Project Title: CHLORINE IN COAL AND ITS RELATIONSHIP WITH BOILER CORROSION

ABSTRACT

Literature and use-history data indicate that high-Cl Illinois coals do not cause boiler corrosion while extensive data developed by the British correlate corrosion with chlorine content and other parameters related to the coal and boiler. The differences in corrosivity in coals may be due to coal properties, to coal blending, or to boiler parameters. The goals of this study focused on coal properties. The goals were to determine the forms of Cl, the characteristics of Cl evolution, and the ash composition of Illinois and British coals; to compare these parameters in Illinois and British coals; and to establish relationships, if any, between these parameters and the corrosivity of the coal.

The results of Cl analyses indicate that the Cl in coal exists in ionic forms, including small amounts of solid NaCl. When heated under air, Illinois coals released hydrogen chloride gas, with maximum evolution occurring between 425 to 475°C, whereas, for British coals, the maximum evolution occurred between 210 and 280°C. Ash analyses indicate that three of the four British coals contain a higher level of soluble sodium related to soluble potassium. A similar relationship was exhibited for the relative corrosion indices (Ic) calculated according to Borio et al. The Ic values for the British coals were 53.94, 15.05, 292.92, and 51.42; for the Illinois coals they were 17.04, 17.50, 11.62, 10.90, and 10.55. Caution should be exercised in interpreting corrosion indices reported in this study since they constitute an extrapolation outside their original correlation. This is because the soluble Na₂O measured in this study was higher than the maximum values measured by Borio et al.
EXECUTIVE SUMMARY

The question of whether or not chlorine in Illinois coals really causes corrosion has had an impact on the marketability of the coal. Literature and use history have suggested that some high-chlorine Illinois coals do not cause boiler corrosion. On the other hand, extensive data developed by the British correlate corrosion with chlorine content, other parameters of coals, and the type of boiler. Although methods such as blending coals of low and high chlorine content have been used in Britain to control corrosion, the presence of chlorine in Illinois coals, because of the extensive British data and other literature, has been a concern for the end users and boiler manufacturers. Market concerns should find relief and the use of Illinois coals should increase, if it can be shown scientifically that Illinois coals do not cause boiler corrosion. Such scientific study should also explain differences in corrosivity between British and Illinois coals. The differences in the corrosivity of coals may be due to properties of the coal, to coal blends, or to parameters of the boilers in which they are burned. This study focused on the effect of coal properties on corrosivity. The goals of this project were to determine the forms of Cl, the evolution characteristics of Cl, and the ash composition of Illinois and British coals; to compare these characteristics in Illinois and British coals; and to establish the relationship, if any, between these parameters and the corrosivity of the coal.

This was a cooperative effort among the ISGS; RU, Houston, TX; UK, Lexington, KY; and WKU, Bowling Green, KY.

Specific objectives were:

A. To determine the types of chlorine- and sulfur-containing compounds in coals by an X-ray Absorption Near Edge Spectroscopic (XANES) method and to determine the total chlorine, total sulfur, and inorganic forms of sulfur by ASTM methods.

B. To examine the chemical composition of coals and to predict the coal corrosion potential based on the ash composition of coals.

C. To compare, using XANES, the distribution and chemical state or states of chlorine in coals which have been reported to have different corrosion potentials.

D. To conduct thermogravimetry with Fourier transform infrared (TGA-FTIR) spectrometry and to examine the evolution characteristics of chlorine-containing compounds in coals under pyrolysis and oxidation conditions.
E. To conduct step-wise pyrolysis while using multi-surface matrix isolation-Fourier transform infrared (MI-FTIR) analyses and to examine the behavior during pyrolysis of heteroatoms, especially Cl compounds, that are present in coal.

F. To establish the relationships, if any, among the forms of chlorine in coals, the evolution characteristics of chlorine in coals, the chemical composition of coals, and the corrosion potential of the coals.

Both destructive temperature-programmed thermogravimetry with fourier transform infrared (TGA-FTIR) and non-destructive X-ray absorption near-edge structure (XANES) techniques were used to examine the forms and the evolution profiles of chlorine-containing compounds in coals. The results from XANES analysis indicate that chlorine in coal exists in ionic forms including small amounts of solid sodium chloride. The HCl evolution profiles obtained from oxidation of the four British coal samples indicate that British coals release HCl gas at temperatures from 150 to 450°C with the maximum HCl evolution temperature between 210°C and 280°C. On the other hand, Illinois coals release HCl gas at temperatures from 150 to 600°C with the maximum HCl evolution temperature between 410°C and 450°C.

The results of ash analyses indicate that British coals contain a higher level of soluble sodium with respect to soluble potassium. The soluble Na-to-K ratios calculated as oxides on a dry coal basis (Na₂O/K₂O) for the British coals were 9.53, 1.86, 56.67, and 9.00, whereas, the ratios for the Illinois coals were 2.20, 2.31, 1.16, 1.02, and 0.92. A similar relationship was exhibited for the relative corrosion indices (I₉) calculated according to Borio et al. The I₉ values for the British coals were 53.94, 15.05, 292.92, and 51.42; for the Illinois coals, the values were 17.04, 17.50, 11.62, 10.90, and 10.55. However, the soluble Na₂O measured in this study were higher than the maximum values measured in the study of Borio et al. and caution should be exercised in interpreting those results because they constitute an extrapolation outside their original correlation.

Overall, the results indicate that the Cl ions in the Illinois coals are more strongly bound than those in the British coals, and suggests that the way in which Cl ions are associated in Illinois coals is different from that in the British coals. This difference, plus the difference in the ratios of the acid-soluble alkali metals, may contribute to the corrosivity differences of the two coal types.
GOALS AND OBJECTIVES

The goals of this study were (1) to determine the forms of Cl, the evolution characteristics of Cl, and the ash composition of Illinois and British coals; (2) to compare these characteristics in Illinois and British coals; and (3) to establish the relationships, if any, between these characteristics and the corrosivity of the coal.

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A. To determine the types of chlorine- and sulfur-containing compounds in coals by an X-ray Absorption Near Edge Spectroscopic (XANES) method and to determine the total chlorine, total sulfur, and inorganic forms of sulfur by ASTM methods.

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INTRODUCTION AND BACKGROUND

Literature and use-history data have suggested that high-Cl Illinois coal does not cause boiler corrosion (Hamling and Kaegi, 1984, Wright et al, 1994, Abbott et al, 1994) while extensive data have been developed by the British which
attribute the rate of corrosion to the Cl content as well as other parameters of coal, such as alkaline content, and coal boiler materials (Reid, 1971, Gibb, 1983, Meadowcroft and manning, 1983, Raask, 1985, Latham et al, 1991, Oakey et al, 1991, and Bakker et al, 1990). Although methods such as blending coals of low and high chlorine content have been used in Britain to control corrosion, the presence of chlorine in Illinois coals, because of the extensive British data and other literature, has been a concern for the end users and boiler manufacturers. Market concerns should find relief and the use of Illinois coals should increase, if it can be shown scientifically that Illinois coals do not cause boiler corrosion. Such scientific study should also explain differences in corrosivity between British and Illinois coals.

A study of the materials for future fossil fuel fired steam generators was conducted by Bakker et al (1990). They indicated that superheater corrosion, in general, can be attributed to five factors. These factors are (1) the amount of liquid sulfate deposited, (2) the sulfur content of the coal, (3) the Cl content of the coal, (4) the temperature of the superheater tube wall, and (5) the chemical composition of the alloy. They also indicated that superheater corrosion was most common, in the U.K., where it was attributed to the high level of Cl in the British coals. The total Cl content in coal has been used in Great Britain for predicting the corrosivity of a coal. It has been indicated, however, that high-Cl Illinois coals do not create the serious corrosion problems which the British coals have shown during combustion. Since these two studies involve two different coals and two different boilers, it is not clear whether the differences in observed corrosion were due to the properties of the coals, or to boiler parameters. For example, the chemical forms of Cl, their behavior during combustion, and their interaction with sulfur and other components of coal may play roles in the corrosivity of a coal with high Cl content. Also, boiler-tube corrosion may be affected by the temperatures of the tubes, the materials from which the boiler tubes were constructed, properties of the coal, and whether a coal that produced corrosion was blended with one that did not.

This study focused on the fundamental effects of Cl and other elements in coals with different corrosion potentials.
EXPERIMENTAL

Task 1. Prepare whole coal samples and Cl-containing standard samples (ISGS).

Five Illinois coals and four British coals were collected for this project. Five pounds of coal, ground to -200 mesh (C-33068) was obtained from Dr. Anthony G. Fonseca of the Consolidated Coal Company. Four additional Illinois Basin coals (C-33873, C-33874, C33875, and C-33876) were obtained from Dr. I. Demir. These 60-mesh sample were approximately 300 g each. All samples were split to amounts needed for analysis and preserved in the facilities of the Coal Sample Bank Program.

Four high-Cl coals were obtained from Great Britain. Selection was based on availability and upon the most frequently used and studied coals. Sampling was accomplished with the assistance of the Coal Research Establishment Technical Services in Great Britain. Two coal sample (C-33499 and C-33500) were obtained from mine. The other two samples (C-33501 and C-33502) were purchased from the CRE Technical Service Coal Bank. These samples were ground to 60 mesh, split to sizes needed for analysis and preserved in the facilities of the Coal Sample Bank Program.

Task 2. Determine the forms of Cl and sulfur in coals by XANES and total Cl, total sulfur, and inorganic forms of sulfur by ASTM analyses. (ISGS/UK)

Total Cl in coal was determined with a Leco model Cl-350 chlorine analyzer. Carbon, hydrogen, and nitrogen were determined with a Leco model CHN-600 carbon, hydrogen, nitrogen analyzer. Proximate analysis, total sulfur, and inorganic forms of sulfur were completed using ASTM procedures (D-3172, D-4239, and D-2492, ASTM 1991). The forms of Cl was determined by XANES analysis.

Task 3. Conduct a complete chemical analysis and examine mineral matter, major, minor, and trace elements in coals with different corrosion potential (ISGS).

Ashing of coals and determination of coal ash composition. Approximately 2 grams of coal was dried at 110°C for two hours to determine moisture content. Then, a separate coal sample was ashed at 750°C to determine the ash content. About 0.6 grams of coal ash was then blended with about 5.4 grams of 50% lithium metaborate/50% lithium tetraborate flux in a 95% Pt-5% Au crucible and fused in a furnace at 1000°C for 15 minutes.
This was followed by a short-cycle fusion in a Claisse Fluxer-Bis using a propane burner. After fusion, the fluxer automatically poured the molten mixture into a 30-mm diameter 95% Pt-5% Au mold in which a glass disk specimen was formed upon cooling. The specimen was analyzed using a Rigaku 3371 WDXRF spectrometer with an end-window rhodium X-ray tube. Concentrations of components in the coal ash were calculated by the computer which control the spectrometer, and which used calibration curves based on natural and artificial standards plus LaChance-Trail matrix correction coefficients.

**Determination of acid-soluble sodium and potassium in coal.**
Two grams of the coal sample, weighed to the nearest milligram, was placed in a 250-ml Erlenmeyer flask which contained 40 ml of 5% HCl solution. The flask was then fitted with an air-cooled condenser and the sample was digested for 16 hours at a gentle boil. The sample was then cooled, filtered through Whatman #40 filter paper, and washed at least four times with small amounts of distilled water. Next, the filtrate was diluted to 100 ml in a volumetric flask. Sodium and potassium were determined using an atomic absorption flame spectrophotometer.

**Task 4.** Compare, using XANES, the distribution and chemical state or states of Cl in coals which have been reported to behave differently with respect to corrosion problems during combustion (ISGS/UK).

The XANES results obtained in Task 2 were examined, and the results from the Illinois and British coals were compared.

**Task 5.** Analyze the evolution profile of Cl-containing compounds in coals under pyrolysis and oxidation conditions (ISGS/WKU).

Temperature-programmed thermogravimetry, in conjunction with Fourier transform infrared spectrometer (TGA-FTIR), was used to obtain the characteristics of the thermal evolution of HCl gas from the coals under both oxidation and pyrolysis conditions. Simultaneous TGA/FTIR techniques were based on a combined analytical method in which thermogravimetry (TGA) was used in conjunction with Fourier transform infrared spectroscopy (FTIR). By using the combined TGA/FTIR instrumental system, the volatile species produced in a Dupont-951 TGA during pyrolysis or combustion of a coal sample were analyzed by a Perkin Elmer-1650 FTIR spectrometer. The system was able to continuously measure the mass change of the coal sample with temperature increasing at a heating rate of 10°C/min. The system was also able to identify qualitatively and determine quantitatively the individual
gaseous species emitted during coal pyrolysis or combustion. The sample chamber in the TGA furnace is connected to the 100x24 mm gas cell in the FTIR spectrometer through a teflon tube. Both the teflon line and gas cell can be heated up to 250°C by heating coils, and the temperature of the gas cell can be controlled continuously. The time lag in the flow of evolved gas between the sample chamber and the gas cell is one minute with a flow of oxygen-free nitrogen of 50 ml/min during pyrolysis or with a flow of air of 50 ml/min during oxidation. The FTIR spectrum can be collected automatically every minute, through the temperature range of 80 to 800°C, by using the LabScan software. Data were collected from the temperature range of 150°C to 600°C for oxidation and 200°C to 500°C for pyrolysis.

A sample size of 300 mg was used for all the TGA/FTIR experiments. The evolution profiles of HCl under oxidation and pyrolysis condition were examined with respect to temperatures.

Task 6. Examine the behavior of heteroatoms, especially Cl compounds, that are present in coal during pyrolysis conditions (ISGS/RU).

Pyrolysis with multi-surface matrix isolation-Fourier transform infrared spectrometer (MI-FTIR) was conducted using a nitrogen atmosphere for one Illinois coal and one British coal. Isothermal flash pyrolysis analysis was not performed due to the limitation of precise control of the shortest heating time and the amount of volatiles needed for detection by FTIR. This part of the research was replaced by additional tests of acid-soluble alkali metal determination (see task 3).

Task 7. Establish the relationship, if any, among the evolution characteristics of Cl in coals, the forms of Cl in coals, the chemical components of coals, and the corrosion problems of coals during coal combustion (ISGS/RU/UK).

The analyses for forms of Cl by XANES from task 2, the chemical composition of coals from task 3, and the evolution behavior of Cl-containing compounds in these two coals from task 4 & 5 were evaluated with respect to their corrosion potentials.
RESULTS AND DISCUSSION

CHEMICAL ANALYSES

The results on forms of sulfur analyses for two Illinois and three British coal samples by XANES method are shown in Table 1. The data from the proximate, ultimate, and sulfur forms for all nine coals by ASTM method are listed in Table 2. The Cl content and calorific value are also presented. The ash composition and acid-soluble alkali metals analyses on four British and five Illinois coals are also listed in Table 2.

Table 1: Forms of sulfur (wt%) in coals by XANES analysis.

<table>
<thead>
<tr>
<th>Forms of Sulfur</th>
<th>British coals</th>
<th>Illinois coals</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C-33499</td>
<td>C-33500</td>
</tr>
<tr>
<td>Pyritic S</td>
<td>1.00</td>
<td>0.38</td>
</tr>
<tr>
<td>Sulfide</td>
<td>0.24</td>
<td>0.14</td>
</tr>
<tr>
<td>Thioph. S</td>
<td>0.75</td>
<td>0.72</td>
</tr>
<tr>
<td>Sulfoxide</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Sulfate</td>
<td>0.04</td>
<td>0.01</td>
</tr>
<tr>
<td>Sulfone</td>
<td>ND</td>
<td>ND</td>
</tr>
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</table>

ND: Not detectable
### Table 2: Chemical analysis of coal and coal ash and calculations of corrosion potential

<table>
<thead>
<tr>
<th>Proximate and other standard analysis of coal samples</th>
<th>C-33499</th>
<th>C-33500</th>
<th>C-33501</th>
<th>C-33502</th>
<th>C-33068</th>
<th>C-33873</th>
<th>C-33874</th>
<th>C-33875</th>
<th>C-33876</th>
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<td>Moist</td>
<td>4.55</td>
<td>4.16</td>
<td>8.84</td>
<td>3.21</td>
<td>3.52</td>
<td>14.97</td>
<td>7.86</td>
<td>9.31</td>
<td>6.61</td>
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<td>Vol</td>
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<td>29.20</td>
<td>39.10</td>
<td>35.54</td>
<td>35.17</td>
<td>40.19</td>
<td>38.50</td>
<td>31.89</td>
<td>36.06</td>
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<tr>
<td>Fe/C</td>
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<td>48.66</td>
<td>58.68</td>
<td>61.33</td>
<td>59.37</td>
<td>50.23</td>
<td>50.75</td>
<td>52.27</td>
<td>55.98</td>
</tr>
<tr>
<td>H</td>
<td>4.64</td>
<td>4.15</td>
<td>4.90</td>
<td>5.09</td>
<td>4.97</td>
<td>4.96</td>
<td>4.83</td>
<td>4.59</td>
<td>5.01</td>
</tr>
<tr>
<td>C</td>
<td>70.07</td>
<td>64.56</td>
<td>79.57</td>
<td>82.36</td>
<td>77.70</td>
<td>70.16</td>
<td>71.37</td>
<td>68.60</td>
<td>74.49</td>
</tr>
<tr>
<td>N</td>
<td>1.51</td>
<td>1.43</td>
<td>1.62</td>
<td>1.75</td>
<td>1.71</td>
<td>1.26</td>
<td>1.24</td>
<td>1.38</td>
<td>1.47</td>
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<tr>
<td>TotS</td>
<td>2.04</td>
<td>1.26</td>
<td>0.86</td>
<td>0.91</td>
<td>0.97</td>
<td>4.42</td>
<td>3.66</td>
<td>1.00</td>
<td>2.90</td>
</tr>
<tr>
<td>OrgS</td>
<td>1.13</td>
<td>0.82</td>
<td>0.71</td>
<td>0.66</td>
<td>0.58</td>
<td>2.96</td>
<td>2.29</td>
<td>0.53</td>
<td>1.76</td>
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<tr>
<td>SuS</td>
<td>0.05</td>
<td>0.03</td>
<td>0.04</td>
<td>0.02</td>
<td>0.03</td>
<td>0.12</td>
<td>0.14</td>
<td>0.10</td>
<td>0.14</td>
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<td>FYRS</td>
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<td>0.99</td>
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<td>TCL</td>
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<td>1.15</td>
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<td>0.22</td>
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<td>0.45</td>
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<td>11319</td>
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<td>14383</td>
<td>13603</td>
<td>12653</td>
<td>12685</td>
<td>12120</td>
<td>13238</td>
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</tbody>
</table>

### Major oxides in coal ash (dry coal basis)

<table>
<thead>
<tr>
<th></th>
<th>C-33499</th>
<th>C-33500</th>
<th>C-33501</th>
<th>C-33502</th>
<th>C-33068</th>
<th>C-33873</th>
<th>C-33874</th>
<th>C-33875</th>
<th>C-33876</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>7.58</td>
<td>12.14</td>
<td>0.61</td>
<td>1.03</td>
<td>2.79</td>
<td>4.42</td>
<td>4.74</td>
<td>9.52</td>
<td>4.05</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>3.65</td>
<td>5.97</td>
<td>0.50</td>
<td>0.79</td>
<td>1.26</td>
<td>1.76</td>
<td>1.89</td>
<td>4.03</td>
<td>1.74</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>1.74</td>
<td>1.50</td>
<td>0.31</td>
<td>0.86</td>
<td>0.60</td>
<td>2.16</td>
<td>2.05</td>
<td>1.00</td>
<td>1.61</td>
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<tr>
<td>CaO</td>
<td>0.59</td>
<td>0.40</td>
<td>0.68</td>
<td>0.31</td>
<td>0.12</td>
<td>0.31</td>
<td>0.43</td>
<td>0.37</td>
<td>0.21</td>
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<tr>
<td>MgO</td>
<td>0.22</td>
<td>0.40</td>
<td>0.06</td>
<td>0.08</td>
<td>0.06</td>
<td>0.10</td>
<td>0.09</td>
<td>0.19</td>
<td>0.08</td>
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<tr>
<td>K₂O</td>
<td>0.48</td>
<td>0.89</td>
<td>&lt;0.01</td>
<td>0.02</td>
<td>0.12</td>
<td>0.21</td>
<td>0.19</td>
<td>0.43</td>
<td>0.20</td>
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<tr>
<td>Na₂O</td>
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<td>0.31</td>
<td>0.34</td>
<td>0.10</td>
<td>0.12</td>
<td>0.18</td>
<td>0.66</td>
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<td>TiO₂</td>
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<td>0.03</td>
<td>0.02</td>
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<td>0.01</td>
<td>0.09</td>
<td>0.20</td>
<td>0.09</td>
</tr>
<tr>
<td>P₂O₅</td>
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<td>0.05</td>
<td>0.07</td>
<td>0.04</td>
<td>0.01</td>
<td>0.01</td>
<td>0.02</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>MnO</td>
<td>0.01</td>
<td>0.02</td>
<td>&lt;0.01</td>
<td>0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
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<tr>
<td>SO₃</td>
<td>0.48</td>
<td>0.25</td>
<td>0.75</td>
<td>0.10</td>
<td>&lt;0.01</td>
<td>0.11</td>
<td>0.28</td>
<td>0.29</td>
<td>0.08</td>
</tr>
</tbody>
</table>

### Acid soluble alkali metals in coal (dry coal basis) and coal relative corrosion index

| (Na₂O)ₘₐ | 0.162   | 0.197   | 0.340   | 0.072   | 0.112   | 0.180   | 0.050   | 0.130   | 0.062   |
| (K₂O)ₘₐ  | 0.017   | 0.106   | 0.006   | 0.008   | 0.051   | 0.078   | 0.043   | 0.128   | 0.067   |
| Na/K (mole)| 14.45   | 2.82    | 85.91   | 13.64   | 33.3    | 3.50    | 1.76    | 1.54    | 1.40    |
| Na₂O/K₂O(ₘₐ)| 9.53    | 1.86    | 56.67   | 9.00    | 2.20    | 2.31    | 1.16    | 1.02    | 0.92    |
| Iₐ       | 53.94   | 15.05   | 292.92  | 51.42   | 17.04   | 17.50   | 11.62   | 10.90   | 10.55   |

*as: acid-soluble*
FORMS OF CHLORINE IN COALS
- by X-ray Absorption Near-Edge Structure (XANES)

The XANES spectra of the British and Illinois coals are shown in Figure 1. Based on the XANES spectra of standard compounds (Huggins and Huffman, 1994), a strong broad peak at about 1 eV followed by a second, much weaker, broad peak at about 20 eV is indicative of an ionic form of Cl. XANES analysis is presently not able to differentiate between the types of positive counter ions that are associated with ionic chloride. However, the appearance of a sharp peak at 12.5 eV is indicative of solid sodium chloride. As seen in these XANES spectra, all of the coal samples contained ionic Cl. A small peak shown at 12.5 eV is indicative of the appearance of solid sodium chloride. Sodium chloride was observed in only two of the British coals and none of the Illinois coals.

![Graph showing XANES spectra for British and Illinois coals](image)

**Figure 1:** XANES spectra of three British coals and three Illinois coals
ASH COMPOSITION OF COALS

The study by Borio et al. (1969) showed that alkali metals, alkaline earths, iron, and sulfur were the most significant constituents relative to high temperature corrosion (Borio et al., 1969 and Meadowcroft, 1989). Because alkali metals generally comprise small portion of the coal, they are usually the most sensitive corrosion indicators. Alkali metal concentration, measured by an acid leaching process, was also found to give a better estimation of alkali metal concentration for reaction in forming molten alkali-iron-trisulfate, a corrosive complex. Certain relationships were developed by Borio et al (1969), in which the amount of acid soluble sodium and potassium (calculated as oxides) in the coal and the amount of calcium oxide and magnesiu oxide obtained as ash in coal were used to calculate the relative corrosion indices of coals (Eq. 1).

\[ I_c = 5.96 + 5.07 \frac{Na_2O}{K_2O} - 0.42(CaO + MgO) \quad (Borio \text{ et al.}, 1969) \]

(1)

In this study, the ratio on the amount of acid-soluble sodium to the amount of acid-soluble potassium, \((Na_2O/K_2O)_{as}\), as well as the relative corrosion indices, \(I_c\), were obtained according to the relationships developed by Borio et al (1969). The results (Table 2) indicate that, with the exception of one coal (C-33500), the weight ratios of \((Na_2O/K_2O)_{as}\) are higher for the British coals than for the Illinois coals. A similar relationship is indicated for the relative corrosion indices \(I_c\). The \(I_c\)'s are higher for those British coals than for the Illinois coals.

When applying current analysis data to the formula established by Borio et al (1969) for relative corrosion index, one should be very careful about interpreting the resulting values. This is because none of the coals analyzed by Borio et al (1969) had soluble sodium oxide in amounts greater than 0.1% on the dry coal basis, whereas, as indicated in Table 2, six of the nine coals analyzed in this investigation had soluble sodium oxide greater than 0.1%. The absolute values of \(I_c\) for the four coals should not be used in grading coal corrosion potential according to the framework defined by Borio et al (1969). The values, however, may give a relative measure on boiler corrosion that could derive from alkali metals and alkali-earth metals in coal.
THE EVOLUTION CHARACTERISTICS OF CHLORINE IN COALS
- by Temperature-Programmed Thermogravimetry with Fourier Transform Infrared (TGA-FTIR)

HCl evolution profiles during combustion-The HCl evolution profiles for the British coals and four Illinois coals determined by TGA-FTIR are presented in Figure 2. The results indicate that the coals release their Cl as HCl gas. British coals release this gas beginning at 150°C and ending at approximately 450°C. The maximum HCl evolution temperature occurs in a range from 210°C to 280°C. Illinois coals release HCl gas beginning at 150°C and ending at approximately 600°C. The maximum HCl evolution temperature occurs in a range from 410 to 450°C.

![Figure 2: The HCl evolution profiles for British Coals and Illinois coals during combustion.](image)

A comparison of the HCl evolution profiles during combustion of Illinois and British coals indicates that the British coal release gas at lower temperature than Illinois coal. This is true for all Illinois and all British coals based on analyses of nine samples. This difference may be due to the differences in forms of Cl in coals or the differences in pore size distribution of the coals, which needs further investigation.

Carbon dioxide evolution profiles during combustion-The carbon dioxide evolution profiles, as determined by TGA-FTIR, for the three British coals are shown in Figure 3, and for three of the Illinois coals are shown in Figure 4. The profiles for British and Illinois coals are very similar, and all coals show a maximum rate of CO₂ release around 410°C. The data
Figure 3: CO₂ evolution profiles of three British coals.

Figure 4: CO₂ evolution profiles of three Illinois coals.

Indicate that Cl, for British coals, is released when CO₂ evolution is low. In other words, Cl in the British coals is released before the coal is combusted. On the other hand, Cl in the Illinois coals is released after the CO₂ maximum and in the range of high CO₂ evolution. In other words, Cl in the
Illinois coals is released during coal combustion.

Weight loss profile during combustion-TGA was used to determine the mass changes of coal samples during temperature programmed oxidation. The results indicate that both British and Illinois coals show a similarity of three-stage mass variations. A typical weight-loss profile is shown in Figure 5. At the initial stage of heating, from ambient to 150°C, the sample weight is reduced slightly. This is attributed to the loss of moisture. Further heating from 150 to 300°C, resulting in a slight increase in sample weight (1.5 - 2.2 %). This weight gain may be attributed to oxygen being absorbed during mild oxidation of the coal. The sample weight is substantially reduced (80 to 95%) by further heating from 300 to 600°C. At this stage, an extensive degradation and combustion of the coal sample have taken place.

Figure 5: The TGA curve and its first derivative for a typical coal.

When heated under air, both Illinois and British coals exhibited similar burning characteristics. They all exhibited maximum rate of mass loss at temperatures around 470°C. This is also the temperature at which CO₂ has its maximum evolution. A comparison between these mass loss profiles and those previously described for CO₂ and for Cl evolution shows an interesting phenomenon. The results indicate that Cl in the British coals is released before optimum volatile matter evolution and coal combustion, whereas, Cl in the Illinois coals is released during optimum volatile matter evolution and coal combustion.

Profiles of HCl evolution during pyrolysis-Figure 6 shows the HCl evolution profile determined by TGA-FTIR for both Illinois and British coals during pyrolysis. In general, the evolution of HCl gas occurs at the temperature from 300 to 410°C. These data indicate that the temperature of maximum release of chlorine was lower for the British coals than for the Illinois
coals. However, the difference in the evolution of chlorine observed under pyrolysis condition is not as obvious as those observed under oxidation condition. This may suggest that Illinois coals are more easily oxidized, and Cl in the oxidized Illinois coals is more strongly bound than Cl in the less oxidized British coals.

![Graph showing HCl evolution profiles of British and Illinois coals during pyrolysis by TGA-FTIR.](image)

**Figure 6:** HCl evolution profiles of British and Illinois coals during pyrolysis by TGA-FTIR.

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**EVOLUTION OF CHLORINE AND VOLATILES FROM COALS  
- by Step-Wise Pyrolysis with Multi-Surface Matrix  
Isolation-Fourier Transform Infrared**

Profiles of volatiles evolution from coals during pyrolysis- The profiles of volatiles evolution from one Illinois coal and one British coal under nitrogen were examined by step-wise pyrolysis with multi-surface matrix isolation-Fourier transform infrared spectrometry. The results are shown in Figures 7 and Figure 8, respectively. The three-dimensional graphs indicate that Illinois coal produced more tar (2700 to 3000 cm⁻¹) than British coal.

Profiles of HCl evolution from coals during pyrolysis-The data collected by step-wise pyrolysis with multi-surface matrix
Figure 7: The 3-D graph of volatiles evolved during stepwise pyrolysis of an Illinois coal (C-33875).

Figure 8: The 3-D graph of volatiles evolved during stepwise pyrolysis of a British coal (C-33499).

isolation-Fourier transform infrared spectrometry were further examined for HCl evolution. The HCl evolution profiles of the Illinois
coal and the British coal are shown in Figure 9. The profiles indicate that most of the HCl gas evolves at the temperatures from 300 to 400°C for the Illinois coal and from 240° to 636°C for the British coal. It is difficult to make a direct comparison between these results and those obtained from the TGA-FTIR data for evolution of chlorine from the coal under pyrolysis conditions. The later (Fig. 7) showed a slight difference in the temperature of maximum release of Cl from the Illinois coals and British coals. The temperature of maximum release of chlorine was a slightly lower for the British coals than for the Illinois coals.

SUMMARY AND CONCLUSIONS

At elevated temperatures and under oxidizing conditions, both British and Illinois coals released hydrogen chloride gas. The Illinois coals, however, released the gas at higher temperatures, with maximum evolution around 425 to 475°C. The British coals released HCl gas at lower temperature with maximum evolution temperatures occurring between 210 and 280°C. Cl exists in ionic form in the coals from both countries. Three of the British coal samples contained higher concentrations of soluble sodium in comparison to soluble potassium than the Illinois coal samples. The ratio of soluble sodium to soluble potassium, calculated as oxides (Na₂O-to-K₂O) for the British coals were 9.53, 1.86, 56.67, and
9.0, whereas, the ratios for the Illinois coals were 2.20, 1.16, 1.02 and 0.92. A similar relationship was indicated for the relative corrosion indices (I_x) as defined by Borio et al (1969). The I_x's for the British coals were 53.94, 15.05, 292.92, and 51.42; for the Illinois coals, the values were 17.04, 17.50, 11.62, 10.90 and 10.55.

The difference in the HCl evolution temperature between the Illinois and British coals suggests that the way in which Cl ions are associated in Illinois coals is different from that in the British coals. This difference, plus the difference in the amounts of alkali metals, may contribute to the corrosivity differences of the two coal types. Further study is recommended to examine if, or how, the interaction of Cl with other species, such as mineral matter, in the coal could affect the corrosion potential of a coal.

REFERENCES


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