TECHNICAL REPORT

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Project Title: HIGH TEMPERATURE CORROSION DURING USE OF CHLORINE
CONTAINING COAL

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ABSTRACT

The goal of this project is to characterize the role of chlorine in coal on the high temperature corrosion processes which can occur in coal combustion and conversion processes. The experiments include laboratory tests performed in well-controlled high temperature environments and field tests in industrial coal fired boilers. Evaluation of samples of boiler tubes which have been recovered from boilers which used both high and low chlorine coals does not indicate that the higher chlorine levels are associated with accelerated corrosion of either water wall tubes or superheater tubes in pulverized coal boilers. Laboratory testing of metal coupons in combustion gas environments produced from low sulfur, high chlorine coal IBC-109 and high sulfur-low chlorine coal IBC-101 has been performed at 800°C. No significant differences in corrosion are evident. Further testing at other temperatures and gas compositions is underway.

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EXECUTIVE SUMMARY

Illinois basin coals have the highest chlorine contents of any coals mined in North America in addition to high sulfur contents. The perception on the part of many coal users that chlorine in coal contributes to boiler corrosion is a hindrance to the marketing of Illinois coal. Although this perception is widespread, it is not supported by any definitive data, and a recent conference on chlorine in coal concluded that there is no clear knowledge of whether chlorine in coal can accelerate corrosion in combustion, gasification, or other energy conversion systems. The goal of this program is to investigate the corrosion of several important high temperature structural materials in environments produced by the combustion of coals, and to clarify the role of chlorine in these processes.

The research includes laboratory exposure tests under well controlled conditions as well as field tests in industrial boilers. Corrosion tests are performed on well characterized metal specimens in environments generated by combusting high sulfur, low chlorine coal (IBC-101) and low sulfur, high chlorine coal (IBC-109) at controlled fuel to air ratios and temperatures. Coal specimens have been ground to less than 200 mesh and combusted under conditions which simulate pulverized coal combustion with 10% excess air. Test coupons of low carbon steel, 2 1/4Cr-1Mo steel, AISI 310 stainless steel, and alloy 800 have been exposed to combustion gases produced from the coals at 800°C. The low carbon steel and the 2 1/4 Cr-1Mo steel oxidized much more than the stainless steel or alloy 800 on the basis of weight change and external scale formation. The relative amounts of corrosion experienced by the four metals were consistent with the known corrosion resistances of the alloys. For all of the alloys, the combustion gases from the IBC-109 coal produced less corrosion than the combustion gases from the IBC-101 coal over 24 hour exposures, although they produced slightly more corrosion over two hour exposures. The kinetics of the corrosion process will be examined in more detail in the next quarter using an improved coal feeding device to provide better reproducibility in fuel to air ratios. A small amount of internal intergranular corrosion was detected in the alloy 800H specimen exposed to the combustion gases from the IBC-109 coal for 24 hours, but no internal attack was detected in any of the other specimens after any period of exposure. The role of chlorine and fuel to air ratio in internal attack of the highly alloyed materials will be investigated in more detail.

Evaluation of test coupons which have been exposed to combustion gases from coal in working boilers is addressed in a second phase of the program. Tubes have been collected and evaluated from several pulverized coal boilers which burned Illinois coals. The results obtained to date do not indicate that there is any correlation between chlorine content of coal and fireside corrosion in pulverized coal boilers. Test coupons of low carbon steel, 1 1/4Cr-1/2Mo steel, 2 1/4Cr-1Mo steel, and AISI 304 stainless steel were placed in the low temperature superheater of that boiler for recovery and further evaluation next year. Discussions are underway with another company regarding placement of test coupons and recovery of exposed boiler tubes from a fluidized bed combustion boiler.

OBJECTIVES

The goal of this project is to characterize the conditions under which corrosion in coal fired boilers and coal conversion systems can be produced by chlorine in coal and to investigate the mechanisms of this corrosion. The program focusses on high temperature fireside corrosion and includes laboratory scale tests under well controlled conditions in the laboratory as well as coupon tests in utility boilers using high and low sulfur coal. In order to meet these objectives, a laboratory furnace is used to expose coupons of important structural materials to combustion gases under well characterized conditions. The apparatus permits control of the temperature, feed rate of well characterized coal, and composition and feed rate of the other combustion gases. Exposure tests are performed over a range of fuel to air ratios, temperatures, and other relevant parameters and the response of the materials is characterized using weight change and microstructural examination. The laboratory work is supplemented by coupon testing in industrial boilers to verify that the corrosion mechanisms identified in the laboratory correspond to the corrosion observed in practice.

INTRODUCTION AND BACKGROUND

Illinois basin coals have the highest chlorine contents of any coals mined in North America in addition to high sulfur contents. The perception on the part of many coal users that chlorine in coal contributes to boiler corrosion problems is a hindrance to the marketing of Illinois coal. Although this perception is widespread, it is not clear that it is correct, because chlorine containing coals have been used in many appli-

cations without serious problems. The materials degradation processes which occur in many coal combustion and conversion systems are complex and there is presently no clear knowledge of whether chlorine in coal can accelerate corrosion in combustion or in gasifiers or other coal conversion systems.

This research program addresses the influence of chlorine in coal on corrosion processes experienced by important structural materials in atmospheres produced by combustion of coal. The research is performed in two sections: (1) Laboratory studies and (2) in plant coupon tests. In the laboratory studies, care is taken to insure that the materials are exposed only to the gaseous atmosphere produced by combustion of the coal so that damage by erosion or other degradation processes is avoided. The mechanisms and rates of corrosion will be characterized as a function of the material, temperature and composition of the atmosphere. The results will provide definitive information on the effects of chlorine on corrosion in atmospheres typical of coal combustion and conversion systems, so that the significance of chlorine to high temperature corrosion problems can be assessed. The plant tests provide verification of the laboratory generated data, as well as documenting data on the actual effects of varying chlorine levels in coal on corrosion problems experienced by coal users.

EXPERIMENTAL PROCEDURES

The laboratory experiments consist of exposures of well characterized materials to gas environments produced by combustion of coals under well characterized conditions. They are performed in a specially designed

furnace in which the composition of the corrosive environment can be accurately controlled. A minimum temperature of 700°C in the combustion zone of the furnace is required to assure complete combustion of the coal. Several firebrick plates are supported in the combustion furnace on a stainless steel rod to prevent the coal from falling into the test furnace before the combustion is complete. The combustion gases then flow downward through the furnace, passing over the samples in the lower furnace zone before leaving the furnace through a long fused quartz tube located at the bottom of the test furnace. The small diameter of the exhaust tube does not present a hazard for plugging because the coal/air mixture has been completely combusted before it reaches this location.

In order to minimize the coal consumption and the the amount of ash buildup in the furnaces, the experiments have been run with very low rates of coal feeding (5 grams/hour). A vibratory feeder is used to maintain the powder flow, however variations in the feeding rate provided by the vibratory unit have resulted in undesirable variations in the fuel to air ratio. After visiting AccuRate, Inc., of Whitewater, WI, one of the few commercial organizations with experience with feeding powders at such low rates, and obtaining permission for the necessary budget modification, an order has been placed for a small scale screw-type feeder which has demonstrated an ability to feed powdered coal at low and accurate rates for extended periods of time as shown in Figure 1.

RESULTS AND DISCUSSION

1. Laboratory Corrosion Tests

MATERIAL TESTING REPORT / GRAPH

COAL

Figure 1. Coal feeding curve for IBC-109 coal ground to 200 mesh using AccuRate Model 102 solids feeding device.

A series of tests have been performed in the laboratory test furnace at 800°C using the vibratory coal feeder operating at approximately 5 g/hr and feeding both low chlorine IBC-101 coal and high chlorine IBC-109 coal and combusting with approximately 10% excess air. Test coupons of four test alloys (1010 carbon steel, F-22 2 1/4 Cr - 1 Mo steel, AISI 310 stainless steel, and alloy 800) have been exposed for periods of 2 and 24 hours. Table 1 summarizes the changes in mass measured on the specimens after each test. The corrosion occurred in the form of growth of oxide scales on the specimens as expected based on the thermodynamic calculations performed for the high excess air combustion gas mixture. The differences in amount of corrosion among the different alloys are consistent with the known corrosion resistances of the four materials in high temperature oxidizing environments.

TABLE I
CHANGE IN MASS OF TEST COUPONS AFTER EXPOSURE
IN LABORATORY FURNACE (mg/cm^2)

	C1010	F-22	310	800
1. IBC-101 10% excess air T= 800 C (2 hour test)	+11.8	+15.9	+0.2	+0.1
2. IBC-109 10% excess air T=800 C (2 hour test)	+19.3	+12.1	+3.4	+1.8
3. IBC-101 10% excess air T= 800 C (24 hour test)	-61.0	+17.0	+0.5	+0.2
4. IBC-109 10% excess air T= 800 C (24 hour test)	+7.8	+7.0	+0.2	NA

The overall amounts of attack among the materials are consistent with the expected behavior of the alloys. The 1010 steel and F-22 low alloy steels were severely oxidized at this temperature leading to large changes in weight. There was some spallation of the corrosion products from the 1010 specimen exposed to the gas mixture from the IBC101 coal in the 24 hour experiment and from the F-22 specimen from the 2 hour experiment, which caused the masses of the samples to decrease rather than increase after exposure. The mass changes of the samples exposed to the combustion gases from IBC-109 coal were larger than those for those exposed to combustion gases from IBC-101 coal after 2 hour exposures but

were smaller after 24 hour exposures. This may indicate that the details of the corrosion processes are different in the two environments. Because of the variations in coal feeding rate encountered when the vibratory feeder was used in these tests, the composition of the gas may have changed during the experiments and duplicate tests will be performed using the new feeding equipment in order to verify these results.

Some spallation may have also occurred from the specimens exposed to the IBC-109 coal in the 24 hour tests. Figure 2 is a scanning electron micrograph of the surface of the corrosion products formed on the 1010 steel after 24 hours of exposure to the combustion gases produced by IBC-109 coal showing a region where the oxide is separating from the underlying metal. EDS microanalysis will be performed on the material in order to identify the corrosion products in detail. Metallographic examination of the remaining metal in the test coupons will be performed in order to clarify the amount of metal consumed in each coupon.

The more highly alloyed materials showed little net change in mass as expected. As was the case for the low alloy steels, the change in mass for the 310 and 800H alloys exposed to combustion gases from IBC-109 coal for 2 hours was greater than that for specimens exposed to combustion gases from IBC-101 coal, while after 24 hours of exposure, the results were reversed. Metallographic examination of the specimens after exposure showed very little net metal consumption as would be expected on the basis of the small weight changes. In a few regions on the alloy 800H specimen exposed to the combustion gases from the IBC-109 coal for 24 hours, a small amount of intergranular internal attack was apparent as

Figure 2. Scanning electron micrograph of 1010 carbon steel specimen after 24 hours exposure to combustion gases from IBC-109 coal showing spallation of oxide.

Figure 3. Optical micrograph showing internal attack in alloy 800H specimen after 24 hours exposure to combustion gases from IBC-109 coal. Attack penetrates along grain boundaries.

Figure 4. Scanning electron micrograph showing external corrosion products formed on alloy 800H specimen after 24 hours exposure to combustion gases formed from IBC-109 coal.

shown in Figure 3. Most other regions showed no internal attack. Alloy 800H is known to be particularly susceptible to this form of internal corrosion in environments which contain chlorine. Similar, but more severe internal attack has been produced when alloy 800H specimens were corroded in high purity laboratory gas mixtures of CO₂, Cl₂ and Ar with low oxygen potentials at 800°C. The role of oxygen and chlorine potentials in this attack may be of particular importance and will be aggressively investigated. No internal attack was detected in 800H specimens exposed to the combustion gases produced by IBC-101 coal or in the specimen exposed for a shorter time to the IBC-109 coal. The oxide scale formed on this specimen was a typical chromium rich oxide as shown in the scanning electron micrograph in Figure 4. No internal attack was detected in the 310 stainless steel specimens exposed to the combustion gases produced by either coal.

2. Evaluation of Test Coupons from Operating Plants

Negotiations are still ongoing with several companies regarding placement of test coupons and/or recovery of tubing which had seen long term, well documented service. We are particularly interested in performing tests in a fluidized bed combustor burning coals with various chlorine contents. We have approached the operator of a fluidized bed combustion unit in Illinois regarding possible cooperation and are awaiting their response.

CONCLUSION AND RECOMMENDATION

Examination of exposed tubes recovered from boilers burning coals with chlorine contents ranging from 0.07% to 0.5% Cl have not indicated that

the higher chlorine coals cause more severe corrosion of either superheater tubes or water wall tubes. Additional coupon tests are ongoing in other pulverized coal boilers and are planned for fluidized bed combustion boilers in the coming year.

Laboratory furnace tests of four common boiler materials are ongoing. Initial tests in combustion gases from IBC-101 and IBC109 coals burned with 10% excess air at 800°C indicate less corrosion with the higher chlorine coal over 24 hours and less corrosion with the higher sulfur coal over two hours. A small amount of internal attack was detected in the 800H specimen. The results are not yet sufficient to provide an overall comparison of the fireside corrosion problems to be expected from the two coals. Further tests at other temperatures and fuel to air ratios are in progress.

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