ABSTRACT

The goal of the first year's work of this project was to characterize the evolution of gaseous sulfur and chlorine species during coal pyrolysis and combustion. Two techniques were developed to identify the gaseous species and to determine gas evolution profiles: (1) temperature-programmed heating and gas-combustion in conjunction with a quadrupole gas analyzer (QGA), and (2) thermogravimetry in combination with Fourier transform infrared analysis (TG-FTIR).

Using the pyrolysis-QGA system, samples of coal were heated from ambient temperature to 800°C at a rate of 20°C/min in the pyrolysis chamber under a nitrogen atmosphere. The volatile products were carried with the nitrogen flow to the combustion chamber which was maintained at 850°C under a constant flow of oxygen. For Illinois coals (IBC-101, -103, and -109), HCl was the only chlorine species identified by the QGA. The HCl release profiles for the coals showed a broad peak between 250°C and 600°C with a maximum at 445°C. Neutron activation analysis of pyrolysis residues showed that 98 percent of the chlorine in raw coal was volatilized. Thus, it may be inferred that the chlorine in Illinois coals is released rapidly as HCl, not as sodium chloride (NaCl), during combustion in a utility/industrial boiler. In contrast to chlorine, the sulfur release profile for IBC-109 showed three peaks: the first sulfur peak at about 350°C was probably derived from elemental sulfur, the main peak at 475°C corresponded to the release of organic sulfur, and the third peak at 600°C resulted from the decomposition of pyrite. The low-temperature peak was absent for fresh samples. Sulfur dioxide (SO₂) was the major sulfur species in combustion gases under an oxidizing condition; additional gaseous sulfur species (COS and H₂S) were observed when the atmosphere was changed to a reducing condition.

The TG-FTIR and TG-IC techniques were used to characterize gaseous species that were evolved during pyrolysis and combustion of Illinois coals. Gas evolution profiles of sulfur (H₂S, SO₂, and COS), chlorine (HCl), and nitrogen (NH₃ and HCN) species were determined. COS may be formed by the reactions of CO and CO₂ with H₂S in the gas phase and by the reaction of CO with pyrite.
EXECUTIVE SUMMARY

The purpose of this project is to study the behavior of sulfur and chlorine during pyrolysis and combustion of Illinois coals, and to better understand the mechanism of boiler corrosion caused by sulfur and chlorine in coal. Identifying the gaseous sulfur and chlorine species in combustion gases and determining their release profiles during coal pyrolysis and combustion under specific conditions are important because the corrosion mechanism depends on the formation of corrosive volatile compounds and their reactions with solid ash phases and boiler equipment. But research in this area has hitherto been hindered by the lack of appropriate techniques to determine the sulfur and chlorine species in combustion gases.

Our approach to attack this problem is to develop two experimental techniques:

- Temperature-programmed heating and gas combustion in conjunction with a quadrupole gas analyzer (pyrolysis/combustion-QGA),
- Thermogravimetry in conjunction with Fourier-transform infrared spectroscopy (TG-FTIR).

Using these techniques we have investigated the evolution of chlorine during pyrolysis and combustion of high-chlorine coal IBC-109 and other Illinois coals. The HCl gas is identified by the QGA based on its mass number and by FTIR spectroscopy based on its absorbance at specific wavenumbers. Mass balance is monitored by chloride ion-selective electrode and high-performance ion chromatography. The pyrolysis residues are analyzed for Na and Cl by neutron activation analysis. We conclude that chlorine in Illinois coals is released rapidly as HCl, not as sodium chloride (NaCl), during combustion. We have also performed experiments to show that chlorine in a weathered sample starts to release at slightly lower temperature (260°C) than that in a fresh sample of coal IBC-109 (320°C).

Sulfur release profiles were determined for Illinois coals by pyrolysis/combustion-QGA and TG-FTIR techniques. Three sulfur evolution peaks are observed for a slightly weathered sample of IBC-109. The 475°C and 600°C peaks are assigned to the release of organic sulfur and pyrite decomposition. The low-temperature (350°C) peak is absent from the fresh sample. We have demonstrated that this low-temperature peak is a result of elemental sulfur being released.

Sulfur species observed in the pyrolysis and combustion gases (SO₂, COS and H₂S) are controlled by the oxidation condition of the atmosphere in the combustion chamber. The data suggest that COS is formed by reaction of CO and CO₂ with H₂S and pyrite. The gaseous species observed provide us a guide to the composition of combustion gases we use to study boiler corrosion during the second year of the project.
OBJECTIVES

The purpose of the project is to study the behavior of sulfur and chlorine in Illinois coal during pyrolysis and combustion and their effects on boiler corrosion. The specific goals of the project are to:

- Develop experimental methods to identify gaseous sulfur and chlorine species evolved during coal pyrolysis and combustion under atmosphere-controlled, temperature-programmed conditions.
- Determine sulfur species in combustion gases under oxidizing and reducing conditions.
- Determine mineralogical and chemical composition of slag and ash samples from boilers and relate chlorine level in coal to boiler corrosion rate.
- Perform simulated corrosion tests to determine effects of chloride concentration in combustion gas (which in turn depends on the chlorine content in coal) on corrosion rate of steels.
- Evaluate practical, remedial measures to solve problem of chlorine-enhanced corrosion.

INTRODUCTION AND BACKGROUND

A better understanding of the behavior of sulfur and chlorine during coal combustion is needed for elucidating the mechanism of boiler corrosion. The research in this area has hitherto been hindered by the lack of suitable techniques for determining volatile sulfur and chlorine compounds in combustion gases. To meet this demand, our primary goal during the first year of this project is to develop techniques to identify the gaseous species and determine gas evolution profiles. Two techniques were developed:

- Temperature-programmed heating and gas combustion in conjunction with a quadrupole gas analyzer (pyrolysis/combustion-QGA),
- Thermogravimetry in conjunction with Fourier-transform infrared spectroscopy (TG-FTIR).

Using these techniques we identified the forms of sulfur, chlorine, and other gases evolved during coal pyrolysis and combustion and determined gas evolution profiles. The composition of combustion gases will be used in the experimental studies of equipment corrosion during coal combustion.
EXPERIMENTAL PROCEDURES

Samples

Coal samples from the Illinois Basin Coal Sample Program were used in the experiments: IBC-102 (3.30% sulfur, 0.02% chlorine), IBC-103 (2.30% sulfur, 0.18% chlorine), IBC-105 (4.55% sulfur, 0.10% chlorine), IBC-106 (3.77% sulfur, 0.02% chlorine), and IBC-109 (1.13% sulfur, 0.42% chlorine).

Pyrolysis-quadrupole gas analysis (QGA) experiments

Major components of the pyrolysis-combustion system include a quartz tube reactor, a gas flow controller, two split-tube furnaces, a programmable temperature controller, 75-μm capillary tubing connecting a Dycor QGA to the pyrolysis-combustion system, and a microcomputer (Figure 1). Approximately 0.5-1.0 gram of coal is heated (temperature programmed) under a controlled atmosphere in the quartz-tube reactor which consists of two consecutive chambers. The coal is heated in the first (pyrolysis) chamber under a nitrogen atmosphere, and the volatile products are carried with the nitrogen flow to the second (combustion) chamber maintained at 850°C under a constant flow of oxygen. The volatiles flowing into the second chamber are combusted. The gaseous products are sampled through a capillary tubing and monitored with a quadrupole gas analyzer (Hackley and Chou, 1992; Chou et al., 1992a). The different gaseous species are identified in the QGA by monitoring the atomic mass associated with different species (Table 1 in Chou et al., 1992b). The data from the QGA and temperature controller are then transmitted to a microcomputer. A chloride ion-selective electrode (ISE) in conjunction with Orion pH/volt meter was used to determine the chloride in the trapping solution. The technique provided an independent supporting method for determining the chloride evolution profile during coal pyrolysis. The method of calibration was described in a previous report (Chou et al., 1992a). The char residues were analyzed for sodium and chlorine by neutron activation analysis. The evolved SO₂ gas was collected in the 3% H₂O₂ solution and sulfur content was determined quantitatively.

Forms of sulfur in coal were determined as follows. A sample of coal (1-2 g) was boiled with dilute HCl for 40 minutes to dissolve sulfate, which was determined gravimetrically by adding BaCl₂ solution to precipitate BaSO₄. Elemental sulfur was extracted with perchloroethylene (PCE) and converted to Ag₂S using the lithium aluminum hydride (LAH) method. The pyritic sulfur was extracted with reductive LAH and determined as Ag₂S. The remaining coal was combusted at 1350°C to determine organic sulfur content.
Thermogravimetry (TG)-Fourier transform infrared (FTIR) spectroscopy experimental procedures

The experimental setup is shown in Figure 2 (Shao et al., 1992a, b). The system consists of a DuPont 951 thermogravimetric analyzer (TGA) in conjunction with a Perkin-Elmer 1650 FTIR spectrometer. In the pyrolysis experiment, a coal sample (about 30-100 mg) is heated in the combustion chamber of the TGA. The gases released from the coal are transported with the carrier gas through the transfer line (1-mm Teflon tubing) to the 100 X 24 mm gas cell of the FTIR spectrometer. Both the Teflon line and the gas cell are heated with a heating coil to 250°C. Thermogravimetry provides a means for measurement of heating conditions and weight changes. The TG-FTIR system is capable of continuously monitoring the weight change of a coal sample as well as quantitatively determining the gases evolved during pyrolysis and combustion: carbon dioxide (CO$_2$, 2360 cm$^{-1}$), carbon monoxide (CO, 2175 cm$^{-1}$), sulfur dioxide (SO$_2$, 1378 cm$^{-1}$), carbon oxysulfide (COS, 2073 cm$^{-1}$), water (H$_2$O, 1683 cm$^{-1}$), ammonia (NH$_3$, 966 cm$^{-1}$), hydrogen cyanide (HCN, 713 cm$^{-1}$), hydrogen sulfide (H$_2$S, 1268 cm$^{-1}$), nitrogen monoxide (NO, 2050 cm$^{-1}$), nitrogen dioxide (NO$_2$, 1468 cm$^{-1}$), methane (CH$_4$, 1304 cm$^{-1}$), ethylene (C$_2$H$_4$, 950 cm$^{-1}$), propylene (C$_3$H$_6$, 912 cm$^{-1}$), hydrochloric chloride (HCl, 2772 cm$^{-1}$). The FTIR spectrum can be taken every minute, including the time it takes to store the spectrum on the computer. Calibration of the FTIR was made using pure gases or prepared gas mixtures. The FTIR spectra of pure gases (CH$_4$, SO$_2$, CO$_2$, H$_2$O, CO, H$_2$S, and HCl) are shown in Figure 3. The pyrolysis was conducted with nitrogen carrier gas at a flow rate of 25 mL/min and a heating rate of 10°C/min from 20°C - 900°C. The FTIR scanning period was four seconds.

TG-ion chromatographic analysis. The sample size of coal was increased to 2 grams, and the coal was heated in a container in the combustion chamber of the TGA. The weight loss was not monitored when the TGA was operated for this purpose because there was too much sample to be placed in the weighing boat. The volatiles (including sulfur and chlorine species) released during programmed heating (at 10°C/min from 20°C to 900°C) were transported with the carrier gas (N$_2$, at a flow rate of 50 mL/min) through a three-stage trap which consisted of three bottles of 50 mL 0.1%-sodium carbonate solution. The gases were collected at 50°C intervals. The chloride and sulfur contents were then determined using a Shimadzu HIC-6A ion chromatograph.

Pyrolysis residues. Samples of pyrolysis residues from TG-FTIR experiments were analyzed for sodium and chlorine by neutron activation analysis.
RESULTS AND DISCUSSION

Chlorine evolution from coal by pyrolysis/gas combustion-quadrupole gas analysis (QGA) experiments

Four temperature-programmed pyrolysis experiments (Run 92012-92015) on high-chlorine coal IBC-109 were conducted at a heating rate of 20°C/min to determine the precision of the HCl evolution profiles (Figure 4). The QGA profiles of HCl indicate that HCl begins to evolve from coal IBC-109 at approximately 250°C (±10°C). The maximum rate of HCl release occurs at approximately 445°C. The peak levels off at 600°C. The variable intensities of the HCl profiles in Figure 4 are the result of different amounts of coal sample used in the experiments.

A typical HCl evolution profile of coal IBC-109 obtained by pyrolysis/gas combustion-QGA is shown along with the data of chloride concentration in the trap solution as determined by the chloride ISE analysis (Figure 5). The chloride concentration in the solution increases with increasing pyrolysis temperature, and the trend levels off at 600°C. The amount of chloride in the solution accounts for all the chlorine in the starting material. The chloride ISE data together with the HCl release profile indicate that the HCl release from coal IBC-109 was virtually completed at approximately 600°C.

When volatile material was released during coal pyrolysis, a significant amount of solid residue (char) was left over. Four char residues from the pyrolysis experiments were analyzed for sodium and chlorine by neutron activation analysis (Table 2 in Chou et al., 1992b). The four runs were conducted under identical conditions in two separate days. The first two runs completed in the same day showed a slightly systematic difference in the char yield than the next two runs, which were also conducted in the same day. Chlorine in coal is highly volatile; only 1.6% - 2.2% of chlorine in feed coal was retained in char; near 98% of the chlorine was volatilized during coal pyrolysis. Sodium, on the other hand, showed much less volatility than chlorine. Below a pyrolysis temperature of 800°C, sodium was totally retained in char. Sodium occurs in clay minerals and pore water in coal; it apparently reacted with other inorganic constituents to form solid phases stable at 800°C.

HCl release profiles of fresh and weathered samples

The coal sample of IBC-109 used in the preceding experiments was dry ground from 63% - 8 mesh to -60 mesh in the Holmes grinder about two years (July 19, 1990) before the pyrolysis experiment; the sample is slightly weathered. Another pyrolysis experiment was conducted on July 31, 1992 on a fresh sample of the same coal (ground to -60 mesh in a mortar). Figure 6 shows the HCl evolution profile of the fresh sample as compared with the old sample. The fresh sample shows a clearly sharper peak; HCl starts to evolve at 320°C as compared to 260°C of the old sample. The difference in peak maximum is small; the fresh sample is about 10°C higher than the weathered sample.
Sulfur release profile during temperature-programmed heating with QGA

Coal IBC-109. The SO₂ profiles determined by QGA in the four replicate pyrolyses of coal IBC-109 are shown in Figure 7. Like the HCl QGA data, the SO₂ profiles show good reproducibility. The shape of the profiles is very similar for each replicate run and appears to be characteristic of coal IBC-109. The profiles show three peaks: an initial peak at approximately 350°C, a major peak at approximately 475°C and a final peak at approximately 600°C. QGA profiles of SO₂ during pyrolysis of other Illinois basin coals usually only contain two peaks, one associated with organic sulfur between 400°C to 500°C and a second associated with the release of pyritic sulfur between 550°C to 600°C (Hackley et al., 1990). The low-temperature peak observed with coal IBC-109 is repeatable and may indicate the presence of a third form of sulfur compound in the sample analyzed.

Because the sample of IBC-109 used earlier was slightly weathered, we conducted a pyrolysis experiment on a fresh sample of the same coal (run 56a on August 1, 1992). The results are shown in Figure 8A. The fresh sample shows two peaks at 486°C and 615°C. The weathered sample shows a slight shift of these two large peaks (480°C and 596°C). In addition there is a low-temperature peak at 357°C. To determine whether this peak is caused by elemental sulfur and iron sulfate formed from pyrite during coal weathering, pyrolysis experiments were conducted on elemental sulfur (Aldrich, 99.999%) and ferric sulfate [Fe₃(SO₄)₂·xH₂O]. The results showed that elemental sulfur was released between 200°C and 360°C with a peak maximum at 320°C, and ferric sulfate between 600°C and 750°C with a peak maximum at 705°C. It appears that elemental sulfur is likely the cause of the 357°C peak on the sulfur evolution profile. The elemental sulfur contents in fresh and weathered samples of IBC-109 are 0.027% and 0.10% respectively (Table 1).

Figure 8B shows the sulfur evolution profile for a fresh coal (1 g) plus 1.7 mg elemental sulfur. The profile of the mixture is similar to that of the weathered coal, although the low-temperature peak of the mixture is at 320°C, slightly lower than the 357°C peak of the weathered coal. The relative intensity of the third peak of the coal-elemental sulfur mixture is stronger than that of the fresh coal which is shown in Figure 8A. The char yields of the fresh and weathered samples are 63.3% and 68.2% respectively. There are 39% and 42% of the sulfur in raw coal volatilized during pyrolysis of fresh and weathered samples of IBC-109 respectively (Table 2).

Coal IBC-102. Additional experiments have been carried out on coal IBC-102. There is much more SO₂ released from this high sulfur coal and the SO₂ peaks are very strong and easily detected by the QGA. It is shown earlier that the sulfur release profile of IBC-102 is quite different from IBC-109 (Chou et al., 1992b). While the SO₂ profile from coal IBC-102 has only two peaks, which is similar to other Illinois Basin coals, the position of the peaks relative to pyrolysis temperature
are very different from most other Illinois bituminous coals (Hackley et al., 1990). The first peak, which is very strong, occurs at a relatively low temperature of approximately 340°C. The second peak, usually considered pyritic sulfur, occurs at approximately 450°C, significantly lower than normally observed for pyritic sulfur. However, this sample IBC-102-A has been exposed to air since July 12, 1987, and it is significantly weathered.

Table 1. Forms of sulfur in fresh and weathered samples of coals IBC-109 and IBC-102.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sulfate</th>
<th>Elemental S</th>
<th>Pyritic S</th>
<th>Organic S</th>
<th>Sum</th>
<th>Total S*</th>
</tr>
</thead>
<tbody>
<tr>
<td>IBC-102</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fresh</td>
<td>0.14</td>
<td>0.048</td>
<td>1.85</td>
<td>0.96</td>
<td>3.00</td>
<td>3.29</td>
</tr>
<tr>
<td>Weathered</td>
<td>1.28</td>
<td>0.25</td>
<td>0.12</td>
<td>1.01</td>
<td>2.66</td>
<td>3.18</td>
</tr>
<tr>
<td>IBC-109</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fresh</td>
<td>0.033</td>
<td>0.027</td>
<td>0.41</td>
<td>0.60</td>
<td>1.07</td>
<td>1.12</td>
</tr>
<tr>
<td>Weathered</td>
<td>0.21</td>
<td>0.10</td>
<td>0.15</td>
<td>0.64</td>
<td>1.10</td>
<td>1.09</td>
</tr>
</tbody>
</table>

*Total sulfur was determined independently to check on the sum of sulfur forms.

Table 2. Percent sulfur volatilized during pyrolysis and collected in hydrogen peroxide solution and % sulfur remained in char for fresh and weathered samples of coals IBC-109 and IBC-102.

<table>
<thead>
<tr>
<th></th>
<th>% total sulfur volatilized</th>
<th>% char</th>
<th>% total sulfur in char</th>
</tr>
</thead>
<tbody>
<tr>
<td>IBC-102</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fresh</td>
<td>37</td>
<td>55.9</td>
<td>63</td>
</tr>
<tr>
<td>Weathered</td>
<td>45</td>
<td>62.7</td>
<td>55</td>
</tr>
<tr>
<td>IBC-109</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fresh</td>
<td>39</td>
<td>63.3</td>
<td>61</td>
</tr>
<tr>
<td>Weathered</td>
<td>42</td>
<td>68.2</td>
<td>58</td>
</tr>
</tbody>
</table>

Two additional pyrolysis experiments were conducted for a 66-day old sample (IBC-102-B) and a fresh sample (IBC-102-C). The fresh sample shows two peaks at 498°C and 641°C, similar to other fresh Illinois coals (Figure 9A). The 66-day old sample shows significant broadening of the 475°C peak toward the low-temperature side. The three profiles shown in Figure 9A indicate a progressive increase of the low temperature peak due to weathering.
Figure 9B shows the sulfur evolution profile of a mixture of fresh sample of coal IBC-102 (1 g) plus 4.7-mg elemental sulfur. The low-temperature half of the profile resembles that of the weathered coal. Thus, the low-temperature peak of the weathered coal represents elemental sulfur which is formed from pyrite during its long-term exposure in the air. The elemental sulfur contents in fresh and weathered samples of coal IBC-102 are 0.048% and 0.25% respectively (Table 1). The char yield is 55.9% and 62.7% respectively, and 37% and 45% of sulfur in raw coal are volatilized during pyrolysis of fresh and weathered samples of IBC-102 (Table 2).

Gaseous sulfur compounds in combustion gases

Experiments were conducted to determine the sulfur species in the combustion gases under oxidizing and reducing conditions. We showed earlier that sulfur dioxide (SO₂) was released from coal IBC-109 primarily between 250°C and 650°C when the coal was heated from the ambient to 850°C.

Figure 10A shows the profiles for SO₂ and COS under oxidizing and reducing conditions. When the oxygen concentration in the combustion chamber never fell below 5 percent (Run 3) SO₂ was observed as a major sulfur species. When a reducing condition occurred in the combustion chamber during the major release of volatiles (Run 4), the SO₂ profile was disturbed and a COS peak was observed.

The H₂S profile is more difficult to comprehend because of the presence of oxygen isotope ¹⁸O in the oxygen flow (Hackley and Chou, 1992). The combination of ¹⁸O and ¹⁶O gives a mass of 34 for oxygen (¹⁶O¹⁸O), the same as H₂S. However, when the combustion is in a reducing condition as O₂ is consumed, the profile of mass 34 represents H₂S.

Figure 10B shows the gas release profiles for sulfur species under reducing condition which occurred between 450°C and 600°C when the oxygen flow to the combustion chamber was turned off. The contrasting behavior of H₂S and COS during the period of oxygen depletion is shown; COS starts to appear and increases rapidly at 450°C when SO₂ decreases. Thus, when oxygen fugacity in combustion gases drops, an appreciable amount of H₂S reacts with CO to form COS. The amount of H₂S also increases in this period of oxygen depletion. The curve of mass numbers 34 represent ¹⁶O¹⁸O except in the temperature range between 450°C and 600°C, during which it represents H₂³⁷S. The appearance of gaseous species with mass 36 during this period (450°C-600°C) is H₂³⁴S.

Thus, sulfur species formed in the combustion gases are controlled by the oxidation condition in the combustion chamber. The experiments indicate that sulfur dioxide (SO₂) is the predominant sulfur species observed during combustion of pyrolysis volatiles. In some of the experiments, during the major release of volatiles between 450°C and 550°C, all oxygen in the pyrolysis system was consumed and a reducing condition occurred which resulted in the detection of additional sulfur.
species (COS and \( \text{H}_2\text{S} \)).

**TG/DTG analysis of coal**

Thermogravimetric analysis of coal IBC-109 was conducted during pyrolysis under a nitrogen atmosphere and during combustion when the coal was heated with air as the carrier gas. The TG and DTG heating curves are shown in Figure 11. During pyrolysis the first peak occurs at about 63°C (I) due to loss of moisture. The maximum rate of mass loss occurs at 434°C (II) reflecting the major release of volatile matter. After 500°C, the volatile loss continues at a slow rate until 940°C. The cumulative yield of volatile matter is 33.3%.

The TG/DTG profile during combustion in air for coal IBC-109 is also shown in Figure 11. The first peak occurs at about 65°C on the DTG curve due to loss of moisture. A negative deflection follows in the temperature range of 200°C-300°C caused by a gain in weight due to solid state oxidation of the organic matter. The amount of weight gain is approximately 0.5% of the sample weight. From point 1 to point 2 (about 300°C-360°C), the rate of weight loss rises linearly as the volatile matter release accelerates with increasing temperature. When the temperature reaches 360°C the combustion becomes the major process, causing the rate of weight loss to increase abruptly. It reaches a maximum at point 3, 471°C (\( T_{\text{MAX}} \)), on the DTG curve. This "peak temperature" of weight loss is an important parameter for assessing the combustibility of coal. Beyond the peak temperature, the rate falls rapidly and smoothly to zero rate at point 4 (about 582°C). Approximately 9.56% of mass is left in the combustion residue. Two shoulders on the left side of the peak temperature are probably due to sample swelling into an impermeable mass, thus it reduces the oxygen accessibility and combustion rate.

**Volatile release during pyrolysis by TG/FTIR technique**

The TG/FTIR spectra of pyrolysis gases at 490°C for coals IBC-109 and IBC-106 are shown in Figure 12. The gases released during pyrolysis of coal IBC-109 under a nitrogen atmosphere are observed: HCl, \( \text{H}_2\text{S} \), SO\(_2\), COS, CH\(_4\), CO, CO\(_2\), H\(_2\)O, NH\(_3\), HCN, C\(_2\)H\(_6\), and C\(_3\)H\(_6\) (Figure 13A). The temperature range during which each gas is evolved is marked with thin and thick lines. The thick line indicates the period when greater than 50% of the maximum absorbance is observed. Methane is the dominant gaseous species under the pyrolysis conditions. Most gases reaches a peak maximum at 440°C which corresponds to the maximum rate of weight loss on the DTG curves (Figure 11). All these gaseous species are observed for three other Illinois Basin coals (IBC-103, -105, and -106).

The gaseous species identified during combustion of IBC-109 in the air are HCl, SO\(_2\), COS, CH\(_4\), CO, CO\(_2\), H\(_2\)O and NO\(_2\) (Figure 13B). Carbon dioxide is the dominant gaseous species during combustion. The release of other gases coincides mostly with CO\(_2\). Moisture in coal (H\(_2\)O) is released from 80°C-120°C, and H\(_2\)O as reaction product is again observed between 275°C and 580°C during pyrolysis. The major release of COS
coincides with CO. The origin of COS will be discussed in a later section.

**TG-FTIR study of HCl evolution during pyrolysis**

We have previously chosen the 2943 cm\(^{-1}\) peak, the most intense peak in the FTIR spectrum of pure HCl gas, to identify HCl in pyrolysis gases, but this peak has an interference from methane (Shao et al., 1992a,b). Mathematical corrections were made to exclude the contribution from methane. In addition to methane, this peak also has interference from paraffin. To correct for the paraffin contribution is very tedious because the correction factor depends on the composition of each coal.

Three additional wavenumbers, 2772 cm\(^{-1}\), 2798 cm\(^{-1}\), and 2726 cm\(^{-1}\), are now used to identify HCl. These peaks are not interfered by methane and paraffin gases. Because the intensity of these peaks are not as strong as the 2943 cm\(^{-1}\) peak, a larger sample (100 mg) is used.

Figure 14A shows three HCl evolution profiles for coal IBC-109 using these wavenumbers. Release of chlorine as HCl from coal occurs within the temperature range of approximately 325\(^\circ\)C-625\(^\circ\)C during pyrolysis. The peak maximum is at 440\(^\circ\)C, which is the maximum devolatilization rate (Figure 11). A shoulder (475\(^\circ\)-525\(^\circ\)) exists on the higher temperature side of this broad peak, indicating there is another peak unresolved at about 500\(^\circ\)C. The two peaks observed on the FTIR spectra indicate that TG-FTIR technique may be used in resolving chemical forms of chlorine in high-chlorine coals.

A TG-FTIR experiment was performed for low-chlorine coal IBC-106 (0.02\% Cl) (Figure 14B). The absorbance for the HCl gas is at the background level. Further combustion experiments on high-chlorine coal IBC-109 show that the HCl release profile during combustion is similar to that during pyrolysis. The peak maximum is at 400\(^\circ\)C on the combustion profile, slightly lower than that in the pyrolysis profile.

**Sodium and chlorine contents in pyrolysis residues**

Four samples of pyrolysis residues were analyzed for sodium and chlorine by neutron activation analysis (Table 3 in Chou et al., 1992b). Percentage of char produced ranges from 56.1\% to 64.7\%. The chlorine concentration in chars is between 55 ppm and 93 ppm. The amount of chlorine retained in the chars are between 1.6\% and 3.7\% of the original chlorine content for three coals IBC-103, -105, and -109. These three coals have a chlorine content between 0.1\% and 0.367\% (as-received basis). For coal IBC-106 with a very low chlorine content (0.018\% Cl), a significant fraction of the original chlorine (29\%) is retained in the char. The Na concentration in chars is between 330 ppm and 1580 ppm, which account for 75\% to 97\% of the sodium in raw coal. It seems that part of the sodium is volatilized from IBC-105 which has the highest sodium content (1,300 ppm Na) among the four samples.
TG-FTIR study of sulfur species during pyrolysis and combustion

$\text{H}_2\text{S}$. The gaseous sulfur species ($\text{H}_2\text{S}$, $\text{SO}_2$, and $\text{COS}$) are observed during coal pyrolysis. $\text{H}_2\text{S}$ is a major sulfur species under the pyrolysis condition. The $\text{H}_2\text{S}$ release profiles of coals IBC-106 and IBC-109 (1268 cm$^{-1}$) are shown in Figure 15A. Both coals have similar $\text{H}_2\text{S}$ release profiles, showing a major peak between 325°C and 500°C and an extended shoulder from 500°C to 700°C. The former is derived from organic sulfur, and the latter is probably due to the hydrolyses of the pyritic sulfur. $\text{H}_2\text{S}$ is not observed during combustion under an oxidizing condition.

$\text{SO}_2$. During combustion, sulfur dioxide is the major sulfur species evolved from coal. The $\text{SO}_2$ release profiles of coals IBC-106 and IBC-109 during pyrolysis are shown in Figure 15B. For high-sulfur coal IBC-106, four peaks are observed at 320°C, 440°C, 500°C and 550°C. This is the same coal weathered sample weathered analyzed at ISGS, the 320°C peak is related to the presence of elemental sulfur in coal. The main peak at 440°C is the result of the release of organic sulfur. The 550°C peak is likely the result of the decomposition of pyrite. The peak at 500°C is probably related to the decomposition of iron sulfate, but more work is need to verify it.

$\text{COS}$. The gas evolution profile of $\text{COS}$ (at wavenumber 2073 cm$^{-1}$) are obtained during pyrolysis and combustion. Figure 16 shows the COS release profiles during pyrolysis of coals IBC-109 and IBC-106. Two major temperature ranges of COS release are observed. The first region (1) is between 350°C and 500°C and the second region (2) between 500°C and 750°C.

The results may be interpreted as follows: the release of COS in region 1 is mainly due to the reaction of $\text{H}_2\text{S}$ with CO or $\text{CO}_2$ in the pyrolysis gas:

\[
\text{H}_2\text{S} (g) + \text{CO} (g) \rightarrow \text{COS} (g) + \text{H}_2 (g)
\]

\[
\text{H}_2\text{S} (g) + \text{CO}_2 (g) \rightarrow \text{COS} (g) + \text{H}_2\text{O} (g)
\]

The release of COS in the temperature region 2 (a composite peak) may be a result of reaction of CO gas with $\text{FeS}_2$:

\[
\text{FeS}_2 (s) + \text{CO} (g) \rightarrow \text{COS} (g) + \text{FeS} (s)
\]

CONCLUSIONS AND RECOMMENDATIONS

1. We have developed two experimental methods to identify gaseous sulfur and chlorine species evolved during coal pyrolysis and combustion under the atmosphere-controlled and temperature-programmed conditions: (a) temperature-programmed heating and gas combustion in conjunction with a quadrupole gas analyzer (QGA), and (b)
thermogravimetric analysis in conjunction with Fourier-transform infrared spectroscopy (TG-FTIR).

2. Replicate HCl evolution profiles of high-chlorine coal IBC-109 are obtained using pyrolysis/gas combustion apparatus with a quadrupole gas analyzer. The chlorine in coal is released solely as HCl and the HCl release profile shows a broad peak between 250°C and 600°C with a maximum at 445°C. The mass balance during pyrolysis was determined by quantitative monitoring of chloride concentration in the trap solution using a chloride ion selective electrode. Thus, it may be inferred that the chlorine in Illinois coals is released rapidly as HCl, not as sodium chloride (NaCl), during combustion in a utility/industrial boiler.

3. Neutron activation analysis for sodium and chlorine in the pyrolysis residues showed that 98% of the chlorine in coal is volatilized during pyrolysis to 800°C and all the sodium is retained in the chars. The fresh sample shows a sharper peak; HCl starts to evolve at 320°C from the fresh sample as compared to 260°C from the weathered sample of coal IBC-109.

4. The sulfur release profile shows three peaks: the sulfur released around 350°C may be derived from elemental sulfur, the main peak at 475°C corresponds to the release of organic sulfur, and the third peak at 600°C results from the decomposition of pyrite.

5. Pyrolysis of a mixture of fresh coal and elemental sulfur demonstrates that the low-temperature peak on the sulfur evolution profile of weathered coal is primarily due to elemental sulfur formed from decomposition of pyrite during weathering.

6. Sulfur dioxide (SO₂) is the major sulfur species in combustion gases under an oxidizing condition. Additional gaseous sulfur species (COS and H₂S) are observed when the atmosphere in the combustion chamber is changed to a reducing condition.

7. Thermogravimetric-Fourier transform infrared spectroscopy technique (TG-FTIR) provided important information about the evolution of gaseous species (CO, CO₂, H₂S, SO₂, COS, H₂O, HCl, NH₃, HCN, CH₄, C₂H₂, C₂H₄, and C₃H₆) from coal during pyrolysis and combustion.

8. The TG-FTIR and TG-IC data on chlorine evolution support the conclusion that chlorine in Illinois coal is volatilized as HCl during both pyrolysis and combustion. The temperature range for HCl evolution is between 300°C and 600°C. The HCl evolution profile shows two peaks reflecting the release of different forms of chlorine. The TG-FTIR technique may be a potential technique for resolving the mode of occurrence of chlorine in coal.

9. H₂S is the major sulfur species evolved during coal pyrolysis. SO₂ is the sulfur species during coal combustion. COS is observed in both pyrolysis and combustion. It may be formed by the
reactions of CO and CO₂ with H₂S in the gas phase and the reaction of CO with pyrite.

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REFERENCES


Figure 1. The experimental setup for temperature-programmed pyrolysis/gas combustion coupled with a quadrupole gas analyzer (QGA).
Figure 2. Flow diagram of the thermogravimetric analyzer, Fourier-transform infrared spectrometer, and high-performance ion chromatography (TG-FTIR-HIC) system for studying the behavior of chlorine, sulfur, and other volatiles during coal pyrolysis and combustion.
Figure 3. FTIR spectra of seven pure gases.
Figure 4. The HCl release profiles determined by quadrupole gas analysis (mass number 36) in four temperature-programmed pyrolysis experiments (runs 92012-92015) on high-chlorine coal IBC-109 (0.42% chlorine on dry basis). The heating rate is 20°C/min. The HCl gas evolution from the coal begins at approximately 250°C (±10°C). The maximum rate of HCl release occurs at approximately 445°C; and at 600°C the release of HCl is nearly complete. The different intensities of the HCl profiles are related to amounts of coal sample used in the experiments.
Figure 5. A typical HCl evolution profile (curve) obtained by QGA for coal IBC-109 compared with the trend of increasing chloride concentration in the solution (squares). A chloride ion-selective electrode (ISE) is used in quantitative monitoring of the chloride evolved during coal pyrolysis. Both the ISE trend and the QGA profile indicate that the HCl is released between 250°C and 600°C. The chloride evolved from the coal is accounted for by the chloride dissolved in the solution.
Figure 6. HCl evolution profiles of a weathered sample and a fresh sample of coal IBC-109.
Figure 7. Sulfur evolution profiles were obtained by four replicate pyrolysis experiments on coal IBC-109. Volatilized sulfur species were converted to $\text{SO}_2$ and monitored with a QGA. The shape of the profiles is very similar for each replicate run and appears to be characteristic of the coal IBC-109. There are basically three peaks shown in the $\text{SO}_2$ profiles: an initial peak at approximately $350^\circ\text{C}$, a major peak at approximately $475^\circ\text{C}$, and a final peak at approximately $600^\circ\text{C}$. These three peaks indicate that three kinds of sulfur species were released at different temperatures: elemental sulfur, organic sulfur, and pyritic sulfur.
Figure 8A. Sulfur evolution profiles of a weathered sample and a fresh sample of coal IBC-109.

Figure 8B. Sulfur evolution profile of a mixture of fresh sample (1.1 g) plus 1.7 mg elemental sulfur as compared with a weathered sample of coal IBC-109.
Figure 9A. Sulfur evolution profiles of a fresh sample, and two weathered samples of coal IBC-102.

Figure 9B. Sulfur evolution profiles of a mixture of fresh sample (1.1 g) plus 4.7 mg elemental sulfur as compared with a weathered sample of coal IBC-102.
Figure 10A. Volatile sulfur species in combustion gases controlled by the atmosphere in the combustion chamber. SO$_2$ is the predominant sulfur species under an oxidizing condition during which the excess oxygen concentration in the combustion chamber never fell below 5% (run 3). When the combustion atmosphere was changed to a reducing condition during the major release of volatiles (run 4), gaseous COS and H$_2$S were detected.

Figure 10B. Gas release profiles for sulfur species under reducing condition. The contrasting behavior of H$_2$S and COS is shown. The profile of mass 34 shows a H$_2$S peak when the O$_2$ is consumed during the experiment. Also observed is the peak of species mass-36 representing H$_2^{34}$S. As the rate of volatile gases released from the coal sample decreases and the O$_2$ concentration is no longer completely consumed, the peaks of COS and H$_2$S disappear.
Figure 11. Thermogravimetric (TG) and differential thermal gravimetric (DTG) analyses during pyrolysis (in nitrogen) and combustion (in air) of coal IBC-109.
Figure 12. TG-FTIR spectra of pyrolysis gases of coals IBC-109 and IBC-106 at 490°C.
Figure 13A. Temperature ranges of gas evolution during pyrolysis of coal IBC-109.

Figure 13B. Temperature ranges of gas evolution from coal IBC-109 during combustion.
Figure 14A. Comparison of HCl release profiles of IBC-109 (0.42% Cl) at three wavenumbers during pyrolysis by TG-FTIR technique.

Figure 14B. Comparison of HCl release profiles of coals IBC-109 (0.42% Cl) and IBC-106 during pyrolysis by TG-FTIR technique.
Figure 15A. H₂S release profiles for coals IBC 106 (3.77% S) and IBC-109 (1.13% S) during pyrolysis by TG-FTIR technique at 1268 cm⁻¹.

Figure 15A. SO₂ release profiles for coals IBC-106 (3.77% S) and IBC-109 (1.13% S) during pyrolysis at 1378 cm⁻¹ by TG-FTIR technique.
Figure 16. COS release profiles of coals IBC-106 (3.77% S) and IBC-109 (1.13% S) at 2073 cm⁻¹ by TG-FTIR technique.