale [0.059 mils (1.5 μm)].

2.3.4. A210-C Test Boiler Tubes

The overview of five tubes after 1,000-hour exposure during Phase I and II in the FBC system is shown in Figure 9. The black spot (arrow) can be observed at the top position of every tube. The surface temperature of the black spot is around 700°F (370°C). No spallation occurred in this area for the five test runs. Severe spallation was found at the high temperature [1050°F (565°C)] region for three tubes after the 1,000-hour runs in the case of coals 98011, 98111 and 99626. However, the most severe spallation occurred in the test tube during the test of coal 97025. During the test of 99425, the tube showed the lowest corrosion, due to the low sulfur and chlorine content of the coal.

The effect of coals on the changes in thickness of the cooled test tubes at the top and bottom positions during Phase I and II is shown in Figure 10-(a,b). The results indicate that surface temperature of the cooled test tubes plays the most important role in the variation of thickness of the test tube. As illustrated in Figure 10-(a,b), corrosion at the top position of

all the test tubes is not significantly changed after 1000-hour test runs at 700°F (370°C) in comparison with that at the other location exposed at higher temperature. This is the temperature at which the tube is used as an evaporating tube in the TVA 160 MWe FBC Plant. Moreover, at 700°F (370°C), erosion at the top [Figure 10-(a), not facing the flow] of the tube can also be neglected in this test. In the case of temperatures below 700°F (370°C), thickness gains were observed at the top of the tubes for the five tests with the coals. These gains may be due to the ash products and metal oxidation. When firing a coal with both high sulfur and chlorine content, like coal 99626, an apparent thickness loss was found even at the location of lower surface temperature. A distribution of the thickness variation in the surrounding of tube is presented in Figure 10-(c). Significant thickness loss could only be observed at the bottom of tube in the coal 99626 run.

Another 1,000-hour corrosion blank test with a boiler tube (A210-C) heated in an electric furnace under a simulated flue gas atmosphere (without SO_x and HCl) was completed. The tube was designed for two different experiments by having two separate parts divided by an inner plate. One side was heated under a nitrogen atmosphere. The other side was heated in a flue gas atmosphere (15% CO₂, 5% O₂, and 1% CO, in nitrogen). The purposes of this test were to study the deterioration rate of the A210-C tube in an inert atmosphere (N₂) at 700°F (370°C), and to study the corrosion rate of the A210-C tube in a flue gas atmosphere (without SO₂ and HCl) at 700°F (370°C). By comparing the data from the two parts of the tube heated in the same furnace at the same temperature, the corrosion rate of the tube in a flue gas atmosphere (without SO₂ and HCl) can be determined. The temperature conditions were 725°F (385°C) in the electric furnace, with a temperature of 650°F (345°C) to 760°F (405°C) at the surface of boiler tube. The measured results showed a 0.07% thickness wastage in a nitrogen atmosphere after the 1,000-hour run. A 0.22% thickness loss was determined in the case of simulated flue gas in the electric furnace. The 0.15% difference between the two sets of data can be attributed to the oxidation rate for the flue gas (without SO₂ and HCl) at 700°F (370°C). The calculated oxidation rate is therefore 3.47 mils/year.

In order to better understand corrosion affected by gaseous sulfur and chloride atmospheres at the lower metal surface temperature [370°C(700°F)], two pieces of samples were cut from each tube. One piece is at a position facing the gas flow and the other is at the opposite side position. A total of 10 pieces of samples were cut from the five tubes obtained from Phase I and II, mounted, polished and carbon-coated before SEM/EDX analysis. When exposed at 700°F (370°C) in the flue gas atmospheres produced from firing five coals, the corrosion behavior of the A210 tubes is significantly different. Figure 11-(a) shows the average thickness of the corrosion scale (including possible ash products in some cases) at the top and the bottom locations of five cooled test tubes after 1,000 hours exposure during Phase I and II in the FBC system. It is evident that the position at the top of erosion blank tube (coal 99425 test) gives the best corrosion resistance as compared to the other tubes at the corresponding position. In contrast to the erosion blank run, the tube obtained from coal 99626 test should have the worst corrosion behavior since the tube was exposed to the atmosphere with both the highest SO₂ (286 ppm) and HCl (85.4 ppm) content. However, the thickness of its corrosion scale is only about 1.181 mils (30 μm), even lower than those of coal 97025 and coal 98011 tests. In this case, the possibility of spallation of part of the outer corrosion products can not be excluded. It also may be due to the interaction between SO₂ and HCl.²² On the position at the bottom of the tubes, the thickness of the corrosion scale of the 6th test is in general near 0.197 mils (5 μm). But at some locations, the corrosion products were observed penetrating into the steel with a maximum depth of 1.575 mils (40 μm). The internal corrosion is believed to be related to an inward attack of corrosive gaseous or solid phases along the defects in the carbon steel substrate.

Figure 11-(b-f) shows the SEM/EDX cross sections of the corrosion scale at the top position of the A210C tube exposed during Phase I and II. The results show that the scale is generally comprised of Fe (> 95 wt. %, except the 7th test) and minor or trace elements whose contents are much different for the tubes. For the 3rd run tube [Figure 11-(b)], its corrosion scale exhibits a porous structure. EDX results show that there is a somewhat different composition at position 1 than at position 2. The corrosion scale at position 1 is presumed to be an ash product layer because of the relatively higher concentrations of Ca (4.75% by wt.), S (3.32%), K (1.05%) as well as Si (2.30%) that is found there. For the 4th tube [Figure 11-(c)], a cracking band (black area) parallel and close to the inner interface of the corrosion product and the substrate is observed. Figure 11-(d) is the cross-sectional image of the corrosion scale of the 5th test tube. The trace of S can not be probed. But, it is interesting that a dark band with over 1.6 % Mn (indicated by arrows) can be seen along the inner interface. For the erosion blank (6th) test tube, no Cl and S can be found. In the case of the 7th test run, a high content of S (6.42%), Ca (5.50 %) and Si (2.64%) is detected at position 1 in Figure 11-(f), with 6.04% O and 2.87% S at position 2, and 3.77% O at position 3. The concentration of Fe is in a range of 85-95%. This is obviously lower than that in other corrosion scales formed on the other tubes. Cracking can also be seen in the corrosion scale near the interface and parallel to the inner interface. The same result is observed in Figure 11-(c). Based on the SEM cross-sectional images of the corrosion scale at the bottom position of the tubes, it was found that the scale of corrosion products is thinner at the bottom position than that at the top position. The reason may be related to the effect of erosion which causes spallation faster and easier.

3. Ash Deposits

In order to study the relationship between metal corrosion and ash deposits (not from reaction with metal), a total 170 ash deposits were collected from the test coupon surfaces and analyzed during Phase I and II. The analysis included determination of metal concentrations by ICP-AES spectroscopy, determination of sulfur content with a LECO SC-432, and determination of chloride by bomb decomposition (LECO AC-350) and ion chromatography (Dionex DX-120). The major components in the deposits were calcium-based compounds, with sulfur content next at around 10-15%, and chloride content following at 0.02-0.4%. It was concluded that the calcium sorbent in the FBC system can capture not only the sulfur but also the chloride effectively. This effect help bring the gas phase chloride concentration in the FBC system down to a level of less than 60 ppm and likely does not contribute significantly to metal corrosion in the FBC system.

Ash deposits were only observed on the top of the coupons for the coal 97025 test run. However, ash deposits were formed only on the bottom part of the coupons that faced the flow direction for the other four test runs. These ash deposit layers need highly adhesive forces to keep their shape. The layers may protect the alloy from erosion effects in the FBC system. The color of the ash deposits were pale gray, pale yellow, pale red, pale white and deep red for the five different runs during Phase I and II. The amount of ash deposits for the fourth test run were much more than those of the other four runs. This may be due to the higher (almost twice as much) amount of sodium and potassium in the ash deposits for the second coal compared to the other four coals, as shown in Figure 12-(a). This supports the belief that the content of alkali metal in the ash is the most important factor to consider in the formation of the molten phase on the surfaces of the metal. The effect of the type of coal on the sulfur content in ash deposits for the three alloys is shown in Figure 12-(b-d). It is clearly indicated that the sulfur content in the ash deposit is dependent on the limestone/coal

feeding rate. High limestone feeding rates can cause high sulfur contents in the ash deposits for all three alloys. In the case of the 6th run, coal 99426 had the lowest sulfur and chlorine contents among the five coals. However, more than 11% sulfur was analyzed in the deposits, which is higher than the results from the 3rd, 4th and 5th tests. This run was made for an erosion blank test. During this test, the limestone feeding ratio was kept the same as that used for 3% sulfur content in coal. When the limestone feeding rate is almost constant, with an increase in sulfur content in the coal, sulfur content in the ash deposits generally increase, such as the sulfur contents in deposits collected from the 7th run is always higher than those from the 6th run.

It also can be seen from Figures 12-(b-d), in the first 250 hours of the test burns, the sulfur content in the ash deposits reaches almost the same value for different coupons. For example, the sulfur content reaches 14% for the three alloys in the case of the 7th test run. These data may indicate that the initial ash deposit did not depend on the material in the coupon. Then, the concentration of sulfur gradually decreases or increases to reach the minimum or maximum point after various exposure times which depend on the type of alloys and coals. For example, in the 3rd coal (97025) 1,000-hour test run, the sulfur content in the ash deposit of 304SS increases to a maximum around 500 hours, then falls to a minimum around 750 hours. For 347SS, only a minimum point was found around 750 hours. For 309SS, the sulfur content in the ash deposit remains almost constant. No peak appears on the curve.

The behavior of chromium is very similar to that of sulfur. This may be due to some sulfur penetrating into the metal coupons to react with chromium. Then, the sulfur and chromium concentrations increase again. This may be due to the new metal layer which formed when spallation occurred. The amount of chromium in the ash deposits is ten times that provided by the coal. This is an indication that spallation of the metal coupons occurred during the entire experimental period. This is also supported by the results of the thickness measurements on the coupons. The only difference is the magnitude of the spallation at different times. This is the major reason causing the different levels of sulfur and chromium in the ash deposits. There is no specific common trend to describe the behavior of chloride in the ash deposits. It was noticed that the concentration of chloride in the ash deposits does not increase when the high chlorine content coal was used. The level of chloride in the ash deposits for the third run (high sulfur and low chlorine) is even higher than that of the other three high chlorine coals after 750 hours, as shown in Figure 12-(e). Another common phenomenon is that the sulfur content in the coals influences the chloride contents in the deposit. The average chloride content for all three alloys decreased when the sulfur content in the coal increased within the 1,000-hour tests. For instance, the deposits collected from coal 99626 has the lowest average chloride content among the five coals. The concentration of calcium in the deposits is almost constant for each coal, as illustrated in Figure 12-(f). Higher concentrations of calcium in the ash deposits for the sixth and seventh coals are observed, which corresponds to the limestone/coal feeding rate for five runs. High limestone/coal feeding rates result in high calcium contents in the deposit. Therefore, the major compounds in the ash deposits are calcium-based products in the FBC system while firing high sulfur coals.

CONCLUSIONS AND RECOMMENDATIONS

1. No significant corrosion was found for all seven 1,000-hour runs in 0.1 MW_{th} WKU-FBC facility. The maximum metal loss for stainless steel is 10.5 μm (3.62×10^{-3} inch/year) per 1000 hours exposure time at the surface temperatures used in the study.

2. No chloride compounds were found in the corrosion scales or on the metal surfaces of the alloy samples after exposure to the flue gases from firing coals with various chlorine and sulfur contents in an FBC system. The alkalis (K, Na) were only observed on the surfaces of the alloys.
3. In the outer layer of the corrosion scale, high sulfur contents were associated with calcium, silica and magnesium, which indicated that the fly ash may react further after being deposited on the metal surface. The high sulfur concentration also correlated with the formation of a high Cr-containing inner layer in the corrosion scale.
4. Ash deposits and erosion are two serious factors to accelerate metal corrosion in FBC systems.
5. The major components in the deposits found on the metal coupons after firing coals with different chlorine and sulfur contents were calcium-based compounds, with sulfur contents around 10-15%, and chloride contents from 0.5-5%. It is concluded that the calcium sorbent in the FBC system can capture not only the sulfur but also the chloride effectively, and as a result gives rise to a decrease of the gas phase chloride concentration in the FBC system down to a level of less than 60 ppm. This concentration is below the typical threshold level (200-300 ppm) required for inducing corrosion and is unlikely to contribute much to corrosion of the metal in the FBC system.
6. Comparing the three alloys, 309SS is more likely to resist attack by chloride and sulfur which would enrich these elements in its ash deposit layers.
7. No significant wastage [$82\mu\text{m}$ (28.28×10^{-3} inch/year) per 1000 hours exposure time] of the top of the A210-C test tube was observed for five test runs when the surface temperature was 370°C (700°F) during Phase I and II. The temperature is the most important factor affecting the corrosion. The sulfur content in the coal may play a secondary role.

FUTURE WORK

As for future research on high temperature corrosion in FBC system firing of high chlorine and high sulfur coal, we would like to propose a project to determine what is the optimal (critical) operating conditions to not cause corrosion problems when high chlorine coals are used. It is believed this can be accomplished by controlling the Ca/(S+Cl) ratio and flue gas velocity in the combustor. It is well known the desired temperature for capturing SO_2 and HCl by calcium-based sorbents is around 850°C and less than 650°C , respectively. In the FBC system, the sorbent reacts with SO_2 first in the dense fluidized zone. If the limestone feeding rate is chosen based only on the sulfur content in the case of firing high chlorine coal, the amount of limestone will be too low to capture HCl effectively in the freeboard. As a consequence, high HCl concentrations will remain in flue gas. For the proposed project, one or two high chlorine coals can be selected. The study can be carried out by making a change in test conditions by feeding the coal and limestone with three different Ca/(S+Cl) molar ratios and with three flue gas velocities. The results from the project will help us determine the critical operating conditions to minimize corrosion when high chlorine coal is used in an FBC system.

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Appendixes

Table 1. Analytical Composition (Percent by Weight) of Three Alloy Metals and A210-C Tube.

| <u>Element</u> | <u>SS304</u> | <u>SS309</u> | <u>SS347</u> | <u>A210-C</u> |
|----------------|-------------------|--------------------|--------------|---------------|
| C | 0.05 | 0.058 | 0.045 | 0.35 |
| Cr | 18.39 | 23.28 | 18.03 | |
| Cu | 0.41 | 0.90 | 0.14 | |
| Mn | 1.84 | 1.78 | 1.20 | 1.06 |
| Mo | 0.36 | 0.14 | 0.17 | |
| Ni | 8.11 | 13.41 | 9.79 | |
| P | 0.032 | 0.017 | 0.018 | 0.035 |
| S | 0.001 | 0.011 | 0.014 | 0.035 |
| Si | 0.46 | 0.44 | 0.52 | 0.01 |
| Fe | 70.3 | 59.7 | 70.0 | 98.5 |
| Other | N-0.06 Co-0.03 | N-0.059 Co-0.21 | N-0.029 | |

Table 3-2. Analytical Values^a for the Coals Used in the Study.

| Phase 0 (1995-1997) | | Phase I (1998-1999) | | | Phase II (1999) | |
|---------------------|-----------------|---------------------|-----------------|-----------------|-----------------|-----------------|
| <u>95011</u> | <u>95031</u> | <u>97025</u> | <u>98011</u> | <u>98111</u> | <u>99426</u> | <u>99626</u> |
| 1 st | 2 nd | 3 th | 4 th | 5 th | 6 th | 7 th |
| | | | | | | |

| | | | | | | | |
|------------------------|-------|-------|-------|-------|-------|-------|-------|
| Proximate Analysis | | | | | | | |
| % Moisture | 10.07 | 8.32 | 4.56 | 10.63 | 10.25 | 2.33 | 6.96 |
| % Ash | 9.37 | 10.78 | 10.97 | 10.10 | 9.67 | 8.70 | 13.81 |
| % Volatile Matter | 43.34 | 37.21 | 36.25 | 34.03 | 34.84 | 36.98 | 34.14 |
| % Fixed Carbon | 47.29 | 52.02 | 52.78 | 55.87 | 55.49 | 54.32 | 52.05 |
| Ultimate Analysis | | | | | | | |
| % Ash | 9.37 | 10.78 | 10.79 | 10.10 | 9.67 | 8.70 | 13.81 |
| % Carbon | 74.08 | 72.16 | 74.69 | 75.59 | 74.18 | 76.25 | 69.53 |
| % Hydrogen | 5.08 | 4.82 | 4.95 | 4.52 | 4.73 | 4.89 | 4.49 |
| % Nitrogen | 1.54 | 1.54 | 1.63 | 1.51 | 1.59 | 1.79 | 1.55 |
| % Sulfur | 3.2 | 2.38 | 3.06 | 1.09 | 1.68 | 0.97 | 4.48 |
| % Oxygen | 6.72 | 7.57 | 4.50 | 6.73 | 7.72 | 7.37 | 5.73 |
| Miscellaneous Analysis | | | | | | | |
| Chlorine (%) | 0.012 | 0.31 | 0.21 | 0.47 | 0.42 | 0.026 | 0.41 |
| Fluorine (ppm) | | | | | 94 | 168 | 131 |
| Mercury (ppb) | | | 88 | 53 | 83 | 79 | 224 |
| BTU/pound | 13203 | 12842 | 13152 | 13017 | 13226 | 13655 | 12406 |

^a Moisture is as-received, all other values are reported on a dry basis.

Table 3-3. Analysis of Ashes Prepared from the Coals Used in the Study.

| <u>Metal Oxides</u> | <u>95011</u> | <u>95031</u> | <u>97025</u> | <u>98011</u> | <u>98111</u> | <u>99426</u> | <u>99626</u> |
|--------------------------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|
| SiO ₂ | 49.22 | 47.32 | 38.51 | 54.66 | 49.03 | 52.47 | 31.36 |
| P ₂ O ₅ | 3.36 | 4.46 | 0.785 | 1.87 | 4.49 | 2.52 | 3.21 |
| CaO | 1.86 | 1.62 | 3.75 | 1.96 | 2.63 | 3.27 | 6.13 |
| K ₂ O | 4.14 | 5.03 | 1.48 | 2.91 | 2.87 | 1.92 | 1.39 |
| TiO ₂ | 1.11 | 1.14 | 1.00 | 1.23 | 1.17 | 1.71 | 0.67 |
| Fe ₂ O ₃ | 19.90 | 17.04 | 26.98 | 9.01 | 15.44 | 5.35 | 36.41 |
| Na ₂ O | 0.58 | 1.90 | 0.41 | 1.60 | 1.13 | 0.38 | 0.98 |

| | | | | | | | |
|--------------------------------|-------|-------|-------|-------|-------|-------|-------|
| MgO | 0.70 | 0.80 | 0.92 | 1.08 | 0.65 | 0.82 | 1.42 |
| Al ₂ O ₃ | 17.12 | 18.18 | 19.52 | 23.76 | 23.33 | 27.90 | 12.73 |
| MnO ₂ | 0.02 | 0.02 | 0.01 | 0.03 | 0.03 | 0.023 | 0.06 |

Table 3-4. Summary of Steady-State Run Conditions.

| | <u>1st run</u> | <u>2nd run</u> | <u>3rd run</u> | <u>4th run</u> | <u>5th run</u> | <u>6th run</u> | <u>7th run</u> |
|-------------------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|
| Fuel feed rate (kg/h) | 8.41 | 10.44 | 7.50 | 7.95 | 8.21 | 8.16 | 7.26 |
| Limestone feed rate (kg/h) | 2.21 | 2.21 | 1.61 | 1.02 | 1.43 | 2.72 | 3.22 |
| Ca/(S+Cl) molar ratio | 3.10 | 3.10 | 2.88 | 3.15 | 3.19 | 9.21 | 3.05 |
| Temperature (K) | | | | | | | |
| Bed temperature | | | 1113 | 1173 | 1223 | | |
| At 0.56 meter* | | | 1108 | 1168 | 1218 | | |
| At 0.97 meter | | | 1073 | 1133 | 1193 | | |
| At 1.90 meter | | | 943 | 1013 | 1078 | | |
| At 2.60 meter | | | 958 | 1023 | 1088 | | |
| At 3.30 meter | | | 843 | 923 | 978 | | |
| SO ₂ Concentration (ppm) | | | | | | | |
| Coupon | | | 245 | 174 | 114 | 53 | 282 |
| A210-C tube | | | 260 | 220 | 137 | 68 | 286 |

| | | | | | | | |
|---------------------------------------|------|------|------|------|------|--|--|
| HCl Concentration (ppm) | | | | | | | |
| Coupon | 44.3 | 65.7 | 55.3 | 2.8 | 55.1 | | |
| A210-C tube | 56.8 | 84.8 | 68.2 | 13.0 | 85.4 | | |
| O ₂ Concentration (vol. %) | | | | | | | |
| Coupon | 4.7 | 4.5 | 5.02 | 4.71 | 4.79 | | |
| A210-C tube | 5.2 | 4.8 | 5.11 | 4.90 | 5.05 | | |
| CO Concentration (ppm) | | | | | | | |
| Coupon | 156 | 214 | 156 | 113 | 173 | | |
| A210-C tube | 170 | 222 | 187 | 164 | 244 | | |
| Moisture Concentration (vol.%) | | | | | | | |
| Coupon | 4.21 | 3.51 | 4.24 | 5.13 | 7.27 | | |
| A210-C tube | 4.42 | 3.14 | 3.98 | 4.68 | 7.26 | | |

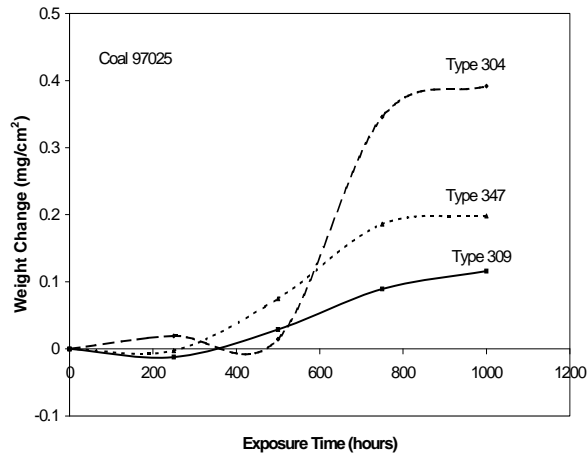
Table 5. The Final Metal Loss after 1,000 Hours Exposed to 0.1MWth WKU-FBC System.

| | Phase 0 (1995-1997) | | Phase I (1998-1999) | | | Phase II (1999) | |
|----------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| | <u>95011</u> 1 st | <u>95031</u> 2 nd | <u>97025</u> 3 th | <u>98011</u> 4 th | <u>98111</u> 5 th | <u>99425</u> 6 th | <u>99626</u> 7 th |
| Ultimate Analysis | | | | | | | |
| % Ash | 9.37 | 10.78 | 10.79 | 10.10 | 9.67 | 8.70 | 13.81 |
| % Sulfur | 3.2 | 2.38 | 3.06 | 1.09 | 1.68 | 0.97 | 4.48 |
| % Chlorine | 0.012 | 0.31 | 0.21 | 0.47 | 0.42 | 0.026 | 0.41 |
| BTU/pound | 13203 | 12842 | 13152 | 13017 | 13226 | 13655 | 12406 |
| Thickness of coupon (mm) | | | | | | | |
| Alloy 304 | | | | | | | |
| Initial | 2.325 | 2.620 | 2.696 | 2.725 | 2.755 | 2.905 | 2.876 |
| After 1,000 hours test | 2.310 | 2.603 | 2.680 | 2.716 | 2.740 | 2.901 | 2.861 |
| Metal loss (µm) | 7.5 | 8.5 | 8.0 | 4.5 | 7.5 | 2.0 | 7.5 |
| Metal loss per year** (µm) | 65.70 | 74.46 | 70.08 | 39.42 | 65.70 | 17.52 | 65.70 |
| Alloy 309 | | | | | | | |
| Initial | 2.625 | 3.411 | 3.255 | 3.230 | 2.581 | 3.266 | 3.305 |
| After 1,000 hours test | 2.620 | 3.406 | 3.251 | 3.227 | 2.577 | 3.264 | 3.293 |
| Metal loss (µm) | 2.5 | 2.5 | 2.0 | 1.5 | 2.0 | 1.0 | 6.0 |

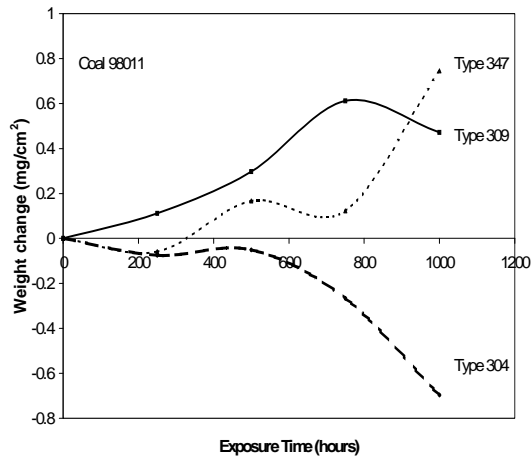
| | | | | | | | |
|---------------------------------------|-------|-------|-------|-------|-------|-------|-------|
| Metal loss per year(μm) | 21.90 | 21.90 | 17.52 | 13.14 | 17.52 | 8.76 | 52.56 |
| Alloy 347 | | | | | | | |
| Initial | 2.343 | 3.141 | 2.926 | 2.901 | 2.897 | 3.041 | 3.110 |
| After 1,000 hours test | 2.331 | 3.125 | 2.911 | 2.896 | 2.890 | 3.038 | 3.094 |
| Metal loss (μm) | 6.0 | 8.0 | 7.5 | 2.5 | 3.5 | 1.5 | 8.0 |
| Metal loss per year (μm) | 52.56 | 70.08 | 65.70 | 21.90 | 30.66 | 13.14 | 70.08 |

-----^a
 Moisture is as-received, all other values are reported on a dry basis.

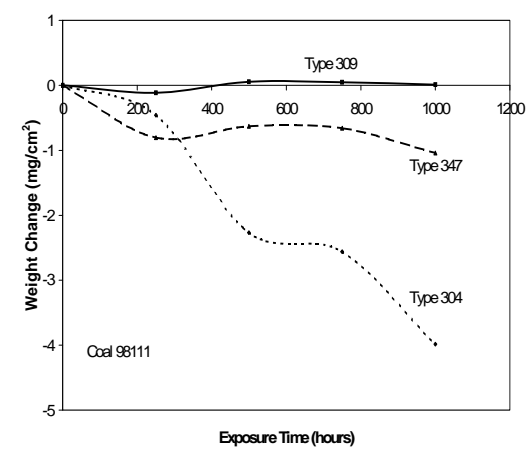
**Based on full time run (8760 hours/year)



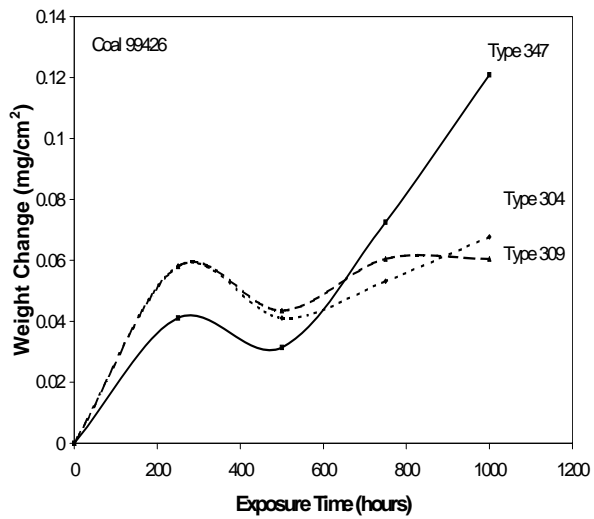
(a)



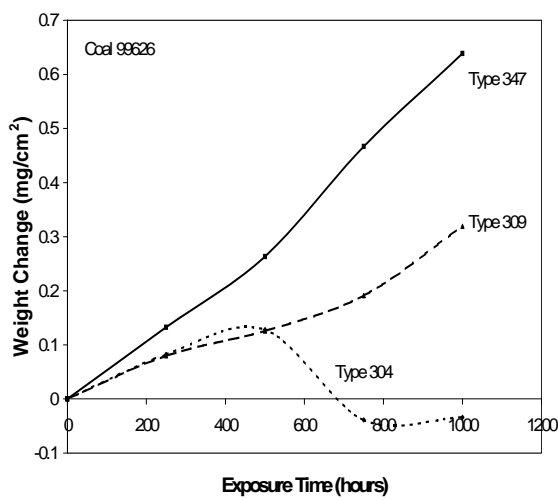
(b)



(c)



(d)



(e)

Figure 2. The weight changes of test coupons during 1,000 hours exposure times while firing five coals in the WKU-FBC system.

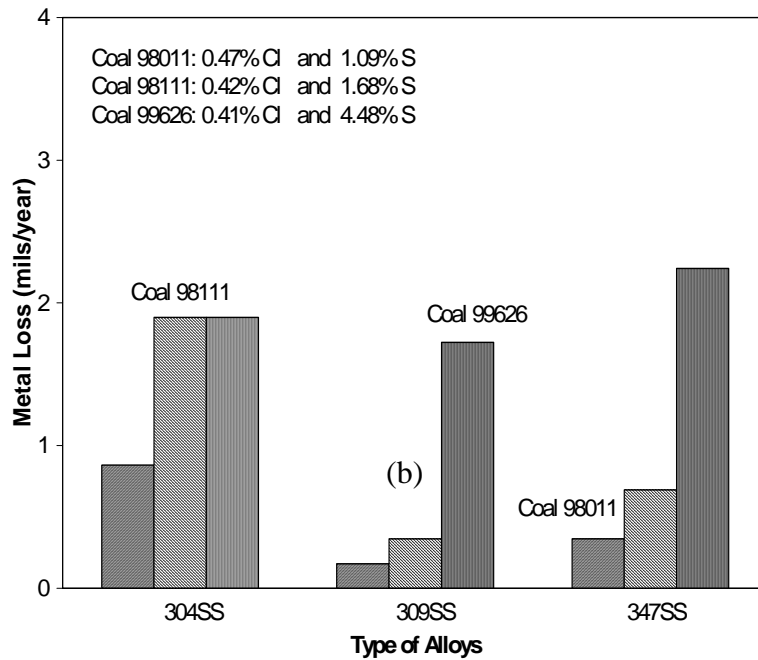
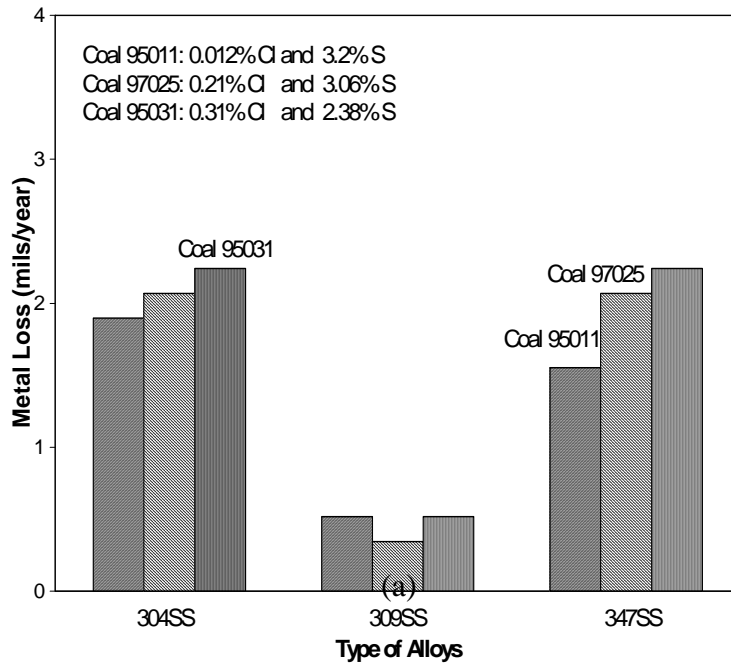


Fig
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in coal on metal (stainless steel) thickness change extrapolated on basis of data of 1,000 hours exposed to WKU-FBC system.

ure 3. The
 ect of chlorine
 sulfur content

on metal (stainless steel) thickness change extrapolated on basis of data of 1,000 hours exposed to WKU-FBC system.

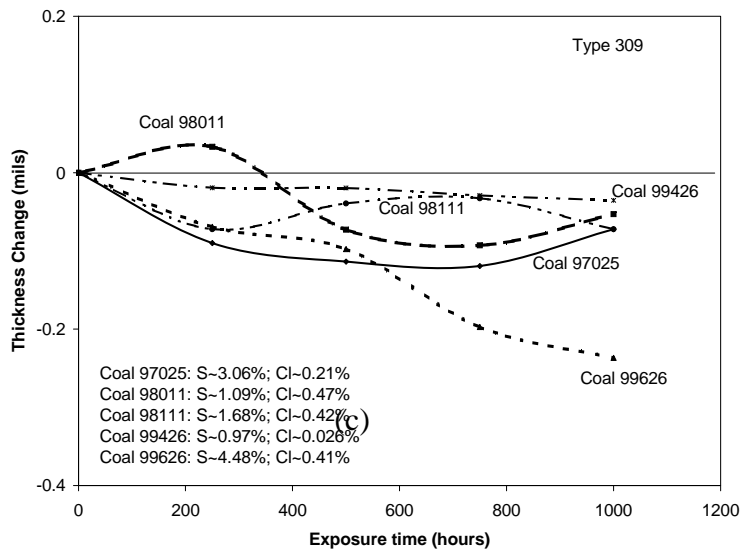
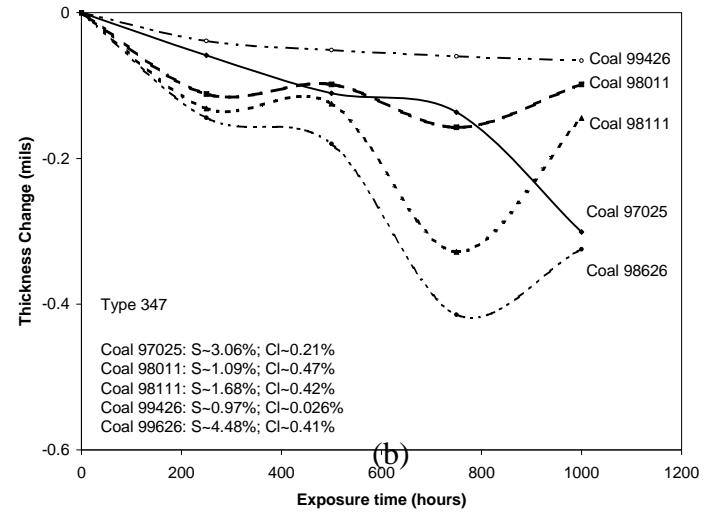
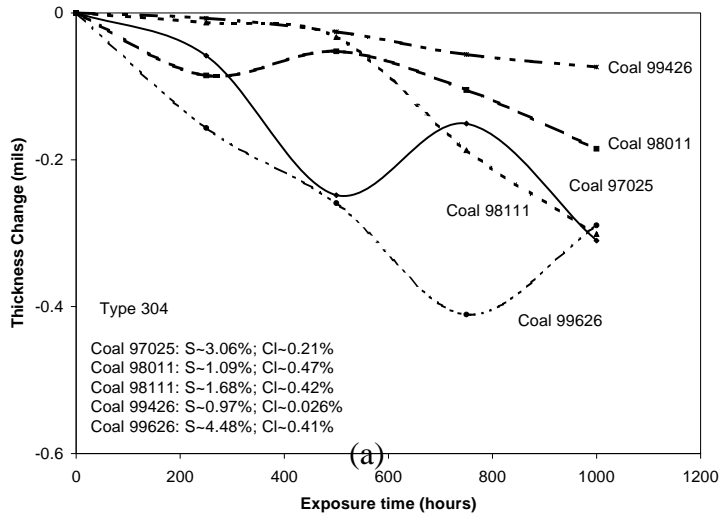


Figure 4. The effect of exposure time on coupon thickness changes in the WKU-FBC system.

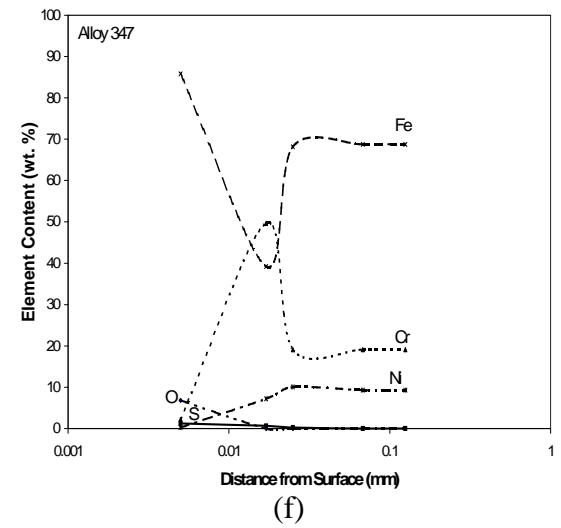
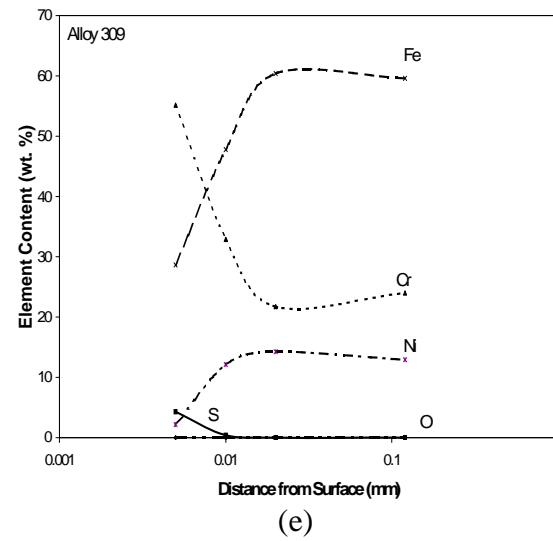
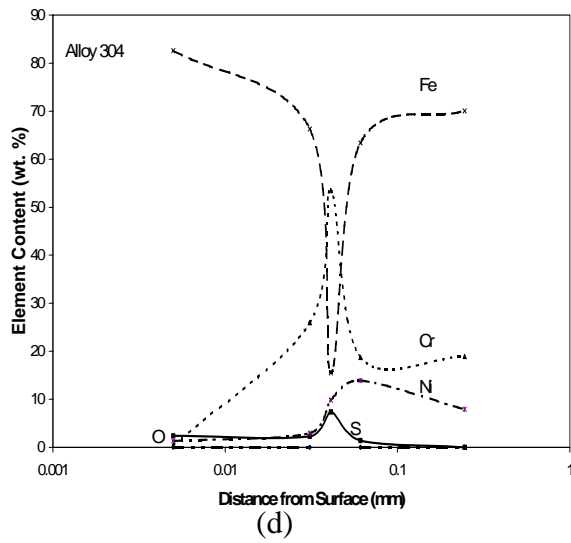
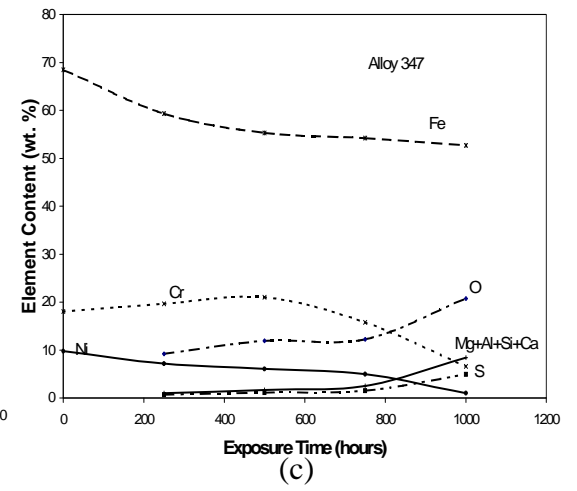
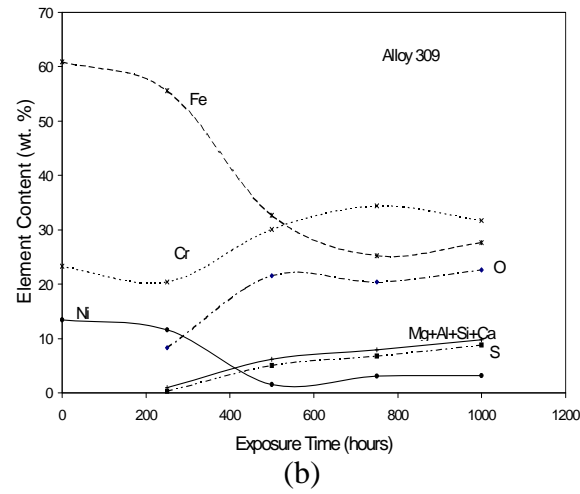
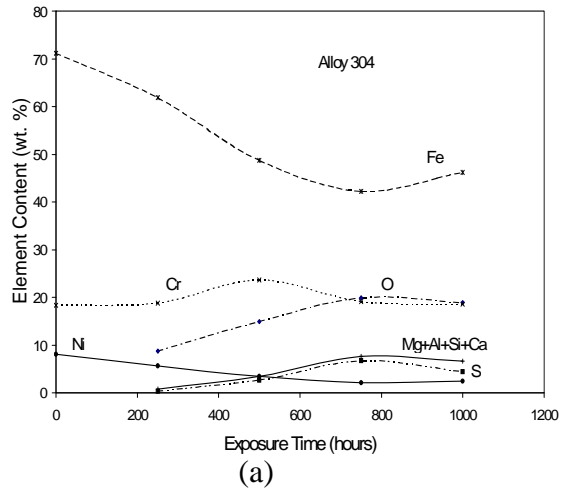
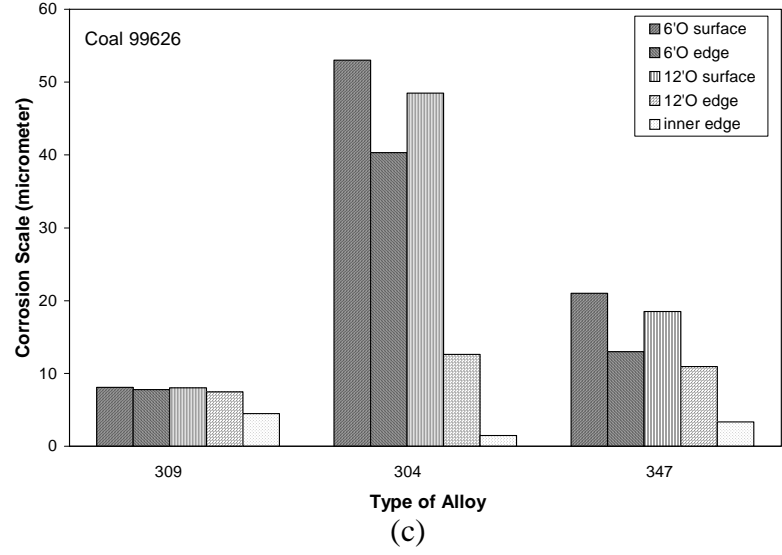
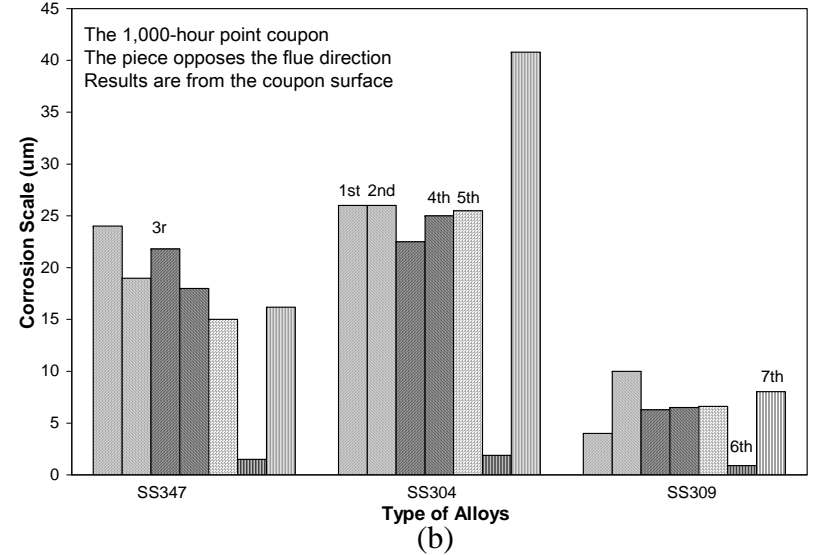
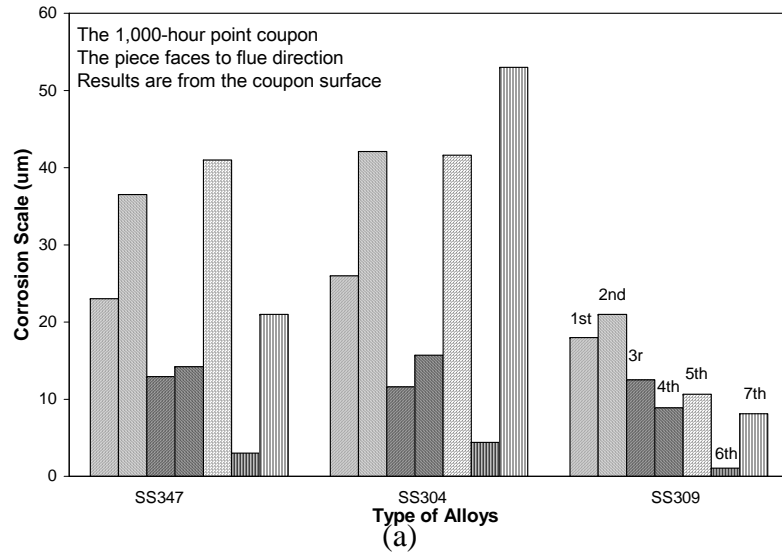
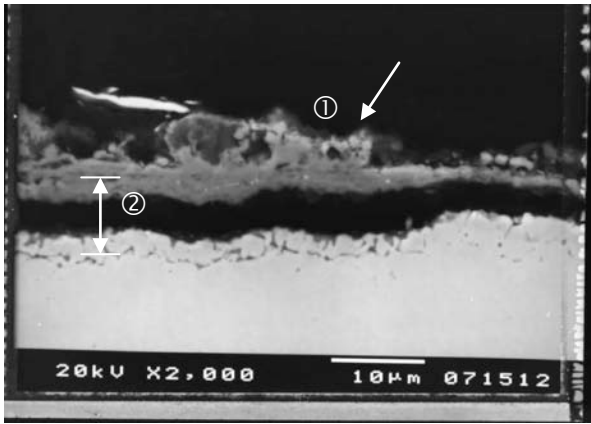


Figure 5. EDX analytical data for coupon surfaces and cross sections.

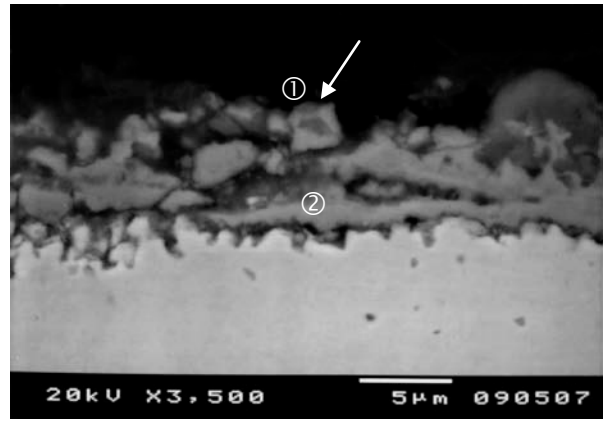


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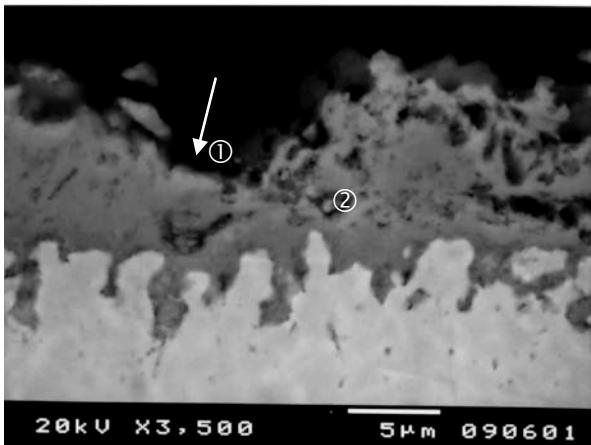
Figure 6. The effect of coals on average thickness of corrosion scale formed in five 1000 hours runs.



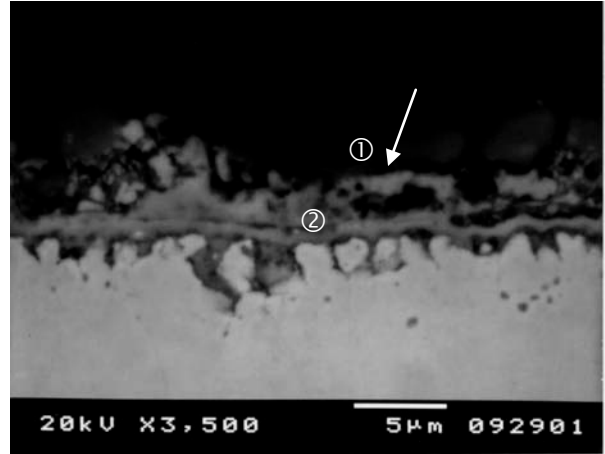
(a)—3rd run, SS309



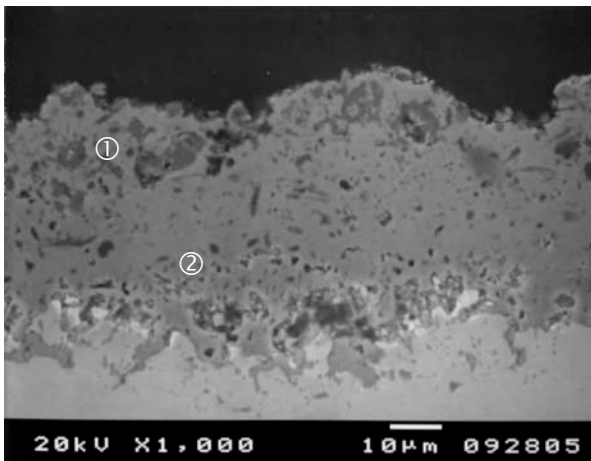
(b)—4th run, SS309



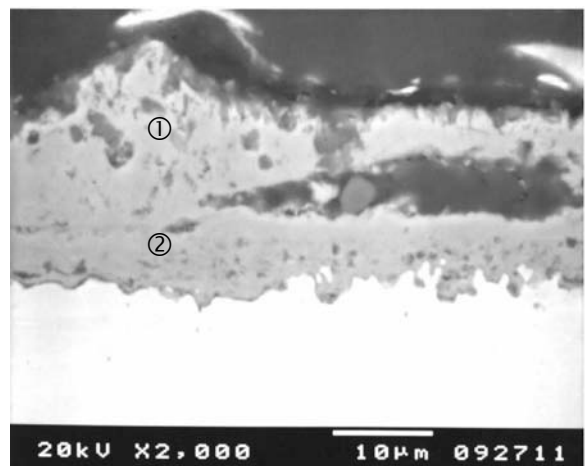
(c)—6th run, SS309



(d)—7th run, SS309



(e)—7th run, SS304



(f)—7th run, SS347

Figure 7. Scale formed after 1000 hours exposure in the WKU-FBC system (6'O position).

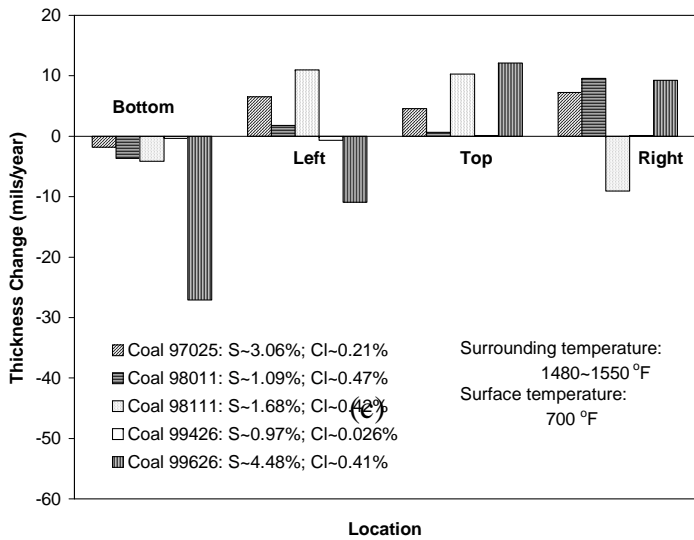
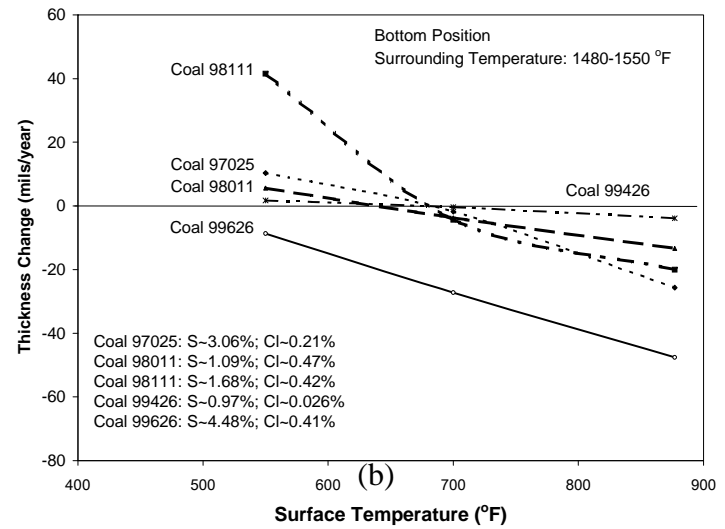
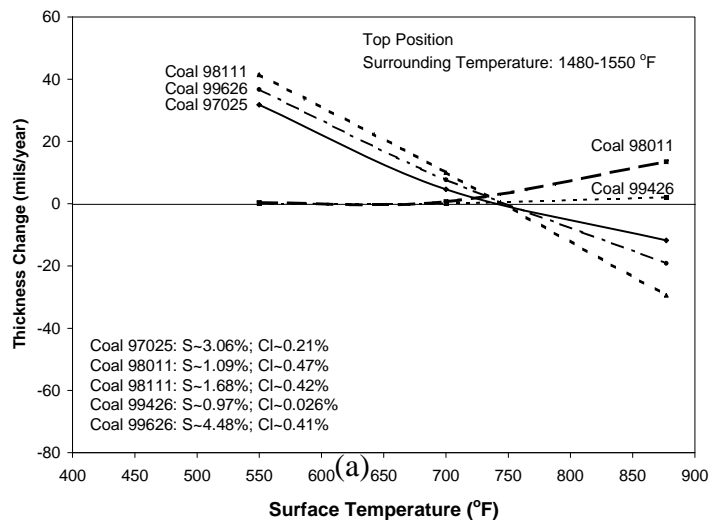
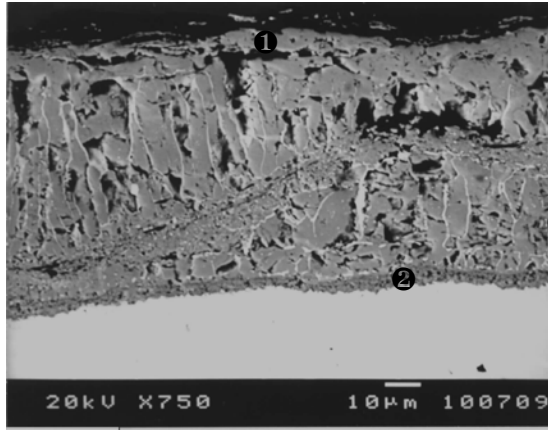
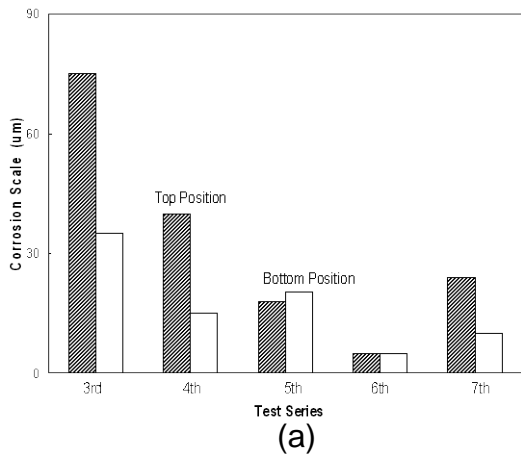
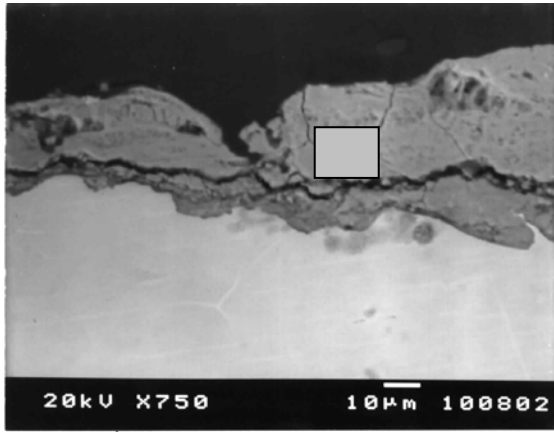


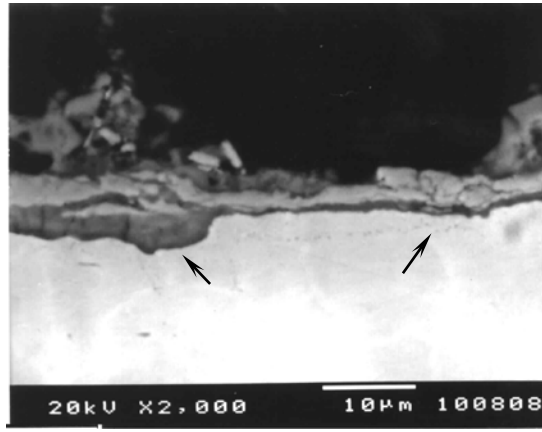
Figure 10. The effect of coals on thickness changes of A210-C evaporating tubes extrapolated on basis of data 1,000 hours exposure in the FBC system.



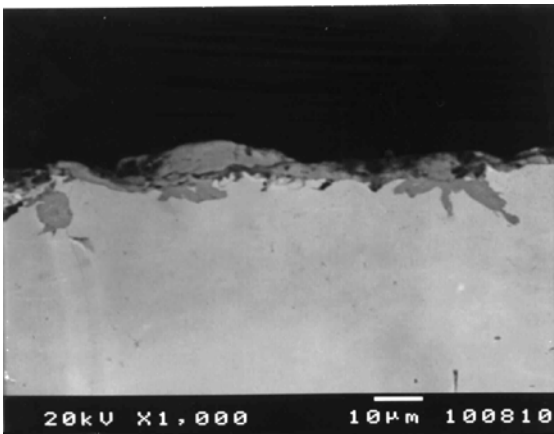
(b)--3rd 1000 hours run



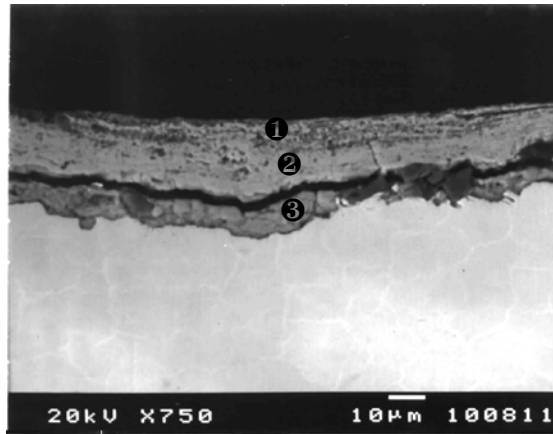
(c)--4th 1000 hours run



(d)--5th 1000 hours run



(e)--6th 1000 hours run



(f)--7th 1000 hours run

Figure 11. The SEM cross-section of corrosive scale of A210-C tube after 1,000 hours exposure time in the WKU-FBC system (12'O position)

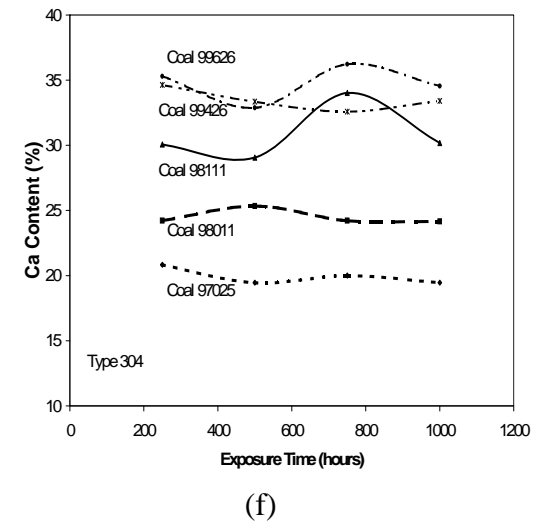
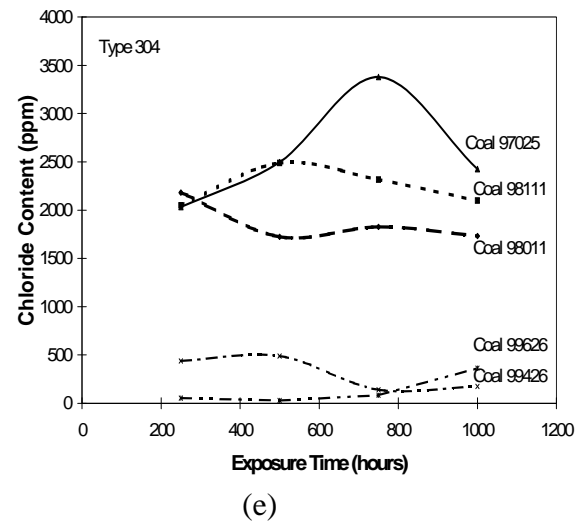
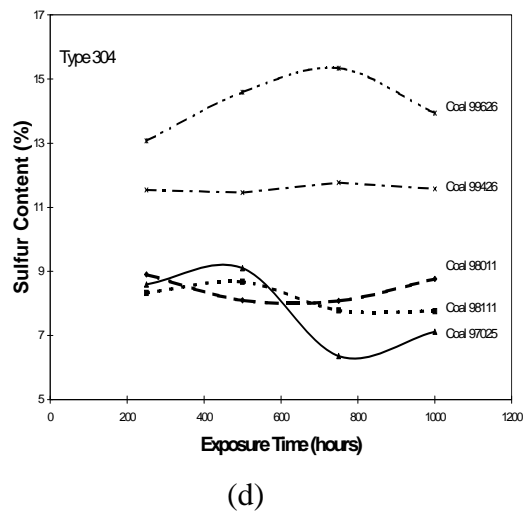
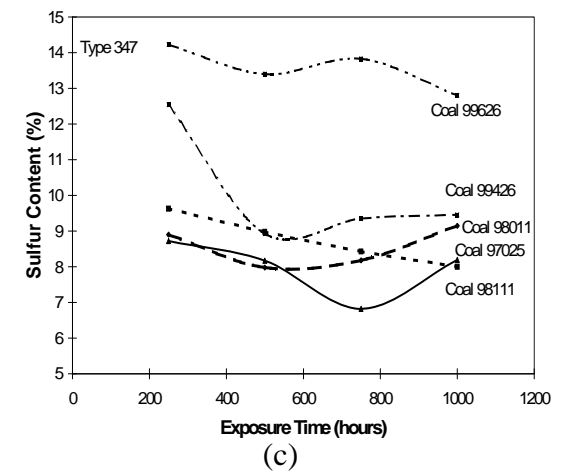
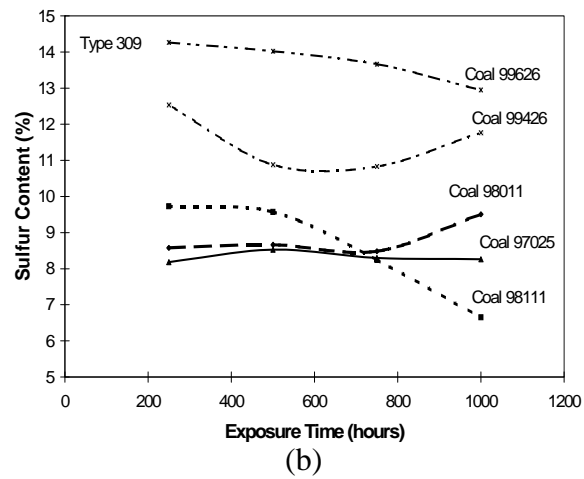
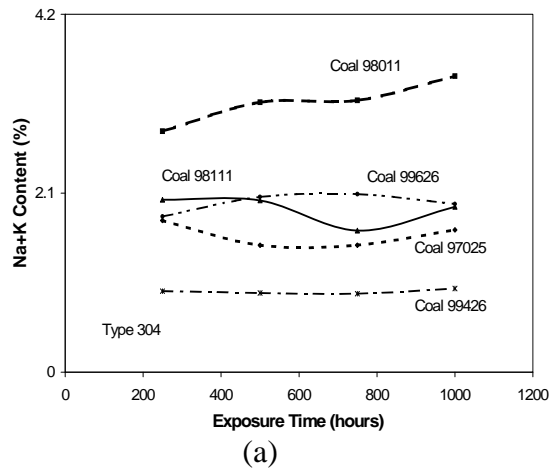


Figure 12. The effect of coals on the elemental contents in the ash deposits.