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TECHNICAL REPORT*
March 1 through May 31, 1993

Project Title: **BEHAVIOR OF SULFUR AND CHLORINE IN COAL
DURING COMBUSTION AND BOILER CORROSION**

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ABSTRACT

The goals of this project are to investigate the behavior of sulfur and chlorine during pyrolysis and combustion of Illinois coals, the chemistry and mineralogy of boiler deposits and the process of ash formation, the effects of combustion gases on boiler materials, and remedial measures to reduce the sulfur and chlorine compounds in combustion gases. During this quarter, experiments were conducted in three areas: HCl evolution during coal pyrolysis, minerals in boiler deposits, and effects of composite gases on boiler materials.

The evolution of HCl during coal pyrolysis and its relation to chlorine forms in raw coal were studied using a temperature-programmed pyrolysis and gas combustion in conjunction with a quadrupole gas analyzer (QGA). Using a new filament source in the QGA significantly improved the sensitivity of HCl detection. The major peak at 445°C showed an increased intensity and a new HCl evolution peak at 600°C was observed during pyrolysis of Illinois coal IBC-109. Pyrolysis of coal IBC-109 spiked with NaCl solution showed a strong peak of HCl evolution above 700°C. In the study of boiler deposits, several sample preparation procedures for X-ray diffraction analysis were developed and six minerals were unambiguously determined in superheater and heater deposits from a power plant in Illinois. Effects of composite gases containing 0.2% HCl on six metals were tested at 600°C and 200°C, and at 100°C with moisture for 400 hours. Similar tests were conducted with a composite gas containing no HCl at 600°C and 200°C. The results allow us to assess the factors controlling the corrosion rate: boiler materials, temperature, concentration of HCl in combustion gases, and chloride condensate on metal surfaces.

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EXECUTIVE SUMMARY

Any corrosion observed in a boiler is an elaborate combination of several factors, which include the amount of liquid sulfate on the superheater tube, the sulfur content of coal, the chlorine content of coal, the temperature of the superheater tube wall, and the chemical composition of the alloy (Bakker et al., 1990). The chlorine content of coal is not the only factor that causes boiler corrosion. An important purpose of this project is to better understand how these factors are related to superheater corrosion and ash deposition in coal-fired power plants. Our approaches include the determination of gaseous species of sulfur and chlorine in combustion gases and their release profiles, chemistry and mineralogy of boiler deposits, and effects of combustion gases on boiler material.

Knowledge about the forms of chlorine in coal and the manner it is released during pyrolysis and combustion is helpful in understanding any role that chlorine has in boiler corrosion. New experiments of determining HCl release profiles were conducted using a temperature-programmed pyrolysis and gas combustion apparatus with a quadrupole gas analyzer (QGA). Using a new filament source in the QGA, the sensitivity of detecting HCl in combustion gases was significantly improved. New experiments on Illinois coal IBC-109 (0.42% Cl on dry basis) showed that in addition to a major peak of HCl evolution between 300°C and 550°C with a peak maximum at 445°C, the HCl release continued to 700°C with a small peak at 600°C. It may result from the reaction of a less volatile chlorine species in coal with the organic matter. Chou (1991) suggested that there are two forms of chlorine in Illinois coals: most of the chlorine occurs as chloride ions adsorbed on inner walls of the pores, the rest of the chlorine is in the form of Na^+Cl^- dissolved in coal moisture in large pores and cracks. To determine the behavior of NaCl during coal pyrolysis, a coal spiked with NaCl solution showed a strong peak of HCl evolution starting at 700°C and extending over 850°C. The absence of this peak in the profiles of coal indicates that only a small fraction of the chlorine in coal occurs as NaCl.

Continued progress was made in the study of mineralogy of boiler deposits by X-ray diffraction analysis. Several procedures for sample preparation (random powder bulk pack, oriented slides, water washing to remove anhydrite, and magnetic component separation) were developed. Six minerals were unambiguously determined in the superheater and heater deposits from a power plant in Illinois: quartz, mullite, anhydrite, hematite, cristobalite, and feldspar.

Effects of combustion gases on six metals with different chromium contents were tested to demonstrate their behavior under various conditions (temperature, concentration of HCl in combustion gases, and chloride condensate on metal surfaces).

OBJECTIVES

The purpose of the project is to study the behavior of sulfur and chlorine during coal pyrolysis and combustion, mineralogical and chemical compositions of boiler deposits, effects of HCl and SO₂ in combustion gases on boiler metals, and remedial measures to reduce the HCl concentration in boiler gases. The specific goals of the project are to:

- Identify gaseous sulfur and chlorine species evolved from coal under various pyrolysis and combustion conditions
- Determine sulfur and chlorine species during coal combustion in oxidizing and reducing atmospheres
- Determine the mineralogical and chemical compositions of superheater and reheater deposits and investigate ash deposition processes
- Characterize the effect of HCl and SO₂ in combustion gases on metals of different Cr contents
- Develop remedial methods for reducing the HCl concentration in combustion gases

INTRODUCTION AND BACKGROUND

Evolution of volatile chlorine species during coal pyrolysis in a nitrogen atmosphere at a heating rate of 20°C/min was investigated. HCl was the only gaseous chlorine species identified in combustion gases. The HCl release profile for Illinois coal IBC-109 (0.42% chlorine on dry basins) showed a broad peak between 250°C and 600°C with a maximum at 445°C. During this quarter, a better sensitivity for HCl detection was achieved by using a new filament source in the quadrupole gas analyzer. Additional experiments were conducted on coal IBC-109 using the equipment with an improved sensitivity for gaseous species. To study the behavior of NaCl component of the chlorine in coal during pyrolysis, experiments on coal combined with NaCl powder and coal spiked with NaCl solution were conducted.

Chemical and mineralogical compositions of deposits from the superheater and reheater in utility boilers are important because corrosion loss of metal tubes may be related to the amounts of the alkali sulfate in boiler tube deposits. Furthermore, the chlorine content in boiler deposits provides information about the behavior and fate of chlorine in the boiler. Six boiler deposits from superheater and reheater tubes in a utility boiler have been examined. Each deposit is

separated into inner and outer portions and analyzed for mineralogical composition by X-ray diffraction, microstructure by scanning electron microscopy, and major, minor, and trace elements by X-ray fluorescence spectrometry and neutron activation analysis. The chemical compositions were reported earlier (Chou et al., 1993). There is considerable variation of chemical compositions among the twelve samples. For example, the CaO content varies from 3.55% to 20.04%, and the SO₃ content from 0.35% to 20.95%, indicating considerable chemical fractionation of ash and volatiles during coal combustion. The chlorine content in the samples is very low. Apparently most of the chlorine is lost during coal combustion because of its high volatility. This is an argument against the hypothesis that chlorine takes part in corrosion of the high-temperature portion of a boiler. During this quarter, considerable effort was made in developing sample preparation procedures for X-ray diffraction analysis for precise identification of minerals.

In the study of the effect of composite gases on boiler materials, corrosion experiments were conducted on six metals exposed to a composite gas containing 0.2% HCl at 600°C and 200°C, and at 100°C with moisture for 400 hours. Another set of experiments was conducted by exposing the metals to a composite gas containing no HCl at 600°C and 200°C for 400 hours. The variation of corrosion rate (relation between weight loss and time) under different conditions is discussed.

EXPERIMENTAL PROCEDURES

HCl evolution from coal during temperature-programmed pyrolysis

The chlorine release profile during coal pyrolysis was determined using a temperature-programmed pyrolysis and gas-combustion apparatus in conjunction with a quadrupole gas analyzer (QGA). The experimental setup and procedures were described previously (Chou et al., 1992). The filament was deteriorated after prolonged usage and the intensity of HCl signal decreased. We later used a new filament source in the QGA, and improved sensitivity of HCl detection was achieved.

Boiler deposits

Six samples of boiler deposits were collected from the final superheater and reheater areas of the Unit 5 boiler, Wood River Power Station, Illinois Power Company. Samples WR5-1, -2, -3, -5, and -6 are from the superheater area, and sample WR5-4 from the reheater area. It is a Combustion Engineering tangential-fired, pulverized coal boiler operating at 1,050°F main steam temperature and 1000°F reheat steam temperature. A

diagram of the boiler with sample locations was included in a previous report (Figure 1 in Chou et al., 1992).

Each of the six samples was examined in the laboratory and separated into inner (comparatively close to the tube surface) and outer portions, with the exception of sample WR5-4 and WR5-6. The inner portion is generally reddish and loosely aggregated, often friable, whereas the outer layer is brownish and relatively compact and firm.

Sample WR5-4 consists of a compact piece of brownish and reddish segments from the outer portion (2-3 cm thick). The brown and red portions were separated for analysis.

Sample WR5-6 consists of a brownish, firm framework filled by brownish grey powder. The grey powder (loosely compacted) was separated and makes up WR5-6b (XRD #3463L) (Table 1).

Separate aliquots of the 12 samples were pulverized to 100 mesh (about 150 μm) powder using a ball mill and analyzed by X-ray diffraction analysis for mineralogical composition and by X-ray fluorescence spectrometry and neutron activation analysis for chemical compositions. Part of the SEM examination and chemical compositions were reported earlier (Chou et al., 1993). The samples and laboratory numbers are listed in Table 1.

X-ray diffraction analysis using random powder bulk packs

All 12 samples were first analyzed as random powder bulk packs by XRD using Cu K-alpha radiation. About 3.5 g of a powder sample was weighted out and wet-ground in propanol for six minutes in a micronizing mill to $<5 \mu\text{m}$. The sample was then poured into a beaker and dried in an oven at 75°C. Upon drying, the powder was packed in a sample holder ready for X-ray scanning. The XRD patterns of the twelve samples of boiler deposits were determined this way (Figure 3a-3f).

Other sample preparation methods

To eliminate some overlapping peaks on the XRD patterns, we tried to selectively dissolve some minerals and magnetically fractionate others. Of the 12 samples, 4 were chosen to be examined as oriented slides and re-examined in random powder bulk pack after a water washing process to remove anhydrite. Two samples were subjected to magnetic separation. The less magnetically susceptible fraction was examined as random powder bulk pack (tail fraction) and the more magnetically susceptible fraction was prepared as a smeared slide (magnetic fraction).

Table 1. Samples

Sample	Description	Chem. Anal. No.	XRD Lab No.
WR5			
-1a	Outer portion	C32825	3463A
-1b	Inner portion	C32826	3463B
WR5			
-2a	Outer portion	C32827	3463C
-2b	Inner portion	C32828	3463D
WR5			
-3a	Outer portion	C32829	3463E
-3b	Inner portion	C32830	3463F
WR5			
-4a	Outer portion, brown	C32831	3463G
-4b	Outer portion, red	C32832	3463H
WR5			
-5a	Outer portion	C32833	3463I
-5b	Inner portion	C32834	3463J
WR5			
-6a	Outer, brown	C32835	3463K
-6b	Inner, gray	C32836	3463L

Oriented slides

In order to distinguish layered silicates and/or minerals with well developed cleavage from other mineral phases, samples WR5-1a (3463A), -3b (3463F), -4b (3463H), and -6b (3463L) were selected to make oriented slides with $<1\ \mu\text{m}$ and $<4\ \mu\text{m}$ particles, respectively. These four samples represent the full range of variation found in the set of 12. The samples were prepared according to the following procedures: put about 5 g powder samples ($<150\ \mu\text{m}$ particles) in 100 ml distilled water; disperse ultrasonically for 1 minute; extract the fluid in the top 1 cm after the sample has settled for 12 minutes for $<4\ \mu\text{m}$ size fraction and 3 hours 10 minutes for $<1\ \mu\text{m}$ size fraction, respectively; put the fluid on a glass slide with an eye dropper, then let the slides dry at room temperature. The dried fine-particle aggregate will be the oriented sample. The XRD pattern of the oriented slide is dominated by gypsum peaks, indicating that anhydrite was dissolved in water and re-crystallized on the slide as gypsum. To observe other minerals, further steps (water washing) were applied to these

samples to remove anhydrite.

Water washing to remove anhydrite

The water washing procedures are as follows: transfer about 3 g of powder sample ($<5\ \mu\text{m}$) to a jar (700 mL) and fill the jar with distilled water, centrifuge the content to settle the undissolved material, pour off the clear solution, refill with distilled water, and repeat these steps 3 times. Monitoring slides were made from the clear solution to check the wash effect. The first two wash solutions crystallized gypsum on the slides, but the third was clear and its XRD pattern showed only the background typical of the amorphous glass of which the slide was made. This indicates that anhydrite is removed by three washing steps. After the water wash, the sample was re-examined as a random powder bulk pack. The washing procedure simplified the XRD patterns for the random powder bulk packs allowing unambiguous identification of hematite and feldspar, and, also, confirmed the anhydrite interpretation.

Figure 4a shows XRD patterns of sample WR5-4b (3463H) before and after water washing. This sample has a high CaO (20.04%) and SO_3 (20.95%) contents. The unwashed sample shows strong anhydrite peaks, which are absent in the washed sample.

Figure 4b shows XRD patterns of sample of WR5-6b (3463L) before and after water washing. This sample has a high Fe_2O_3 (12.1%) and Al_2O_3 (23.03%) contents. The washed sample shows clearly hematite, mullite, quartz and cristobalite peaks.

Magnetic component separation

To reduce the interference between hematite and mullite and confirm the existence of hematite, samples WR5-3b (3463F) and WR5-6b (3463L) were subjected to separation of a magnetic component using a Frantz Isodynamic Magnetic Separator. A sample (about 5 g) was dispersed in 500 mL distilled water. Then, the fluid was circulated through 1 ampere (D.C.) magnetic field in the magnetic separator for 1 hour. A fraction of higher magnetic susceptibility (magnetic portion) and a fraction of lower magnetic susceptibility (tail portion) were collected. After the separation, both portions were water washed, as described above. The tail portion was enough to make a bulk pack sample, whereas the magnetic portion was only enough for a smeared slide. The XRD patterns from both the tail and the magnetic portion are not as good as expected. Though most hematite is in the magnetic portion, the tail portion still contains a little and the magnetic portion also contains other minerals such as mullite. Apparently, hematite and other minerals are aggregated together and the magnetic field (1 ampere) is strong enough to pull the particles containing hematite and mullite into the magnetic portion. On

the other hand, the magnetic field is too weak, or the operation time (1 hour) is too short, or the hematite and mullite are intergrown on a scale too fine to clean out all the hematite from the tail portion.

Effect of composite gases on metals at various temperatures

The purpose of these experiments is to define a set of parameters that outline corrosion effects on metals under simulated boiler conditions. Three variables are considered: HCl concentration, length of exposure time, and temperature under isothermal conditions.

Evaluation of corrosion for any metal is dependent on the length of a particular experimental run. The experiments are run at three different temperatures (100°C, 200°C, and 600°C). The temperature of 600°C is chosen because it simulates a common superheater temperature. The 100°C temperature is chosen to determine the interaction of water, as it condenses or evaporates, with metals on the corrosion rate. Therefore, for the 100°C run, water vapor is introduced to the samples by passing nitrogen gas first through a water bath then to the furnace.

The rate of corrosion is evaluated by weight gain or loss per unit of time. The furnace design is shown in a previous report (Figure 2 of Chou et al., 1992). Experiments were conducted using two composite gases; one contains 0.2% HCl and the other no HCl.

RESULTS AND DISCUSSION

HCl evolution from coal during temperature-programmed pyrolysis

Results of pyrolysis experiments for HCl evolution from coal IBC-109 (1 g) are shown in Figure 1. A typical profile obtained about eight months ago (9/10/92) is represented by profile C. It shows a smooth peak at 445°C and, although the shoulder above 600°C is higher than the background in the temperature below 300°C, there is no peak at 600°C. Profile D has a low intensity, because it was obtained on March 3, 1993 when the filament source in the QGA was deteriorated. Profiles B and A are obtained after a new filament was replaced. Profile B shows a slight indication of increasing HCl intensity at 600°C, and profile A shows a clear peak at 600°C. This series of profiles indicates that the 600°C peak is detected only when the QGA is in its best condition with a high sensitivity.

There are two forms of chlorine in Illinois coals: most of the

chlorine occurs as chloride ions adsorbed on the inner walls of pores, the rest of chlorine is in the form of Na^+Cl^- dissolved in moisture (Chou, 1991). To determine the behavior of NaCl during coal pyrolysis, two pyrolysis tests on mixtures of coal + NaCl were conducted (Figure 2). In the first test, 11 mg of solid NaCl was placed with coal in a pyrolysis vessel, and the profile shows an increase of HCl evolution above 700°C. In the second test, coal was spiked with NaCl solution (25 mg NaCl), and the sample was dried and subjected to a pyrolysis run. The results showed a new HCl evolution peak starting at 700°C and extending over 850°C, probably as a result of the reaction of NaCl with organic matter.

Boiler deposits

The XRD patterns of twelve samples (XRD analysis No. 3463A-L) were shown in Figures 1a-1f. Mineral phases were identified based on their XRD patterns and chemical compositions by X-ray fluorescence analysis (Chou et al., 1993). At least six mineral phases have been identified: quartz, cristobalite, mullite, anhydrite, hematite, and feldspar in most samples. Abundances of the mineral phases vary from sample to sample as indicated by the relative intensity of XRD peaks (Figure 3a-3f).

High-temperature albite seems to best fit the peaks found in WR5-1a (Figure 3a, 3463A). The feldspar in sample -3b (Figure 3c, 3463F) and -6b (Figure 3f, 3463L) matches the pattern for oligoclase. However, there may be more than one mineral in the feldspar group present in these and other samples.

Mullite is absent in WR5-4b (3463H) but present in other samples; cristobalite is at its maximum in WR5-6b (3463L) but is absent in WR5-4b; it seems that cristobalite is inversely proportional to quartz in amount; WR5-3a (3463E) and -3b (3463F) have more hematite than others; -4b has more anhydrite than any of the 12 samples. Because WR5-4a (3463G) and -4b (3463H) were sampled in the reheater area of the boiler and others were from the superheater area, the reheater area may favor anhydrite deposition and the superheater area favor mullite and cristobalite.

Effects of composite gases with 0.2% HCl and with no HCl on corrosion of metals

Six metals listed below were selected for tests:

<u>AISI ID</u>	<u>Composition</u>
C1010	8-13% C, 0.3-0.6% Mn
C1018	15-20% C, 0.6-0.9% Mn

F11	1.25% Cr, 0.5% Mo, LC
F22	2.25% Cr, 1% Mo, LC
310SS	25% Cr, 21% Ni
Alloy 800	21% Cr, 31% Ni

Experiments with a composite gas containing 0.2% HCl. The composite gas is composed of 0.2% HCl, 0.2% SO₂, 4.0% O₂, 14.0% CO₂, and 81.6% N₂. Experiments were conducted at three different temperatures: 600°C, 200°C, and 100°C. Figure 5a shows the weight change of six metals at 600°C during the 400 hour runs. The three metals F11, F22, and C1010 have the greatest weight loss, metal C1010 has a less amount of weight loss, and high-Cr Alloy 800 and 310SS show no weight loss. The results indicate the material effect reflecting that chromium is an inhibitor of corrosion.

The next set of experiments was conducted at 200°C under otherwise similar conditions. The results are shown in Figure 5b. No significant corrosion is observed. Different degrees of corrosion between 600°C and 200°C indicate a strong temperature effect on metal corrosion.

The third set of experiments was conducted at 100°C and with the addition of water vapor (Figure 5c). The Cr-Ni alloys show essentially no weight loss. The other four metals (F11, C1010, F22, and C1018) show different degrees of weight loss and the amounts of weight loss are smaller than those in the case of 600°C. Also during the experiments at 100°C, the weight loss occurs after the metals were exposed to the damp gas for 150 hours. In contrast, the weight loss starts at the beginning the run in the case of the 600°C test.

The rate of weight loss may be obtained by regression analysis of the experimental results, using the equation:

$$L \text{ (weight loss)} = \text{Corrosion rate} \times \text{Time}^{1/2}.$$

The equations for the four metals which show weight loss at 600°C are:

$$\text{C1018} \quad L = 1.71t^{1/2}$$

$$\text{F22} \quad L = 2.87t^{1/2}$$

$$\text{C1010} \quad L = 2.96t^{1/2}$$

$$\text{F11} \quad L = 3.15t^{1/2}$$

The R² values of the four equations are 0.98, 0.98, 0.94, and 0.97, respectively. Figure 6a shows the rate of

corrosion for metal F22. The linear relationship between weight and $t^{1/2}$ demonstrates a first order reaction mechanism. The corrosion rate for the metals increases in the order: C1018 < F22 ≤ C1010 < F11.

The rate of weight loss at 100°C in a damp gas with 0.2% HCl for the four metals can be expressed by the following equations obtained by regression analysis:

$$\text{C1018} \quad L = 0.22 \exp (0.20t^{1/2})$$

$$\text{C1010} \quad L = 0.37 \exp (0.32t^{1/2})$$

$$\text{F11} \quad L = 0.03 \exp (0.37t^{1/2})$$

$$\text{F22} \quad L = 0.01 \exp (0.36t^{1/2})$$

The R^2 values of the four equations are 0.91, 0.95, 0.95, and 0.96, respectively. Figure 6b show the rate of corrosion for metal F22. The corrosion rate increases rapidly after 150 hours. Such exponential relationship between weight loss and $t^{1/2}$ indicates a second order reaction mechanism.

Experiments with a composite gas containing no HCl. The composite gas is composed of 0.2% SO₂, 4.0% O₂, 14.0% CO₂, and 81.8% N₂. Experiments have been completed at two different temperatures: 600°C and 200°C. Figure 7 shows the weight change of six metal samples at 600°C. Metal F22 is the only metal showing significant weight loss (27% at the end of the 400 hour run). Metal F11 shows significant weight gain, 25% at the end of the run, indicating it is oxidized in the composite gas. Metals C1010 and C1018 show a moderate weight gain of 4%. Metals 310SS and alloy 800 (high Cr alloy) show no weight change.

The three metals that show exponential weight change have the following corrosion rate relations:

$$\text{C1018 (weight gain)} \quad L = 0.20 \exp (0.18t^{1/2})$$

$$\text{F11 (weight gain)} \quad L = 0.74 \exp (0.18t^{1/2})$$

$$\text{F22 (weight loss)} \quad L = 0.76 \exp (0.18t^{1/2})$$

The R^2 values of the three equations are 0.98, 0.97, and 0.97, respectively. Thus, the corrosion at 600°C with no HCl in the gas is a second order reaction, different from the first order reaction which occurs at 600°C with the presence of HCl in the gas. The oxidation on the surface of metals C1018 and F11 may act as a protective coating against further corrosion. The similar experiments using composite

gas without HCl were conducted at 200°C. No significant weight change was observed for all six metals (Figure 7).

CONCLUSIONS AND RECOMMENDATIONS

1. Using a new filament source in the QGA significantly improved the sensitivity of HCl detection. New experiments on Illinois coal IBC-109 (0.42% Cl on dry basis) showed that in addition to the major peak on the HCl evolution profile between 300°C and 550°C with a peak maximum at 445°C, the HCl release continued to 700°C with a small peak 600°C. It may result from the reaction of a less volatile chlorine species in coal with the organic matter.

Chou (1991) indicated that there are two forms of chlorine in Illinois coals: most of the chlorine occurs as chloride ions adsorbed on inner walls of the pores, and the rest of the chlorine is in the form of Na^+Cl^- dissolved in moisture. To test the release of NaCl during pyrolysis, a mixture of coal spiked with NaCl solution showed a new HCl evolution peak starting at 700°C and extending over 850°C, probably as a result of the reaction of NaCl with organic matter. HCl evolution profiles of raw coal do not show a high temperature peak above 700°C, indicating that only a small fraction of chlorine in coal occurs in the form of NaCl.

2. With various sample preparation techniques, six minerals have been unambiguously identified in a set of boiler deposit samples. Relative abundances of major minerals in boiler deposits may be estimated using the peaks listed below: mullite (2θ , 16.4°), quartz (20.8°, 50.14°), cristobalite (21.9°), anhydrite (25.45°), hematite (49.5°), feldspar (51.55°).

Further sample treatments will be carried out to improve XRD analysis for studying the minerals in boiler deposits: (1) weak acid dissolution and residue separation, (2) further magnetic component separation using a weak magnetic field for collecting the magnetic portion and a strong magnetic field/long time operation for the clean tail portion; (3) attempts to account for phosphorous in the chemical analysis by identifying a P-bearing phase. Thin sections are being prepared to examine petrographic textures.

3. Corrosion of six metals in a composite gas with 0.2% HCl was tested at 600°C, 200°C, and at 100°C with moisture. Similar tests were conducted with a composite gas containing no HCl at 600°C and 200°C. The results show several important factors of metal corrosion. First,

high-Cr alloys are more corrosion resistant than Cr-Mo steels and C-Mn steels. Second, tests conducted at 600°C show considerably higher corrosion than at 200°C. Third, significant corrosion is observed when the metals were exposed to a damp composite gas containing 0.2% HCl, reflecting damaging chloride condensate on metal surfaces. The presence or absence of HCl in the composite gases affects the behavior of metal corrosion at 600°C. Metal F22 shows a greater degree of weight loss with the presence of HCl. Metal F11 shows a significant corrosion (weight loss) in a composite gas with HCl, but shows oxidation (weight gain) in a composite gas without HCl. Both metals C1010 and C1018 show significant corrosion (weight loss) in a composite gas containing HCl, but only slight oxidation (weight gain) in a composite gas without HCl. Further corrosion tests using 0.01% HCl in a composite gas, equivalent to 0.04% chlorine in raw coal, are underway.

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Figure 1. The HCl evolution profiles during coal pyrolysis, showing a second peak at 600°C when the sensitivity of HCl detection by QGA was improved (case A and B).

Figure 2. The release of HCl during pyrolysis of coal IBC-109 (1 g) first with NaCl (11 mg) and second spiked with NaCl solution.

Figure 3a. XRD patterns of boiler deposits WR5-1a (3463A) and WR5-1b (3463B) by random powder bulk packs, showing the major phases identified quartz (q), cristobalite (Cr), mullite (m), feldspar (f), hematite (h), anhydrite (a).

Figure 3b. Similar to Figure 1a for sample WR5-2a (3463C) and WR5-2b (3463D).

Figure 3c. Similar to Figure 1a for sample WR5-3a (3463E) and WR5-3b (3463F).

Figure 3d. Similar to Figure 1a for sample WR5-4a (3463G) and WR5-4b (3463H). Note strong anhydrite peaks for WR5-4b, which is high in CaO (20.04%).

Figure 3e. Similar to Figure 1a for sample WR5-5a (3463I) and WR5-3b (3463J).

Figure 3f. Similar to Figure 1a for sample WR5-6a (3463K) and WR5-3b (3463L).

Figure 4a. XRD patterns of sample WR5-4b before and after water washing (XRD Lab #3463H and 3463H-washed).

Figure 4a. XRD patterns of sample WR5-6b before and after water washing (XRD Lab #3463L and 3463L-washed).

Figure 5a. Weight loss vs. time for six metals which are exposed to a composite gas (0.2% HCl, 0.2% SO₂, 14% CO₂, 4% O₂, and 81.6% N₂) at 600°C for 400 hours.

Figure 5b. Similar to Figure 5a, but at 200°C.

Figure 5c. Similar to Figure 8a, but at 100°C and in a damp gas. Note significant weight loss for 4 of the metals after exposure to the composite gas for 150 hours.

Figure 6a. The corrosion rate showing first order relation between weight loss and time ($t_{1/2}$) when metal F22 was exposed to a composite gas containing 0.2% HCl at 600°C.

Figure 6b The corrosion rate as indicated by an exponential relation between weight loss and time ($t_{1/2}$) when metal F22 was exposed to a damp gas with 0.2% HCl at 100°C. The corrosion rate increased rapidly after 150 hours.

Figure 7a. Weight change of six metals which are exposed to a composite gas with no HCl (0.2% SO₂, 4.0% O₂, 14.0% CO₂, and 81.8% N₂) at 600°C.

Figure 7b. Similar to Figure 7a, but at 200°C.

PROJECT MANAGEMENT REPORT
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Project Manager: K.K. Ho, Illinois Clean Coal
Institute

COMMENTS

The project has proceeded well. The expenditures are
consistent with the projected amounts.

EXPENDITURES - EXHIBIT B

Projected and Estimated Actual Expenditures by Quarter

Quarter (cumulative by quarter)	Types of Cost	Direct Labor	Materials and Supplies	Travel	Major Equipment	Other Direct Costs	Indirect Costs	Total
Sept. 1, 1992 to Nov. 30, 1992	Projected	4,500	600	0	0	8,000	938	14,038
	Est. Actual	4,500	320	0	0	7,938	903	13,661
Sept. 1, 1992 to Feb. 28, 1993	Projected	9,000	1,200	250	400	18,000	2,140	30,990
	Est. Actual	9,000	1,307	251	0	17,404	2,051	30,013
Sept. 1, 1992 to May 31, 1993	Projected	13,500	1,800	250	400	28,000	3,278	47,228
	Est. Actual	13,975	1,758	251	391	26,842	3,170	46,387
Sept. 1, 1992 to Aug. 31, 1993	Projected	18,344	2,400	500	400	39,753	4,650	66,047
	Est. Actual							

COSTS BY QUARTER

Behavior of Sulfur and Chlorine in Coal During Combustion
and Boiler Corrosion

Months and Quarters

O = Projected Expenditures -----

■ = Actual Expenditures _____

Total CRSC Award \$ 66,047

Schedule of major milestones

September 1, 1992 - August 31, 1993

Milestones:

- A. Employ research assistants
- B. Subcontract WKU
- C. Request and receive samples from utility boilers
- D. Analyze boiler deposits and conduct boiler corrosion studies (Task 3, ISGS)
- E. Perform laboratory corrosion experiments with simulated combustion gases (Task 4, WKU)
- F. Perform combustion tests with TGA and DTA systems with FTIR spectroscopy (Task 5, WKU)
- G. Perform combustion tests for coal with additives with temperature-programmed pyrolysis coupled with quadrupole gas analysis and assess remedial measures (Task 6, ISGS)
- H. Prepare and submit technical reports
- I. Prepare and submit project management reports

**DATE
FILMED**
10 / 7 / 93