THE EFFECT OF COAL CHLORINE AND SULFUR CONTENTS ON HIGH TEMPERATURE CORROSION IN AN AFBC SYSTEM

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INTRODUCTION

The occurrence of furnace wall and superheater corrosion in fluidized bed combustor systems has caused some operational and economic concerns.[1] It is generally accepted that chlorine and sulfur may play roles in this corrosion. In order to predict the performance of high chlorine or high sulfur coals in these combustion systems, it is necessary to have a better understanding of the different corrosion mechanisms in which chlorine and sulfur may be involved.[2] It is also important to evaluate the critical point of coal chlorine content which may cause initial corrosion.

TVA's Shawnee plant observed that the boiler tubes in the primary superheater region of the atmospheric fluidized bed combustion system had wastage/corrosion problems between 1992 and 1993. The boiler tubes were located in the bed area and the wastage was caused by both corrosion and erosion. It is difficult to isolate the factors (such as chlorine content, sulfur content, or erosion) causing this wastage. Also, the gas composition varies a great deal in the primary superheater region. However, the tube wastage problems were resolved after several modifications were made in the AFBC system. The modifications included (1) changing the type of coal to a low chlorine coal, and (2) elevation of the boiler tubes to a higher position in the unit.

Our study was designed to evaluate the role coal chloride may play in causing corrosion of boiler components. The Western Kentucky University AFBC system was configured to simulate the Shawnee Plant's system and especially the secondary superheater region in the TVA plant. This simulation excluded consideration of the erosion problems. Also, TVA did not observe any wastage in this location when they used low chloride content coal. The gas composition of this location is very consistent during constant operation.

EXPERIMENTAL

Two 1,000-hour burns were conducted with the 12-inch (0.3 m) laboratory AFBC system at Western Kentucky University. Operating conditions similar to those used at the 160-MW system at the TVA Shawnee Steam Plant located near Paducah, KY were used. A 1000-hour burn was done with a low-chlorine (0.012% Cl and 3.0% S) western Kentucky # 9 coal, which is the same type of coal as that supplied to the TVA plant during 1993. A second 1000-hour burn was conducted with high-chlorine (0.28% Cl and 2.4% S) Illinois # 6 coal. The limestone came from Kentucky Stone in Princeton, KY. This is the source of the limestone used by the Shawnee plant in their AFBC system during 1993. The major operating parameters were as follows: excess air level -- approximately 1.3; Ca/S ratio -- approximately 3; bed temperature -- approximately 1150 K; and temperature near metal coupons -- approximately 900 K. Four different metal alloys [carbon steel C1020 (0.18% C and 0.05% Cr), 304 SS (18.39% Cr and 8.11% Ni), 309 SS (23.28% Cr and 13.41% Ni), and 347 SS (18.03% Cr and 9.79% Ni)] were studied in this project. Each metal coupon had a 5.08 cm outside diameter, was 0.3175 cm thick, with 1.587 cm diameter hole in center. A set of metal coupons was placed at 3.35 m above the fuel injection port, which is 10 cm below the convective pass heat exchange tubes. Coupons were held in place by a machinable tungsten rod (powder metallurgically prepared) and separated by ceramic mounts. Two sets of each coupons (listed above) made a total of eight coupons for the run. Each specimen within a group was rotated as to position in an array every 250 hours during the test burn. The coupon was weighed before and after the run and examined using SEM. The SEM analysis was performed on a JEOL JSM-5400 SEM. Attached to the SEM for Energy Dispersive X-ray analysis (EDS) was a KEVEX Sigma 1 system with a Quantum detector for elemental analysis down to carbon. The following instrument operating parameters were used for the SEM/EDS analysis: electron beam energy -- 20 KeV; working distance -- 24 mm; sample tilt angle -- 0°.

RESULTS AND DISCUSSION

Only SEM/EDS results on different specimens will be presented in this paper. The results of corrosion with respect to the morphologies of the test coupons (cross section examination) will be reported in the near future.

The C1020 specimen was cracked after 250-hours of operation in both test runs. Figure 1 illustrates the weight change data for the alloys in the first 1000-hour burn with the low chloride coal. The type 347 specimen showed the highest weight gain among the other three samples. However, alloy 304 showed the most oxide scale on the surface and alloy 309 showed the least oxide scale on the surface. These observations are based on the color (reddish) and SEM studies. Also, slight scale failures were observed in all three samples. The degree of scale failure is in the following order: 304 > 347 > 309 (the least). This is the reason for the fluctuation of weight change shown for alloy 304. The weight gain is due to the oxidation and the weight loss is due to the scale failure. The two reactions compete with each other.

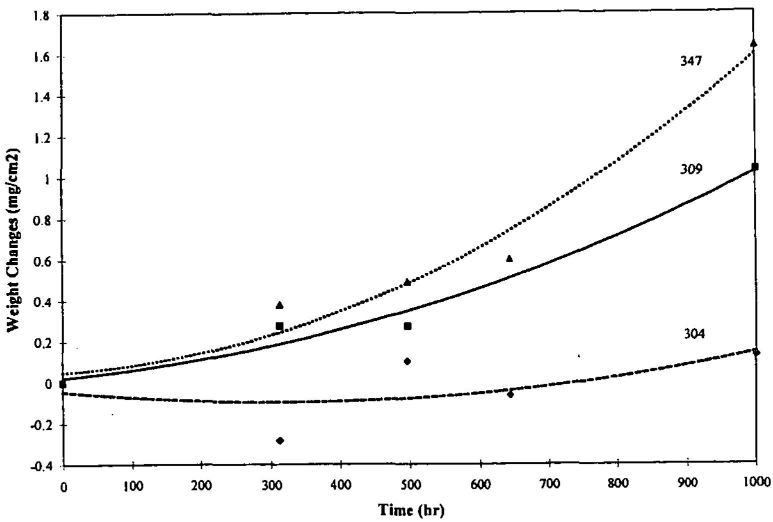

Figure 1. The effect of time of exposure to AFBC combustion gases on the weight of metal coupons.

The scale failure might be due to the sulfur attack and the effect of erosion. The EDS results indicated that the amount of sulfur, calcium and sodium on the surface increased with burning time, as is illustrated in Figures 2 and 3. A certain amount of fly ash passed through the specimens the entire time during the run. Thus, the effect of erosion should also be taken into consideration. The alloy 309 is the best (less oxide scale and scale failure) corrosion resistant material among the three samples under our experimental conditions. It may be due to the high amount of chromium in the compositions.

Figure 4 shows the weight change data for the alloy in the second 1000-hour burn with the higher chlorine coal (0.28% Cl). The weight gain was observed in the case of 309 and 347 before 500 hours. In the case of the 304 alloy, the weight almost remained constant in the first stages of the test burn. There is no chloride (EDS results) observed on the surface of coupons before 500 hours, as is illustrated in Figures 5 and 6. The small amount of scale failure was observed on all three samples, which is similar to the results obtained with the low chlorine coal in the first 1000-hour test. However, the weight loss was observed in all three coupons after 500 hours. The chloride also was identified on the surface of the coupons. Based on the mapping results, the chloride is evenly distributed on the surface of the coupons. There is no concentration of chloride on the spot of scale failure. There are more scale failures observed in this test run than was observed in the first test run. This suggests that chlorine may enhance attack on the metal coupons, but the data is not conclusive.

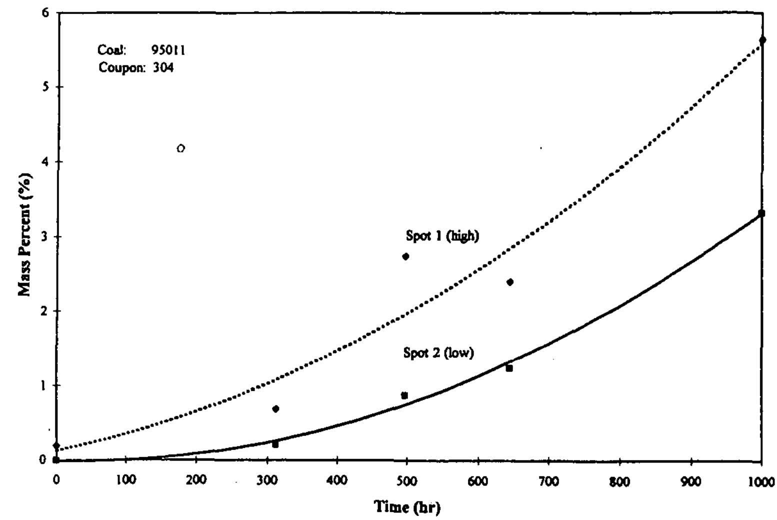

Figure 2. The effect of time of exposure to AFBC combustion gases on the sulfur concentration on metal coupons.

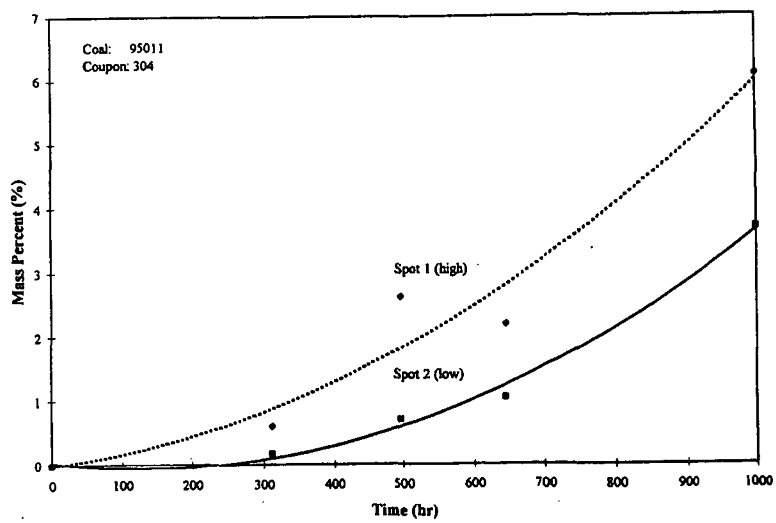

Figure 3. The effect of time of exposure to AFBC combustion gases on the calcium concentration on metal coupons.

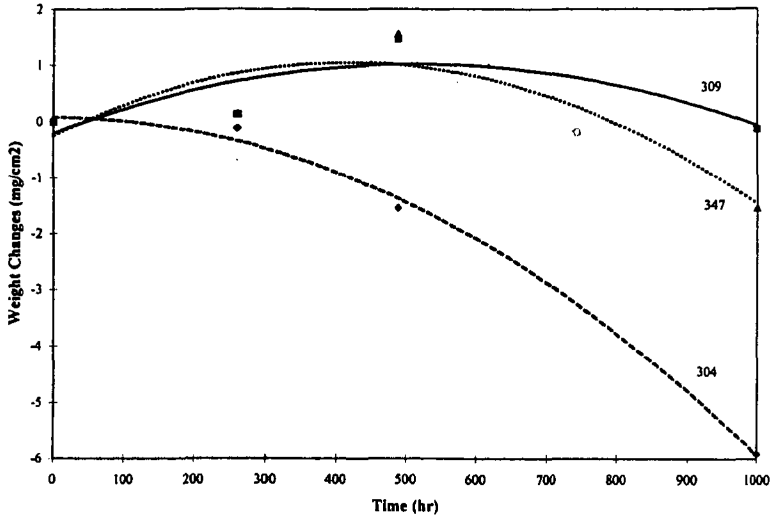

Figure 4. The effect of time of exposure to AFBC combustion gases on the weight changes of metal coupons.

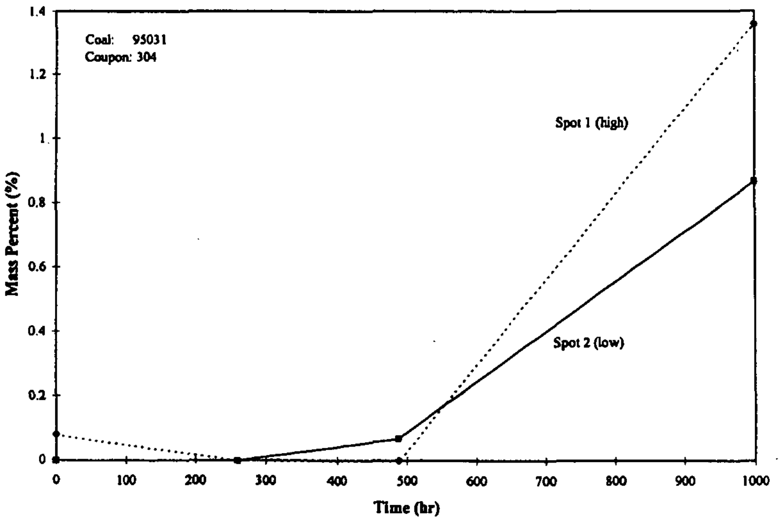

Figure 5. The effect of time of exposure to AFBC combustion gases on the chloride concentration on metal coupons.

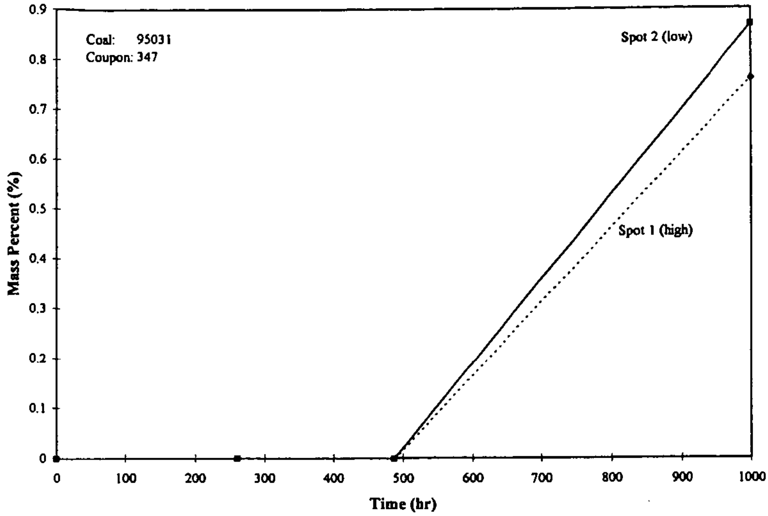

Figure 6. The effect of time of exposure to AFBC combustion gases on the chloride concentration on metal coupons.

CONCLUSIONS

Based on the data presented in this paper the following statements and observations can be made.

- High chromium (~ 23%) 309 alloy steels forming Cr_2O_3 on the surface possessed the greatest corrosion resistance of the four materials tested.
- Scale failure was observed in both 1000-hour test burns with low and high chlorine coals. The second test burn with the high chlorine coal showed more scale failure than that obtained with the first run with the low chlorine coal.
- Chlorine in the coal may enhance the scale failure but the evidence is not conclusive.

ACKNOWLEDGMENTS

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