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Project Title: **EFFECTS OF CHLORINE IN COAL ON FURNACE WALL CORROSION
UNDER LOW-NO_x CONDITIONS**

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ABSTRACT

Since the late 1960s, the British literature has correlated corrosion of utility boilers with the total amount of Cl in coals, and has indicated accelerated corrosion when using coals with Cl content of 0.3% or greater. The US experience, on the other hand, has indicated that Cl in high-Cl coals is not a major cause of corrosion. Nevertheless, because of the British data, many US boiler manufacturers have recommended a maximum Cl level of 0.3% for burning US coals. This limit decreases the market potential of high-Cl Illinois coals. In 1998, a joint study by the ISGS, MTI, ICCI, and U.S. DOE focused on high-temperature superheater and reheater tube wall corrosion that occurred under oxidation conditions. Pilot-scale combustion corrosion tests were conducted on a high-Cl Illinois coal, a high-Cl British coal, and a low-Cl baseline Illinois coal. The results showed no evidence of a correlation between coal Cl content and rate of corrosion, but showed a correlation between the rate of corrosion and the metal temperature used. The same conclusion was recently published by a joint study by PowerGen in the United Kingdom and the Electric Power Research Institute in the United States. They concluded that under oxidizing conditions, increasing the chlorine content of the coal burned was not expected to increase the tube corrosion rate, and the resulting corrosion rates were dependent only upon metal temperatures.

The purpose of this continuing research is to determine the significant effect, if any, of Cl in coal on corrosion of the furnace wall under substoichiometric (low-NO_x) combustion conditions. Two pilot-scale combustion corrosion tests using high- (0.41%) and low- (0.10%) Cl Illinois coals were conducted. The corrosion rates were measured using conventional probes, made of T22 metal-alloy, for a duration that would give reliable comparisons. Combustion of the high- and low-Cl coal resulted in the same maximum loss on T22 tube wall thickness. However, the average tube wall thickness loss was more pronounced in the low-Cl coal test than in the high-Cl coal test. In addition, no chloride deposition was observed in the corrosion sample obtained from the high-Cl coal test.

The results obtained from combusting coal under reducing conditions were consistent with those of the previous study under oxidizing conditions. Under both conditions, no increase in the corrosion rate was observed with an increased Cl content in the coal. The relationship between corrosion rate and metal temperature was studied under oxidation conditions. However, temperature dependence of the corrosion rate under reducing conditions was not a part of this study.

Pages 1 to 12 contain proprietary information.

EXECUTIVE SUMMARY

Many British studies have associated accelerated fireside corrosion on tubes of utility boilers with the high Cl content in coal (Bettelheim et al. 1980). Their corrosion data suggested that the corrosion rate of boiler tubes increased proportionately with increasing Cl concentration in coal. Based on the results of these studies, US boiler manufacturers and utilities consider coals containing more than 0.3% Cl to be potentially corrosive. This 0.3% limit was primarily based on engineering studies extrapolating the British coal data to the probable corrosive behavior of US coal. The 0.3%

limit on Cl has discouraged the burning of many Illinois Basin coals in utility boilers.

A survey jointly conducted by the Electric Power Research Institute (EPRI) and ICCI (Doane et al. 1994) indicated that some US utilities have had decades of experience burning high-Cl coals in PC-fired boilers. Although fireside corrosion problems have been reported, none of them could be directly related to the presence of Cl in coal. Furthermore, the corrosivity of two Illinois coals, one with a high Cl content of 0.31% Cl and the other with a low Cl content of 0.16%, was determined by Monroe et al. (1994) under pilot-scale combustion tests. The results showed that the corrosion rate of the high Cl coal was actually slower than the corrosion rate of the low Cl coal. In that study, resistance corrosion probes instead of conventional probes were used in the tests, and corrosion rates were based on measurements of electrical resistance over the period of the tests. Also, during the tests for the high-Cl coal, equipment malfunction caused high-temperature excursion, which increased the relative corrosion rates. Resistance probes are particularly sensitive to short temperature increases and are also sensitive to the temperature gradients along the probes. These temperature gradients of the probes were unavoidable during the tests in both oxidizing and reducing zones. The overall results showed that the high-Cl Illinois coal was not corrosive under the test conditions. The results, however, could not be used as a basis for redefining recommended limits of Cl in coal for boiler combustion because of the uncertainties created by the high-temperature excursion and the sensitivity of the resistance probes subjected to temperature variations.

A recent study by research teams from the Illinois State Geological Survey (ISGS), McDermott Technology Inc. (MTI), Illinois Clean Coal Institute (ICCI), and U.S. Department of Energy (U.S. DOE) (Chou et al. 1998; 2000) focused on high-temperature superheater/reheater tube wall corrosion that occurred under oxidation conditions. Pilot-scale combustion corrosion tests were conducted with a high-Cl Illinois coal, a high-Cl British coal, and a low-Cl baseline Illinois coal. The corrosion rates were measured using conventional probes under oxidizing conditions as would be experienced by superheater tube walls in a conventional boiler. The results showed no evidence of a correlation between coal Cl content and rate of corrosion, and suggested that high-Cl Illinois coals, like low-Cl coal, could be successfully used in utility boilers if other coal components or boiler properties were understood and controlled. These findings were further confirmed by a joint study by PowerGen in the United Kingdom and the Electric Power Research Institute (EPRI) in the United States (Davis et al. 2000). They concluded that under oxidizing conditions, increasing the Cl content of the coal burned was not expected to increase the tube corrosion rate, and the resulting corrosion rates were dependent only upon metal temperatures.

A review published by British researchers (James and Pinder 1997) correlated the high corrosion wastage observed on the furnace-wall of UK boilers with the high Cl in UK coal. However, they also suggested that factors other than Cl should be considered in the accelerated corrosion mechanism. It was suggested that the accelerated corrosion took place primarily on the furnace wall where substoichiometric combustion conditions and a high heat flux coexisted.

The presence of reducing gases implies that insufficient oxygen has supplied to the combustion zone by improper air/coal mixing, and a high heat flux results in a high metal temperature on the furnace wall. Under insufficient oxygen conditions, the sulfur in coal is primarily converted to sulfide (H_2S) instead of sulfur oxide (SO_x). The H_2S gas is very corrosive and readily sulfidizes conventional furnace-wall alloys. The sulfidation of the furnace-wall alloys is further escalated by a high metal temperature. Therefore, when a high H_2S concentration and a high metal temperature coexist, accelerated corrosion wastage on the furnace wall is expected. A combination of these conditions could have accounted for the majority of the corrosion wastage experienced on the furnace wall of UK boilers.

However, contrary to the general consensus of the British researchers, the laboratory studies by MTI (Kung et al. 1994; 1996) indicated that the addition of HCl to the combustion gases at a level

equivalent to burning high-Cl coal under substoichiometric combustion conditions would not cause additional corrosion on the furnace wall. In fact, the presence of HCl in the low-NO_x combustion gas may retard the sulfide attack. These results were consistent with those under reducing conditions with H₂S present reported by the UK researchers (Latham et al. 1991). No effect of HCl contents up to 800 ppm (corresponding to 1.0% Cl in coal) was observed on the corrosion of steel tubes at 400°C (752° F) and 500° C (932° F) (see also Doane et al. 1994). These findings are of potential importance to the Illinois coal industry, especially the State of Illinois, which has a large reserve of high-Cl coal. However, the laboratory corrosion data available at MTI were insufficient to evaluate the potential beneficial effects from the Cl in coal on low-NO_x burner applications.

The purpose of this study was to conduct pilot-scale tests using conventional probes to measure corrosion rates under reducing/sulfiding conditions that would be experienced by a water-wall in a low-NO_x boiler. The results obtained should help clarify the significance of Cl on furnace-wall corrosion when coal is burned substoichiometrically.

The specific objectives of this study were:

- A. Acquire two Illinois coal samples, one containing high Cl (0.4% to 0.6%) and one containing low Cl (<0.20%) and process and distribute the samples for characterization and combustion tests.
- B. Characterize the properties of the coal samples used, including the occurrence of Cl, sulfur, and alkali metals and their roles, if any, that could affect the chemistry and mechanism of furnace-wall corrosion during combustion under substoichiometric conditions.
- C. Conduct two Stoker boiler burner-rig corrosion tests at the McDermott Technology, Inc. (MTI), and collect samples for metallurgical composition and the rate of corrosion examinations.
- D. Perform metallographic examination of boiler scale and/or deposit and measure rates of corrosion from specimen cross sections.
- E. Interpret the sampling and analytical results, and compare the rates of corrosion of the high-Cl coal with those of the low-Cl coal.

For the pilot-scale combustion tests to be conducted under low-NO_x conditions, modification of the Stoker boiler system at MTI was completed during the first project year. Also, a low-Cl (<0.2% Cl) and a high-Cl Illinois coal (0.4% to 0.6% Cl) were chosen. Combustion of the first coal sample was initiated at the end of the first project year, and the second sample was completed during the second year.

Corrosion samples obtained from both combustion tests were analyzed for metal corrosion and the effects of Cl and/or deposited ash on the rate of corrosion. The results showed that combustion of the high-Cl and low-Cl coal resulted in a similar maximum tube-wall thickness loss. However, the average tube wall thickness loss obtained from burning the low-Cl coal was greater than that obtained from burning the high-Cl coal. The greater corrosion rate for the low-Cl coal may be related to other properties of the coal. A higher sulfur content was observed in the scale produced from burning the low-Cl coal. This difference in sulfur content in the scale may be related to the sulfur content of the coal used. The low-Cl coal used contained a higher sulfur content than the high-Cl coal used. There was no evidence of chloride deposition in the scale produced from burning the high-Cl coal.

The results obtained from combusting coal under reducing conditions were consistent with those of our previous study under oxidizing conditions in that Cl in coal was not detrimental to boiler

corrosion. For combusting coal under both oxidation and reduction conditions, no increase in corrosion rate was observed with an increase of the Cl content in coal. The corrosion rate temperature dependency was observed in the study under oxidation conditions; however, it was not part of this study under reducing conditions. Further studies should focus on testing the corrosivities of high-sulfur, high-Cl coals and low-sulfur, low-Cl coals. In addition, study of the effect of metal temperature on corrosion rate under low NO_x conditions is also warranted. The results of these studies could provide a comprehensive database and a justification for the boiler manufacturers to remove the restriction on Cl content of coals burned in their boilers. This project was a combined effort by research teams from the ISGS and MTI. The ISGS acquired the coal samples, coordinated the research efforts including sample processing, distribution, and characterization, and has prepared the reports for the ICCI. MTI was responsible for conducting Stoker boiler tests, analyzing the corrosion samples obtained, interpreting the data, and providing a final technical report to the ISGS.