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

ICCI Project Number: R90-1/5.2A-1M

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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 between 600°C (1112°F) and 800°C (1472°F). More overall corrosion is produced in the high sulfur environment than in the high chlorine environment. HCl additions of 1000 ppm to Ar-20%CO2-3%H2O accelerate the oxidation of ferritic steels at 600°C but additions of 330 ppm HCl have no measurable effect. Internal attack in CO2 containing environments at 800°C of the austenitic alloys 800 and 310 stainless steel is accelerated by the presence of Cl2 but HCl has much less effect. Both of these results imply that chlorine accelerated corrosion is not likely to occur at chlorine levels typical of Illinois coals.

This project is funded by the U. S. Department of Energy (DOE) and by the Illinois Department of Energy and Natural Resources as part of their cost-shared program.
Illinois basin coals have the highest chlorine contents of any coals mined in North America in addition to high sulfur contents. The perception 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 definitive data. 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 field tests in industrial boilers as well as laboratory exposure tests. Evaluation of test coupons which have been exposed to combustion gases from coal in working boilers have been addressed in the field test portion of the program. Tubes have been collected and evaluated from several power plants with pulverized coal boilers which burned Illinois coals having chlorine contents ranging from 0.07% to 0.5%. Superheater and water wall tubes which had been in service for extended periods were subjected to metallurgical analysis. The results 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 and AISI 304 stainless steel were placed in the low temperature superheater of a boiler burning low chlorine coal in April of 1991. These coupons were recovered in April of 1992 after approximately one year of exposure to the environment. Very little attack of the coupons was detected. This may be due to the relatively low gas temperature at the location where they were attached to the boiler tubes.

Laboratory tests were performed on metal specimens in environments generated by combusting high sulfur, low chlorine coal (IBC-101) and low sulfur, high chlorine coal (IBC-109) at controlled temperatures. The ferritic steels, C1010 and F22 suffer substantial oxidation in both environments as indicated by weight changes after exposures at 600 or 800°C. The environment produced by burning the high sulfur, low chlorine coal (IBC-101) caused more weight change than the environment produced by burning the low sulfur, high chlorine coal (IBC-109) at 600°C. No weight changes were detected in the austenitic alloys 310 stainless steel or Alloy 800.

The experiments were supplemented by tests in artificial combustion environments produced by mixing reagent grade gases including CO₂, Cl₂, HCl, and H₂O. Tests on C1010 and F22 indicate that the HCl level necessary to produce accelerated oxidation in a CO₂ containing environment is between 330 and 1000 ppm. Such HCl levels could be produced by combustion of coals containing between 0.4 and 1.2% Cl. AISI 310 stainless steel and alloy 800 suffer from internal attack at 800°C. The microstructure of the internal corrosion has been characterized and a mechanism is postulated in which the attack occurs by penetration of carbon into the surfaces of the alloys. The carbon ties up the chromium as chromium carbides so that it is not available to produce a protective oxide scale. The chlorine selectively attacks the carbides to produce pores which penetrate the surface. The rate of the internal corrosion process is
affected by the chlorine potential in the environment and the temperature, decreasing as either of these is reduced.
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 focuses 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 addition to the coupon tests, a laboratory furnace was 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. The tests were supplemented by similar tests performed in a furnace containing a mixture of laboratory reagent grade gases with compositions similar to those of the combustion gases at thermodynamic equilibrium. Exposure tests were performed over a range of fuel to air ratios, temperatures, and other relevant parameters and the response of the materials was characterized using weight change and microstructural examination. The results indicate that while chlorine can cause a drastic increase in the rate of high temperature corrosion of chromium containing alloys, the effects are minimal at the chlorine levels expected in coal combustion gases from fuels containing up to 0.5% Cl.

INTRODUCTION AND BACKGROUND

In addition to their high sulfur contents, Illinois basin coals have the highest chlorine contents of any coals mined in North America. The per-
ception on the part of many coal users that chlorine in coal contributes to boiler corrosion problems is a nuisance to the marketing of Illinois coal. Although this perception is widespread, it is not well documented, and chlorine containing coals have been used in many applications 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 problems experienced by important structural materials in atmospheres produced by combustion of coal. The research is performed in two sections: (1) in-plant coupon tests and (2) laboratory studies. In the in-plant coupon tests, the corrosion of metal specimens which were recovered from coal fired power plant boilers which burned Illinois coal with high and low chlorine contents was characterized by metallographic techniques and electron microscopy. Degradation of the material under these conditions is influenced by erosion, creep, and other phenomena in addition to corrosion. These phenomena are influenced by the location of the coupon in the boiler, the load cycle of the plant and other variables which are difficult to control in a commercial power plant setting. In the laboratory studies, care was taken to insure that the materials were 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 were characterized as a function of the test material, temperature and composition of the atmosphere. The results provide 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.

High temperature corrosion processes which can be influenced by chlorine can occur in three locations in a coal-fired pulverized coal boiler. (1) Water Wall Tubes: When the coal and air are injected into the boiler, the space which contains the combustion fireball is contained by four walls of welded steel pipes in which water is boiled to generate steam. The metal temperature in the water walls is typically lower than in other tubes of the boiler (as low as 400°F or 750°F), but the steep temperature drop between the combusting gas and the metal can contribute to formation of deposits which can cause more rapid corrosion than in higher temperature sections of the boiler. Furthermore, because combustion is actually occurring in this part of the boiler, variations in combustion efficiency can cause localized regions of reducing and oxidizing conditions which can contribute to the breakdown of normally protective oxide scales. (2) Superheater Tubes: Located at the top of the combustion zone, the steam is superheated in this location before it is supplied to the turbine. The metal temperature may be as high as 600°C (1112°F) with the gas temperatures being somewhat higher. (3) Back End Corrosion: This corrosion occurs in the ducts and vents carrying the combustion gases out of the furnace after the useful heat has been extracted to the steam. This corrosion is often associated with the formation of low pH aqueous deposits from the cooling gases. It may be influenced by the use of scrubbing solutions for SO2 control.

EXPERIMENTAL PROCEDURES
A. In-Plant Tests

Three power plants participated in the in-plant testing portion of the program: The Dallman power station of Springfield City Water, Light and Power, which burns a low chlorine Illinois coal containing less than 0.07% Cl by weight, the power generation station at Inland Steel Company, which burns a high chlorine Illinois coal containing 0.49 to 0.5% Cl by weight, and another plant which did not give permission for its name to be used and which burns a coal with an intermediate chlorine level. Used boiler tubes were recovered from the superheater and water wall sections of the three boilers and evaluated during the first year of this program. The results of these evaluations were presented in the Annual Technical Report for 1990-1991. Although a small amount of chlorine was detected in the deposits on the water wall tubes from the plant burning the highest chlorine coal, there was not evidence that chlorine caused accelerated corrosion of these tubes. The most serious damage detected was produced by ash particle erosion on the superheater tubes in the plant burning the low chlorine coal.

In addition to recovering sections of used boiler tubes from the Dallman power station in April of 1991, several test coupons were placed in the low temperature superheater region of the boiler at that time. Figure 1 is a schematic diagram of the test coupons. Two of these test coupons were recovered from the boiler during its spring outage in April 1992 and subjected to metallurgical evaluation.

B. Laboratory Corrosion Tests
Figure 1. Schematic diagram of Test coupons placed in low temperature superheater.
The laboratory experiments consisted of exposing well characterized materials to gas environments produced by combustion of coals under well characterized conditions. They were performed in a specially designed furnace in which the composition of the corrosive environment can be accurately controlled. Considerable effort has gone into the design and construction of this unit, and improvements in the performance of the furnace continued throughout the course of the program. Figure 2 is a schematic diagram of the laboratory coal combustion test furnace as it has been operated during the last months of the program. The test furnace consists of a fused silica reaction tube contained in a two zone heating furnace. Pulverized coal (ground to less than 200 mesh in a ball mill) is fed into the furnace using a screw type feeder. A low pressure vacuum pump is used to draw laboratory air into the top of the furnace along with the coal and to insure the steady flow of combustion gases through the system. The top zone of the furnace is maintained at approximately 800°C (1472°F) to initiate combustion of the coal. Ceramic baffles placed in the combustion zone increase the residence time of the coal in this zone of the furnace to insure complete combustion. The combustion gases are then drawn into the lower zone of the furnace which is maintained at the desired test temperature. The test specimens are supported in a ceramic sample holder at the bottom of the test zone. The vacuum pump draws the combustion gases continuously over the test specimens and out of the furnace through a fused silica exhaust tube.

The combustion gases leaving the furnace pass through a teflon tube which is electrically heated to a temperature above 100°C to avoid condensation, and fed into a separate chamber which contains an additional
Figure 2. Schematic diagram of laboratory test furnace.
sample holder. The effects of coal composition on back-end type corrosion can be investigated using the samples in this container which can also be maintained at a controlled temperature. The combustion gases are then drawn through a bubble column, which presently only contains a quantity of low vapor pressure oil to provide a visual check on the gas flow rates through the system. In the long term, we would like to fill the column with wet scrubber solutions to investigate the effects of the combustion gases on the stability of these solutions and corrosion of materials exposed to them. The final gases are exhausted from the pump to a fume hood.

In addition to the coal combustion furnace, an additional test furnace has been committed to the program in which supplementary tests are performed in simulated combustion gases produced by mixing reagent gases. These tests can be performed more rapidly, and have the advantage that the composition of the gas is not dependent on the combustion process. They have been performed to supplement the results obtained in the coal combustion furnace and to verify the effects of the corrosive species found in the coal combustion tests.

RESULTS AND DISCUSSION

1. In-Plant Tests

The test coupons recovered from the Dallman power station after one year of exposure in the low temperature superheater showed no measureable loss in section thickness (i.e. < 0.001 inch thickness change). One test coupon of A106 low-carbon steel tubing and one test coupon of 304 stain-
less steel were examined. A thick build up of ash deposits was found on the outside of each of the coupons. Figure 3 shows a scanning electron micrograph of the deposits from the 304 stainless steel specimen. Energy dispersive X-ray spectroscopy detected only elements which are typical of coal ash. No nickel or chromium were detected, indicating that no elements from the alloy were corroding into the deposit. Metallographic examination of the interiors of the specimens also showed no change from the unexposed condition.

Although 304 stainless steel would usually be expected to be more corrosion resistant than low carbon steel, no significant attack was detected on either specimen after this exposure. Essentially, the conditions in this region of the boiler were not severe enough to produce any attack of either material. It was known at the time that the coupons were placed that the temperatures and erosion conditions at the test location were not as severe as at other locations in the boiler. However, because of the operators concern that debris from severely corroded test coupons could interfere with the operation of the power station, a less aggressive location was selected. It is clear now that test coupons could safely be placed in higher temperature portions of the boiler in future studies.

2. Laboratory Corrosion Tests

Laboratory corrosion tests have been performed with three alloys, the compositions of which are shown in Table I. C1010 is a low carbon steel with a composition close to that of the low carbon boiler tube steel defined by ASME specification A-178. F22 is the pipe designation for the
Low temperature super heater test coupon.

Figure 3. Scanning electron micrograph of deposits on AISI 304 test coupon recovered from low temperature superheater with EDS spectra.
<table>
<thead>
<tr>
<th></th>
<th>C1010</th>
<th>F22</th>
<th>310SS</th>
<th>A800</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.08</td>
<td>0.141</td>
<td>0.06</td>
<td>0.01</td>
</tr>
<tr>
<td>Mn</td>
<td>0.45</td>
<td>0.441</td>
<td>1.94</td>
<td>0.92</td>
</tr>
<tr>
<td>Si</td>
<td></td>
<td>0.218</td>
<td>0.68</td>
<td>0.38</td>
</tr>
<tr>
<td>Mo</td>
<td></td>
<td>1.022</td>
<td>0.16</td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td></td>
<td>2.33</td>
<td>24.87</td>
<td>20.90</td>
</tr>
<tr>
<td>Ni</td>
<td></td>
<td></td>
<td>19.72</td>
<td>30.74</td>
</tr>
<tr>
<td>Ti</td>
<td></td>
<td></td>
<td></td>
<td>0.43</td>
</tr>
</tbody>
</table>
2 l/4Cr – 1 Mo steel defined by ASME specification A-213 Grade T22. Both of these are low cost ferritic materials which are typically used in regions of the boiler where conditions are not severe enough to require the use of highly alloyed materials. 310 stainless steel has the highest chromium and nickel content of any austenitic stainless steel, and therefore is usually considered to have the best corrosion resistance of this class of alloys. Alloy 800 is an austenitic iron based alloy which contains more nickel than usual stainless steels. This alloy is often specified for use in environments which are too corrosive for stainless steels. Both of these alloys are relatively expensive materials which would be used in the parts of a boiler where the conditions are most severe.

Combustion gases have been generated in the furnace by combustion of two coals, the compositions of which are given in Table II. These coals were selected from the inventory of the Illinois Basin Coal Sample Program to represent a low chlorine high sulfur coal (IBC-101) and a high chlorine, low sulfur coal (IBC-109). The coal and ash analyses were provided by the Illinois Geological Survey. Thermodynamic calculations performed with the aid of the SOLGASMIX-PV computer program indicate that when combusted with a stoichiometric amount of air, the IBC-101 coal should produce a combustion gas containing approximately 94 ppm HCl, while the IBC-109 coal should produce a combustion gas containing approximately 320 ppm HCl.

Laboratory furnace exposures were performed for 24 hours on each of the four alloys in combustion gases produced from both coals at 600°C.
<table>
<thead>
<tr>
<th></th>
<th>IBC-101</th>
<th>IBC-109</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>69.30</td>
<td>75.05</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>5.18</td>
<td>4.89</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>1.31</td>
<td>1.74</td>
</tr>
<tr>
<td>Oxygen</td>
<td>9.31</td>
<td>8.53</td>
</tr>
<tr>
<td>Total Sulfur</td>
<td>4.36</td>
<td>1.13</td>
</tr>
<tr>
<td>Total Chlorine</td>
<td>0.12</td>
<td>0.42</td>
</tr>
<tr>
<td>Ash (HT)</td>
<td>10.5</td>
<td>8.2</td>
</tr>
<tr>
<td>$\text{SiO}_2$</td>
<td>49.22</td>
<td>49.84</td>
</tr>
<tr>
<td>$\text{Al}_2\text{O}_3$</td>
<td>17.30</td>
<td>25.62</td>
</tr>
<tr>
<td>$\text{Fe}_2\text{O}_3$</td>
<td>17.00</td>
<td>10.90</td>
</tr>
<tr>
<td>CaO</td>
<td>4.85</td>
<td>2.78</td>
</tr>
<tr>
<td>MgO</td>
<td>0.96</td>
<td>1.20</td>
</tr>
<tr>
<td>$\text{K}_2\text{O}$</td>
<td>2.16</td>
<td>2.84</td>
</tr>
<tr>
<td>$\text{Na}_2\text{O}$</td>
<td>1.38</td>
<td>1.40</td>
</tr>
<tr>
<td>$\text{SO}_3$</td>
<td>4.34</td>
<td>2.18</td>
</tr>
</tbody>
</table>
(1120°F) and 800°C (1472°F). No significant change in mass was detected for either the 310 stainless steel or the alloy 800 specimen after any of the exposures. This is consistent with the known corrosion resistance of these two alloys. The weight changes produced on the C1010 and F22 specimens are summarized in Figure 4. At 800°C, the weight changes were 60 to 80 mg/cm² for the C1010 steel and 40 to 50 mg/cm² for the F22 steel. These large weight changes are to be expected because these materials would not normally be used at such a high temperature. At 900°C, the weight changes are 2 to 4 mg/cm² for the C1010 steel and 0.4 to 1 mg/cm² for the F22 steel. The corrosion rates for the F22 steel in this environment would be acceptable for service in a boiler. Both the C1010 and F22 steels corroded more rapidly in the combustion gas from the high sulfur IBC-101 coal than in the high chlorine IBC-109 coal at this temperature.

Figure 5 shows a scanning electron micrograph of the corrosion products on the surface of the F22 sample after exposure to the combustion gases from the IBC-101 coal for 24 hours at 800°C. As was the case with the specimens from the plant exposure test, the surface is covered by coal ash deposits. Energy dispersive analysis of the deposits indicates that they are composed primarily of elements from the coal ash. A larger amount of iron was detected in these deposits than in the deposits from the plant tests. This is likely to have resulted from the shorter exposure time which meant that the ash deposits were thinner. Some sulfur was detected in the deposits from both coals, but no chlorine was detected in the deposits from either the IBC-101 or IBC-109 coal.
Figure 4. Weight change of C1010 and F22 specimens after 24 hours exposure to combustion gases from IBC-101 and IBC-109 coals.
Figure 5. Scanning electron micrograph of F22 specimen after exposure.

F22 exposed to combustion gas of IBC-101 for 24 hours at 800°C.
Although no significant weight change was observed for either of the highly alloyed materials in the tests, some internal attack was observed in the 310 stainless steel specimen exposed to the combustion gases generated from the IBC-109 coal at 800°C as shown in Figure 6. Internal attack occurs when corrosive species penetrate into the alloy and combine with the reactive elements in the interior of the alloy instead of at the surface. Typically, a region of metal near the surface may be influenced by internal attack. Internal attack can be a serious problem in service because the mechanical strength of the metal may be compromised without producing a change in dimensions which would indicate damage. The internal attack in this specimen penetrated down grain boundaries from the surface and extended up to 15 micrometers into the alloy. It was associated with the formation of a carburized layer just below the deepest penetration as shown in Figure 7.

The role of chlorine in the corrosion of the ferritic steels at 600°C requires further study. Because of the difficulty in collecting accurate kinetic data from the laboratory combustion furnace, the experiments were supplemented by a series of conventional thermogravimetric analyses in which specimens were exposed to reagent gas environments intended to simulate the composition of the combustion gases. The mass of the test specimen was measured continuously during the exposure using a Cahn 2000 electrobalance. The continuous experimental data permits the results to be fit to theoretical rate equations so that theoretical models of the corrosion process can be tested.
Figure 6. Internal attack in 310 stainless steel specimen after 24 hours exposure to combustion gases from IBC-109 coal at 800°C. (unetched specimen at 1000X).
Figure 7. Internal attack in 310 stainless steel specimen after 24 hours exposure to combustion gases from IBC-109 coal at 800°C. Specimen etched to reveal carbides. (1000X)
Thermogravimetric experiments were performed on both C1010 and F22 steels in Ar-20%CO\(_2\)-3%H\(_2\)O at 600°C. This gas mixture was selected to simulate a clean combustion product gas. The results are shown in Figures 8 and 9. Both C1010 and F22 oxidize according to a parabolic rate equation as would be expected if the rate of oxidation is limited by diffusional transport through a growing oxide scale. C1010 oxidizes more rapidly than F22 in agreement with the results of the combustion tests.

A second series of TGA tests were performed in the same gas mixtures with the addition of 1000 ppm HCl. The purpose of these tests was to determine whether HCl can accelerate the oxidation of these steels. The results are shown in Figures 10 and 11. Both C1010 and F22 oxidized more rapidly in the HCl containing gases than in the clean gases. The oxidation kinetics still obeyed parabolic rate laws, but the rate constants for the oxidation processes were higher as shown in Figures 12 and 13. This indicates that the addition of HCl to the environment did not change the rate-determining step in the process but did permit faster transport across the growing scale, possibly by contributing to the porosity of the oxide.

The 1000 ppm HCl experiments verify that HCl can accelerate the oxidation of ferritic alloys, but do not verify that this can occur in the context of coal combustion. Combustion gases containing HCl contents this high could only be produced by combustion of a fuel containing 1.2% Cl or higher. No Illinois coals contain such high concentrations of chlorine. An additional series of experiments was performed in Ar-20%CO\(_2\)-3%H\(_2\)O with 330 ppm HCl. This is approximately the level of HCl
Figure 8. Thermogravimetric results for C1010 steel in Ar-20% CO2 + 3%H2O at 600°C.

Weight Change (mg/cm²)

C1010 Material
Ar + 20% CO2 + 3.0% Water Vapor

600°C

Exposure Time (hrs.)

0 5 10 15 20 25
Figure 9: Thermogravimetric Results for 220 steel in Ar-20% CO₂-3%H₂O at 600°C.
Figure 10: Thermogravimetric results for C1010 steel in AR-20%CO₂-3%H₂O-1000 ppm HCl at 600°C.
Figure 11. Thermogravimetric results for F22 steel in air-20%CO₂-3%H₂O-1000 ppm HCl at 600°C.

Exposure Time (hrs)

Weight Change (mg/cm²)

AR + 20%CO₂ + 0.1%HCI + 3.0% Water Vapour

600°C

F22 Material

#2015
Figure 12. Parabolic plots of TGA results for Cl1010 steel in Ar-20%CO2-3%H2O with and without addition of 1000 ppm HCl at 600°C.

Cl1010 Materials in Ar + 20% CO2 + 3.0% Water Vapor at 600°C
Figure 13. Parabolic plots of TGA results for ZrO₂ and without.

ZrO₂ Weight Changes (mg/cm²)

Materials in AR + 20% CO₂ + 3.0% Water Vapor at 600 °C.
expected in the combustion gases from the 18t 109 coal with a chlorine content of 0.4%. As shown in Figures 14 and 15, the thermogravimetric curves for the two alloys in this environment are virtually identical to those in the tests without HCl. This implies that the amount of HCl necessary to produce accelerated oxidation of steel is between 330 and 1000 ppm and that the minimum chlorine content in the coal to produce accelerated corrosion is between 0.4 and 1.2%.

Internal corrosion was also investigated in the laboratory furnace. This phenomenon is most serious for the highly alloyed materials such as alloy 800 and 310 stainless steel at high temperatures such as 800°C. Figure 16a is an optical micrograph of a cross section of the 310 stainless steel specimen after exposure to Ar-20%CO₂-0.25%Cl₂-2%H₂O for 24 hours at 800°C. It shows internal penetration penetrating into the specimen to a depth of 60 micrometers. This attack is associated with the simultaneous presence of both chlorine and carbon in the environment. Carbon penetrates into the metal producing internal carburization and chlorine follows, attacking the carbides and leaving behind a layer of porous metal. Figure 16b is a similar micrograph after etching the metal to reveal the carbides. The large grains which are surrounded by the internal corrosion are carburized, and a region of carburization precedes the internal corrosion layer growing into the metal. Carburization along grain boundaries is visible penetrating even deeper into the metal.

The importance of chlorine in this corrosion process is indicated by comparing these structures with those produced in the same alloy by exposure to Ar-20%CO₂ at 800°C for the same period of time. Figure 17a shows that
Figure 14. Thermogravimetric results for C1010 steel in AR-20%CO₂-3%H₂O, 0.03%HCl + 3.0% Water Vapor at 600°C.

Reaction: AR + 20%CO₂ + 0.03%HCl + 3.0% Water Vapor

C1010 Material
Figure 15.
Thermogravimetric results for F22 steel in Ar-20%CO2-3%H2O - 330 ppm HCl at 600°C.

Weight Changes (mg/cm²)

Exposure Time (hrs.)

0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0

#2016

F22 Material

Ar + 20% CO₂ + 0.033% HCl + 3.0% Water Vapor

600°C
$310 \text{ SS exposed to } \text{AR} + 20\% \text{ CO}_2 + 0.25\% \text{ Cl}_2 \text{ for 24 hours at } 800^\circ \text{C}$
in (p) and Ni for the micrograph shown
Concentration profiles of Cr, Fe
cross section (with etching)
(q) Optical microstructure of the
(a) No etched surface
24 hours at 800°C
310 SS exposed to AR + 20% CO2 for

(q)
No internal corrosion is produced by this exposure, and the etched micrograph shown in Figure 17 reveals that the amount of internal carburization produced under these conditions is much smaller than in the case where chlorine is present.

These results are consistent with the hypothesis that the principal effect of chlorine in the environment is to reduce the protectiveness of the oxide scale which forms on the alloys. The dense, protective chromium oxide layer which forms on 310 stainless steel or alloy 800 in Ar-CO₂ separates the alloy from the environment and prevents the formation of carbides. In the presence of sufficient chlorine contamination, the oxide is porous and is penetrated by carbon, allowing internal carburization to occur, and internal oxidation and chlorination follow the carburization. This interpretation is supported by the results of X-ray diffraction analyses of corroded 310 stainless steel and alloy 800. Diffraction peaks associated with Cr₃C₂ austenite and carbides have been identified. In the case of 310 stainless steel, sigma phase was also detected in the corroded region.

Internal attack occurs because the normally protective chromium in the alloy is consumed by the simultaneous attack of carbon and chlorine. Figure 18 includes a scanning electron micrograph of the corroded and internally carburized zones of the 310 stainless steel specimen after 24 hours exposure to Ar–20%CO₂–0.25%C1₂ at 800°C and a plot of the elemental composition of the alloy as determined by Energy dispersive X-ray fluorescence microanalysis as a function of distance from the surface. The surface of the specimen is high in chromium because of the presence
For micrograph shown in (e)
(d) Composition profiles of Cr, Fe and Ni
of the cross section
(e) Scanning electron micrograph

310 SS exposed to AR + 20% CO₂ + 0.25% Cl₂ for 24 hours at 800°C

Figure 18. Scanning electron micrograph and elemental composition profile for 310 after internal attack.
of the non-protective chromium oxide layer there. Beneath this is a region extending approximately 50 micrometers below the surface where the chromium content is low and the material has been affected by internal attack. Between approximately 50 micrometers and 100 micrometers below the surface is the carburized layer where the apparent chromium content is slightly enriched, but this chromium is primarily in the form of carbides which do not provide much protection for the alloy. Beyond 100 micrometers into the alloy, the chromium content of the alloy is unaffected. The nickel and iron contents of the alloy vary in the opposite way as the chromium content, being enriched in the chromium depleted porous region and depleted in the carburized region.

The depth of internal attack is affected by the carbon and chlorine potentials in the environment and by temperature, which determines the diffusion coefficient of carbon in the alloy. Figure 19 is a micrograph of the surface region of the 310 stainless steel specimen exposed for 24 hours to Ar-20%CO₂-0.5%HCl at 800°C. Although some internal attack is evident, the depth is only approximately 10 micrometers and the carburized layer extends only an additional 10 micrometers into the alloy. This indicates that the lower chlorine potential in the HCl containing gas is not sufficient to produce the same degree of scale penetration as the Cl₂ containing gas mixture. As was noted for the ferritic alloys at 600°C, chlorine contents sufficiently high to produce this form of corrosion are not likely to be encountered during combustion of even the highest chlorine content coals.
310 SS alloy exposed to Ar + 20% CO₂ + 0.5% HCl for 24 hrs at 800 °C

(a) Unetched surface
(b) Optical micrograph of the cross section (with etching)

Figure 19. Optical micrographs of AISI 310 stainless steel after exposure to Ar-20%CO₂-0.5%HCl at 800 °C.
Similar microstructures and corrosion processes were observed on the specimens exposed at 700°C, but the depth of the attack is smaller, with the penetration being less than 20 microns after 24 hours of exposure to the same gas mixtures. Similar results have been obtained with alloy 800. No internal attack was observed in the 1010 stainless steel or the 2-1/4Cr-1Mo alloy, which suffer from rapid external attack at this temperature.

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. Test coupons recovered from the low temperature superheater region of a coal fired boiler after one year of operation showed no significant attack.

Laboratory furnace tests of four common boiler materials in combustion gases from IBC-101 and IBC109 coals at 700°C and 800°C indicate less overall corrosion with the higher chlorine IBC109 coal than with the higher sulfur IBC-101 coal over 24 hours. Tests performed in reagent Ar-20%CO₂-3%H₂O gas mixtures containing HCl indicate that 1000 ppm HCl produces accelerated oxidation of ferritic steels at 600°C, but no detectable increase in the oxidation rate was found in gas mixtures containing 330 ppm HCl. This implies that the minimum chlorine content in coal necessary to produce accelerated oxidation is between 0.4 and 1.2%. Similar experiments on internal corrosion of austenitic alloys in gas mixtures
containing CO₂ and Cl₂ or HCl indicate that the HCl is much less aggressive than the Cl₂ to the high alloyed steels at 800°C. More internal attack is produced when chlorine is present along with carbon and oxygen at this temperature. This type of attack has also been detected in some of the alloy specimens exposed to gases produced by combustion of high chlorine coal.