Behavior of Chlorine & Sulfur During Coal Pyrolysis & Combustion

Dakang Shao
Western Kentucky University

Follow this and additional works at: https://digitalcommons.wku.edu/theses

Part of the Chemistry Commons

Recommended Citation
https://digitalcommons.wku.edu/theses/2845
Shao,
Dakang
1992
BEHAVIOR OF CHLORINE AND SULFUR
DURING COAL PYROLYSIS AND COMBUSTION

A Thesis
Presented to
the Faculty of the Department of Chemistry
Western Kentucky University
Bowling Green, Kentucky

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

by

Dakang Shao

December 1992
AUTHORIZATION FOR USE OF THESIS

Permission is hereby

☑ granted to the Western Kentucky University Library to make, or allow to be made photocopies, microfilm or other copies of this thesis for appropriate research for scholarly purposes.

☐ reserved to the author for the making of any copies of this thesis except for brief sections for research or scholarly purposes.

Signed: [Signature]

Date: 3-10-93

Please place an "X" in the appropriate box.

This form will be filed with the original of the thesis and will control future use of the thesis.
BEHAVIOR OF CHLORINE AND SULFUR
DURING COAL PYROLYSIS AND COMBUSTION

Recommended February 4, 1973
(Date)

Director of Thesis

Graduate Studies
ACKNOWLEDGEMENTS

It is my pleasure to take this time to thank Dr. Wei-Ping Pan (Department of Chemistry, Western Kentucky University) and Dr. Chen-Lin Chou (Illinois State Geological Survey) for their guidance and patience during my period of research on the thesis. Also, I would like to extend thanks to Mr. Leonard J. Poirier for providing me with the opportunity to acquire practical training with Shimadzu Scientific Instruments, Inc., which enhanced my education. Finally, I wish to give my thanks to the faculty and staff of the Department of Chemistry at Western Kentucky University for their instruction and help during my graduate studies.

This work was prepared with the support, in part by grants made possible by the Illinois Department of Energy and Natural Resources through its Coal Development Board and Center for Research on Sulfur in Coal, and by the U.S. Department of Energy (Grant Number DE-FG22-91334). However, any opinions, findings, conclusions, or recommendations expressed herein are those of the author(s) and do not necessarily reflect the views of IDENR, CRSC, and DOE.
CONTENTS

CHAPTER 1 INTRODUCTION 1

1.1 Chlorine Content in Coal 1

1.2 Chemical Nature and Distribution of Chlorine in Coal 2

1.3 Behavior of Chlorine in Coal during Pyrolysis and Combustion 5

1.4 Chemical Nature and Distribution of Sulfur in Coal 8

1.5 Behavior of Sulfur in Coal during Pyrolysis and Combustion 10

1.6 Objectives of the Study 18

CHAPTER 2 EXPERIMENTAL DESIGNS 19

2.1 Preparation of Samples 19

2.1.1 Illinois Coal Samples 19

2.1.2 Clean Illinois Coal Samples 19

2.1.3 Coal-Sorbent Mixture Samples 20

2.2 Investigation of Coal Pyrolysis and Combustion Using Simultaneous TG/FTIR Techniques 21

2.2.1 Simultaneous TG/FTIR Techniques 21

2.2.2 Calibration of FTIR Spectra by Pure Gas 23

2.2.3 Determination of Gas Release Profiles during Coal Pyrolysis and/or Combustion 23

2.3 Investigation of Release Behavior of Chlorine and Sulfur during Coal Pyrolysis and Combustion by TG/IC Techniques 25

2.3.1 TG/IC Technique 25
2.3.2 Determination of Quantitative Chlorine and Sulfur Release Profiles of Coal Pyrolysis and Combustion

2.3.3 Determination of Chlorine and Sulfur Mass Balance During Combustion of Coal-Sorbent Mixtures

CHAPTER 3 BEHAVIOR OF CHLORINE AND SULFUR IN ILLINOIS COAL DURING PYROLYSIS

3.1 Thermogravimetric Analysis for Illinois Coal Pyrolysis

3.2 FTIR Analysis for Illinois Coal Pyrolysis Gases
   3.2.1 Standard FTIR Spectra of Pure Gases
   3.2.2 Identification of Illinois Coal Pyrolysis Gases
   3.2.3 Evaluation of Pyrolysis Gas Release Profiles

3.3 Sulfur Release During Illinois Coal Pyrolysis by TG/FTIR
   3.3.1 Pyrolysis H₂S Release Profiles
   3.3.2 Pyrolysis COS Release Profiles
   3.3.3 Pyrolysis SO₂ Release Profiles

3.4 Gaseous Chlorine Release during Illinois Coal Pyrolysis
   3.4.1 Pyrolysis HCl Release Profiles by TG/FTIR
   3.4.2 Quantitative Pyrolysis Chlorine Release Profiles and Chlorine Mass Balance by TG/IC

CHAPTER 4 BEHAVIOR OF CHLORINE AND SULFUR IN ILLINOIS COALS DURING COMBUSTION

4.1 Thermogravimetric Analysis for Illinois Coal Combustion

4.2 Illinois Coal Combustion Gas Release Profiles by TG/FTIR

4.3 Gaseous Sulfur Release During Illinois Coal Combustion
4.3.1 Combustion COS Release Profiles by TG/FTIR 94
4.3.2 Combustion SO$_2$ Release Profiles by TG/FTIR 96
4.3.3 Quantitative Combustion Gaseous Sulfur Release Profiles and Sulfur Mass Balance by TG/IC 98

4.4 Gaseous Chlorine Release During Illinois Coal Combustion 101
4.4.1 Combustion HCl Release Profile by TG/FTIR 101
4.4.2 Quantitative Combustion Gaseous Chlorine Release Profiles and Chlorine Mass Balance by TG/IC 103

CHAPTER 5 BEHAVIOR OF CHLORINE AND SULFUR IN LEACHED ILLINOIS COALS DURING COMBUSTION 107

5.1 Thermogravimetric Analysis for Leached Coal Combustion 107
5.1.1 Combustion TG Analysis 107
5.1.2 Combustion DTG Analysis 109

5.2 Gas Release Profile During Leached Coal Combustion by TG/FTIR 112
5.2.1 Combustion CO$_2$ and CO Release Profiles 113
5.2.2 Combustion H$_2$O Release Profiles 118
5.2.3 Combustion CH$_4$ Release Profiles 120

5.3 Gaseous Sulfur Release During Leached Coal Combustion 122
5.3.1 Combustion SO$_2$ Release Profile by TG/FTIR 122
5.3.2 Combustion COS Release Profile by TG/FTIR 122
5.3.3 Quantitative Combustion Gaseous Sulfur Release Profiles and Sulfur Mass Balance by TG/IC 124

5.4 Gaseous Chlorine Release During Leached Coal Combustion 128
5.4.1 Combustion HCl Release Profiles by TG/FTIR 128
5.4.2 Quantitative Combustion Gaseous Chlorine Release Profiles and Chlorine Mass Balance by TG/IC

CHAPTER 6 EFFECT OF SORBENT ADDITION ON BEHAVIOR OF CHLORINE AND SULFUR IN ILLINOIS COAL DURING COMBUSTION

6.1 Dynamic TG/FTIR Analysis for Coal-Sorbent Mixture Combustion

6.1.1 Dynamic Combustion TG Analysis

6.1.2 Behavior of Sulfur in Coal-Sorbent Mixture During Combustion by TG/FTIR

6.1.3 Behavior of Chlorine in Coal-Sorbent Mixture During Combustion

6.3 Rapid TG/IC Analysis for Coal-Sorbent Mixture Combustion

6.3.1 Rapid-Heating TG Analysis

6.3.2 Behavior of Chlorine and Sulfur in Coal-Sorbent Mixture During Rapid-Heating Combustion by TG/IC

CHAPTER 7 CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

7.2 Recommendations

REFERENCES
The behavior of chlorine and sulfur in Illinois coals and during pyrolysis and combustion their forms in the coals were evaluated by combined Thermogravimetry/Fourier Transform Infrared Spectroscopy/Ion Chromatography (TG/FTIR/IC) techniques. It was found that more than 90% of chlorine in Illinois coals was liberated as HCl gas during pyrolysis and combustion in the temperature range of approximately 300° - 600°C, with the amount reaching the maximum around 440°C. Similarity of the HCl and NH₃ release profiles during pyrolysis of IBC-109 indicates that the forms of chlorine in coal is associated closely with the forms of nitrogen, and that the chlorine may be bonded to the basic nitrogen-sites on the inner walls of coal micropores.

Approximately more than 60% of the total sulfur in the coals was evolved mainly as SO₂ and COS in the 250°C-750°C range during combustion. Except for SO₂ and COS, H₂S was a major gaseous sulfur-containing product observed during coal
pyrolysis. The release rates of the gaseous sulfur species reached several peaks at some points within the temperature ranges during pyrolysis and combustion, and these peaks were due to the emissions of several types of the sulfur in different forms present in the coals.

The effect of chlorine removal from high chlorine Illinois coal on its reactivity was also investigated by TG/FTIR/IC techniques. The weight loss behavior of the leached coals was significantly different from that of the raw coal (IBC-109) during combustion. The release profiles of gaseous chlorine (HCl) and sulfur species (SO₂ and COS) of the leached coals are significantly different from those of the raw coal.

The effect of the addition of CaCO₃ and Ca(OH)₂ on the behavior of chlorine and sulfur during combustion of high chlorine and medium sulfur Illinois coal was investigated by TG/FTIR/IC techniques. Thermogravimetry showed no significant difference in weight loss between IBC-109 and its sorbent mixtures, Coal-CaCO₃ and Coal-Ca(OH)₂. However, addition of 5% Ca(OH)₂ or 6% CaCO₃ to IBC-109, may not only reduce emission of chlorine by about 48% or 20%, but also reduce emission of total sulfur by about 68% or 52% during combustion.
CHAPTER 1
INTRODUCTION

1.1 Chlorine Content in Coal

The chlorine content in coals around the world ranges from a few parts per million to about 1 wt% in certain coals from the United Kingdom.\(^1\)\(^2\) The chlorine content in Illinois Basin coals (IBC) varies from less than 0.003 wt% to 0.8 wt\(^%\).\(^3\)\(^4\)\(^32\) The samples of Illinois Basin coals may be divided into three groups according to their chlorine content: low-chlorine coals containing less than 0.15 wt% chlorine, medium-chlorine coals containing 0.15-0.30 wt% chlorine, and high-chlorine coals containing greater than 0.30 wt% chlorine, following the way chlorine content in British coals is grouped.\(^5\)\(^32\)

At least half of the known economically minable coal resources in the Illinois Basin have a high chlorine content greater than 0.3\(^%\).\(^6\)\(^32\) Coal with high chlorine content may be difficult to market because the chlorine may not only enhance boiler corrosion rate of metal tube walls in utility and industrial boilers, but also cause severe environmental pollution.\(^7\) However, assessing the effect of chlorine in coal on boiler corrosion is a complex problem. There are many variables which may synergistically affect the corrosion rate
in a boiler, and there is a lack of data to isolate individual factors.

1.2 Chemical Nature and Distribution of Chlorine in Coal

The chemical nature and distribution of chlorine in coal have been the subject of many studies, generally based on the characterization of aqueous extracts. However, conclusions of these studies vary. The main chemical forms of chlorine present in coal have been proposed as the following:

1) inorganic water soluble chlorides including NaCl, KCl, CaCl₂, and traces of MgCl₂ and FeCl₃,
2) a component of stable complex silicates,
3) chloride ions in the water layers absorbed on the inner surfaces of coal,
4) chloride ions associated with exchangeable cations in clay minerals,
5) water-insoluble chlorine-bearing minerals such as chlorapatite (9CaO•3P₂O₅•CaCl₂) or sodalite [3(Na₂O•Al₂O₃•2SiO₂)•2NaO],
6) chloride ions by an ion exchange linkage,
7) and covalently bound organic chlorine.

After reviewing the chlorine in coal question Watt concluded that it was still not possible to give a clear account of the mode of combination of chlorine.

Few studies have been carried out on the physical distribution of the chlorine through coal. However, Louis, as well as Chapman and Mott concluded from the high chloride
levels in aqueous extracts from the fines of fusain-rich coal that the lithotypes vitrain and clarain were lower in soluble salts than durain. Crumley and McCamley\textsuperscript{27} showed for some British coals that the chlorine content could be closely correlated with the organic matter rather than with the mineral matter in the coal.

In 1981 Chakrabarti\textsuperscript{28} proposed a method to estimate the fraction of the chlorine that is bound to organic molecules in coal. His conclusion that only organic chlorine was liberated by ignition was shown to be wrong by other studies.\textsuperscript{29}

In 1984 Cox et al.\textsuperscript{29} estimated the inorganic-organic chlorine ratio in Herrin No. 6 coal, and concluded that the coal sample contained a total of 0.52 wt% Cl, distributed as follows: 83% inorganic salt, 17% chloride held by an ion exchange mechanism, and 0% covalently bonded chlorine.

In 1988 Martinez-Tarazona et al.\textsuperscript{30} investigated the mode of occurrence of chlorine in two high volatile bituminous coals from the Asturian Central coalfield, with a chlorine content about 0.1 wt%. Direct evidence of the presence of chlorine and its chemical association was gained by scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX). From the results, they concluded that chlorine in the coals studied was mainly localized in the coal matrix associated to organic matter. The highest proportion of chlorine is uniformly distributed in the coal matrix, and was not bonded to any cation. The likely chlorides were not identified and the possible accumulation of chlorine in pores
could not be proved.

In 1990 Demir, Chou et al. investigated the abundances and distribution of sodium and chlorine in lithotypes of Illinois Basin coals. They concluded that the chlorine content is the highest (0.52% Cl) in vitrinite and the lowest (0.25% Cl) in roof shale, whereas the sodium content is the lowest (0.088% Na) in vitrinite and the highest (0.263% Na) in roof shale. The Cl/Na ratio of the lithotypes is significantly greater than that of NaCl, the dominant dissolved salt in the ground water associated with Illinois coals. Chlorine and sodium in the coal samples studied are concentrated in vitrinite and mineral matter, respectively. Part of the Na and a small fraction of the Cl occur as dissolved NaCl in large pores and mesopores, mainly within the mineral matter and inertinite. The organically associated chlorine in coal is adsorbed primarily on the micropore walls.

In 1991 Chou investigated the distribution of chlorine in Illinois coals. He concluded that chlorine in coal is in equilibrium with the chlorine in the associated groundwater because of the close relationship between chlorine content and depth of the coal seam. After analyzing 68 samples of coal lithotypes (vitrain, bright banded coal, subbright banded coal, dull coal and fusain) and other lithologic separates for sodium and chlorine contents, as well as other chemical and maceral compositions, he concluded that the chlorine content of the coal lithotypes varies from 0.13% to 0.58%, and that two forms of chlorine occur in coal: (1) chloride ions (Cl⁻)
occurring as Na\textsuperscript{+}Cl\textsuperscript{-} dissolved in pore water, and (2) chlorine enriched in organic matter, most likely as chloride ions adsorbed on the inner surfaces of micropores in macerals. The adsorbed chloride ions probably occur as hydrogen chloride (HCl) associated with the positively charged nitrogen functional groups, and may be held in the diffuse electrical double layer. The charge of adsorbed chloride ions may be balanced by hydrogen ions, not by sodium ions.

Edgcombe,\textsuperscript{16} Dabell and Pringle,\textsuperscript{17} and Given\textsuperscript{33} suggested that chlorine in coal may be attached to basic N sites as hydrogen chloride. It is generally agreed that the nitrogen in coals occurs almost completely in heterocyclic ring structure.\textsuperscript{34} Although quantitative information on the functionality of nitrogen in coals is lacking in the literature, it is now believed that a part of the nitrogen is present as basic nitrogen (as in pyridine structures) and a part is present in acidic nitrogen (as in pyrrole structure).\textsuperscript{35} Mahajan and Walker\textsuperscript{36} suggested that a certain amount of HCl is bound to the basic nitrogen (as in pyridine structure) in the form of hydrochloride structure in the washed coal after inorganic matter is removed from coal by the acidic-washing treatment (with HCl). However, the acidic nitrogen is not expected to bind HCl like the basic nitrogen.

1.3 Behavior of Chlorine in Coal during Pyrolysis and Combustion

Few studies have been done on the behavior of chlorine in coal during pyrolysis and combustion.
By using the British standard method of chlorine determination, Edgecombe investigated the evolution of chlorine as hydrogen chloride on heating 29 British coals (0.2%-1.0% Cl) in dry air at 200°C for 24 hours. He concluded that more than half of the chlorine in the coals was liberated as HCl in air (combustion) at 200°C, but not in nitrogen (pyrolysis) at the same temperature. He demonstrated that the chlorine evolved was not produced by the decomposition of alkali chlorides. However, he postulated that the volatile chlorine represents that part of the total chlorine which is not present as alkali chlorides, and he also suggested that the volatile chlorine exists in the coal as chloride ions held on the coal substance by ion exchange linkage.

On the contrary, Daybell concluded that chlorine in some British coals is liberated as HCl in oxygen-free nitrogen (pyrolysis) at 200°C. Gibb concluded, however, that British coals give off 97% of its chlorine as HCl in oxygen-free nitrogen (pyrolysis) at 258°C.

In 1983 Herod et al. investigated the evolution of HCl and other volatile species during the mild heat treatment of six UK coals (0.35-0.86% Cl) in helium followed by mass spectrometry (MS). The coals were heated at 2°C/min to 300°C before being heated isothermally for about 24 hours. They concluded that 40-60% of the chlorine is emitted as HCl; no other chlorine-containing volatile species were identified. The HCl losses did not correlate with the initial chlorine contents of the coals. The first-order release of HCl from
the coals suggested that the rate-controlling step may be either diffusion through micropores or breakdown of an ionic complex within the pores. The emission of HCl did not correlate with that of any of the volatile organic compounds and the temperature of appearance of HCl showed no simple pattern. A low-temperature maximum in HCl emission was found for three coals and, in two cases, was associated with steam evolution. The initial HCl surge corresponded to the maximum for water emission, suggesting that steam is carrying some of HCl out of the coals.

Since brine is the most likely source of chlorine in coal, it is possible that chloride ions may exist either as ion pairs (H'Cl- or Na'Cl-) on the coal surface or alternatively bonded as chloride ions to nitrogen-containing organic compounds such as amine cations, [RNH3]+. The loss of chlorine as HCl from either Na'Cl- or organic compounds would require either hydrogen abstraction or combination with a hydrogen ion, probably from water.

Mild heating of coals in nitrogen drives off chlorine as HCl, although slowly. The evidence does not preclude the possibility that covalent chlorine-carbon bonds exist in coal or that small amounts of volatile organic chlorine compounds may be formed on low-temperature devolatilization of coal.

In 1992 C.B. Muchmore et al. investigated chlorine removal from an Illinois high-chlorine coal, IBC-109 (0.42% Cl), with thermal treatment followed by analysis using electrode technique. They concluded that 84.3% of total...
chlorine was removed from the coal by preheating the coal in a nitrogen gas flow at lower temperatures prior to a six-minute reaction at 385°C. They proposed an equation for calculating percent removal of chlorine, which is as follows:

\[
\% \text{ removal of chlorine} = R\{1-\exp[-k(t-t_0)]\}
\]

Where:

- \( R \) = the % ultimate chlorine removal under the reaction conditions
- \( k \) = the first order rate constant, \( \text{hr}^{-1} \).
- \( t \) = the reaction time measured from the beginning of the heating period, \( \text{hr} \).
- \( t_0 \) = the time lag prior to the onset of significant chlorine evolution, \( \text{hr} \).

There is, however, a lack of data concerning dynamic behavior of chlorine evolution during pyrolysis and combustion of Illinois coals.

1.4 Chemical Nature and Distribution of Sulfur in Coal

Several reviews on the sulfur chemistry of coal are available.\(^{41-46} \) It is known that during pyrolysis the extent of the sulfur release and distribution in the pyrolysis products depends on several parameters such as coal type, heating rate, pressure, soak time at the pyrolysis temperature, the form of sulfur in the coal (e.g., inorganic versus organic), intimacy of contact between minerals and the primary products of devolatilization (pyrolysis).\(^{47-53} \)

It is generally accepted that three forms of sulfur occur in coal,\(^{45,55,84} \) organic sulfur (an integral part of the coal structure); pyrites and/or marcasites (generally discrete particles or 'lumps'); and sulfates (as salts of metals such
as calcium or iron). A minor amount of elemental sulfur also occurs in coal.⁸⁴

Sulfates are not usually present in significant quantities in fresh raw coal. However, significant amounts can be formed if the coal has been weathered (i.e., oxidized).

The type and distribution of organic sulfur varies widely in a complex manner in different coals. Roughly 40-70% of the organic sulfur of a coal is in a thiophene structure (and its derivatives). However, there are some serious concerns regarding the validity of the qualification in some of the reported work⁴¹-⁴⁴ in the literature (e.g., failure to consider interferences of FeS₂, and inability to measure complex thiophenic sulfur).

Thiophenes are heteroaromatic compounds with the sulfur as part of an aromatic ring. Sulfides are usually present as aryl sulfides, cyclic sulfide, and aliphatic sulfides.⁴¹-⁴⁴, ⁵⁵ In an aryl sulfides, the sulfur is linked to an aromatic ring. In cyclic sulfides, the sulfur is part of a non-aromatic ring. For high rank coals, disulfides are not believed to be a significant portion of the total sulfur. The amount of thiols is substantially higher in lignites and high volatile coals than in low volatile coals. In summary, the types of organic sulfur in the coal vary with coal rank. The stronger bonding of sulfur present in the higher rank coals renders the sulfur more stable during heat treatment.⁵⁵-⁵⁷

According to Coburn⁵⁸ pyrite is defined as FeS₂, but the name is imprecise because FeS₂ in coal has several forms
1.5 Behavior of Sulfur in Coal during Pyrolysis and Combustion

During the pyrolysis of coals of various types, the mechanisms of sulfur release are influenced by numerous factors such as the forms and types of sulfur present in the coals, coal rank and experimental conditions.

When heated in an inert atmosphere during pyrolysis, the pyrite present in coal decomposes to ferrous sulfide and sulfur by the following reaction:

\[ \text{FeS}_2 \xrightarrow{\text{inert}} \text{FeS} + \text{S} \xrightarrow{500^\circ C} \text{non-vol. sulfur compounds} \] (1-1)

\[ \text{S} \xrightarrow{2\text{coal}-\text{H}} \text{H}_2\text{S} + 2(\text{coal}) \] (1-2)

Conversion of pyrite is limited kinetically. This transformation begins at 450 to 500°C, and is essentially complete at 850°C if the heating rate is sufficiently slow. At elevated temperatures, the pyrite may be reduced by carbon by the following reaction:

\[ 2\text{FeS}_2 \xrightarrow{1000^\circ C} \text{CS}_2 + 2\text{FeS} + (\text{coal}) \] (1-3a)

\[ 2\text{FeS} \xrightarrow{1000^\circ C} 2\text{Fe} + \text{CS}_2 + (\text{coal}) \] (1-3b)

At relatively low temperatures, the pyrite may also be reduced by hydrogen (donated by coal) by the following reaction:
\[
2\text{FeS}_2 + \text{H}_2 \quad \xrightarrow{230 \degree \text{C}} \quad 2\text{FeS}_3 + \text{H}_2\text{S} \quad (1-4a)
\]

\[
\text{Fe}_2\text{S}_3 + \text{H}_2 \quad \xrightarrow{280 \degree \text{C}} \quad 2\text{FeS} + \text{H}_2\text{S} \quad (1-4b)
\]

\[
\text{FeS} + \text{H}_2 \quad \xrightarrow{370 \degree \text{C}} \quad \text{Fe} + \text{H}_2\text{S} \quad (1-4c)
\]

The reactions of pyrite with CH\(_4\), CO or CaSO\(_4\) may occur during pyrolysis according to the following:

\[
4\text{FeS}_2 + \text{CH}_4 \quad \xrightarrow{500 \degree \text{C}} \quad \text{CS}_2 + 4\text{FeS} + 2\text{H}_2\text{S} \quad (1-5)
\]

\[
\text{CaSO}_4 + \text{FeS}_2 + \text{H}_2\text{O} \quad \xrightarrow{} \quad \text{CaO} + \text{FeS} + 2\text{SO}_2 + \text{H}_2 \quad (1-6)
\]

Similar reactions are possible between CO and FeS\(_2\). Some excellent references are available in the literature\(^{46,55-56,59-60}\) which provide further details regarding these reactions.

Most aliphatic sulfur compounds decompose appreciably at about 500\(^\circ\)C. Diethyl sulfides begin decomposing at about 400\(^\circ\)C to form \(\text{H}_2\text{S}\) and mercaptans. Aliphatic and benzylic sulfides, mercaptans, and disulfides lose \(\text{H}_2\text{S}\) between 700 and 800\(^\circ\)C. Aromatic sulfides and mercaptans are relatively stable\(^{61-64,55}\) and yield \(\text{H}_2\text{S}\) and \(\text{CS}_2\) only at a relatively high temperature (800\(^\circ\)C). Examples of the reactions of organic sulfur are summarized in Table 1-1.\(^{61}\)

The volatile matter yield of the lower rank coals is significantly higher than that of the higher rank coals. The lower rank coals with higher volatile matter content may retain less sulfur in the residue (by fixation of sulfur by organic or inorganic coal constituents) than the higher rank coals.
coals. Also, the indigenous mineral matter present in coal (particularly calcium, sodium, or iron compounds) may react

<table>
<thead>
<tr>
<th>Table 1-1. A Summary of Possible Organic Reactions Involving Sulfur Compounds during Coal Devolatilization</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Reaction Diagram" /></td>
</tr>
</tbody>
</table>

and fix sulfur species in the solids during pyrolysis. $^{55}$

In 1932 Snow $^{57}$ investigated the conversion of coal sulfur at various peak temperatures in the presence of different gases, and reported that first traces of $H_2S$ could be observed at a temperature as low as $200\, ^\circ C$.

In 1974 Yergey et al. $^{62}$ performed non-isothermal kinetic studies on sulfur evolution in hydrogen at a relatively slow heating rate (1 to $100\, ^\circ C/min$). They developed a kinetic scheme to describe $H_2S$ evolution in hydrogen.

In 1974 Stinnett et al. $^{63}$ applied the principle of free energy minimization and used the NASA chemical equilibrium
code (CEC) to predict the composition of the fixed-bed exit gases, including the sulfur species.

In 1987 Calkins\textsuperscript{59} studied the conversion of coal and model organic sulfur compounds in a rapidly heated fluid-bed reactor.

In 1978 Attar\textsuperscript{43} investigated the evolution of sulfur gases during coal pyrolysis. The yields and rates of evolution of the sulfur gases depended not only on pyrolysis conditions but also on the coal itself. The organic/inorganic forms of sulfur, as well as the secondary reactions of sulfur gases with solids and with other pyrolysis-generated gases, play an important role.

Monitoring the time- and temperature-dependent evolution of sulfur-containing gases during coal pyrolysis provides insight into the sulfur chemistry affecting the evolution profiles. Programmed-temperature studies of sulfur gas evolution often have been limited to H\textsubscript{2}S.\textsuperscript{43,65} In some cases, all sulfur gases are studied collectively by reducing or oxidizing them to H\textsubscript{2}S or SO\textsubscript{2}.\textsuperscript{66-67}

In 1987 Calkins\textsuperscript{59} studied the evolution of individual sulfur species from a pyroprobe using gas chromatograph/mass spectrometer (GC/MS) and from isothermal flash pyrolysis. Boudou et al.\textsuperscript{68} also identified some individual sulfur gases from isothermal pyrolysis using a Curie-point reactor in combination with MS, GC and GC/MS.

In 1988 M.S. Oh et al.\textsuperscript{69} investigated the evolution of sulfur gases during pyrolysis of eight Argonne premium coal
samples in an inert atmosphere (argon) in the temperature range of 25 to 900°C with a slow heating rate (4.5°C/min). They monitored the real-time evolution of sulfur gases during slow-heating pyrolysis using a triple quadrupole mass spectrometer (TQMS). Their studies demonstrated that sulfur gaseous species were SO$_2$, COS, CS$_2$, H$_2$S, and some organic sulfur gases such as C$_4$H$_4$S, CH$_3$SH, C$_2$C$_5$SH, C$_3$H$_7$SH, CH$_3$C$_4$H$_4$S, C$_2$H$_3$SH and CH$_3$C$_4$H$_3$SH evolved during the coal pyrolysis.

Sulfur dioxide is the only gaseous sulfur species that evolved at temperature lower than 200°C, which implies the existence of loosely bound, trapped, or adsorbed SO$_2$ on the surface of coal. They suggested that SO$_2$ evolution seemed to be very sensitive to pyrolysis conditions and a reaction of SO$_2$ with the stainless steel.

All organic sulfur gases as well as COS, CS$_2$, and H$_2$S were evolved in the temperature range of 400 to 500°C. Their evolution profiles were a poorly defined combination of organic pyrolysis reactions and pyrite reactions. The source of the sulfur could be both sulfur in the organic matrix as well as pyritic sulfur.

The decomposition of pyrite at about 550°C produced H$_2$S, COS and CS$_2$. Both gas-solid reactions and gas-phase secondary reactions are responsible for the formation of the sulfur gases, as shown below:

A. Gas-solid reactions to form H$_2$S, COS, CS$_2$ and thiols:

$$2\text{FeS}_2 + \text{Organic} \rightarrow 2\text{FeS} + \text{H}_2\text{S} + \text{R-SH} \quad (1-7)$$

$$\text{FeS}_2 + \text{CO} \rightarrow \text{COS} + \text{FeS} \quad (1-8)$$
\[2\text{FeS}_2 + \text{coal-C} \rightarrow \text{CS}_2 + 2\text{FeS} + \text{coal} \quad (1-9)\]
\[4\text{FeS}_2 + \text{CH}_4 \rightarrow \text{CS}_2 + 4\text{FeS} + 2\text{H}_2\text{S} \quad (1-10)\]

B. Gas-phase secondary reactions to form COS, CS\(_2\) and thiols:

\[\text{H}_2\text{S} + \text{R} \rightarrow \text{R}'\text{-SH} \quad (1-11)\]
\[\text{H}_2\text{S} + \text{R-OH} \rightarrow \text{R}'\text{-SH} + \text{H}_2\text{O} \quad (1-12)\]
\[\text{H}_2\text{S} + \text{CO} \rightarrow \text{COS} + \text{H}_2 \quad (1-13)\]
\[\text{H}_2\text{S} + \text{CO}_2 \rightarrow \text{COS} + \text{H}_2\text{O} \quad (1-14)\]
\[\text{H}_2\text{S} + \text{COS} \rightarrow \text{CS}_2 + \text{H}_2\text{O} \quad (1-15)\]
\[2\text{COS} \rightarrow \text{CS}_2 + \text{CO}_2 \quad (1-16)\]

The evolution of sulfur gases preceded that of hydrocarbon gases.

In 1989 Khan\(^{70}\) investigated the distribution of coal sulfur into the gaseous, liquid, and solid products that occur during devolatilization (pyrolysis) in an inert atmosphere at a relatively low temperature (about 500°C) of bituminous coal containing various amounts of total, pyritic and organic sulfur. Thirty-two coal samples, mostly in the high volatile range, were investigated in the study. His study demonstrated that 31% (as sum of H\(_2\)S and COS) of the coal sulfur appeared in the gaseous products of the coal pyrolysis, while about 61% of the coal sulfur appeared in char. Hydrogen sulfide and COS were only the gaseous sulfur species found in the pyrolysis gaseous products. The total gaseous sulfur (H\(_2\)S+COS) generated during coal pyrolysis could be correlated with the total coal sulfur using the following equation:

Total sulfur in gas = 0.43(coal\(_{pyr}\))

\([R^2=0.68]\)
Furthermore, total coal sulfur could be utilized to predict the yields of $\text{H}_2\text{S}$ or COS species individually using the following equations:

$$[\text{H}_2\text{S}] = 0.36(\text{coal}_{\text{pys}})$$
$$= 0.53(\text{coal}_{\text{orgs}})$$
$$= 0.17(\text{coal}_{\text{pys}}) + 4.0(\text{coal}_{\text{orgs}})$$

$$[\text{COS}] = 0.071(\text{coal}_{\text{pys}})$$
$$= 0.095(\text{coal}_{\text{orgs}})$$
$$= 0.040(\text{coal}_{\text{pys}}) + 0.063(\text{coal}_{\text{orgs}})$$

The tar sulfur (in liquid) could be correlated to the coal sulfur using the following equation:

Total sulfur in tar = 0.0128(\text{coal}_{\text{pys}})$$
$$= 0.123(\text{coal}_{\text{orgs}})$$
$$= 0.034(\text{coal}_{\text{pys}}) + 0.095(\text{coal}_{\text{orgs}})$$

The char sulfur (in solid) could be predicted by the total coal sulfur using the following equation:

Total S in char = 0.95(\text{coal}_{\text{pys}})$$
$$= 1.09(\text{coal}_{\text{orgs}})$$
$$= 0.70(\text{coal}_{\text{pys}}) + 0.53(\text{coal}_{\text{orgs}})$$

The organic sulfur content of coal plays a strong role in determining the sulfur content of tar or gases. The tar sulfur is primarily attributable to the tightly bound
thiophanic structures present in coal. The pyritic sulfur content of coal, on the other hand, plays a key role in determining the sulfur content of char. It is proposed that 'loosely' bound sulfur (e.g., thiols, sulfides, or disulfides) decomposes at a relatively low temperature (about 500°C) yielding ultimately H$_2$S and COS.

But Khan did not establish and evaluate the release profile of the gaseous sulfur species (e.g., H$_2$S and COS) during the coal pyrolysis.

In 1991 Coburn et al. investigated a mechanism for H$_2$S release during pyrolysis of Illinois #6 coal in argon. They used a temperature programmed, gas evolution technique with an argon sweep of 20 ml/min to study the evolution of H$_2$S detected by a quadrupole MS at different temperatures. At a 10 K/min heating rate, the rate of H$_2$S release from both organic and pyrite by the H-donor mechanism (as shown in reactions 1-17 and 1-18) reaches a maximum at 700 K and then decreases.

\[
\begin{align*}
\text{H-donor} & \\
\text{R-S-H} & \rightarrow \text{H}_2\text{S} + \text{RH} & \text{(1-17)} \\
\text{FeS}_2 & \rightarrow \text{H}_2\text{S} + \text{FeS} & \text{(1-18)}
\end{align*}
\]

The H$_2$S release by the unimolecular decomposition of coal pyrite to FeS and S$_2$ also by the H-donor mechanism (as shown in Reaction 1-19) then occurs sharply at 830 K (557 °C).

\[
\begin{align*}
\text{H-donor} & \\
\text{FeS}_2 & \rightarrow \text{FeS} + \frac{1}{2} \text{S}_2 & \rightarrow \text{H}_2\text{S} + \text{Fe} & \text{(1-19)}
\end{align*}
\]
In 1987 Carangelo et al. investigated hydrocarbon structure and kinetics of gas evolution by using a TG/FTIR technique to study pyrolysis of coal, char, tar and oil shale. They identified the individual gaseous species such as CO, CO₂, H₂O, CH₄, C₂H₆, C₂H₄, C₂H₂, C₃H₈, benzene, heavy paraffins, heavy olefins, HCN, HCl, NH₃, SO₂, CS₂, COS, CH₃OH, CH₃COOH and CH₃COCH₃.

1.6 Objectives of This Study

This study is a part of the on-going project "Behavior of Sulfur and Chlorine in Coal during Combustion and Boiler Corrosion". One important goal of the study is to identify gaseous chlorine and sulfur species from the mixtures of volatile species evolved and the kinetics of their release during coal pyrolysis and combustion. The results should lead to a better understanding of the relation between the chlorine, sulfur and alkali levels in feed coal. In addition, boiler corrosion can be better understood. The purposes of this work were (1) to determine gaseous chlorine and sulfur species as HCl, H₂S, SO₂ and COS evolved during pyrolysis and combustion of Illinois coals, and to evaluate their release behaviors using both simultaneous TG/FTIR technique and TG/IC techniques; (2) to investigate the effect of chlorine-removal from the coal on the combustion-release behavior of the chlorine and sulfur; and (3) to study the effect of sorbent-addition to the coal on the combustion-release behavior of the chlorine and sulfur.
2.1 Preparation of Samples

2.1.1 Illinois Coal Samples

Four coal samples from the Illinois Basin Coal Sample Program were used in the experiments of coal pyrolysis and combustion. The coal samples (called IBC coals for short) contain 0.02 to 0.42% chlorine and 1.13% to 4.54% sulfur on a dry basis. The compositions of the coal samples are shown in Table 2-1.

<table>
<thead>
<tr>
<th>Composition\Coal</th>
<th>IBC-103</th>
<th>IBC-105</th>
<th>IBC-106</th>
<th>IBC-109</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Moisture</td>
<td>4.80</td>
<td>9.16</td>
<td>9.23</td>
<td>8.76</td>
</tr>
<tr>
<td>% Ash</td>
<td>8.70</td>
<td>18.60</td>
<td>9.00</td>
<td>8.20</td>
</tr>
<tr>
<td>% Vol Matter</td>
<td>36.10</td>
<td>36.80</td>
<td>39.70</td>
<td>35.00</td>
</tr>
<tr>
<td>% Carbon</td>
<td>74.48</td>
<td>63.60</td>
<td>71.86</td>
<td>75.05</td>
</tr>
<tr>
<td>% Hydrogen</td>
<td>5.04</td>
<td>4.58</td>
<td>4.93</td>
<td>4.89</td>
</tr>
<tr>
<td>% Nitrogen</td>
<td>1.73</td>
<td>1.22</td>
<td>1.67</td>
<td>1.74</td>
</tr>
<tr>
<td>% Sulfur</td>
<td>2.30</td>
<td>4.55</td>
<td>3.77</td>
<td>1.13</td>
</tr>
<tr>
<td>% Oxygen</td>
<td>7.56</td>
<td>7.39</td>
<td>8.76</td>
<td>8.53</td>
</tr>
<tr>
<td>% Chlorine</td>
<td>0.18</td>
<td>0.10</td>
<td>0.02</td>
<td>0.42</td>
</tr>
</tbody>
</table>

Note: % Moisture is as-determined, and all the other values are on a dry basis.

2.1.2 Leached Illinois Coal Samples

Two water-leached IBC coal samples (Coal-0.23 and Coal-0.07) were used in the experiments to investigate the effects
of chlorine removal from high chlorine coal IBC-109 (0.42% Cl) on the behavior of chlorine release and other properties during their combustion. The chlorine content of two leached-IBC coal is shown in Table 2-2.

Table 2-2. Total chlorine content in two leached-IBC coal samples derived from high chlorine coal IBC-109

<table>
<thead>
<tr>
<th>Coal Sample</th>
<th>Total chlorine content</th>
</tr>
</thead>
<tbody>
<tr>
<td>IBC-109</td>
<td>0.42%</td>
</tr>
<tr>
<td>Coal-0.23</td>
<td>0.23%</td>
</tr>
<tr>
<td>Coal-0.07</td>
<td>0.068%</td>
</tr>
</tbody>
</table>

Note: All the values are on a dry basis.

The chlorine has been removed from high-chlorine coal, IBC-109, by Illinois State Geological Survey (ISGS) Grinding-Leaching System. The leached coal, Coal-0.23, was obtained by grinding and washing high-chlorine coal IBC-109 in water. A second grinding and leaching once again by water produced another leached coal, Coal-0.07. The particle sizes of the two leached coals were unknown as used in the experiments.

2.1.3 Coal-Sorbent Mixture Samples

Two coal-sorbent mixture samples, referred to as combination fuels, were used in the experiments to investigate the reduction of emission of gaseous chlorine and sulfur species from high-chlorine and high-sulfur IBC coals during combustion. Also investigated was the effect of chemical reagent addition to coal on the behavior of chlorine and sulfur release during combustion. Table 2-3 lists components of the IBC coal-sorbent mixture samples.
Table 2-3. Components and Chlorine Content in Coal-Sorbent Mixtures Derived from High Chlorine Coal IBC-109

<table>
<thead>
<tr>
<th>Sample</th>
<th>Component</th>
<th>Total Cl in coal</th>
</tr>
</thead>
<tbody>
<tr>
<td>IBC-109</td>
<td>100% Coal</td>
<td>0.42%</td>
</tr>
<tr>
<td>Coal-CaCO₃</td>
<td>94% Coal+6% CaCO₃</td>
<td>0.39%</td>
</tr>
<tr>
<td>Coal-Ca(OH)₂</td>
<td>95% Coal+5% Ca(OH)₂</td>
<td>0.40%</td>
</tr>
</tbody>
</table>

The coal-sorbent mixtures were prepared in the following manner. A fixed amount of raw coal and a fixed amount of chemical reagent powder such as CaCO₃ or Ca(OH)₂ (Laboratory Reagent, powder; MC&B, Inc.) was placed into an 100-ml container. Each mixture sample was well mixed physically by several metallic mixers in the container, and both were used with an identical amount of coal (on a mass basis) and calcium (on a mmole basis) in the individual experiments.

2.2 Investigation of Coal Pyrolysis and/or Combustion Using Simultaneous TG/FTIR Techniques.

2.2.1 Simultaneous TG/FTIR Techniques

Thermogravimetry (TG) is a dynamic-mass change method in which the mass of a sample is measured as a function of temperature while the sample is subjected to a controlled heating program.

Simultaneous TG/FTIR techniques are based on a combined analytical method in which thermogravimetry (TG) is used in conjunction with Fourier Transform Infrared Spectroscopy (FTIR). While TG is monitoring the mass change of a sample as a function of temperature change, FTIR is able to simultaneously identify qualitatively and/or determine
quantitatively the individual gaseous species evolved from the coal sample at the corresponding temperatures.

By using the combined TG/FTIR instrumental system, the volatile species produced on a DuPont-951 TG during pyrolysis and/or combustion of a coal sample are analyzed by the Perkin Elmer-1650 FTIR spectrometer. The system is able to continuously measure the mass change of the coal sample with the temperature increase at a heating rate of 10°C/min (by TG) as well as to identify qualitatively and/or determine quantitatively the individual gaseous species such as HCl, NH₃, COS, SO₂, H₂S, H₂O, CH₄, C₂H₄, C₃H₆, etc. (by FTIR) emitted during coal pyrolysis and/or combustion. The sample chamber in the TG furnace is connected to the 100 x 24 mm gas cell in the FTIR spectrometer through a 1-mm teflon tube. Both the teflon line and gas cell can be heated by heating coils up to 250°C, and the temperature can be controlled continuously by temperature controllers. The time lag between the sample chamber and the gas cell is one minute with a oxygen-free nitrogen flow at a rate of 50 ml/min during pyrolysis or with a air flow at a rate of 50 ml/min. The FTIR spectrum can be taken manually every minute. In other words, the spectrum can be taken manually every 10°C during heating within the temperature range of 20-850°C. This also includes the time it takes to store the spectrum on the disk. Alternatively, the FTIR spectrometer is also able to automatically scan the pyrolysis and/or combustion gas mixture and the spectra can be taken automatically every minute or every 10°C during heating.
by using the LabScan software. A diagram of simultaneous TG/FTIR instrumental system is shown in Figure 2-1.

2.2.2 Calibration of FTIR Spectra by Pure Gas

Calibration of the FTIR spectra was made by scanning individual pure gases or prepared gas mixtures before the coal pyrolysis and/or combustion was investigated using the TG/FTIR system. The standard FTIR spectra of HCl, H2S, SO2, CO2 and CO were made by scanning their pure gases in the FTIR gas cell. The pure gases were carried by a dry-nitrogen flow at a rate of 50 ml/min through the teflon and gas cell, which were heated isothermally at approximately 120°C. The standard spectrum of CH4 was taken by scanning 5% CH4 in nitrogen, and the standard H2O spectrum taken by scanning steam produced by vaporizing D.I. water.

2.2.3 Determination of Gas Release Profiles during Coal Pyrolysis and/or Combustion

Varying sizes of a coal sample were used in TG-FTIR experiments in order to identify by FTIR all the possible volatile species evolved during pyrolysis or combustion. The pyrolysis or combustion was conducted in the TG furnace tube with an atmosphere of nitrogen or air at a flow rate of 50 ml/min and with a temperature program from ambient to 1000°C at a heating rate of 10°C/min. Meanwhile, the FTIR scanned every minute or 10°C the volatile species produced on TG at a scanning period of four seconds. When approximately 30 mg of a high-chlorine coal sample was used in a pyrolysis
Figure 2-1. A diagram of TG/FTIR/IC instrumental system.
experiment, CH₄, paraffin, CO₂, CO, H₂O, H₂S, COS, SO₂ were the volatile species identified by the FTIR. However, HCl, NH₃ and HCN could not be identified. When approximately 100 mg of the high-chlorine coal was used in the experiment, the volatile species identified contained HCl, NH₃, HCN, NO, CH₄, paraffin, C₂H₄, C₃H₆, CO₂, CO, H₂O, H₂S, COS, SO₂. Similarly, when approximately 30 mg of a high-chlorine coal was used in a combustion experiment, CO₂, CO, H₂O, CH₄, SO₂ and COS were the volatile species observed by the FTIR. However, gaseous HCl and NO₂ could not be observed. The HCl could not be observed by the FTIR unless approximately 300 mg of a high-chlorine coal was employed in the experiment.

The release profiles of the volatile species during pyrolysis or combustion were made by plotting their FTIR peak absorption vs. temperature.

2.3 Investigation of Release Behavior of Chlorine and Sulfur During Coal Pyrolysis and Combustion by TG/IC Technique

2.3.1 TG/IC Technique

The TG/IC technique is based on a combined analytical method, in which thermogravimetry (TG) is able to monitor the mass change of a coal sample with temperature during pyrolysis and/or combustion, and ion chromatography (IC) is able to quantitatively determine the concentration of gaseous chlorine and sulfur species emitted in the same temperature ranges. Figure 2-1 shows the flow diagram of the TG/IC system used in this study in which the TG/FTIR is conducted simultaneously, but the TG/IC is not conducted simultaneously.
2.3.2 Determination of Quantitative Chlorine and Sulfur Release Profiles of Coal Pyrolysis and Combustion

Approximately 250 mg of a high-chlorine coal sample was heated on a sample boat inside the furnace chamber of a DuPont-951 TG in each TG/IC pyrolysis or combustion experiment. The sample was heated from ambient to 850°C at a heating rate of 10°C/min, and the pyrolysis or combustion was conducted in an atmosphere of nitrogen or air at a flow rate of 50 ml/min. The sample chamber on the TG furnace was connected with a series of buffered traps. Carried by a nitrogen or air flow during the pyrolysis or combustion, the volatile species produced on TG was collected in three buffered traps connected in series every 50°C within the temperature range from ambient to 850°C. Thus, the gaseous chlorine and sulfur were trapped as chloride and sulfate ions in approximately 90 ml of the buffer solution (pH = 9.5) containing sodium bicarbonate (70 ppm) -sodium carbonate (16 ppm) and 1.5% H₂O₂. Then, each trapped buffered solution was diluted exactly to 100 ml, filtered through a membrane filter, and analyzed for chloride and sulfate concentration by the Shimadzu HIC-6A ion chromatograph system.

The Shimadzu HIC-6A system consists of a liquid chromatograph (LC-600, a pump), a conductivity detector(CDD-6A), an ion chromatograph (HIC-6A), a column with a guard column (Shim-pack IC-A1) and a data processor for chromatography (Chromatopac-CR501). Before a trapped buffered solution was analyzed for chloride and sulfate concentration, the Shimadzu HIC-6A system was calibrated by analyzing a
standard buffer solution containing 1.00 ppm of chloride and 1.00 ppm sulfate. The standard Cl/S buffer solution was prepared with sodium chloride (Reagent, A.C.S., Crystals; Matheson Coleman & Bell), sodium sulfate (Fisher Laboratory Chemical, Crystals, Cat. No. S-420; Fisher Scientific Company) and pure water. The calibration was conducted by the Absolute Calibration Curve Method (made automatically by CR501) under the following conditions:

1. **Mobile phase**: 2.5 mM phthalic acid (99%, reagent; Mallinckrodt, Inc.)
   
   2.4 mM tris(hydroxymethyl) aminomethane (99.9%, reagent; J.T. Baker Chemical Co.)
   
   pH 4.0

2. **Flow rate**: 1.5 ml/min

3. **Column temperature**: 40°C

4. **Detector parameters**: a) Cell temperature 43°C
   
   b) Measuring range: 0.8 µS/cm
   
   c) Polarity: (+)

5. **Injection volume**: 100 µl

6. **Retention time** (t_R):
   
   a) t_R(Cl^-) = 2.4 min
   
   b) t_R(SO_4^{2-}) = 5.0 min

7. **Concentrations**:
   
   a) Cl = 1.00 ppm
   
   b) S = 1.00 ppm

Then, under the same conditions as used for the calibration, each trapped buffer solution (unknown) was analyzed by IC for chlorine and sulfur content emitted in each 50°C range. As a consequence, the release profiles of gaseous chlorine and
sulfur during coal pyrolysis and/or combustion were established quantitatively by plotting the chlorine or sulfur content vs. temperature (ambient to 850°C).

2.3.3 Determination of Chlorine and Sulfur Mass Balance During Combustion of Coal-Sorbent Mixtures

Approximately 50 mg of a coal-sorbent mixture was used in a rapid-heating combustion. After the sample chamber of the TG furnace was preheated to 800°C, the sample was pushed into the furnace and heated at a heating rate of about 1600°C/min under an atmosphere of air. The volatile species produced during the combustion was carried by an air flow (50 ml/min) through a tubing into four traps connected in series containing 90 ml of Na₂CO₃-NaHCO₃ buffered solution. The gaseous chlorine and sulfur emitted were collected as their anions in the buffered traps. For chlorine and sulfur content emitted during the rapid-heating combustion of the sample, the trapped buffered solutions were analyzed using IC under the same experimental conditions as above. As a result, the mass balance of chlorine and sulfur in the coal-sorbent mixture before and after the rapid-heating combustion was determined by appropriate calculations.
CHAPTER 3

BEHAVIOR OF CHLORINE AND SULFUR IN ILLINOIS COAL DURING PYROLYSIS

3.1 Thermogravimetric Analysis for Illinois Coal Pyrolysis

As shown in Figures 3-1 and 3-2, the TG/DTG curves obtained by heating approximately 30 mg of the Illinois coal samples illustrate the behavior of decomposition of the samples during pyrolysis from ambient to 950°C. Table 3-1 summarizes the thermogravimetric (TG/DTG) analysis results.

Table 3-1. Thermogravimetric (TG/DTG) Results of Illinois Coals during Pyrolysis

<table>
<thead>
<tr>
<th>Coal</th>
<th>Temp</th>
<th>Wt Loss</th>
<th>T_max a</th>
<th>Wt Loss R_max b</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(°C)</td>
<td>(%)</td>
<td>(°C)</td>
<td>(%/min)</td>
</tr>
<tr>
<td>IBC-103</td>
<td>22-150</td>
<td>3.79</td>
<td>62.5</td>
<td>0.54</td>
</tr>
<tr>
<td></td>
<td>150-350</td>
<td>1.41</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>350-940</td>
<td>30.35</td>
<td>425.5</td>
<td>2.42</td>
</tr>
<tr>
<td>IBC-105</td>
<td>22-150</td>
<td>7.46</td>
<td>60.1</td>
<td>1.08</td>
</tr>
<tr>
<td></td>
<td>150-350</td>
<td>1.36</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>350-940</td>
<td>30.49</td>
<td>411.2</td>
<td>2.37</td>
</tr>
<tr>
<td>IBC-106</td>
<td>22-150</td>
<td>7.49</td>
<td>62.7</td>
<td>1.24</td>
</tr>
<tr>
<td></td>
<td>150-350</td>
<td>1.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>350-940</td>
<td>34.60</td>
<td>452.2</td>
<td>1.69</td>
</tr>
<tr>
<td>IBC-109</td>
<td>22-150</td>
<td>3.86</td>
<td>60.9</td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td>150-350</td>
<td>1.93</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>350-940</td>
<td>27.45</td>
<td>433.5</td>
<td>1.79</td>
</tr>
</tbody>
</table>

a) T_max is a temperature at which the maximum rate of weight loss occurs.
b) Wt Loss R_max is a maximum rate of weight loss.
Figure 3-1. TG curves of Illinois coals during pyrolysis.
Figure 3-2. DTG curves of Illinois coals during pyrolysis.
The four coal samples have similar behavior of thermal decomposition during pyrolysis, but the amount of the weight loss varies from one to another, with different maximum rates and $T_{\text{MAX}}$'s. The $T_{\text{MAX}}$ is the temperature at which the maximum rate of the weight loss occurs. Significant weight loss occurs for all the coal samples in two major temperature ranges: 22-150°C and 350-940°C. In the 22-150°C range in which the first significant weight loss takes place, the two high-chlorine coals, IBC-109 (0.42% Cl) and IBC-103 (0.18% Cl), have almost the same amount of weight loss, 3.86% and 3.89%, respectively. Nearly the same amount of weight loss, 7.53% and 7.49%, occurs for the two low-chlorine coals, IBC-105 (0.10% Cl) and IBC-106 (0.02% Cl), respectively. However, the amounts of weight loss for the former two coals are less than that for the latter two coals. The first weight loss results from the vaporization of inherent water held in the capillaries of varying radii in the coals.26 It is obvious that IBC-105 and IBC-106 contain more inherent water than the other two coals.

The second significant weight loss for the four Illinois coals occurs in the same temperature range of approximately 350°C-950°C, with the amount in the order of IBC-109 (27.45%) < IBC-103 (30.35%) < IBC-105 (30.49%) < IBC-106 (34.60%), respectively, as shown in Table 3-1. Yet, IBC-109 (the highest-chlorine coal) and IBC-106 (the lowest-chlorine coal) have very close maximum rates of weight loss (1.79%/min and 1.69%/min, respectively) and close $T_{\text{MAX}}$'s (433° and 452°C,
respectively). The two coals IBC-103 and IBC-105 (the medium-chlorine coals) have weight loss rates of 2.42%/min and 2.37%/min at 426° and 411°C, respectively. The weight losses in the 350-950°C temperature range correspond basically to the loss of the volatile species resulting from decomposition of the coals, and are comparable to the values of the volatile matter loss determined using LECO MAC-400 Analyzer (30.82% for IBC-109, 32.56% for IBC-103, 31.83% for IBC-105 and 33.51% for IBC-106 on an as-received basis).

It is interesting to note that within the temperature range of 22-940°C, the observed total weight loss for the four coals increases in an order, IBC-109 (33.24%) < IBC-103 (35.77%) < IBC-105 (39.31%) < IBC-106 (43.10%). Also, due to the loss of the volatile species from coal in the temperature range of 150-940°C, the amount of weight loss for the coals increases in the same order as above: IBC-109 (29.38%) < IBC-103 (31.76%) < IBC-105 (31.85%) < IBC-106 (35.61%). On the other hand, the chlorine content in the four coals increases in an opposite order, IBC-106 (0.02% Cl) < IBC-105 (0.10% Cl) < IBC-103 (0.18% Cl) < IBC-109 (0.42% Cl). In other words, the larger the amount of the total weight loss or the higher the content of the volatile species, the higher the chlorine content in the coal. This might give information about the forms of chlorine present in the coals. Furthermore, similar behavior of the weight change during pyrolysis between a high chlorine coal IBC-109 (0.42% Cl) and medium chlorine coal IBC-103 (0.18% Cl), and between two low chlorine coals IBC-105
(0.10% Cl) and IBC-106 (0.02% Cl), might also provide information about the forms of chlorine present in Illinois coals.

3.2 FTIR Analysis for Illinois Coal Pyrolysis Gases

3.2.1 Standard FTIR Spectra of Pure Gases

In order to identify individual gases from the volatile species produced during coal pyrolysis, the pure gases HCl, H$_2$S, SO$_2$, CH$_4$, CO, CO$_2$ and H$_2$O, which were suspected to be present in the volatile species, were analyzed by FTIR, and their standard FTIR spectra are shown in Figure 3-3. The FTIR spectra of other individual gases were obtained from the literature. Table 3-2 summarizes wavenumbers (cm$^{-1}$) of the absorption bands and their strongest peaks (P$_{\text{Max}}$) in the standard FTIR spectra of the pure gases.

As shown in Figure 3-3 and Table 3-2, it is obvious that overlapping of the absorption regions and peak maxima occurs if the coal pyrolysis-evolved volatile species consist of these individual gases. Such absorption region overlapping makes it difficult to identify some individual gases in the pyrolysis and combustion gas mixture.

3.2.2 Identification of Illinois Coal Pyrolysis Gases

The volatile species evolved during pyrolysis of Illinois coals were monitored and identified by FTIR spectroscopy. Figures 3-4a and 3-4b show the combined FTIR spectra of the volatile species evolved from high-chlorine coal IBC-109,
Table 3-2. Wavenumbers of Absorption Bands and Peaks of Some Pure Gases in Their Standard FTIR Spectra

<table>
<thead>
<tr>
<th>Gas</th>
<th>Region I</th>
<th>P&lt;sub&gt;MAX&lt;/sub&gt;</th>
<th>Region II</th>
<th>P&lt;sub&gt;MAX&lt;/sub&gt;</th>
<th>Region III</th>
<th>P&lt;sub&gt;MAX&lt;/sub&gt;</th>
<th>Region IV</th>
<th>P&lt;sub&gt;MAX&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>3760-3524</td>
<td>3729</td>
<td>2398-2210</td>
<td>2360</td>
<td>748-591</td>
<td>670</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>2235-2142</td>
<td>2172</td>
<td>2142-2025</td>
<td>2116</td>
<td>1580-1281</td>
<td>1506</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>4000-3452</td>
<td>3851</td>
<td>1956-1589</td>
<td>1652</td>
<td>1583-1048</td>
<td>1268</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH&lt;sub&gt;4&lt;/sub&gt;</td>
<td>3218-2836</td>
<td>3014*</td>
<td>1396-1177</td>
<td>1304*</td>
<td>1322-1065</td>
<td>1164</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;S</td>
<td>4000-3530</td>
<td>3062</td>
<td>2854-2567</td>
<td>2712</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>2534-2217</td>
<td>2511</td>
<td>1413-1296</td>
<td>1374</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCl</td>
<td>3116-2893</td>
<td>2962</td>
<td>2873-2565</td>
<td>2798</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* The maximum peak is a spike.

within the temperature range from ambient to 850°C during pyrolysis. The other three coals have similar combined spectra as above.

By comparing with the standard FTIR spectra of pure gases (Figure 3-3) and referring to the literature, individual gases were able to be identified from the volatile species evolved from coal pyrolysis. Liberated in varying temperature ranges during pyrolysis of Illinois coals, the individual gases include carbon monoxide, carbon dioxide, carbonyl sulfide, sulfur dioxide, hydrogen sulfide, ammonia, hydrogen cyanide, nitrogen monoxide, nitrogen dioxide, water moisture, propylene, ethylene, methane, paraffin and hydrogen chloride. Table 3-3 lists wavenumbers of absorption peaks selected to...
Figure 3-4a. Typical combined FTIR spectra of volatile species emitted from high-chlorine coal IBC-109 between 200° and 490°C during pyrolysis.
Figure 3-4b. Typical combined FTIR spectra of volatile species emitted from high-chlorine coal 18C-109 between 500° and 850°C during pyrolysis.
Table 3-3. Wavenumbers of Absorption Peaks Chosen to Identify the Individual Gaseous Species from the Coal Pyrolysis Gases.

<table>
<thead>
<tr>
<th>Volatile species</th>
<th>Wavenumber</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon dioxide, CO₂</td>
<td>2356 cm⁻¹</td>
</tr>
<tr>
<td>Carbon monoxide, CO</td>
<td>2178 cm⁻¹</td>
</tr>
<tr>
<td>Water, H₂O</td>
<td>1683 cm⁻¹</td>
</tr>
<tr>
<td>Methane, CH₄</td>
<td>1304 cm⁻¹</td>
</tr>
<tr>
<td>Ethylene, C₂H₄</td>
<td>950 cm⁻¹</td>
</tr>
<tr>
<td>Propylene, C₃H₆</td>
<td>912 cm⁻¹</td>
</tr>
<tr>
<td>Paraffin</td>
<td>2967 cm⁻¹</td>
</tr>
<tr>
<td>Ammonia, NH₃</td>
<td>965 cm⁻¹</td>
</tr>
<tr>
<td>Hydrogen cyanide, HCN</td>
<td>713 cm⁻¹</td>
</tr>
<tr>
<td>Nitrogen monoxide, NO</td>
<td>2050 cm⁻¹</td>
</tr>
<tr>
<td>Nitrogen dioxide, NO₂</td>
<td>1468 cm⁻¹</td>
</tr>
<tr>
<td>Hydrogen sulfide, H₂S</td>
<td>1268 cm⁻¹</td>
</tr>
<tr>
<td>Carbonyl sulfide, COS</td>
<td>2073 cm⁻¹</td>
</tr>
<tr>
<td>Sulfur dioxide, SO₂</td>
<td>1374 cm⁻¹</td>
</tr>
<tr>
<td>Hydrogen chloride, HCl</td>
<td>2798 cm⁻¹</td>
</tr>
</tbody>
</table>

identify the individual gases from the volatile species.

The COS absorption region (around 2073 cm⁻¹) overlaps completely with CO absorption region II (2142-2025 cm⁻¹), as shown in Figure 3-3 and Table 3-2. Fortunately, the intensity of the COS maximum absorption peak (2073 cm⁻¹) is stronger enough than that of CO absorption band II so that COS is able to be easily observed in the FTIR spectra of the volatile species.

However, it is difficult to identify H₂S from the volatile species because two strong absorption regions of H₂S overlap with CO₂, H₂O, CH₄, as shown in their standard FTIR spectra (Figure 3-3 and Table 3-2). Since strong H₂S absorption region I (4000-3530 cm⁻¹) overlaps completely with both CO₂ absorption region I (3760-3524 cm⁻¹) and H₂O absorption region I (4000-3452 cm⁻¹), it is impossible to resolve H₂S in this
combined absorption region. Although strong H₂S absorption region III (1583-1048 cm⁻¹) mainly overlaps partially with the strong CH₄ absorption region II (1396-1177 cm⁻¹), the intensity of the H₂S maximum absorption peak (1292 cm⁻¹) is much lower than that of CH₄ in absorption region II. As a consequence, H₂S could not be identified directly from CH₄ absorption region II, and one is able only to identify the species indirectly from the CH₄ with appropriate correction. This determination will be discussed later.

Identification of HCl from the volatile species is not simple. It is evident that the chlorine in coal will be liberated as HCl upon isothermal heating at a certain temperature during both pyrolysis and combustion. Evolution of HCl during pyrolysis of the high-chlorine coal, IBC-109, could not be determined by FTIR when a small sample size (30 mg) was used in the experiment. When the sample size was increased from 30 mg to 100 mg and the heating line between the TG sample chamber and FTIR gas cell was improved, it was possible to observe HCl at the 2798 cm⁻¹ peak rather than at the maximum absorption peak (2819 cm⁻¹) in its absorption band II (2873-2565 cm⁻¹). There are two reasons why the HCl was not determined easily by FTIR: (1) The chlorine content in coal is so low (0.42% Cl in high chlorine coal IBC-109) that the concentration of HCl in the pyrolysis gases is also so low that it could not be easily detected by FTIR under our experiment conditions and instrumental sensitivity, and (2) Since a significant amount of water was formed during
pyrolysis, the HCl could be dissolved in the water and condensed on the tubing wall between the TG sample chamber and FTIR gas cell. The second factor is the most important one that dominates the successful determination of the HCl by FTIR.

The HCl absorption region I (3116-2893 cm\(^{-1}\)) overlaps completely with the CH\(_4\) absorption band I (3218-2836 cm\(^{-1}\)) and the paraffin absorption region. Furthermore, the absorbance intensity of HCl absorption band I is much lower than those of both CH\(_4\) absorption region I and the paraffin absorption region. Thus, no peaks in the HCl absorption region I could be used to identify the HCl from the combination of CH\(_4\) and paraffin. However, HCl absorption region II (2873-2565 cm\(^{-1}\)) only overlaps partially with both CH\(_4\) absorption region I and the paraffin absorption region. Several peaks in the HCl absorption region II can be used to determine the HCl. Since the maximum peak (2819 cm\(^{-1}\)) in HCl absorption region II is merged into both the CH\(_4\) absorption region I and the paraffin absorption region, it is not possible to determine the HCl release profile. By contrast, although the 2798 cm\(^{-1}\) peak in HCl absorption region II, the absorbance intensity of which is only a little lower than that of the 2819 cm\(^{-1}\) peak, overlaps slightly with both CH\(_4\) absorption region I and/or paraffin absorption region, its absorbance intensity is quite larger than those of CH\(_4\) region I and/or paraffin region. Therefore the HCl 2798 cm\(^{-1}\) peak can be used to determine the HCl release profile.
3.2.3 Pyrolysis Gas Release Profiles for Illinois Coals

Figure 3-5 shows a qualitative summary of the evolution of all the individual gases identified from the volatile species during pyrolysis of high-chlorine coal IBC-109. The range of evolution of each gas is marked using thin and thick solid lines. The thick solid lines indicate the absorbance intensity greater than 50% of the maximum absorbance for each gas. The emission of most individual gases occurs between 400° and 600°C, which corresponds to the second significant weight loss caused by devolatilization of the coal during pyrolysis, as shown on the TG curves (Figure 3-1). The released amounts of most of the individual gases reach the peak maxima around 440°C, which match the maximum weight loss of coal devolatilization, as shown on DTG curves (Figure 3-2). It is evident that the dominant product is methane (CH₄) during pyrolysis of IBC-109 under the experimental conditions. All the gaseous species mentioned above are also observed for pyrolysis of the other three raw Illinois coals (IBC-103, IBC-105 and IBC-106) under the same experimental conditions.

The release profiles of CO₂, CO, CH₄, C₂H₄, C₃H₆, H₂O, HCN, NH₃, NO and NO₂ during pyrolysis of high-chlorine coal IBC-109 are illustrated in Figures 3-6 and 3-7, respectively. These release profiles were established directly by plotting their peak absorbance intensities vs. temperature within the temperature range 20-950°C during pyrolysis. Figures 3-6 and 3-7 show the typical release profiles of the gaseous species produced during the pyrolysis of an Illinois coal sample, and
Figure 3-5. Qualitative illustration of gaseous species evolution during pyrolysis of IBC-109 as determined by FTIR.
Figure 3-6. Gas release profiles of CO₂, CO, CH₄, C₂H₄, C₃H₆ and Paraffin for IBC-109 pyrolysis, as determined by TG/FTIR using a 30 mg sample.
Figure 3-7. Gas release profiles of $\text{H}_2\text{O}$, HCN, $\text{NH}_3$, NO and NO$_2$ for IBC-109 pyrolysis, as determined by TG/FTIR using a 30 mg sample.
the other three Illinois coals give similar release profiles of pyrolysis gaseous species. The gas release profiles determined by TG/FTIR give us qualitative information about coal decomposition during pyrolysis. It appears that the pyrolysis of IBC-109 generates carbon dioxide between 200° and 900°C, with most CO₂ given off between 350° and 600°C, and between 680° and 850°C. The CO release profile is similar to the CO₂ release profile, but the amount of CO released is much less than that of CO₂ (approximately 1:5). It appears that the evolution of CO is probably associated with the CO₂ evolution. In other words, the CO₂ and CO probably come from the same source in the coal matrix.

The gases C₂H₄, C₃H₆ and paraffin have release profiles with the same shape, which indicate that they are produced between 300° and 600°C with the maximum amount at 440°C during the pyrolysis. However, the released amount of paraffin is much greater than that of C₂H₄ and C₃H₆ (approximately 4:1), whereas the amount of C₂H₄ and C₃H₆ is almost the same. The CH₄ release profile indicates that CH₄ is generated between 350° and 800°C and its rate reaches the maximum around 500°C. The CH₄ is a dominant product of the pyrolysis. It is evident that the organic matter in the coal seems to decompose to smaller molecules of hydrocarbons as paraffin, C₂H₄ and C₃H₆, and the smaller molecules of hydrocarbons decompose to CH₄.

As shown in the H₂O release profile (Figure 3-7), H₂O is produced between 300° and 550°C with the maximum amount at 430°C. The H₂O evolution results from the thermal
decomposition of organic constituents of coal with oxygen-contained function groups, and the H₂O is called decomposition water.²⁶ The release profiles of NH₃, HCN, NO and NO₂ (Figure 3-7) illustrate that coal pyrolysis randomly gives off gaseous nitrogen species between 250° and 850°C. The nitrogen might exist in several forms in the coal.

3.3 Sulfur Release during Illinois Coal Pyrolysis by TG/FTIR

It is well known that sulfur in coal occurs in several forms. Table 3-4 summarizes data about the forms of sulfur and their content present in four raw Illinois coals, as analyzed by ASTM D 2492.

<table>
<thead>
<tr>
<th>Coal</th>
<th>Total Sulfur</th>
<th>Pyritic Sulfur</th>
<th>Sulfate Sulfur</th>
<th>Organic Sulfur</th>
</tr>
</thead>
<tbody>
<tr>
<td>IBC-103</td>
<td>2.30%</td>
<td>1.11%</td>
<td>0.02%</td>
<td>1.16%</td>
</tr>
<tr>
<td>IBC-105</td>
<td>4.55%</td>
<td>2.52%</td>
<td>0.00%</td>
<td>2.03%</td>
</tr>
<tr>
<td>IBC-106</td>
<td>3.77%</td>
<td>1.86%</td>
<td>0.01%</td>
<td>1.90%</td>
</tr>
<tr>
<td>IBC-109</td>
<td>1.13%</td>
<td>0.50%</td>
<td>0.00%</td>
<td>0.63%</td>
</tr>
</tbody>
</table>

Note: All the values are on a dry basis.

Since there are several forms of sulfur present in Illinois coals, several gaseous sulfur species such H₂S and SO₂ can be produced by the decomposition of the coals under the pyrolysis conditions. By referring to the standard FTIR spectra of H₂S and SO₂ gases (Figure 3-3) and to the literature, we did observe three kinds of gaseous sulfur species, H₂S, SO₂ and COS under our pyrolysis conditions.
3.3.1 Pyrolysis H$_2$S Release Profiles

Hydrogen sulfide, H$_2$S, may be a dominant sulfur-containing product from coal under pyrolysis conditions. Unfortunately, the H$_2$S absorption peaks could not be clearly observed in the FTIR spectra of pyrolysis volatiles because they overlap with the strong absorption regions of other gaseous species such as CO$_2$, H$_2$O, SO$_2$ and CH$_4$ in different wavenumber ranges, as shown in their standard spectra (Figure 3-3). The strong H$_2$S absorption peaks in its absorption region I (4000-3530 cm$^{-1}$) are completely merged into strong CO$_2$ absorption region I (3760-3524 cm$^{-1}$) and H$_2$O absorption region I (4000-3452 cm$^{-1}$), as shown in Table 3-2. Thus, none of the absorption peaks in H$_2$S absorption region I could be resolved from those of CO$_2$ and H$_2$O. The H$_2$S absorption band II (2854-2567 cm$^{-1}$) seems to have a little overlapping with the absorption regions of the other gaseous species, but its absorbance intensities is probably too weak to resolve under the instrumental sensitivity.

As discussed earlier, strong H$_2$S absorption region III (1583-1048 cm$^{-1}$) has a partial overlapping mainly with the CH$_4$ absorption band II (1396-1777 cm$^{-1}$), and the peaks in this region have quite strong absorbance intensities. Thus, it is reasonable to use the strongest peak (at 1268 cm$^{-1}$) in region III to determine the H$_2$S release profile. However, CH$_4$ gas also absorbs around the 1268 cm$^{-1}$ peak, and we are only able to establish the combined H$_2$S/CH$_4$ release profile by using this peak. By plotting the absorbance intensity of the 1268 cm$^{-1}$
peak vs. temperature, the combined $\text{H}_2\text{S}/\text{CH}_4$ release profiles at 1268 cm$^{-1}$ of high-sulfur coal IBC-106 (3.77% S) and low-sulfur coal IBC-109 were produced, as shown in Figure 3-8.

The combined $\text{H}_2\text{S}/\text{CH}_4$ release profiles of IBC-106 and IBC-109 are quite similar, and both have three significant peaks around 440$^\circ$C, 510$^\circ$C and 570$^\circ$C. According to the $\text{CH}_4$ and $\text{H}_2\text{S}$ standard FTIR spectra as well as the $\text{CH}_4$ release profiles of both coals, made by using the 1304 cm$^{-1}$ spike peak, as shown in Figure 3-9, the 510$^\circ$C peak on the combined $\text{H}_2\text{S}/\text{CH}_4$ release profiles is mainly due to the contribution of the absorbance intensities of the $\text{CH}_4$-1268 cm$^{-1}$ absorption peak, whereas the 440$^\circ$C and 570$^\circ$C peaks may correspond to the contribution of the absorbance intensities of the $\text{H}_2\text{S}$-1268 cm$^{-1}$ FTIR peak.

However, it is possible to calculate the contribution of the $\text{CH}_4$ release profile made by the 1268 cm$^{-1}$ absorption peak to the combined $\text{H}_2\text{S}/\text{CH}_4$ release profile made with the same absorption peak in the following way. We know the absorbance intensities of the $\text{CH}_4$ 1304 cm$^{-1}$ peak, which are given by the FTIR spectra of the gaseous species mixture at varying temperatures within the temperature range of 200$^\circ$ to 750$^\circ$C (Figures 3-4a and 3-4b). In the $\text{CH}_4$ standard FTIR spectrum (Figure 3-2) we know the absorbance intensities of both the 1304 cm$^{-1}$ and 1268 cm$^{-1}$ absorption peak. Thus, we are able to calculate the ratio of the absorbance intensities of the 1268 cm$^{-1}$ peak to the 1304 cm$^{-1}$ peak for the $\text{CH}_4$, and the ratio is equal to 0.16. By multiplying the $\text{CH}_4$-1304 cm$^{-1}$ peak absorbance intensities by this ratio at varying temperatures,
Figure 3-8. Pyrolysis combined H₂S-CH₄ release profiles made with the 1268 cm⁻¹ absorption peaks for coals IBC-106 and IBC-109, as determined by TG/FTIR (sample size: 30 mg).
Figure 3-9. Pyrolysis CH₄ release profiles made with the 1304 cm⁻¹ absorption peaks for IBC-106 and IBC-109, as determined by TG/FTIR (sample size: 30 mg).
the net CH$_4$-1268 cm$^{-1}$ peak absorbance intensities will be given a particular temperature range. Finally, we are able to establish the net CH$_4$-1268 cm$^{-1}$ release profile by plotting the net CH$_4$-1268 cm$^{-1}$ peak absorbance intensities vs. temperature. Thus, the resulting net combustion CH$_4$-1268 cm$^{-1}$ release profiles for IBC-106 and IBC-109 are shown in Figure 3-10, respectively. Like the CH$_4$-1304 cm$^{-1}$ release profiles (Figure 3-9), the net CH$_4$-1268 cm$^{-1}$ release profiles for both coals also have significantly large 510°C peaks with a slight difference in absorbance intensity from one coal to another.

The net CH$_4$-1268 cm$^{-1}$ release profile indicates the contribution of CH$_4$ to the combined H$_2$S/CH$_4$ release profile made with the 1268 cm$^{-1}$ absorption peak. Evidently, the 510°C peak on the combined H$_2$S/CH$_4$ release profile (Figure 3-8) is mainly due to the contribution of CH$_4$. Thus, by subtracting the net CH$_4$-1268 cm$^{-1}$ release profile (Figure 3-10) from the combined H$_2$S/CH$_4$ release profile (Figure 3-8) at the 1268 cm$^{-1}$, the net H$_2$S release profile is obtained within the 200-750°C range. The calculation of the absorbance intensities of the net H$_2$S release profile for IBC-109 and corresponding data are illustrated in Table 3-5. The resulting net H$_2$S release profiles of IBC-106 and IBC-109 are shown in Figure 3-11. The net H$_2$S release profiles of the other two coals, IBC-103 and IBC-105, established with a similar calculation, are similar to those of IBC-106 and IBC-109.

As indicated on their net H$_2$S release profiles, both IBC-109 and IBC-106 have three significant peaks around 440°C,
Figure 3-10. Calculated pyrolysis net CH₄/1268 cm⁻¹ release profiles for IBC-106 and IBC-109.
### Table 3-5. Calculation of Absorbance Intensities of Net Combustion H\textsubscript{2}S Release Profile for IBC-109 and Resulting Data

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>(A_{\text{H2S/CH4}})\textsuperscript{a} @1268cm\textsuperscript{-1}</th>
<th>(A_{\text{CH4}})\textsuperscript{b} @1304cm\textsuperscript{-1}</th>
<th>Net (A_{\text{CH4}})\textsuperscript{c} @1268cm\textsuperscript{-1}</th>
<th>Net (A_{\text{H2S}})\textsuperscript{d} @1268cm\textsuperscript{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>0.02</td>
<td>0.10</td>
<td>0.02</td>
<td>0.00</td>
</tr>
<tr>
<td>220</td>
<td>0.08</td>
<td>0.50</td>
<td>0.08</td>
<td>0.00</td>
</tr>
<tr>
<td>240</td>
<td>0.10</td>
<td>0.50</td>
<td>0.08</td>
<td>0.02</td>
</tr>
<tr>
<td>260</td>
<td>0.10</td>
<td>0.55</td>
<td>0.09</td>
<td>0.01</td>
</tr>
<tr>
<td>280</td>
<td>0.11</td>
<td>0.45</td>
<td>0.07</td>
<td>0.04</td>
</tr>
<tr>
<td>300</td>
<td>0.14</td>
<td>0.65</td>
<td>0.10</td>
<td>0.04</td>
</tr>
<tr>
<td>320</td>
<td>0.27</td>
<td>1.01</td>
<td>0.16</td>
<td>0.11</td>
</tr>
<tr>
<td>340</td>
<td>0.40</td>
<td>1.23</td>
<td>0.20</td>
<td>0.20</td>
</tr>
<tr>
<td>360</td>
<td>0.56</td>
<td>1.65</td>
<td>0.26</td>
<td>0.30</td>
</tr>
<tr>
<td>370</td>
<td>0.64</td>
<td>2.19</td>
<td>0.35</td>
<td>0.29</td>
</tr>
<tr>
<td>380</td>
<td>0.84</td>
<td>2.56</td>
<td>0.41</td>
<td>0.43</td>
</tr>
<tr>
<td>390</td>
<td>1.23</td>
<td>3.13</td>
<td>0.50</td>
<td>0.68</td>
</tr>
<tr>
<td>400</td>
<td>1.58</td>
<td>3.68</td>
<td>0.59</td>
<td>0.99</td>
</tr>
<tr>
<td>410</td>
<td>2.41</td>
<td>6.72</td>
<td>1.08</td>
<td>1.33</td>
</tr>
<tr>
<td>420</td>
<td>3.45</td>
<td>9.06</td>
<td>1.45</td>
<td>1.96</td>
</tr>
<tr>
<td>430</td>
<td>4.49</td>
<td>12.15</td>
<td>1.94</td>
<td>2.55</td>
</tr>
<tr>
<td>440</td>
<td>5.86</td>
<td>14.38</td>
<td>2.30</td>
<td>3.16</td>
</tr>
<tr>
<td>450</td>
<td>5.40</td>
<td>16.86</td>
<td>2.70</td>
<td>2.70</td>
</tr>
<tr>
<td>460</td>
<td>4.81</td>
<td>19.68</td>
<td>3.15</td>
<td>2.14</td>
</tr>
<tr>
<td>470</td>
<td>5.37</td>
<td>22.82</td>
<td>3.65</td>
<td>1.72</td>
</tr>
<tr>
<td>480</td>
<td>5.64</td>
<td>25.00</td>
<td>4.00</td>
<td>1.64</td>
</tr>
<tr>
<td>490</td>
<td>5.87</td>
<td>27.14</td>
<td>4.32</td>
<td>1.55</td>
</tr>
<tr>
<td>500</td>
<td>5.94</td>
<td>28.94</td>
<td>4.65</td>
<td>1.29</td>
</tr>
<tr>
<td>510</td>
<td>5.96</td>
<td>30.25</td>
<td>4.84</td>
<td>1.12</td>
</tr>
<tr>
<td>520</td>
<td>5.76</td>
<td>30.13</td>
<td>4.82</td>
<td>0.94</td>
</tr>
<tr>
<td>530</td>
<td>5.38</td>
<td>29.55</td>
<td>4.73</td>
<td>0.65</td>
</tr>
<tr>
<td>540</td>
<td>5.31</td>
<td>28.75</td>
<td>4.60</td>
<td>0.71</td>
</tr>
<tr>
<td>550</td>
<td>5.07</td>
<td>27.03</td>
<td>4.32</td>
<td>0.75</td>
</tr>
<tr>
<td>570</td>
<td>5.08</td>
<td>25.42</td>
<td>4.07</td>
<td>1.01</td>
</tr>
<tr>
<td>590</td>
<td>4.65</td>
<td>21.74</td>
<td>3.49</td>
<td>1.17</td>
</tr>
<tr>
<td>610</td>
<td>3.84</td>
<td>17.48</td>
<td>2.80</td>
<td>1.04</td>
</tr>
<tr>
<td>630</td>
<td>2.85</td>
<td>13.58</td>
<td>2.17</td>
<td>0.68</td>
</tr>
<tr>
<td>650</td>
<td>2.06</td>
<td>9.77</td>
<td>1.56</td>
<td>0.50</td>
</tr>
<tr>
<td>670</td>
<td>1.39</td>
<td>6.25</td>
<td>1.00</td>
<td>0.39</td>
</tr>
<tr>
<td>690</td>
<td>0.82</td>
<td>3.41</td>
<td>0.55</td>
<td>0.27</td>
</tr>
<tr>
<td>710</td>
<td>0.35</td>
<td>1.20</td>
<td>0.19</td>
<td>0.16</td>
</tr>
<tr>
<td>730</td>
<td>0.17</td>
<td>0.50</td>
<td>0.08</td>
<td>0.09</td>
</tr>
<tr>
<td>750</td>
<td>0.01</td>
<td>0.05</td>
<td>0.01</td>
<td>0.00</td>
</tr>
</tbody>
</table>

\(a\) \(A_{\text{H2S/CH4}}\) is the absorbance intensity of the combined \(H_2S/CH_4\) 1268 cm\textsuperscript{-1} peak; \(b\) \(A_{\text{CH4}}\) is the absorbance intensity of the \(CH_4\) 1304cm\textsuperscript{-1} peak; \(c\) Net \(A_{\text{CH4}}\) is the net absorbance intensity of the \(CH_4\) 1268 cm\textsuperscript{-1} peak and given by 0.16 x \(A_{\text{CH4}1304\text{cm}^{-1}}\); \(d\) Net \(A_{\text{H2S}}\) is the net absorbance intensity of the \(H_2S\) 1268 cm\textsuperscript{-1} peak and given by (\(A_{\text{H2S}1268\text{cm}^{-1}}\) - Net \(A_{\text{CH4}1268\text{cm}^{-1}}\)).
Figure 3-11. Calculated pyrolysis net H₂S release profiles for IBC-106 and IBC-109, as determined by TG/FTIR (sample size: 30 mg).
490°C and 590°C, respectively. The 440°C peak is the largest peak and it is probably due to both the emission of the organic sulfur species as H₂S, and the emission of the pyrite sulfur as H₂S. The decomposition of the organic aromatic sulfur species is responsible mainly for the 490°C peak, whereas the higher temperature peak of 590°C, which is much smaller than the 440°C, corresponds mainly to the release of the pyritic sulfur as H₂S.

Coburn et al. studied the mechanism for the H₂S release from Illinois #6 high-sulfur coal (4.83% S) during pyrolysis. As obtained by a programmed temperature, gas evolution technique and a quadrupole mass spectrometer (QPMS), the H₂S release profile of Illinois #6 coal did have two significantly large peaks at about 440°C and 590°C, respectively. The H₂S release profile of IBC-106 (3.77% S) (Figure 3-11) obtained in our experiments matches their results very well, and also has two significantly large peaks around 440°C and 590°C. But the 440°C peak in the IBC-106 H₂S release profile is much larger than that at 590°C, whereas the 440°C peak in the Illinois #6 H₂S release profile is much smaller than the 590°C peak. The different conditions used in the experiments may have produced the different results.

Coburn et al. suggested a mechanism for the H₂S release from Illinois #6 coal during pyrolysis, as follows:

1. Formation of H₂S from organic sulfur species:

   \[
   R-S-H + H-Donor \rightarrow H_2S + RH \quad (3-1)
   \]
2. Formation of $H_2S$ from pyrite sulfur species:

\[
\begin{align*}
\text{H-Donor} & \quad \text{FeS}_2 \quad \rightarrow \quad H_2S + \text{FeS} \\
\text{FeS}_2 \quad \leftrightarrow \quad \text{FeS} + \frac{1}{2}S_2 \quad \rightarrow \quad H_2S \\
\text{Hydrolysis} & \quad 3\text{FeS} + 4\text{H}_2\text{O} \quad \rightarrow \quad 3H_2S + \text{Fe}_3\text{O}_4 + H_2
\end{align*}
\]

(3-2)

(3-3)

(3-4)

The 440°C peak on the $H_2S$ release profile of Illinois #6 coal is mainly due to the decomposition of the organic sulfur species (reaction 3-1). The 590°C peak is mainly due to the decomposition of the pyrite sulfur species (reactions 3-2 to 3-14). It is commonly believed that pyrite contributes to both low and high temperature $H_2S$ release as suggested by Oh et al. and Khan. Khan wrote the following expression for $[H_2S]$ on heating various coals to 500°C under his experimental conditions:

\[
[H_2S] = 0.17(\text{Coal}_{\text{pyr.}}) + 0.40(\text{Coal}_{\text{org.}}); \quad R^2 = 0.94
\]

where $R$ is a correlation coefficient.

Thus, Coburn et al. suggested that reaction 3-2 seems to best characterize low temperature formation of $H_2S$ from pyrite. Hence, the 440° peak is mainly due to the decomposition of both the organic sulfur species (reaction 3-1) and the pyrite sulfur species (mainly reaction 3-2).

Under our experimental conditions, we suggest a more detailed mechanism for the $H_2S$ release from Illinois coals during pyrolysis, as described below:
1. Formation of $H_2S$ from aliphatic organic sulfur species:

a) From aliphatic disulfides:

$$H\text{-Donor}$$

$$R-S-S-R \rightarrow 2H_2S + 2RH \quad (3-5)$$

b) From aliphatic sulfides:

$$H\text{-Donor}$$

$$R-S-R \rightarrow H_2S + 2RH \quad (3-6)$$

2. Formation of $H_2S$ from Aromatic Organic Sulfur Species:

a) From aromatic disulfides:

$$H\text{-Donor}$$

$$Ar-S-S-Ar \rightarrow 2H_2S + 2ArH \quad (3-7)$$

b) From aromatic-aliphatic disulfides:

$$H\text{-Donor}$$

$$Ar-S-S-R \rightarrow 2H_2S + ArH + RH \quad (3-8)$$

c) From aromatic-aliphatic monosulfides:

$$H\text{-Donor}$$

$$Ar-S-R \rightarrow H_2S + ArH + RH \quad (3-9)$$

d) From aromatic monosulfides:

$$H\text{-Donor}$$

$$Ar-S-Ar \rightarrow 2H_2S + 2ArH \quad (3-10)$$

3. Formation of $H_2S$ from pyrite sulfur species:

a) $FeS_2 \rightarrow H_2S + FeS \quad (3-11)$

b) $FeS_2 \rightarrow FeS + 1/2S_2 \rightarrow H_2S + FeS \quad (3-12)$

Hydrolysis

$$3FeS_2 + 4H_2O \rightarrow 4H_2S + Fe_3O_4 + S_2 \quad (3-13)$$

Hydrolysis

$$3FeS + 4H_2O \rightarrow 3H_2S + Fe_3O_4 + H_2 \quad (3-14)$$
Thus, the low-temperature decomposition of both the organic sulfur species and pyritic sulfur species may generate H$_2$S pyrolysis of raw Illinois coals under our experimental conditions, and results in the lower temperature peaks of 440°C on the net H$_2$S release profiles, according to Coburn et al. and Khan. The organic sulfur species which undergo pyrolysis decomposition at relatively low temperature may include aliphatic disulfides, aliphatic sulfides, aromatic disulfides, aromatic-aliphatic disulfides and some aromatic-aliphatic monosulfides. Reactions 3-5 to 3-9 probably control the formation of H$_2$S from the decomposition of thesis compounds. As controlled by reactions 3-11 and 3-12, the decomposition of some of the pyritic sulfur species could also take place to liberate H$_2$S at relatively low temperature of 440°C under the pyrolysis conditions. As a consequence, the combination of H$_2$S formulated from both the organic and pyritic sulfur species decomposition contributes to the large 440°C peaks on the net H$_2$S release profiles.

The decomposition of the aromatic monosulfides and some of the aromatic-aliphatic sulfur species might occur at relatively high temperature (around 490°C) to give off H$_2$S, and the formulation of the H$_2$S is controlled by reactions 3-9 and 3-10, leading to the small 490°C peaks on the net H$_2$S release profiles. Finally, the small 590°C peaks on the net H$_2$S release profiles are mainly due to the emission of H$_2$S by hydrolysis of a small part of pyritic sulfur species, which takes place at relatively high temperature (around 590°C) and
is controlled by reactions 3-13 and 3-14.

3.3.2 Pyrolysis COS Release Profiles

For many years, COS has been a sulfur-containing species of interest released during coal pyrolysis and combustion. According to the literature, the COS absorption region occurs around the 2073 cm\(^{-1}\) peak in its FTIR spectrum, and the 2073 cm\(^{-1}\) peak has its strongest absorbance intensity. As we have seen in the CO standard FTIR spectrum (Figure 3-3 and Table 3-2), there are two CO absorption regions; region I ranges from 2235 cm\(^{-1}\) to 22142 cm\(^{-1}\), with the maximum absorption peak at 2178 cm\(^{-1}\), and region II from 2142 cm\(^{-1}\) to 2025 cm\(^{-1}\) with its maximum absorption peak at 2116 cm\(^{-1}\).

Obviously, the COS absorption region completely overlaps the CO absorption region II in the FTIR spectra of the coal pyrolysis gas mixture (Figure 3-4). Fortunately, the absorbance intensity of the COS-2073 cm\(^{-1}\) absorption peak is much stronger than that of CO absorption region II. Therefore, the COS-2073 cm\(^{-1}\) absorption peak is observed clearly in the FTIR spectra, and its absorbance intensities will not be affected significantly by that of CO absorption region II. Thus, the pyrolysis COS release profile of Illinois coals can be established easily by plotting the absorbance intensity of the COS 2073 cm\(^{-1}\) absorption peak vs. temperature. The resulting pyrolysis COS release profiles of IBC-109 and IBC-106 are shown in Figure 12. The COS release profiles are similar for both of the coals and show three
Figure 3-12. Pyrolysis COS release profiles for IBC-109 and IBC-106 made by using the 2703 cm⁻¹ absorption peaks, as determined by TG/FTIR using a 30 mg sample.
significant peaks around 430°, 560° and 610°C. The largest 420°C peaks are mainly due to the release of COS from the sulfur sources of both the organic and pyritic sulfur species in the coals. The smaller 560°C and 610°C peaks correspond mainly to the emission of COS from the sulfur sources of different types of pyritic sulfur species in the coals. The other two Illinois coals, IBC-103 and IBC-105, also have the pyrolysis COS release profiles similar to those of IBC-109 and IBC-106.

Oh et al.⁶⁹ employed GC/TQMS techniques to analyze the release of the sulfur species as COS from the pyrolysis of Illinois No. 6 coal (5.40% S_tot), which is one of eight Argonne premium coal samples used in their experiments. They found that the yields and rates of evolution of the sulfur gases depended not only on the pyrolysis conditions but also on the coal itself.⁴³ As established under their experimental conditions (slow-heating pyrolysis with a programmed-temperature range of 20°-800°C), the COS release profile of Illinois No. 6 coal has two large peaks around 400° and 600°C. The 600°C peak is significantly larger than the 400°C peak. They suggested a mechanism for the reactions controlling the COS release from the coal. The reactions to form COS could be both gas-solid and gas phase secondary reactions:

1. Formation of COS from Gas Phase Reactions:

   \[
   \begin{align*}
   H_2S + CO & \rightarrow COS + H_2 & \text{(3-15)} \\
   H_2S + CO_2 & \rightarrow COS + H_2O & \text{(3-16)}
   \end{align*}
   \]
2. Formation of COS from Gas-Solid Reactions:

\[ \text{FeS}_2 + \text{CO} \rightarrow \text{COS} + \text{FeS} \quad (3-17) \]

3. Elimination of COS:

\[ \text{H}_2\text{S} + \text{COS} \rightarrow \text{CS}_2 + \text{H}_2\text{O} \quad (3-18) \]
\[ 2\text{COS} \rightarrow \text{CS}_2 + \text{CO}_2 \quad (3-19) \]

Accordingly, the 400°C peak of Illinois # 6 coal is mainly due to reactions 3-15 and 3-16, in which H₂S is released from the decomposition of the organic sulfur species, as discussed above. The 600°C peak is mainly due to reaction 3-17 in which the COS is released mainly from the decomposition of the pyritic sulfur species.

Our experiments show that the COS release profiles of raw Illinois coals (Figure 3-12) have two relatively large peaks around 430°C and 560°C, and a small broad peak around 610°C. According to Oh et al., the larger 430°C peaks are probably due to the combined release of COS from two different sources of sulfur species, the organic sulfur species and the pyritic sulfur species. The release of COS from the aromatic sulfur species is controlled by the gas-phase reaction of CO and/or CO₂ with H₂S (reactions 3-15 and 3-16), and the H₂S is produced from the decomposition of different types of the organic sulfur species, as discussed above. The release of COS from one type of the pyritic sulfur species is also controlled by the reaction of CO with H₂S (reaction 3-15), but the H₂S is produced from the decomposition of the pyritic sulfur species. The large 560°C and small broad 610°C peaks are probably due
to the release of COS by the gas-solid reactions of CO with two different types of the pyritic sulfur species (isometric pyrite and thorhombic marcasite), and reaction 3-17 controls the COS release.

According to Ferm,\textsuperscript{76} reaction 3-18 occurs at temperature between 340°C and 900°C, and reaction 3-19 is slow but its rate reaches a maximum at 600°C. Thus, these two reactions compete with the formation of COS between 350° and 900°C, and they probably dominate around 550 and 600°C. This probably leads to the smaller 560 and 610°C peaks on the COS release profiles of Illinois coals.

As discussed above, the formation of COS should be related closely to the formation of H\textsubscript{2}S under the pyrolysis conditions (reactions 3-15, 3-16 and 3-17). By comparing the COS and net H\textsubscript{2}S release profiles of IBC-106 shown in Figure 3-13, we do find that the COS profile is very similar with the H\textsubscript{2}S profile in the temperature range of 300-700°C, except the absence of the 560°C peak on the H\textsubscript{2}S profile. This is evidence that reactions 3-15, 3-16 and 3-17 do control the formation of COS and the elimination of H\textsubscript{2}S during the pyrolysis.

3.3.3 Pyrolysis SO\textsubscript{2} Release Profiles

Sulfur dioxide (SO\textsubscript{2}) is a main gaseous sulfur-containing species released during coal pyrolysis and combustion.\textsuperscript{69} The SO\textsubscript{2} release profile during pyrolysis of Illinois coal can be established by using the strongest absorption peak (1374 cm\textsuperscript{-1}) of SO\textsubscript{2} in its absorption region II (1413-1296 cm\textsuperscript{-1}) according
Figure 3-13. Comparison of pyrolysis COS and net $\text{H}_2\text{S}$ release profiles for IBC-106 (sample size: 30 mg).
to the SO\textsubscript{2} standard FTIR spectrum (Figure 3-3 and Table 3-2). Although SO\textsubscript{2} absorption region II overlaps partially with CH\textsubscript{4} absorption region II (1396-1177 cm\textsuperscript{-1}), the absorbance intensities of the SO\textsubscript{2}-1374 cm\textsuperscript{-1} absorption peak are much stronger than those of the absorption peaks in CH\textsubscript{4} absorption region II. Thus, the pyrolysis SO\textsubscript{2} release profiles of Illinois coals were established by plotting the absorbance intensity of the SO\textsubscript{2}-1374 cm\textsuperscript{-1} absorption peak vs. temperature. Figure 3-14 shows the pyrolysis SO\textsubscript{2} release profiles of IBC-109 and IBC-106. The pyrolysis SO\textsubscript{2} release profiles are similar for both coals with the difference in their absorbance intensities, and three broad peaks around 320°, 440° and 550° on the profiles. The other two Illinois coals, IBC-103 and IBC-105, have similar pyrolysis SO\textsubscript{2} release profiles.

The small broad 320°C peak on the SO\textsubscript{2} release profile is mainly due to the SO\textsubscript{2} release from the decomposition of aliphatic and/or elemental sulfur species which take place easily at relatively low temperatures. The large broad 440°C peak is probably due to the SO\textsubscript{2} release from the decomposition of both aromatic and pyritic sulfur species in the coals. The large broad 550°C peak may be mainly due to the SO\textsubscript{2} release from the decomposition of pyritic sulfur species.\textsuperscript{71}

### 3.4 Gaseous Chlorine Release during Illinois Coal Pyrolysis

#### 3.4.1 Pyrolysis HCl Release Profiles by TG/FTIR

As previously reported,\textsuperscript{74,77-79} the 2962 cm\textsuperscript{-1} absorption peak in HCl absorption region I (Figure 3-3 and Table 3-2), which
Figure 3-14. Pyrolysis SO$_2$ release profiles for IBC-106 and IBC-109 made with the 1374 cm$^{-1}$ absorption peaks, as determined by TG/FTIR using a 30 mg sample.
has the strongest absorbance intensity of all the HCl absorption peaks in the FTIR spectra, was chosen for the identification of HCl evolved from coal pyrolysis. An attempt was made to exclude the contribution of CH₄ to the overlapping 2962 cm⁻¹ absorption peak. Although it is a time consuming method, it is still a successful method, as we have seen in establishing the net H₂S release profile discussed earlier. However, it is very difficult to calculate the contribution of paraffin to the combined 2962 cm⁻¹ peak because a great deal of paraffin is produced during coal pyrolysis and it also absorbs around the 2962 cm⁻¹ peak. Thus, the 2962 cm⁻¹ peak cannot be used to identify the HCl and determine its release profile. In this case, the 2798 cm⁻¹, 2772 cm⁻¹ and 2726 cm⁻¹ absorption peaks of HCl, which are three strong absorption peaks in HCl absorption region II in the FTIR spectra (Figure 3-3 and Table 3-2), have been adopted for the identification of HCl. These peaks do not interfere with CH₄ and paraffin or other gaseous species in the FTIR spectra of the pyrolysis gas mixture. Since the intensities of these peaks are not as strong as the 2962 cm⁻¹ peak, a 100 mg sample was used the pyrolysis experiments.

Figure 3-15 illustrates the pyrolysis HCl release profiles of the high-chlorine coal, IBC-109, made by using three different absorption peaks, 2798 cm⁻¹, 2772 cm⁻¹ and 2726 cm⁻¹. The profiles indicate that the evolution of chlorine as HCl in high-chlorine coal IBC-109 occurs approximately between 250°C and 700°C. The HCl release rate reaches the maximum at
Figure 3-15. Pyrolysis HCl release profiles of high-chlorine coal IBC-109 made by using three different FTIR absorption peaks and a 100 mg sample, as determined by TG/FTIR.
440°C which matches closely $T_{\text{max}}$ (434°C) on the DTG curve of IBC-109 (Figure 3-2) at which the maximum devolatilization rate occurs. The comparison of the pyrolysis HCl release profiles between high-chlorine coal IBC-109 (0.42% Cl) and low-chlorine coal IBC-106 (0.02% Cl) are shown in Figure 3-16. The IBC-106 HCl profile indicates that the amount of HCl emission was very low during pyrolysis because of its low chlorine content.

Why is the chlorine in coal liberated as HCl within the temperature range 300-600°C under the pyrolysis conditions? Why does its release rate reach the maximum at relatively high temperature (440°C)? What kind of the form does the chlorine exist in coal?

According to Herod et al., some of the chlorine in coal may be bonded as chloride ions to functional groups of the organic compounds on the coal surface. The functional groups could be basic nitrogen groups such as $-R_2N$, $-HRN$ or pyridine-$N$, and the chloride ions could be bonded to them in the forms of hydrochloride such as $\text{[pyridine-NH}^+]\text{Cl}^-$, $\text{[-R}_2\text{NH}^+]\text{Cl}^-$ and/or $\text{[-HRNH}^+]\text{Cl}^-$. Thus, on heating the coal below 440°C, some of the chlorine in the coal associated as hydrochloride bound to the basic N groups on the coal surfaces will decompose to give off HCl. The emission of the HCl requires the abstraction of hydrogen and/or combination with the hydrogen ion. The hydrogens probably come from the hydrochloride themselves, the pore water driven off from the coal pores and/or from the brine on the coal surface, free
Figure 3-16. Comparison of pyrolysis HCl release profiles for high chlorine coal IBC-109 (0.42% Cl) and low chlorine coal IBC-106 (0.02% Cl) made by using the 2798 cm⁻¹ FTIR absorption peak and a 100 mg sample, as determined by TG/FTIR.
hydrogen adsorbed on the coal surface, decomposition of simple hydrocarbons, or other H-donor species.

In summary, under our experimental conditions, we could suggest a mechanism for the formation of HCl below 440°C from the some of the chlorine in the coal bonded as chloride ions to the nitrogen functional groups of the organic compounds on the coal surface.

\[
[surf-R_2NH']Cl^– \xrightarrow{\text{slow}} [surf-R_2NH'] + Cl^– (\text{gas}) <440^\circ C \tag{3-20}
\]

\[
[surf-R_2NH']Cl^– \xrightarrow{\text{slow}} [surf-R_2NH'] + Cl^– (\text{gas}) <440^\circ C \tag{3-21}
\]

\[
[surf-C_2H_4NH']Cl^– \xrightarrow{\text{slow}} [surf-C_2H_4NH'] + Cl^– (\text{gas}) <440^\circ C \tag{3-22}
\]

\[
[surf-C_2H_4NH']Cl^– \xrightarrow{\text{slow}} [surf-C_2H_4NH'] + Cl^– (\text{gas}) <440^\circ C \tag{3-23}
\]

\[
[surf-R_2NH'] + Cl^– (\text{gas}) \xrightarrow{\text{fast}} [surf-R_2N] + HCl(\text{gas}) <440^\circ C \tag{3-24}
\]

\[
[surf-R_2NH'] + Cl^– (\text{gas}) \xrightarrow{\text{fast}} [surf-R_2N] + HCl(\text{gas}) <440^\circ C \tag{3-25}
\]

\[
[surf-C_2H_4NH'] + Cl^– (\text{gas}) \xrightarrow{\text{fast}} [surf-C_2H_4N] + HCl(\text{gas}) <440^\circ C \tag{3-26}
\]

\[
[surf-C_2H_4NH'] + Cl^– (\text{gas}) \xrightarrow{\text{fast}} [surf-C_2H_4N] + HCl(\text{gas}) <440^\circ C \tag{3-27}
\]

\[
Cl^– (\text{gas}) + H_2O(\text{gas}) \xrightarrow{\text{fast}} HCl(\text{gas}) + OH^– (\text{gas}) <440^\circ C \tag{3-28}
\]

\[
Cl^– (\text{gas}) + H_2O(\text{gas}) \xrightarrow{\text{fast}} HCl(\text{gas}) + OH^– (\text{gas}) <440^\circ C \tag{3-29}
\]
According to Walker et al., coals and chars are highly microporous materials. Their porosity is of the aperture-cavity type and a large proportion of the total surface area and pore volume is accessible through apertures 0.49-0.52 nm in size. Evidently, most of the chlorine species in coal are associated with the organic matter on the inner walls of the micropores of the coal matrix as the chloride ions by an ion exchange linkage. It is generally agreed that the ion exchange linkage is the basic nitrogen site to which the chloride ions are attached in the form of hydrochloride (HCl). However, most of the nitrogen is believed to occur in a heterocyclic ring structure such as pyridine ring structure. But it is also possible that some of the nitrogen in the coal occurs in the form of the other basic nitrogen functional groups such as aliphatic nitrogen functional groups (-NR₂, -NHR and -NH₂) and aromatic nitrogen functional groups (-NAR and -NHAR).

Thus, most of the chlorine in the coal evolved as HCl around 440°C exists most likely in the form of the chloride ions associated tightly by an ion exchange linkage with the basic nitrogen sites (-pyridine-N, -NR₂, -NHR, -NH₂, -NAR and -NARH). These basic nitrogen sites are most likely attached to the inner walls of micropores in the coal matrix (the macerals). According to Chou, these chloride ions probably also occur as hydrochloride (HCl) associated tightly
with the positively charged nitrogen functional groups, and may be held in the diffuse electrical double layer.

We can further suggest that the inner walls of the coal micropores are probably composed of the pyridine-N and/or the other basic nitrogen sites (−NR₂, −NRH, −NH₂, −NArR and −NArH). Some of the basic nitrogen sites may occur as the basic nitrogen functional groups of the organic amines (−pyridine-N, −NR₂, −NRH, −NH₂, −NArR and −NArH) faced forward to the centers of the micropores. Some of the basic nitrogen sites may occur as nitrogen-bridge units (still in the forms of the basic nitrogen functional groups of the organic amines) such as −NR−, −NH−, −NH−, −NAr−, −NAr− or −N− which may serve as the linkages between the large or small organic molecules constructing the inner walls of the coal micropores. In this context, the inner walls of the micropores enrich a great number of the basic nitrogen sites. It is these basic nitrogen sites that have a great ability to form stable organic ammonium chloride species (or organic ammonium chloride salt species) such as [−pyridine−N⁺H]Cl⁻, [−HN⁺R₂]Cl⁻, [−HN⁺RH]Cl⁻, [−HN⁺NH₂]Cl⁻, [−HN⁺ArR]Cl⁻ and −HN⁺ArHCl⁻, and/or [−HN⁺R−]Cl⁻, [−HN⁺H−]Cl⁻, [−HN⁺Ar−]Cl⁻, or [−HN−]Cl⁻ by the reactions of the basic nitrogen sites as the organic amines with the acidic chlorine species such as HCl. Thus, it is possible that most of the chlorine species in the coal as the chloride anions are associated very tightly with the nitrogen cation species on the inner walls of the coal micropores by the ion bond interactions. It is also possible that the
chloride ions are adsorbed very tightly between the diffuse electrical layers by the electrostatic interactions according to Chou,\textsuperscript{32} or between the positive-charged layers by the interactions of the ion bonds or coordination bonds. However, these suggestions should be based on the prerequisite that the coal is of the layer structure to a certain extent, and the layers should also attach the nitrogen cation species or other positive-charged species on their surface.

In order to dissociate the ionic bonds between the chloride anions and the nitrogen cation species on the inner walls of the coal micropores, relatively high energy is certainly required. Therefore, the dissociations of these ionic bonds could happen only at relatively high temperature such as 440°C. Still, relatively high energy is required to overcome the electrostatic or coordination interactions between the chloride anions (Cl\textsuperscript{-}) and the diffuse electrical or positive-charged layers in the coal. This could also happen only at relatively high temperatures.

Furthermore, as discussed earlier, pyrolysis of high chlorine coal IBC-109 produces a relatively small amount of the dry-volatile matter with a relatively higher T\textsubscript{max} (440°C), compared with the other three coals. This indicates that IBC-109 may have a relatively dense coal matrix, and therefore it probably consists of a greater number of small micropores than large pores. This may increase the difficulty of the HCl emission from the chlorine species adsorbed on the inner walls of the coal micropores.
In summary, most of the chlorine in the coal is difficult to remove during pyrolysis unless enough energy is present to break the various strong interactions between the chlorine species and the inner walls of the coal micropores and/or the diffuse electrical or positive-charged layers in the coal. Thus, as the coal is heated to around 440°C ($T_{MAX}$), the dry volatile matter is being produced. In the meantime, the coal matrix structure begins decomposing and the coal micropores and/or coal layers also start breaking. Around 440°C, most of the dry volatile matter has been emitted from the coal, and the coal matrix structure is almost completely destroyed, as well as most of the coal micropores and/or coal layers have been broken. Obviously, the breaking or decomposition of the organic ammonium chloride salt species attached to the inner walls of the coal micropores and/or the surfaces of the coal layers takes place as the breakdown of the coal micropores and/or coal layers takes place. On the other hand, around a high temperature such as 440°C, the dissociation may occur by breaking ionic, covalent and coordination bonds, or electrostatic interactions existing between the chloride ions ($\text{Cl}^-$) and the nitrogen cationic species attached to the inner walls of the coal micropores and/or the surfaces of the coal layers.

As a result, associated tightly with the nitrogen cations (attached to the inner walls of the coal micropores and/or the surfaces of the coal layers), most of the chlorine species in the form of the chloride anions are driven off as HCl around
this temperature (440°C). The emission of HCl needs a source of sufficient hydrogens or hydrogen ions. It is at 440°C that sufficient hydrocarbon species (such as paraffin, aliphatic and aromatic species), water, pyridine and/or amine species as well as other hydrogen donors such as H₂S are produced as the volatile matter, and their decomposition donates a great deal of hydrogen as free hydrogen radicals or ions.

In summary, under our pyrolysis experimental conditions, a mechanism may be suggested for the formation of HCl around 440°C from the chlorine species as the chloride ions (Cl⁻) associated tightly with the nitrogen cation species attached on the inner walls of the coal micropores and/or the surfaces of the coal layers:

\[
\text{[MPIW-P-NH}^+ \text{]Cl}^- \overset{\text{slow}}{\underset{440^\circ C}{\longrightarrow}} \text{NH}_4^+ + \text{Cl}^- + \text{VM(RH,R',H}_2\text{O,H}_2\text{S,etc.)} \quad (3-31)
\]

\[
\text{[MPIW-P-N11}^+ \text{]Cl}^- \overset{\text{slow}}{\underset{440^\circ C}{\longrightarrow}} \text{NH}_4^+ + \text{Cl}^- + \text{VM(RH,R',H}_2\text{O,H}_2\text{S,etc.)} \quad (3-32)
\]

where MPIW = Micropore inner wall,

\[P = \text{Pyridine species,} \]
\[\text{VM = Volatile matter.} \]

\[
\text{[MPIW-A-NH}^+ \text{]Cl}^- \overset{\text{slow}}{\underset{440^\circ C}{\longrightarrow}} \text{NH}_4^+ + \text{Cl}^- + \text{VM(RH,R',H}_2\text{O,H}_2\text{S,etc.)} \quad (3-33)
\]

\[
\text{[MPIW-A-NH}^+ \text{]Cl}^- \overset{\text{slow}}{\underset{440^\circ C}{\longrightarrow}} \text{NH}_4^+ + \text{Cl}^- + \text{VM(RH,R',H}_2\text{O,H}_2\text{S,etc.)} \quad (3-34)
\]

where A = Amine species.
The emission of HCl at this temperature is probably the first-order release, and therefore, the breakdown of the nitrogen-cation sites may be the rate-controlling step. As shown in Figure 3-17, the similarity of the HCl and NH₃ release profiles of IBC-109 in the temperature range of approximately 390-690°C gives supporting evidence for the mechanism.
Figure 3-17. Comparison of pyrolysis HCl and NH₃ release profiles for high chlorine coal IBC-109 (0.42% Cl), as determined by TG/FTIR using a 100 mg sample.
3.4.2 Quantitative Pyrolysis Chlorine Release Profiles and Chlorine Mass Balance by TG/IC

In order to determine quantitatively the pyrolysis gaseous chlorine release profile of high-chlorine coal IBC-109 (0.42% Cl) by the TG/IC technique, a 250 mg sample size was used in the experiments. The 250 mg is the upper limit amount of the coal which can undergo complete decomposition under the experimental conditions. Table 3-6 summarizes the data of the average release rates of the gaseous chlorine in each 50°C range within the temperature range of 175-775°C during pyrolysis of IBC-109. For calculating the chlorine mass

Table 3-6. Average Release Rates of Gaseous Chlorine in Each 50°C Range within the 175-775°C Range during Pyrolysis of IBC-109, as Determined by TG/IC Using a 250 mg Sample.

<table>
<thead>
<tr>
<th>Temperature Range (°C)</th>
<th>Average Temperature (°C)</th>
<th>Cl Release Amount (%/50°C or %/5 min)</th>
<th>Average Cl Release Rate (%/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150-199</td>
<td>175</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>200-249</td>
<td>225</td>
<td>1.90</td>
<td>0.38</td>
</tr>
<tr>
<td>250-299</td>
<td>275</td>
<td>5.10</td>
<td>1.02</td>
</tr>
<tr>
<td>300-349</td>
<td>325</td>
<td>8.38</td>
<td>1.68</td>
</tr>
<tr>
<td>350-399</td>
<td>375</td>
<td>11.99</td>
<td>2.40</td>
</tr>
<tr>
<td>400-449</td>
<td>425</td>
<td>15.18</td>
<td>3.04</td>
</tr>
<tr>
<td>450-499</td>
<td>475</td>
<td>14.89</td>
<td>2.98</td>
</tr>
<tr>
<td>500-549</td>
<td>525</td>
<td>11.81</td>
<td>2.36</td>
</tr>
<tr>
<td>550-599</td>
<td>575</td>
<td>9.58</td>
<td>1.92</td>
</tr>
<tr>
<td>600-649</td>
<td>625</td>
<td>6.95</td>
<td>1.39</td>
</tr>
<tr>
<td>650-699</td>
<td>675</td>
<td>4.02</td>
<td>0.80</td>
</tr>
<tr>
<td>700-749</td>
<td>725</td>
<td>1.50</td>
<td>0.30</td>
</tr>
<tr>
<td>750-799</td>
<td>775</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>91.30 %</td>
<td></td>
</tr>
</tbody>
</table>

Notes:

a) Total chlorine in sample = 0.42% x 1000(µg/mg) x 250(mg) = 1050 (µg).
b) The total chlorine released = 958 (µg) or 91.30% vs. total chlorine in sample [958(µg) x 100/1050 (µg) = 19.30%].
balance during the combustion and relevant standard deviation, three individual runs have been done to determine the total chlorine evolved, and the results are listed in Table 3-7.

Table 3-7. Results of Chlorine Mass Balance during Combustion of IBC-109 and Standard Deviation, as Determined by TG/IC.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Total Cl Evolved (%)</th>
<th>Std. Dev.</th>
<th>% Std. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>91.3</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>2</td>
<td>91.0</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>3</td>
<td>91.5</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>Average</td>
<td>91.3</td>
<td>0.2</td>
<td>0.2</td>
</tr>
</tbody>
</table>

The resulting gaseous chlorine release profile for the high-chlorine coal of IBC-109 (0.42% Cl) during pyrolysis is illustrated in Figure 3-18.

The profile indicates quantitatively that the emission of the chlorine in the coal occurs as gaseous chlorine species approximately between 200° and 750°C, and the chlorine release rate reaches the maximum in the 400°-450°C. The result matches the FTIR results very well (Figure 3-15). More than 90% of the total chlorine in the coal was given off during pyrolysis under our experimental conditions. However, approximately 63% of the total released gaseous chlorine has been liberated below 500°C. Furthermore, the pyrolysis residues of four Illinois coals were analyzed for sodium and chlorine by neutron activation analysis (NAA).80 Most of the chlorine (96-98%) in coals IBC-103 (0.18% Cl), IBC-105 (0.10% Cl) and IBC-109 (0.42% Cl) was volatilized during pyrolysis. For coal IBC-106, which has a very low chlorine content (0.02% Cl),
Figure 3-18. Pyrolysis gaseous chlorine release profile for high chlorine coal IBC-109, as determined by TG-IC using a 250 mg sample.
a small amount, but significant fraction of the total chlorine (29%), was retained in its char.

As obtained by the combined TG/FTIR/IC techniques under our experimental conditions, the results of the gaseous sulfur and chlorine evolution during pyrolysis of Illinois coals are comparable with those given by Chou et al. who used the temperature-controlled pyrolysis technique combined with quadruple gas analyzer (QGA) and ion selective electrode (ISE).
4.1 Thermogravimetric Analysis for Illinois Coal Combustion

On heating approximately 30 mg of the coal samples in air within the temperature range of ambient-800°C at a 10°C/min heating rate, similar combustion TG/DTG curves were obtained for four Illinois coals IBC-103, -105, -106 and -109, as shown in Figures 4-1 and 4-2. Table 4-1 summarizes the corresponding TG/DTG data of coal mass change with increasing heating temperature during combustion.

The TG curves indicate that there are three significant mass changes for the four coals within the temperature range during pyrolysis. The first mass changes, which are mass losses, occur between 20°C and 151°C, and are mainly due to the vaporization of inherent water in the coals. The mass loss amounts in this temperature range for the four coals are approximately 4.71-7.66% of the sample weights (Table 4-1). The second set of mass changes, which are mass gains, take place between 150°C and 300°C, and they are mainly due to the gas-solid phase oxidation of the organic matter in the coals by air under the combustion conditions. These reactions were not observed under the pyrolysis conditions (Figure 3-2 and Table 3-1). The mass gain for the coals is 1.02-1.84% of the
Figure 4-1. Combustion TG curves of coals IBC-103, IBC-105, IBC-106 and IBC-109 with a 10°C/min heating rate.
Figure 4-2. Combustion DTG curves of coals IBC-103, IBC-105, IBC-106 and IBC-109 with a 10°C/min heating rate.
Table 4-1. Combustion TG/DTG Results of Illinois Coals

<table>
<thead>
<tr>
<th>Coal</th>
<th>Temp</th>
<th>Wt Loss</th>
<th>T&lt;sub&gt;MAX&lt;/sub&gt;&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Wt Loss R&lt;sub&gt;MAX&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(°C)</td>
<td>(%)</td>
<td>(°C)</td>
<td>(%)/min</td>
</tr>
<tr>
<td>IBC-103</td>
<td>22-151</td>
<td>4.71</td>
<td>64.9</td>
<td>0.67</td>
</tr>
<tr>
<td></td>
<td>151-300</td>
<td>-1.84</td>
<td>427.9(I)</td>
<td>5.84</td>
</tr>
<tr>
<td></td>
<td>300-589</td>
<td>91.26</td>
<td>448.2(II)</td>
<td>6.07</td>
</tr>
<tr>
<td></td>
<td>589-800</td>
<td>0.10</td>
<td>478.4(III)</td>
<td>6.62</td>
</tr>
<tr>
<td>IBC-105</td>
<td>20-151</td>
<td>7.62</td>
<td>67.3</td>
<td>1.15</td>
</tr>
<tr>
<td></td>
<td>151-300</td>
<td>-1.02</td>
<td>399.0(I)</td>
<td>6.77</td>
</tr>
<tr>
<td></td>
<td>300-582</td>
<td>75.21</td>
<td>430.3(II)</td>
<td>5.91</td>
</tr>
<tr>
<td></td>
<td>579-800</td>
<td>1.00</td>
<td>469.6(III)</td>
<td>5.03</td>
</tr>
<tr>
<td>IBC-106</td>
<td>19-151</td>
<td>7.66</td>
<td>62.5</td>
<td>1.36</td>
</tr>
<tr>
<td></td>
<td>151-291</td>
<td>-1.52</td>
<td>372.6(I)</td>
<td>8.81</td>
</tr>
<tr>
<td></td>
<td>291-579</td>
<td>86.32</td>
<td>401.4(II)</td>
<td>6.10</td>
</tr>
<tr>
<td></td>
<td>579-800</td>
<td>0.18</td>
<td>449.5(III)</td>
<td>5.45</td>
</tr>
<tr>
<td>IBC-109</td>
<td>20-151</td>
<td>5.01</td>
<td>64.9</td>
<td>0.68</td>
</tr>
<tr>
<td></td>
<td>151-300</td>
<td>-1.63</td>
<td>430.3(I)</td>
<td>5.58</td>
</tr>
<tr>
<td></td>
<td>300-582</td>
<td>87.50</td>
<td>454.3(II)</td>
<td>6.28</td>
</tr>
<tr>
<td></td>
<td>582-800</td>
<td>0.27</td>
<td>471.2(III)</td>
<td>6.79</td>
</tr>
</tbody>
</table>

a) T<sub>MAX</sub> is the temperature at which the maximum rate of weight loss occurs.

b) Wt Loss R<sub>MAX</sub> is the maximum rate of weight loss.

sample weights (Table 4-1). The third mass change, which is mass loss again and the most important in the study, occurs in the temperature range of 300-580°C. This loss probably results from both the pyrolysis devolatilization of the coals and combustion reactions of the coal matrixes. The amount of mass loss in this temperature range varies from 75.21% to 91.26% of the sample weights for the four coals.

As indicated on the DTG curves (Figure 4-2), there are
three main peaks for each coal which occur at different temperature (Table 4-1). The temperature at which the rate of the mass loss is at maximum (the peak maximum) is labelled $T_{\text{MAX}}^\text{I}$. The pyrolysis devolatilization is responsible for the first peak maximum at $T_{\text{MAX}}^\text{I}$ (Table 4-1) for each coal. As the temperature rises to approximately 300°C, the sample weight begins to decrease rapidly as the evolution of the volatile matter takes place. Thereafter, the rate of the mass loss increases relatively linearly as the volatile matter release accelerates with increasing temperature until the volatile matter loss reaches a peak at $T_{\text{MAX}}^\text{I}$. Then, the mass loss rate decreases as the volatile matter release decreases until the combustion emission of the volatile species starts just below $T_{\text{MAX}}^\text{II}$. Around $T_{\text{MAX}}^\text{II}$ both the pyrolysis volatile matter and combustion volatile species release probably occurs at the same time, but the combustion volatile species release dominates. As the weight loss rate increases to the third peak maximum at $T_{\text{MAX}}^\text{III}$, the net combustion evolution rate of the volatile species reaches the peak maximum. It is the $T_{\text{MAX}}^\text{III}$ that is the most important parameter which is used directly in the assessment of coal combustibility. The second peak maximum at $T_{\text{MAX}}^\text{II}$ might also be due to the sample swelling into an impermeable mass, thus reducing the oxygen accessibility and making combustion relatively slow. It is interesting that the $T_{\text{MAX}}^\text{III}$'s of IBC-103 and IBC-109, which are relatively high-chlorine and low-sulfur coals, are higher than those of IBC-105 and IBC-106, which are relatively low-
chlorine and high-sulfur coals. Thus, coals IBC-103 and IBC-109 have apparently greater combustibility than IBC-105 and IBC-106. Approximately 5.77-17.19% of the sample masses are left in the combustion residues of the four coals, which are comparable with the ash contents of the coals determined by ASTM standard method (Table 2-1).

4.2 Illinois Coal Combustion Gas Release Profiles by TG/FTIR

As identified by FTIR, the gaseous species evolved during combustion of Illinois coals under our experimental conditions includes carbon dioxide (CO₂), carbon monoxide (CO), water (H₂O), methane (CH₄), paraffin, nitrogen oxide (NO₂), sulfur dioxide (SO₂), carbonyl sulfide (COS) and hydrogen chloride (HCl). However, volatile species observed under the pyrolysis conditions, such as H₂S, C₂H₄, C₃H₆, NH₃, HCN and NO, were not observed under the combustion conditions. The wavenumbers of the FTIR absorption peaks chosen to identify the combustion gaseous species are summarized in Table 4-2.

Table 4-2. Wavenumbers of Absorption Peaks Chosen to Identify the Coal Combustion Gaseous Species.

<table>
<thead>
<tr>
<th>Gaseous species</th>
<th>Peak Wavenumber</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon dioxide, CO₂</td>
<td>2360 cm⁻¹</td>
</tr>
<tr>
<td>Carbon monoxide, CO</td>
<td>2175 cm⁻¹</td>
</tr>
<tr>
<td>Water, H₂O</td>
<td>1507 cm⁻¹</td>
</tr>
<tr>
<td>Methane, CH₄</td>
<td>3014 cm⁻¹</td>
</tr>
<tr>
<td>Paraffin</td>
<td>2943 cm⁻¹</td>
</tr>
<tr>
<td>Nitrogen dioxide, NO₂</td>
<td>1468 cm⁻¹</td>
</tr>
<tr>
<td>Carbonyl sulfide, COS</td>
<td>2073 cm⁻¹</td>
</tr>
<tr>
<td>Sulfur dioxide, SO₂</td>
<td>1374 cm⁻¹</td>
</tr>
<tr>
<td>Hydrogen chloride, HCl</td>
<td>2798 cm⁻¹</td>
</tr>
</tbody>
</table>
Figure 4-3 shows qualitatively the gaseous products evolved from the combustion of IBC-109 in an air atmosphere. The range of evolution of each gas is marked by the thin and thick solid lines. The thick lines indicate the absorbance intensities greater than 50% of the maximum absorbance intensity for each gas. The figure indicates that combustion of IBC-109 emits the gases between 300° and 600°C and most of these gases are evolved between 440° and 480°C, which correspond to the T$_{max}$'s on the DTG curve. The figure also shows that the dominant gas products are CO$_2$ and H$_2$O which result from the combustion reactions of the organic matter in the coal. The other three coals of IBC-103, -105 and -106 also have similar release behavior for the gaseous species during their combustion.

As a typical example of the combustion gaseous species release profiles of Illinois coals, Figures 4-4 and 4-5 shows the combustion gas release profiles of CO$_2$, CO, H$_2$O, CH$_4$ and paraffin from high-chlorine coal IBC-109 constructed from their FTIR peak absorbance intensities vs. heating temperature. All the profiles look like the DTG curve of IBC-109 (Figure 4-1) and have peak maxima between 400° and 500°C which corresponds to the T$_{max}$'s on the DTG curve. The H$_2$O profile (Figure 4-4) also has a peak at approximately 70°C which matches the T$_{max}$ (65°C) in the first mass loss temperature range of 20-150°C. A significantly large peak occurs at 300°C on the CO profile (Figure 4-4). This peak is mainly due to the pyrolysis evolution of CO caused by
Figure 4-3. Qualitative evolution of gaseous species during combustion of IBC-109, as determined by TG/FTIR using a 30 mg sample.
Figure 4-4. Combustion CO$_2$, CO and H$_2$O release profiles of IBC-109, as determined by TG/FTIR using a 30 mg sample.
Figure 4-5. Combustion CH₄, paraffin release profiles of IBC-109, as determined by TG/FTIR using a 30 mg sample.
decomposition of the oxygen-containing organic matter in the coal. The CH$_4$ and paraffin profiles indicate that coal combustion give off a much less amount of CH$_4$ and paraffin, especially paraffin, than coal pyrolysis (Figure 3-5). This is because most of the CH$_4$ and paraffin will be burned in air under the combustion conditions as they evolve by the decomposition of organic matter in the coal. The other three coals IBC-103, -105 and -106 have similar gas release profiles during combustion under the same experimental conditions.

4.3 Gaseous Sulfur Release during Illinois Coal Combustion

4.3.1 Combustion COS Release Profiles by TG/FTIR

The evolution of gaseous sulfur as COS was observed during combustion of Illinois coals by TG/FTIR using a 30 mg sample. The resulting combustion COS release profiles of high sulfur coal IBC-106 (3.77% S) and medium sulfur coal IBC-109 (1.13% S) are illustrated in Figure 4-6. The profiles have a shape similar to the DTG curve of both coals (Figure 4-1). There are two large peaks at approximately 300°C and 360°C and a small broad peak around 400°C on the IBC-106 COS profile. The 300°C peak is mainly due to the pyrolysis-like emission of COS formulated by reaction of CO (or CO$_2$) with H$_2$S at relatively low temperature under the combustion conditions, which is controlled by reactions 3-15 and 3-16, as previously discussed. The H$_2$S probably comes from the pyrolysis decomposition of both the organic and pyritic sulfur species, which is controlled by reactions 3-1 to 3-3. However, the
Figure 4-6. Comparison of combustion COS release profiles of high sulfur coal IBC-106 (3.77% S) and medium sulfur coal IBC-109 (1.13% S), as determined by TG/FTIR using a 30 mg sample.
360° and 400°C peaks are mainly due to the evolution of COS produced by the reaction of CO with FeS₂ under the combustion conditions, which is controlled by reaction 3-17.

By contrast, the IBC-109 COS profile only has two significant peaks: a relatively small peak at 300°C and a large broad peak around 440°C. Like the IBC-106 300°C peak, the IBC-109 300°C peak is also mainly due to the reaction of H₂S with CO or CO₂. Similar to the IBC-106 360°C and 400°C peaks, the IBC-109 440°C peak is mainly due to the reaction of FeS₂ with CO.

Coal combustion liberates a greater amount of COS than coal pyrolysis, as indicated in Figures 3-12 and 4-6. Still, the emission of the COS during combustion of Illinois coals takes place earlier than during pyrolysis.

4.3.2 Combustion SO₂ Release Profiles by TG/FTIR

As compared to coal pyrolysis, sulfur dioxide (SO₂) is the main gaseous sulfur species released during coal combustion under the experimental conditions. The combustion SO₂ release profiles of high-sulfur coal IBC-106 and low-sulfur coal are shown in Figure 4-7. Three significant peaks are observed at 280°C, 340°C and 440°C for IBC-109. The 280°C peak is mainly due to the aliphatic sulfur species, whereas the 340°C peak is due to the aromatic sulfur species in the coals under the combustion conditions. The 440°C peak may result from the pyritic sulfur species. The relevant three peaks on the IBC-106 SO₂ profile shift to higher temperature
Figure 4-7. Comparison of combustion SO$_2$ release profiles of high sulfur coal IBC-106 and medium sulfur coal IBC-109, as determined by TG/FTIR using a 30 mg sample.
by 20°C, the IBC-106 360°C peak is much larger than its 300°C and 450°C peaks, and it is also due to part of the pyritic sulfur species, except for aromatic sulfur species.

Compared with pyrolysis, combustion of Illinois coals give off a much greater amount of SO₂, and the emission of the SO₂ occurs earlier under the combustion conditions (Figures 3-4 and 4-7).

4.3.3 Quantitative Combustion Gaseous Sulfur Release Profiles and Sulfur Mass Balance by TG/IC

The quantitative release profile of combustion gaseous sulfur species for IBC-109 (1.13% S) has been determined by TG/IC technique using a 250 mg sample. It is noted that the TG/IC data was taken every 50°C interval (or every 5 min) instead of every 10°C (or every one minute) used in the TG/FTIR experiments. The profile was based on the determination of SO₄²⁻, which was obtained by oxidizing the combustion gaseous sulfur species with H₂O₂. The calculation and corresponding data for the average release rates of the combustion gaseous sulfur species are given in Table 4-3, and the resulting profile is shown in Figure 4-8. The sulfur mass balance during combustion of the coal has been calculated based, on three individual runs to determine the total sulfur released within the temperature range of 20-800°C under the same experimental conditions. Table 4-4 illustrates the resulting data and standard deviation.

The IC gaseous sulfur profile also has three peaks around 325°, 425°C and 525°C, which match quite well the FTIR results
Table 4-3. Average Release Rates of Gaseous Sulfur in each 50°C Range within the 175-775°C Range during Combustion of IBC-109, as Determined by TG/IC Using a 250 mg Sample.

<table>
<thead>
<tr>
<th>Temp. Range (°C)</th>
<th>Average Temp. (°C)</th>
<th>S Release Amount (%/50°C or %/5min)</th>
<th>Average S Release Rate (%/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150-199</td>
<td>175</td>
<td>0.26</td>
<td>0.05</td>
</tr>
<tr>
<td>200-249</td>
<td>225</td>
<td>0.90</td>
<td>0.18</td>
</tr>
<tr>
<td>250-299</td>
<td>275</td>
<td>1.60</td>
<td>0.32</td>
</tr>
<tr>
<td>300-349</td>
<td>325</td>
<td>6.00</td>
<td>1.20</td>
</tr>
<tr>
<td>350-399</td>
<td>375</td>
<td>7.12</td>
<td>1.54</td>
</tr>
<tr>
<td>400-449</td>
<td>425</td>
<td>17.24</td>
<td>3.45</td>
</tr>
<tr>
<td>450-499</td>
<td>475</td>
<td>13.82</td>
<td>2.76</td>
</tr>
<tr>
<td>500-549</td>
<td>525</td>
<td>10.99</td>
<td>2.20</td>
</tr>
<tr>
<td>550-599</td>
<td>575</td>
<td>4.31</td>
<td>0.86</td>
</tr>
<tr>
<td>600-649</td>
<td>625</td>
<td>2.02</td>
<td>0.40</td>
</tr>
<tr>
<td>650-699</td>
<td>675</td>
<td>1.18</td>
<td>0.31</td>
</tr>
<tr>
<td>700-749</td>
<td>725</td>
<td>0.74</td>
<td>0.15</td>
</tr>
<tr>
<td>750-799</td>
<td>775</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>67.07 %</td>
<td></td>
</tr>
</tbody>
</table>

Notes:

a) Total sulfur in the sample = 1.13% x 1000(µg/mg) x 250(mg) = 2825(µg).

b) Total sulfur released = 1895 (µg) or 67.07% vs. total sulfur in the sample [1895(µg) x 100/1350(1g) = 67.07%].

Table 4-4. Data of Sulfur Mass Balance during combustion of IBC-109 and Standard Deviation, as determined by TG/IC.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Total S Evolved (%)</th>
<th>Std. Dev.</th>
<th>% Std. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>67.1</td>
<td>0.3</td>
<td>0.4</td>
</tr>
<tr>
<td>2</td>
<td>67.3</td>
<td>0.2</td>
<td>0.4</td>
</tr>
<tr>
<td>3</td>
<td>67.7</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>Average</td>
<td>67.4</td>
<td>0.3</td>
<td>0.4</td>
</tr>
</tbody>
</table>

with regard to profiles of the gaseous sulfur species such as SO₂ and COS (Figures 4-6 and 4-7). However, the separation of the three peaks on the IC profile is not as pronounced as those on the FTIR profiles (Figures 4-6 and 4-7). The longer sampling range (every 50°C) used in the IC experiments may be
Figure 4-8. Quantitative combustion gaseous sulfur release profile of medium sulfur coal IBC-109 (1.13% Cl), based on the determination of $\text{SO}_4^{2-}$ by TG/IC using a 250 mg sample.
responsible for the poor resolution of the peaks, as compared with the FTIR experiments with the short sampling range (every 10°C).

The sulfur mass balance indicates that approximately 67% of the total sulfur has been liberated as gaseous sulfur species during combustion, and 33% of the total sulfur might be still left in the residue. If the sulfur content in the residue could be determined by an appropriate method, the sulfur mass balance would be better understood.

4.4 Gaseous Chlorine Release during Illinois Coal Combustion

4.4.1 Combustion HCl Release Profiles by TG/FTIR

Since a much greater amount of water is produced during combustion than pyrolysis of Illinois coals, the condensation of HCl with the water on the walls of the tubing becomes a severe problem. Even a 100 mg sample of high-chlorine coal IBC-109 (0.42% Cl) is not enough to observe the HCl by FTIR under the combustion conditions. Thus, a 300 mg sample of IBC-109 was used under improved combustion conditions, which was to heat the entire gas transfer line to 160°C. The HCl is observed clearly at the absorption peaks of 2798 cm⁻¹, 2772 cm⁻¹ and 2726 cm⁻¹ using these conditions. As established by using the 2798 cm⁻¹ FTIR peak, the combustion HCl release profiles of high-chlorine coal IBC-109 and low-chlorine coal IBC-106 (0.02% Cl) are shown in Figure 4-9. The IBC-109 HCl profile indicates that the chlorine in the coal is liberated as HCl approximately between 250°C and 700°C, and its release
Figure 4-9. Comparison of combustion HCl release profiles of high-chlorine coal IBC-109 and low-chlorine coal IBC-106 determined by TG/FTIR using a 300 mg sample.
amount reaches the peak maximum around 440°C. This result matches the pyrolysis result above, and it is also comparable with the result obtained by Chou et al. However, the IBC-106 HCl profile indicates that little gaseous chlorine is given off as HCl during combustion of IBC-106 under the same experimental conditions.

4.4.2 Quantitative Combustion Gaseous Chlorine Release Profiles and Chlorine Mass Balance by TG/IC

The combustion HCl release profile of high-chlorine coal IBC-109 has been also analyzed quantitatively using the TG/IC technique. When a 250 mg sample of IBC-109 was heated on the TG system under the improved combustion conditions, the combustion gas mixture was collected in a series of the trap solutions of Na₂CO₃-NaHCO₃ buffer. The trap solutions were analyzed by IC for the chlorine content evolved in each 50°C interval within the temperature range of ambient to 800°C, and the average chlorine release rate in each 50°C was calculated. Then, by plotting the average chlorine release rate in each 50°C vs. temperature, the quantitative combustion gaseous chlorine release profile of IBC-109 was obtained. Table 4-5 illustrates the calculation and corresponding data for the chlorine release rates in 50°C ranges within the temperature range during combustion of IBC-109. Figure 4-10 shows the resulting quantitative release profile of combustion gaseous chlorine species for high chlorine coal IBC-109. Three individual runs have been conducted to determine the chlorine mass balance in the coal during combustion, and the standard
The deviation has been calculated. The results are listed in Table 4-6.

The profile and the chlorine mass balance indicate that approximately 97% of the total chlorine in the sample is evolved as gaseous chlorine species mainly between 300°C and 700°C.

Table 4-5. Average Release Rates of Gaseous Chlorine in Each 50°C Range within the 175-775°C Range during Combustion of IBC-109, as Determined by TG/IC Using a 250 mg Sample.

<table>
<thead>
<tr>
<th>Temp. Range (°C)</th>
<th>Average Temp. (°C)</th>
<th>Cl Release Amount (%/50°C or %/5min)</th>
<th>Average Cl Release Rate (%/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150-199</td>
<td>175</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>200-249</td>
<td>225</td>
<td>0.61</td>
<td>0.12</td>
</tr>
<tr>
<td>250-299</td>
<td>275</td>
<td>3.01</td>
<td>0.60</td>
</tr>
<tr>
<td>300-349</td>
<td>325</td>
<td>7.72</td>
<td>1.54</td>
</tr>
<tr>
<td>350-399</td>
<td>375</td>
<td>13.99</td>
<td>2.80</td>
</tr>
<tr>
<td>400-449</td>
<td>425</td>
<td>22.12</td>
<td>4.42</td>
</tr>
<tr>
<td>450-499</td>
<td>475</td>
<td>19.84</td>
<td>3.97</td>
</tr>
<tr>
<td>500-549</td>
<td>525</td>
<td>16.25</td>
<td>3.25</td>
</tr>
<tr>
<td>550-599</td>
<td>575</td>
<td>8.70</td>
<td>1.74</td>
</tr>
<tr>
<td>600-649</td>
<td>625</td>
<td>2.96</td>
<td>0.59</td>
</tr>
<tr>
<td>650-699</td>
<td>675</td>
<td>1.80</td>
<td>0.36</td>
</tr>
<tr>
<td>700-749</td>
<td>725</td>
<td>0.18</td>
<td>0.04</td>
</tr>
<tr>
<td>750-799</td>
<td>775</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>97.18 %</td>
<td></td>
</tr>
</tbody>
</table>

Notes:
a) Total chlorine in sample = 0.42% x 1000 (µg/mg) x 250 (mg) = 1050 (µg).
b) Total chlorine released = 1020 (µg) or 97.18% vs. total chlorine in sample [1020(µg) x 100/1050(µg) = 97.18%].

Table 4-6. Data of Chlorine Mass Balance during Combustion of IBC-109 and the Standard Deviation, as Determined by TG/IC.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Total Cl Evolved (%)</th>
<th>Std. Dev.</th>
<th>% Std. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>97.2</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>2</td>
<td>97.3</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>3</td>
<td>97.7</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Average</td>
<td>97.4</td>
<td>0.2</td>
<td>0.2</td>
</tr>
</tbody>
</table>
Figure 4-10. Quantitative combustion gaseous chlorine release profile of high-chlorine coal IBC-109 (0.42% Cl), as determined by TG/IC using a 250 mg sample.
600°C during combustion of high-chlorine coal IBC-109 (0.42% Cl), and the chlorine release rate reaches a maximum in the temperature range of 400-450°C. However, almost 70% of the total released gaseous chlorine (97.18%) has been given off just below 500°C which corresponds to $T_{\text{MAX-III}}$ (471°C) on the DTG curve of IBC-109. The gaseous chlorine profile determined by TG/IC matches well the HCl profile obtained by TG/FTIR.

In summary, the TG/IC method provides quantitative results and the TG/FTIR method provides semi-quantitative results about the behavior of chlorine and sulfur in coal during combustion. The quantitative results concerning the behavior of the chlorine release during coal combustion determined by TG/IC are comparable with the results obtained by Chou et al. who used the temperature-controlled combustion technique combined with quadruple gas analyzer (QGA) and ion selective electrode (ISE).
CHAPTER 5

BEHAVIOR OF CHLORINE AND SULFUR IN LEACHED ILLINOIS COAL DURING COMBUSTION

This chapter includes the discussion of the possible changes in the coal burning and gas evolution profiles during combustion following the removal of chlorine from high-chlorine coal IBC-109 (0.42% Cl). The chlorine was removed from IBC-109 by C. L. Chou, Illinois State Geological Survey (ISGS), using a grinding-leaching system. The chlorine content was reduced in IBC-109 from 0.42% (Coal-0.42) to 0.23% (Coal-0.23), and then from 0.23% to 0.068% (Coal-0.07). 85

5.1 Thermogravimetric Analysis for Leached Coal Combustion

5.1.1 Combustion TG Analysis

The leached coals were heated in the TG furnace from ambient temperature to 800°C at a heating rate of 10°C/min and an air flow rate of 50 ml/min. The resulting combustion TG profiles of Coal-0.42, Coal-0.23 and Coal-0.07 are shown in Figure 5-1. After the vaporization of inherent water in the coal, the mass of the coal increases, which is due to the oxygen chemisorption at the beginning of the combustion process. The chemisorption occurs between 200°C and 300°C causing Coal-0.42 to experience a 1.36% weight gain. Compared with the raw coal (Coal-0.42), the leached coals (Coal-0.23
Figure 5-1. Combustion TG profiles for Coal-0.42, Coal-0.23, and Coal-0.07 at a heating rate of 10°C/min.
and Coal-0.07) absorb less oxygen in the more narrow and lower temperature ranges, as illustrated in Table 5-1. This effect is probably attributed to the larger surface area of the leached coal, compared with its parent coal, Coal-0.42.

Table 5-1. Combustion TG Results for Raw Coal Coal-0.42 and Leached Coals Coal-0.23 and Coal-0.07

<table>
<thead>
<tr>
<th>Sample</th>
<th>(T_g^a) (°C)</th>
<th>Mass Gain (%)</th>
<th>(T_i^b) (°C)</th>
<th>(T_{1/2}^c) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal-0.42</td>
<td>229-321</td>
<td>1.36</td>
<td>324</td>
<td>469</td>
</tr>
<tr>
<td>Coal-0.23</td>
<td>212-279</td>
<td>1.08</td>
<td>245</td>
<td>431</td>
</tr>
<tr>
<td>Coal-0.07</td>
<td>178-245</td>
<td>1.17</td>
<td>243</td>
<td>415</td>
</tr>
</tbody>
</table>

a) \(T_g^a\) is chemisorption temperature at which the mass gain occurs; b) \(T_i\) is the initial decomposition temperature; and c) \(T_{1/2}\) is the temperature at 50% conversion (on a daf basis).

After the chemisorption of oxygen by the coal, the sample weight begins to decrease as the volatile matter loss starts. The initial decomposition temperature (\(T_i\)) and the 50% conversion temperature of the leached coals shift to much lower temperature, compared with Coal-0.42 (see table 5-1). These phenomena are probably due to the increasing reactivity of the leached coals as a result of smaller particle size. Approximately 10% of mass is left in the residue of Coal-0.42, whereas the amounts of the residues of Coal-0.23 and Coal-0.07 are 9.6% and 7.9%, respectively.

5.1.2 Combustion DTG Analysis

The combustion DTG curves of Coal-0.42, Coal-0.23 and Coal-0.07 are shown in Figure 5-2, and the corresponding data is given in Table 5-2. As indicated on the DTG curves of the leached coals, both the leached coal samples exhibit two
Figure 5-2. Combustion DTG curves of raw coal Coal-0.42 and leached coals Coal-0.23 and Coal-0.07 at a heating rate of 10°C/min.
Table 5-2. Data of the Combustion DTG Analysis for Coal-0.42, Coal-0.23 and Coal-0.07 at a Heating Rate of 10°C/min

<table>
<thead>
<tr>
<th>Sample \ Parameters</th>
<th>(T_{MAX}^{a}) (°C)</th>
<th>Wt Loss Rate(^b) (%/min)</th>
<th>Wt Loss(^b) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal-0.42</td>
<td>281</td>
<td>1.3</td>
<td>1.25</td>
</tr>
<tr>
<td>Coal-0.23</td>
<td>250</td>
<td>4.4</td>
<td>4.05</td>
</tr>
<tr>
<td>Coal-0.07</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample \ Parameters</th>
<th>(T_{Ax}^{-II}^{a}) (°C)</th>
<th>Wt Loss Rate(^b) (%/min)</th>
<th>Wt Loss(^b) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal-0.42</td>
<td>336</td>
<td>2.3</td>
<td>6.25</td>
</tr>
<tr>
<td>Coal-0.23</td>
<td>320</td>
<td>9.8</td>
<td>11.70</td>
</tr>
<tr>
<td>Coal-0.07</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample \ Parameters</th>
<th>(T_{ma}^{-III}^{a}) (°C)</th>
<th>Wt Loss Rate(^b) (%/min)</th>
<th>Wt Loss(^b) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal-0.42</td>
<td>430</td>
<td>5.5</td>
<td>28.5</td>
</tr>
<tr>
<td>Coal-0.23</td>
<td>389</td>
<td>8.7</td>
<td>19.9</td>
</tr>
<tr>
<td>Coal-0.07</td>
<td>375</td>
<td>11.2</td>
<td>15.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample \ Parameters</th>
<th>(T_{mAlc}^{IV}^{a}) (°C)</th>
<th>Wt Loss Rate(^b) (%/min)</th>
<th>Wt Loss(^b) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal-0.42</td>
<td>471</td>
<td>6.8</td>
<td>63.4</td>
</tr>
<tr>
<td>Coal-0.23</td>
<td>418</td>
<td>6.6</td>
<td>61.8</td>
</tr>
<tr>
<td>Coal-0.07</td>
<td>413</td>
<td>6.4</td>
<td>61.5</td>
</tr>
</tbody>
</table>

Note: a) \(T_{MAX}\) is the peak maximum temperature in each stage.  
   b) The values are on a dry basis.

additional distinct peak maxima at 281°C and 336°C for Coal-0.23 and 250°C and 320°C for Coal-0.07. These two thermal decomposition stages are not observed during combustion of Coal-0.42.

It is obvious that the grinding process of Coal-0.42 has reduced the coal particle size to some extent. This process
may produce several types of the coal particle sizes being present in the leached coals of Coal-0.23 and Coal-0.07. It is the different sizes of the coal particles in the leached coals that are probably responsible for the existence of more thermal decomposition and/or combustion stages during combustion, compared with their parent coal, Coal-0.42, which has a 60-mesh size of the coal particles. The smaller the coal particles, the earlier the thermal decomposition and/or combustion of the coal particles takes place. Thus, corresponding to the first thermal decomposition stage, the first peak maxima at $T_{\text{max}}^{\text{-I}}$ (281°C for Coal-0.23 and 250°C for Coal-0.07) is mainly due to the thermal decomposition of the relatively small size of the particles in the clean coal. The second stage corresponding to the second peak maxima at $T_{\text{max}}^{\text{-II}}$ (336°C for Coal-0.23 and 320°C for Coal-0.07) is mainly due to the thermal decomposition of a larger size of the coal particles, compared with the first stage. In the third stage, much sharper and higher weight loss rates are observed for the clean coals. In the fourth stage, the major combustion area for the clean coals occurs at a much lower temperature, compared with Coal-0.42.

5.2 Gas Release during Leached Coal Combustion by TG/FTIR

Identified by FTIR, the gaseous species evolved during the combustion of both leached coals, Coal-0.23 and Coal-0.07, mainly include CO$_2$, CO, H$_2$O, CH$_4$, SO$_2$, COS and HCl. The FTIR absorption peaks illustrated in Table 4-2 were also selected
to identify these gaseous species. The combustion release behavior of these gaseous species for both leached coals closely resembles each other, but they are quite different from those of the parent coal, Coal-0.42. Each gas release profile has three peak maxima occurring roughly at the same temperatures as the $T_{max}$'s for the weight loss rates on the combustion DTG curves of the leached coals (Figure 5-2 and Table 5-2).

5.2.1 Combustion CO$_2$ and CO Release Profiles

The comparison of combustion CO$_2$ release profiles for raw coal Coal-0.42 and leached coal Coal-0.07 is shown in Figure 5-3. Carbon dioxide (CO$_2$) is the dominant gas product of coal combustion, and its release yield reflects directly the combustibility of a coal. The CO$_2$ release profile of leached coal Coal-0.07 is quite different from that of raw coal Coal-0.42. The CO$_2$ profile of raw coal Coal-0.42 has a large broad peak between 380°C and 540°C (at 50% absorbance), whereas that of leached coal Coal-0.07 has a large broad peak between 360°C and 470°C, a small narrow peak at 250°C, as well as a large narrow peak at 310°C. As discussed previously, the 250°C and 310°C peaks on the CO$_2$ profile of leached coal Coal-0.07 are mainly due to the early thermal decomposition and/or combustion of its coal particles smaller than those of raw coal Coal-0.42. Furthermore, the average total absorbance area under the Coal-0.07 CO$_2$ profile seems to be larger than that under the Coal-0.42 CO$_2$ profile. This implies that the
Figure 5-3. Comparison of combustion CO₂ release profiles between leached coal Coal-0.07 and raw coal Coal-0.42, as determined by TG/FTIR using a 50 mg sample.
Coal-0.07 combustion gives off more CO$_2$ than Coal-0.42. Thus, Coal-0.07 is more combustible than Coal-0.42. However, it appears that the Coal-0.07 combustion takes place earlier than the Coal-0.42, as indicated by their CO$_2$ profiles. Thus, the combustion durability of Coal-0.07 seems to be lower than that of Coal-0.42. In other words, Coal-0.07 may be burned up more rapidly during combustion than Coal-0.42. The low combustion durability is not desired for a coal of good quality.

The comparison of combustion CO release profiles between raw coal Coal-0.42 and leached coal Coal-0.07 is shown in Figure 5-4. The large narrow 250°C peak on the Coal-0.07 CO profile, which does not exist on the CO profile of the raw coal, is mainly due to the first stage of the thermal decomposition and/or combustion emission, which is not desired for a quality coal. The 390°C peak on the Coal-0.07 CO profile is much smaller than the corresponding peak (440°C) on the Coal-0.42 CO profile. During combustion, the leached coal gives off much less CO than the raw coal within the main combustion temperature range of 350-550°C, which is desired for a good coal used as a combustible fuel.

The CO/CO$_2$ ratio is an important parameter to evaluate a coal. The comparison of the CO/CO$_2$ ratio plots between the leached coal of Coal-0.07 and the raw coal of Coal-0.42 is shown in Figure 5-5. For Coal-0.42, the CO/CO$_2$ ratio is approximately 0.09 at 250°C, which is mainly due to the devolatilization, and it decreases to near zero between 350°C and 600°C, which mainly results from the oxidative pyrolysis.
Figure 5-4. Comparison of combustion CO release profiles between leached coal Coal-0.07 and raw coal Coal-0.42, as determined by TG/FTIR using a 50 mg sample.
Figure 5-5. Comparison of combustion CO/CO₂ release ratio profiles between leached coal Coal-0.07 and raw coal Coal-0.42, as determined by TG/FTIR using a 50 mg sample.
During the oxidative pyrolysis stage, the generation of \( \text{CO}_2 \) from coal is much greater than that of CO. For leached coal Coal-0.07, the shape of the CO/\( \text{CO}_2 \) release ratio profile is very similar to that of raw coal Coal-0.42. However, the CO/\( \text{CO}_2 \) ratio of Coal-0.07 is approximately 0.05 at 250\(^\circ\)C, which is lower than that (0.09) of Coal-0.42, and it appears that Coal-0.07 generates relatively less CO in its devolatilization stage, compared with the raw coal. The CO/\( \text{CO}_2 \) ratio of Coal-0.07, then, drops to near zero just above 300\(^\circ\)C, which takes place earlier than in the case of the raw coal. Thus, the leached coal shows a significant decrease in the CO/\( \text{CO}_2 \) release ratio as well as their CO/\( \text{CO}_2 \) release ratio profiles shift to a lower temperature, compared with the raw coal. Therefore, the leached coal combustion produces more \( \text{CO}_2 \) and less CO than the raw coal, and the leached coal has higher combustibility but lower combustion durability than the raw coal.

5.2.2 Combustion \( \text{H}_2\text{O} \) Release Profiles

The comparison of the combustion \( \text{H}_2\text{O} \) release profiles between the leached coal (Coal-0.07) and raw coal (Coal-0.42) is shown in Figure 5-6. The Coal-0.07 profile still shows three peak maxima at 290\(^\circ\)C, 330\(^\circ\)C and 380\(^\circ\)C. However, the three peak maxima are not pronounced enough to be separated from each other, compared with \( \text{CO}_2 \) and CO. Some water might condense somewhere in the gas-train path between the TG sample chamber and the FTIR gas cell.
Figure 5-6. Comparison of combustion H$_2$O release profiles between leached coal Coal-0.07 and raw coal Coal-0.42, as determined by TG-FTIR on a basis of a 50 mg sample.
5.2.3 Combustion CH\textsubscript{4} Release Profiles

The comparison of the combustion CH\textsubscript{4} release profiles between the leached coal (Coal-0.07) and the raw coal (Coal-0.42) is shown in Figure 5-7, as determined by TG/FTIR using a 30 mg sample. The 250°C, 310°C, 370°C and 440°C peaks on the Coal-0.07 CH\textsubscript{4} profile is mainly due to varying stages of the thermal decomposition, and correspond to the peaks at different T\textsubscript{MAX}'s on the DTG curve of Coal-0.07. The 250°C peak is significantly larger than other three peaks and results from the coal devolatilization at relatively low temperature. However, the Coal-0.42 CH\textsubscript{4} profile only has a large broad peak at 440°C, which is mainly due to the CH\textsubscript{4} emission of the coal oxidative pyrolysis within the major combustion temperature range (380°-500°C). The 440°C peak of the raw coal seems to be split into several peaks in the case of leached coal Coal-0.07, as shown in the Coal-0.07 CH\textsubscript{4} profile. As a result, the Coal-0.07 440°C peak has become much smaller and its absorbance intensity is approximately 10 times lower, as compared with the raw coal (Coal-0.42). Furthermore, the total area estimated under the Coal-0.07 CH\textsubscript{4} profile is much smaller than that of the raw coal. Thus, the leached coal generates much less CH\textsubscript{4} within the major combustion temperature range (380-500°C) than the raw coal. Much more combustible matter, such as CH\textsubscript{4}, in the leached coal tends to be burned, as compared with its parent coal.
Figure 5-7. Comparison of combustion CH\textsubscript{4} release profiles between leached coal Coal-0.07 and raw coal Coal-0.42, as determined by TG/FTIR using a 50 mg sample.
5.3 Gaseous Sulfur Release during Leached Coal Combustion

5.3.1 Combustion SO$_2$ Release Profiles by TG/FTIR

As determined by TG/FTIR using a 50 mg sample, SO$_2$ is also a major product of the gaseous sulfur species produced during combustion of the leached coal. The comparison of the combustion SO$_2$ release profiles between leached coal Coal-0.07 and raw coal Coal-0.42, is shown in Figure 5-8. Three well separated peaks exist at 250°C, 320° and 380°C on the profile of the leached coal (Coal-0.07), as compared with the raw coal (Coal-0.42), and these three peaks are probably due to the oxidative pyrolysis emission of aliphatic, aromatic and pyritic sulfur species. It appears that more organic sulfur species in the leached coal has been liberated as SO$_2$ at 250°C and 320°C, compared to the raw coal. As discussed previously, the 440°C peak on the Coal-0.42 SO$_2$ profile is probably due to the combined release of SO$_2$ from both aromatic and pyritic sulfur species in the coal. The observation that the Coal-0.07 440°C peak is much smaller than that of Coal-0.42 may imply that a less amount of the aromatic sulfur in the leached coal emits as SO$_2$ at this temperature, as compared with its parent coal. It seems that the chlorine removal process caused the evolution of organic sulfur species as SO$_2$ at lower temperatures than the raw coal.

5.3.2 Combustion COS Release Profiles by TG/FTIR

As determined by TG/FTIR analysis using a 50 mg sample, the combustion COS release profiles of leached coal Coal-0.07
Figure 5-8. Comparison of combustion SO$_2$ release profiles between leached coal Coal-0.07 and raw coal Coal-0.42, as determined by TG/FTIR on a basis of a 50 mg sample.
and raw coal Coal-0.42 are shown in Figure 5-9. Three well separated peaks exist at 250°C, 320°C and 400°C, on the COS profile of the leached coal, whereas two broad peaks occur around 290°C and 440°C on the COS profile of the raw coal (Coal-0.42). The three peaks on Coal-0.07 profile may be due to the oxidative decomposition emission of aliphatic, aromatic and pyritic sulfur species in the leached coal, respectively. As we have seen in the case of the SO$_2$ release, the treatment of the grinding-leaching process has also made the organic sulfur species in the leached coal release as COS more at relatively lower temperatures, compared with the raw coal.

5.3.3 Quantitative Combustion Gaseous Sulfur Release Profiles by TG/IC

The quantitative combustion gaseous sulfur release profiles of the leached coals (Coal-0.07 and Coal-0.23) have been established using the TG/IC technique and a 250 mg sample under the same experimental conditions as used in the case of the raw coal (Coal-0.42). The comparison of the quantitative release profiles of the combustion gaseous sulfur species between the leached coal and raw coal is shown in Figure 5-10. The average release rates of the gaseous sulfur species in each 50°C interval within the temperature range of 175-775°C are listed in Table 5-3. The average sulfur mass balance has been calculated, based on three runs, to determine the total sulfur evolved within the 20°-800°C range during combustion of the leached coals. The resulting data, as well as the standard deviation are summarized in Table 5-4.
Figure 5-9. Comparison of combustion COS release profiles between leached coal Coal-0.07 and raw coal Coal-0.42, as determined by TG/FTIR on a basis of a 50 mg sample.
Figure 5-10. Comparison of combustion gaseous sulfur release profiles between the leached coals (Coal-0.07 and Coal-0.23) and the raw coal (Coal-0.42), as determined by TG/IC using a 250 mg sample.
Table 5-3. Average Release Rates of Gaseous Sulfur in Each 50°C Range within the 175°C-775°C Range during Combustion of Leached Coals, as Determined by TG/IC Using a 250 mg Sample.

<table>
<thead>
<tr>
<th>Temp. Range (°C)</th>
<th>Average Temp. (°C)</th>
<th>Average Gaseous S Release Rate (%/min) Coal-0.07</th>
<th>Coal-0.23</th>
<th>Coal-0.42</th>
</tr>
</thead>
<tbody>
<tr>
<td>150-199</td>
<td>175</td>
<td>0.01</td>
<td>0.06</td>
<td>0.05</td>
</tr>
<tr>
<td>200-249</td>
<td>225</td>
<td>0.81</td>
<td>0.40</td>
<td>0.18</td>
</tr>
<tr>
<td>250-299</td>
<td>275</td>
<td>0.09</td>
<td>0.10</td>
<td>0.32</td>
</tr>
<tr>
<td>300-349</td>
<td>325</td>
<td>2.15</td>
<td>1.78</td>
<td>1.20</td>
</tr>
<tr>
<td>350-399</td>
<td>375</td>
<td>1.85</td>
<td>1.64</td>
<td>1.54</td>
</tr>
<tr>
<td>400-449</td>
<td>425</td>
<td>4.63</td>
<td>4.53</td>
<td>3.45</td>
</tr>
<tr>
<td>450-499</td>
<td>475</td>
<td>2.74</td>
<td>3.38</td>
<td>2.76</td>
</tr>
<tr>
<td>500-549</td>
<td>525</td>
<td>1.16</td>
<td>1.31</td>
<td>2.20</td>
</tr>
<tr>
<td>550-599</td>
<td>575</td>
<td>0.37</td>
<td>0.57</td>
<td>0.86</td>
</tr>
<tr>
<td>600-649</td>
<td>625</td>
<td>0.22</td>
<td>0.28</td>
<td>0.40</td>
</tr>
<tr>
<td>650-699</td>
<td>675</td>
<td>0.21</td>
<td>0.21</td>
<td>0.31</td>
</tr>
<tr>
<td>700-749</td>
<td>725</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>750-799</td>
<td>775</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Notes:
a) Total sulfur in sample = 1.13% x 1000(µg/mg) x 250(mg) = 2825 (µg).
b) Total sulfur released is 1895 (µg) or 67.07% for Coal-0.42, 2043 (µg) or 72.32% for Coal-0.23 and 2053 (µg) or 72.67% for Coal-0.07 vs. total sulfur in the sample.

Table 5-4. Results of sulfur mass balance for leached coal combustion determined by TG-IC and the standard deviation.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Coal-0.07</th>
<th>Coal-0.23</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total S Evolved (%)</td>
<td>Std. Dev.</td>
</tr>
<tr>
<td>1</td>
<td>72.3</td>
<td>0.3</td>
</tr>
<tr>
<td>2</td>
<td>72.0</td>
<td>0.4</td>
</tr>
<tr>
<td>3</td>
<td>72.6</td>
<td>0.2</td>
</tr>
<tr>
<td>AVE</td>
<td>72.3</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Two leached coals (Coal-0.07 and Coal-0.23) have similar gaseous sulfur profiles, which also resemble the profile of the raw coal (Coal-0.42). The TG/IC gaseous sulfur profiles do not show the 225°C and 325°C peaks as clearly as the
corresponding peaks in the TG/FTIR release profiles of the gaseous sulfur species such as SO\textsubscript{2} and COS (Figures 5-8 and 5-9). There are probably two reasons. First, the sampling range (every 50°C) in the case of IC is longer than in the case of FTIR (every 10°C), and this may make the peaks broad and flat. Secondly, not all of the gaseous sulfur species could have been converted to the detectable SO\textsubscript{4}\textsuperscript{2-} ions by IC under the experimental conditions, and this would lead to a relative smaller amount of the evolved sulfur recovered by IC than it should be.

The sulfur mass balance indicates that approximately 72% of the total sulfur has been emitted from the leached coals during combustion, and this amount might be lower than it should be because the escape of some gaseous sulfur species might take place under the TG/IC experimental conditions. If we could determine the sulfur content in the residue, the amount of the escaped sulfur could be calculated. Furthermore, the leached coal gives off a little more gaseous sulfur by approximately 5% than its parent coal during combustion, and this supports the FTIR results above.

5.4 Gaseous Chlorine Release during Leached Coal Combustion

5.4.1 Combustion HCl Release Profiles by TG/FTIR

Hydrogen chloride (HCl) was observed during combustion of the leached coal using the TG/FTIR technique and a 300 mg sample under the same experimental conditions used for the raw coal. Comparison of the combustion HCl release profiles
between the leached coals (Coal-0.07 and Coal-0.23) and the raw coal (Coal-0.42) is shown in Figure 5-11. Three broad peaks exist at 270°C, 360°C and 420°C on the Coal-0.23 HCl profile, corresponding to the 281°C, 336°C and 418°C peak maxima on the DTG curve of Coal-0.23, which are related to the first, second and fourth stages of thermal decomposition and/or combustion. These three peaks are mainly due to the emission of HCl from the thermal decomposition. However, there is no peak around 380°C on the Coal-0.23 HCl profile, which corresponds to the 389°C peak maximum in the third stage of combustion on the DTG curve. As discussed previously, the treatment of the parent coal (Coal-0.42) by the grinding-leaching process has also made the chlorine in the leached coal release at relatively lower temperature. As a result, the behavior of chlorine in the leached coal is different during combustion from the raw coal. Furthermore, as indicated on the profile, the ratio of peak area under the curves of Coal-0.42 and Coal-0.23 is approximately 1.7, whereas the ratio of the chlorine content between Coal-0.42 and Coal-0.23 is 1.8. There is excellent agreement between the elemental analysis and the TG-FTIR analysis. The Coal-0.07 HCl profile indicates that little HCl release has been observed during combustion.
Figure 5-11. Comparison of combustion HCl release profiles between the leached coals (Coal-0.07 and Coal-0.23) and the raw coal (Coal-0.42), as determined by TG/FTIR using a 300 mg sample.
5.4.2 Quantitative Combustion Gaseous Chlorine Release Profiles by TG/IC

Based on the determination of chloride ion (Cl⁻) by IC, the data for average gaseous chlorine release rates in each 50°C interval within the temperature range of 175°-775°C during combustion of the leached coals are illustrated in Table 5-5.

Table 5-5. Average Release Rates of Gaseous Chlorine in Each 50°C Range within the 175-775°C range during Combustion of Leached Coals, as Determined by TG/IC Using a 250 mg Sample.

<table>
<thead>
<tr>
<th>Temp. Range (°C)</th>
<th>Average Temp (°C)</th>
<th>Average Gaseous Cl Release Rate (µg/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Coal-0.07</td>
</tr>
<tr>
<td>150-199</td>
<td>175</td>
<td>0.00</td>
</tr>
<tr>
<td>200-249</td>
<td>225</td>
<td>3.42</td>
</tr>
<tr>
<td>250-299</td>
<td>275</td>
<td>2.87</td>
</tr>
<tr>
<td>300-349</td>
<td>325</td>
<td>6.40</td>
</tr>
<tr>
<td>350-399</td>
<td>375</td>
<td>3.19</td>
</tr>
<tr>
<td>400-449</td>
<td>425</td>
<td>6.36</td>
</tr>
<tr>
<td>450-499</td>
<td>475</td>
<td>4.22</td>
</tr>
<tr>
<td>500-549</td>
<td>525</td>
<td>2.38</td>
</tr>
<tr>
<td>550-599</td>
<td>575</td>
<td>1.43</td>
</tr>
<tr>
<td>600-649</td>
<td>625</td>
<td>1.38</td>
</tr>
<tr>
<td>650-699</td>
<td>675</td>
<td>0.84</td>
</tr>
<tr>
<td>700-749</td>
<td>725</td>
<td>0.35</td>
</tr>
<tr>
<td>750-799</td>
<td>775</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Notes:
a) Total chlorine in the sample is 1050 (µg) for Coal-0.42, 576 (µg) for Coal-0.23 and 169 (µg) for Coal-0.07.
b) Total chlorine released is 1020 (µg) for Coal-0.42, 562 (µg) for Coal-0.23 and 164 (µg) for Coal-0.07.

The resulting quantitative gaseous chlorine release profiles of the leached coals (Coal-0.23 and Coal-0.07) and their parent coal (Coal-0.42) during combustion are shown in Figure 5-12. The chlorine mass balance of the clean coals during combustion is summarized in Table 5-6, which is determined by IC analysis of the total chlorine evolved during combustion.
Figure 5-12. Comparison of quantitative release profiles of combustion gaseous chlorine between the leached coals (Coal-0.07 and Coal-0.23) and the raw coal (Coal-0.42), as determined by TG/IC using a 300 mg sample.
The combustion chlorine release profiles obtained by TG-IC indicate that the emission of chlorine in the leached coals (Coal-0.23 and Coal-0.07) occurs within the temperature range of 200°-600°C during combustion. The chlorine release amount has three broad peaks around 225°C, 325°C and 425°C, which correspond to the first, second and fourth thermal decomposition and/or combustion stages on the combustion DTG profiles of the leached coals (Figure 5-2 and Table 5-2). However, the third thermal decomposition or combustion stage occurring around 380°C on the DTG curves is not reflected on the IC chlorine profile of the leached coals.

The IC chlorine profiles match well the FTIR HCl profiles for all the leached coals (Coal-0.23 and Coal-0.07) and the raw coal (Coal-0.42). Both of the IC and FTIR chlorine profiles show that the total amount of chlorine released decreases during combustion of the leached coals, and that the emission of chlorine in the leached coals shifts to lower temperature, as compared with the raw coal. However, compared with the FTIR HCl profile (Figure 5-11), the three peaks on
the IC chlorine profile of the leached coal (Coal-0.23) are less pronounced due to the longer sampling time used in the TG/IC method than in the TG/FTIR method.

As determined by TG/IC technique, the chlorine mass balance during combustion of the leached coals (Table 5-6) indicates that approximately 97% of total chlorine in the leached coals is released during combustion. Approximately 86% of the total released chlorine has been evolved below 500°C for the leached coals, and this amount is greater than that (approximately 70%) in case of the raw coal (see section 4.3.2).
CHAPTER 6

EFFECT OF SORBENT ADDITION ON BEHAVIOR OF CHLORINE AND SULFUR IN ILLINOIS COAL DURING COMBUSTION

This chapter deals with the behavior and reactivity of chemical reagents CaCO$_3$ and Ca(OH)$_2$ while they are employed as sorbents to control the release of gaseous chlorine and sulfur species in the temperature range of 25°C-800°C by the dynamic TG/FTIR and rapid TG/IC methods.

6.1 Dynamic TG/FTIR Analysis for Coal-Sorbent Mixture Combustion

6.1.1 Dynamic Combustion TG Analysis

Commercial powder samples of CaCO$_3$ and Ca(OH)$_2$ were mixed with high-chlorine and low-sulfur coal IBC-109 (0.42% Cl and 1.13% S), respectively. The coal and sorbent are well mixed physically in a 100 ml container with several metal mixers. The sorbent/coal mass ratios of the Coal-Ca(OH)$_2$ and Coal-CaCO$_3$ mixtures are 4.76% and 6.33%, respectively. Both mixtures contain an identical molar amount of calcium.

In the dynamic TG/FTIR method, the mixture sample is heated from ambient temperature to 800°C at a heating rate of 10°C/min under an air flow rate of 50 ml/min. Combustion gases are analyzed simultaneously by FTIR.

Individual TG analysis in air for each component making
up the various combination fuels were initially carried out, and the resulting TG curves are illustrated in Figure 6-1. The CaCO₃ TG curve shows only one major weight loss region (approximately 44%) which is mainly attributed to the calcination of the calcium carbonate giving off CO₂ above 600°C, as shown in the following equation:

\[
\text{Calcination} \quad \frac{\text{CaCO}_3}{\gg 600^\circ C} \xrightarrow[]{} \text{CaO} + \text{CO}_2 \quad (6-1)
\]

The TG curve of Ca(OH)$_2$ shows two major weight loss regions. The first weight loss of 21% occurs between 350°C and 450°C, which is attributed to the conversion of Ca(OH)$_2$ to CaO, by the following equation:

\[
\text{Dehydration} \quad \frac{\text{Ca(OH)}_2}{350-450^\circ C} \xrightarrow[]{} \text{CaO} + \text{H}_2\text{O} \quad (6-2)
\]

The second minor weight loss of 3% takes place between 450°C and 650°C, which is probably due to the weight loss of the impurities in the sample. The TG curve of coal IBC-109 indicates two major weight loss regions. The first weight loss (20°-150°C) corresponds to 5% inherent moisture loss followed by the second weight loss of 84% (150°-800°C) containing two overlapping DTG peaks at 430°C and 471°C, respectively (Figure 5-2 and Table 5-2).

The combustion thermograms of the original coal, IBC-109 and its mixtures with sorbents, Coal-CaCO$_3$ and Coal-Ca(OH)$_2$, are shown in Figure 6-2. As indicated by the TG results, there is no significant difference between the coal and its
Figure 6-1. Combustion TG curves of components making up the various combination fuels, with a heating rate of 10°C/min.
Figure 6-2. Combustion TG curves of original coal, IBC-109, and its mixtures with sorbents, Coal-CaCO₃ and Coal-Ca(OH)₂, with a heating rate of 10°C/min.
mixture samples. For example, the temperature for the 50% mass loss for coal IBC-109, coal-sorbent mixtures Coal-CaCO$_3$ and Coal-C(OH)$_2$ is 457°C, 457°C and 447°C, respectively.

6.1.2 Behavior of Sulfur in Coal-Sorbent Mixtures During Combustion by TG/FTIR

The comparison of combustion SO$_2$ release profiles between original coal, IBC-109, and the coal-sorbent mixtures, Coal-CaCO$_3$ and Coal-Ca(OH)$_2$, are shown in Figure 6-3. The profiles are determined by TG/FTIR on a 30 mg sample. The profiles indicate that the release behavior of sulfur (as SO$_2$) in the three samples during combustion are very similar, and that there is a large peak at 440°C, a medium broad peak around 350°C, a small broad and flat peak around 300°C and a shoulder peak around 530°C for each sample. These peaks may be attributed to the emission of SO$_2$ from aliphatic, aromatic and pyritic sulfur in coal. It should be mentioned that the corresponding peaks on the Coal-Ca(OH)$_2$ profile are lower in absorbance intensities and shift to lower temperatures, as compared with other two profiles. Still, the medium broad peak at 350°C is diminished on the Coal-Ca(OH)$_2$ profile.

The relative sulfur mass balance has been estimated for the three samples. The ratio of area under the profile curves of IBC-109, Coal-CaCO$_3$ and Coal-Ca(OH)$_2$ is 1.00:0.73:0.38, which implies that the gaseous sulfur releases from Coal-CaCO$_3$ and Coal-Ca(OH)$_2$ during combustion have decreased by approximately 58% and 68%, respectively, as compared with the raw coal (IBC-109). Thus, Ca(OH)$_2$ is a more reactive sorbent
Figure 6-3. Comparison of combustion SO$_2$ release profiles between coal IBC-109 and its mixtures with sorbents, Coal-CaCO$_3$ and Coal-Ca(OH)$_2$, as determined by TG/FTIR using an identical amount of coal mass (50 mg) as well as calcium mmole.
than CaCO₃ to reduce the gaseous sulfur release during coal combustion.

The mechanisms for the capture of SO₂ by CaCO₃ and Ca(OH)₂ are explained by the following reactions:\textsuperscript{81,82}

\[
\begin{align*}
\text{Calcination} & : & \text{CaCO}_3 & \rightarrow & \text{CaO} + \text{CO}_2 & >600^\circ\text{C} \\
\text{Dehydration} & : & \text{Ca(OH)}_2 & \rightarrow & \text{CaO} + \text{H}_2\text{O} & 350^\circ-450^\circ\text{C} \\
\text{Sulfation} & : & \text{CaO} + \text{SO}_2 & \rightarrow & \text{CaSO}_3 & 300^\circ-650^\circ\text{C} \\
\text{Sulfation} & : & 2\text{CaSO}_3 + \text{O}_2 & \rightarrow & 2\text{CaSO}_4 & <650^\circ\text{C} \\
\text{Sulfation} & : & 2\text{CaSO}_3 + \text{SO}_2 & \rightarrow & 2\text{CaSO}_4 + \text{S} & <650^\circ\text{C} \\
\text{Sulfation} & : & \text{CaSO}_3 + \text{SO}_3 & \rightarrow & \text{CaSO}_4 + \text{SO}_2 & <650^\circ\text{C} \\
\text{Sulfation} & : & 4\text{CaSO}_3 & \rightarrow & \text{CaS} + 3\text{CaSO}_4 & >650^\circ\text{C} \\
\text{Sulfation} & : & \text{CaS} + 2\text{O}_2 & \rightarrow & \text{CaSO}_4 & >650^\circ\text{C} \\
\text{Sulfation} & : & \text{CaS} + 4\text{SO}_3 & \rightarrow & \text{CaSO}_4 + 4\text{SO}_2 & >650^\circ\text{C}
\end{align*}
\]

Thus, reactions 6-1 and 6-3 to 6-9 may mainly control the SO₂ release with the capture of SO₂ by CaCO₃ during combustion, whereas reactions 6-2, and 6-3 to 6-9 probably control the SO₂ release with the capture of SO₂ by Ca(OH)₂. Obviously, Ca(OH)₂ has more chances to capture SO₂ than CaCO₃ (reaction 6-
3) because the conversion of the former to CaO occurs at lower temperature than the latter. Hence, the total amount of sulfur evolved from Coal-Ca(OH)$_2$ is much less than from Coal-CaCO$_3$, as shown in Figure 6-3.

6.1.3 Behavior of Chlorine in Coal-Sorbent Mixture During Combustion by TG/FTIR

Comparison of combustion HCl release profiles of coal IBC-109 and its mixtures, Coal-Ca(OH)$_2$ and Coal-CaCO$_3$, is shown in Figure 6-4. The profiles have been determined by TG/FTIR using an identical amount of coal mass (300 mg) as well as calcium mmole. As indicated in the HCl profiles, the behavior of chlorine in the coal-sorbent mixtures is similar to that of chlorine in the original coal. In other words, the chlorine in all the three samples is liberated as HCl between approximately 300° and 600°C, and the HCl emission reaches the peak maxima at 440°C with different absorbance intensities for the three samples.

It is estimated that the ratio of area under the profile curves of coal IBC-109, Coal-CaCO$_3$ and Coal-Ca(OH)$_2$ is approximately 1.00:0.80:0.52. This implies that the coal-sorbent mixtures, coal-CaCO$_3$ and Ca(OH)$_2$, have given off a less amount of HCl by approximately 20% and 48% during combustion, compared with the raw coal (IBC-109). Thus, Ca(OH)$_2$ is a more reactive sorbent than CaCO$_3$ to reduce the gaseous chlorine release during coal combustion.

The mechanisms for the reduction of HCl released from the coal by sorbents CaCO$_3$ and Ca(OH)$_2$ may be explained as follows:
Figure 6-4. Comparison of combustion HCl release profiles between coal IBC-109 and its sorbent mixtures, Coal-CaCO3, and Coal-Ca(OH)2, as determined by TG/FTIR using an identical amount of coal mass (300 mg) as well as calcium mmole.
Calcination

\[
\text{CaCO}_3 \xrightarrow{\text{Calcination}} \text{CaO} + \text{CO}_2 \\
> 600^\circ\text{C} (6-1)
\]

Dehydration

\[
\text{Ca(OH)}_2 \xrightarrow{\text{Dehydration}} \text{CaO} + \text{H}_2\text{O} \\
350^\circ-450^\circ\text{C} (6-2)
\]

\[
2\text{CaO} + 2\text{HCl} \rightarrow 2\text{CaCl}_2 + \text{H}_2\text{O} (6-10)
\]

reaction 6-1 or 6-2 is probably a rate-determining step, and \(\text{CaCl}_2\) does not vaporize at relatively low temperature. Thus, the \(\text{HCl}\) release from the samples is reduced with \(\text{HCl}\) captured \(\text{CaO}\), which are controlled by reactions 6-1, 6-2 and 6-10 during combustion of Coal-\(\text{CaCO}_3\) and Coal-\(\text{Ca(OH)}_2\). Obviously, \(\text{Ca(OH)}_2\) is able to decrease the \(\text{HCl}\) release more than \(\text{CaCO}_3\), because the \(\text{Ca(OH)}_2\) is able to be converted to \(\text{CaO}\) at much lower temperature than \(\text{CaCO}_3\).

In summary, \(\text{Ca(OH)}_2\) is more reactive than \(\text{CaCO}_3\) in capturing \(\text{SO}_2\) and \(\text{HCl}\). Also, \(\text{Ca(OH)}_2\) is more reactive in the capture of \(\text{SO}_2\) than that of \(\text{HCl}\). This behavior is principally attributed to the difference in the porous structures of \(\text{CaO}\), according to Gullet and Bruce.\(^{83}\) \(\text{CaO}\) obtained from \(\text{CaCO}_3\) would seem to have pores with a cylindrical structure, whereas that obtained from \(\text{Ca(OH)}_2\) appears to have pores with slit or plate-like structure; furthermore, the cylindrical pores should have a smaller radius than the plate-like pores. Hence, \(\text{CaO}\) obtained from \(\text{Ca(OH)}_2\) is more reactive and able to capture more \(\text{SO}_2\) and \(\text{HCl}\), as compared with that obtained from \(\text{CaCO}_3\).
6.3 Rapid TG/IC Analysis for Coal-Sorbent Mixture Combustion

6.3.1 Rapid-Heating Combustion TG Analysis

In the rapid TG-IC method, the sample chamber on the TG furnace is preheated to 800°C, then the mixture sample is pushed into the chamber. As the mixture sample is being pushed into the furnace, the sample is being heated at an estimated heating rate of 1600 °C/min. Meanwhile, the combustion-evolved gas mixture is collected completely in a series of the trap solutions, and the trap solutions then are further treated and analyzed by IC for the total content of chlorine and sulfur evolved during combustion.

Figure 6-5 shows the rapid TG results of coal IBC-109 and its mixtures with sorbents, Coal-CaCO₃ and Coal-Ca(OH)₂, using a 50 mg coal-mass as well as an identical amount of calcium mmole. There is no significant difference between the raw coal (IBC-109) and its mixtures [Coal-CaCO₃ and Coal-Ca(OH)₂].

6.3.2 Behavior of Chlorine and Sulfur in Coal-Sorbent Mixture during Rapid-Heating Combustion by TG/IC

Based on the determination of chloride and sulfate ions (Cl⁻ and SO₄²⁻) by IC using 50 mg of coal and an identical amount of calcium mmole, the amounts of total gaseous chlorine and sulfur evolved during rapid-heating combustion of the samples are summarized in Tables 6-1 and 6-2. As determined by IC, the ratio of the total chlorine released during combustion of IBC-109 and its sorbent mixtures, Coal-CaCO₃ and Coal-Ca(OH)₂ is 1.00:0.71:0.56, and the ratio for SO₂ is 1.00:0.60:0.32. The ratios obtained by the rapid TG/IC method
Figure 6-5. Rapid combustion TG results of original coal, IBC-109, and its sorbent mixtures, Coal-CaCO₃ and Coal-Ca(OH)₂, with a rapid-heating rate of 1600°C/min and isothermal at 800°C for 20 min (sample size: 50 mg).
Table 6-1. IC Results for Total Gaseous Sulfur Released during Rapid-Heating Combustion of Coal IBC-109 and Its Sorbent Mixtures

<table>
<thead>
<tr>
<th>Sample</th>
<th>Run</th>
<th>Rel. $S_{tot}$ (%)</th>
<th>Std.Dev.</th>
<th>% Std.Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>IBC-109</td>
<td>1</td>
<td>67.0</td>
<td>0.3</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>67.2</td>
<td>0.2</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>67.5</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>AVE</td>
<td>67.2</td>
<td>0.3</td>
<td>0.4</td>
</tr>
<tr>
<td>Coal-CaCO$_3$</td>
<td>1</td>
<td>40.7</td>
<td>0.3</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>40.3</td>
<td>0.1</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>40.1</td>
<td>0.2</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>AVE</td>
<td>40.4</td>
<td>0.2</td>
<td>0.5</td>
</tr>
<tr>
<td>Coal-Ca(OH)$_2$</td>
<td>1</td>
<td>21.3</td>
<td>0.1</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>21.2</td>
<td>0.2</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>21.5</td>
<td>0.1</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>AVE</td>
<td>21.3</td>
<td>0.1</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Table 6-2. IC Results for Total Gaseous Chlorine Released during Rapid-Heating Combustion of Coal IBC-109 and Its Sorbent Mixtures

<table>
<thead>
<tr>
<th>Sample</th>
<th>Run</th>
<th>Rel.$Cl_{tot}$ (%)</th>
<th>Std.Dev.</th>
<th>% Std.Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>IBC-109</td>
<td>1</td>
<td>97.8</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>97.3</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>97.9</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>AVE</td>
<td>97.7</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Coal-CaCO$_3$</td>
<td>1</td>
<td>69.7</td>
<td>0.3</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>69.4</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>69.1</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>AVE</td>
<td>69.4</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Coal-Ca(OH)$_2$</td>
<td>1</td>
<td>54.0</td>
<td>0.3</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>54.2</td>
<td>0.2</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>54.6</td>
<td>0.2</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>AVE</td>
<td>54.2</td>
<td>0.2</td>
<td>0.5</td>
</tr>
</tbody>
</table>

is different from that obtained by the dynamic TG/FTIR method (1.00:0.73:0.38). In other words, the effect of the TG methods (mainly regarding the heating program) on the capture of $SO_2$ and $HCl$ by different sorbents is significant. In the
case of Coal-CaCO$_3$, the capture activity for SO$_2$ and HCl increases in the rapid TG/IC method in which the furnace temperature is at 800°C before the sample is pushed into it. This temperature is higher than the decomposition temperature of CaCO$_3$ (around 650°C), and causes CaCO$_3$ to decompose rapidly to form CaO. In the case of Coal-Ca(OH)$_2$, the capture activity for SO$_2$ and HCl is not significantly different between the two methods because of the low decomposition temperature of Ca(OH)$_2$ (around 350°C).
CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

1. More than 95% of chlorine in Illinois coal is evolved mainly as HCl between 300°C and 600°C during pyrolysis and combustion, with an amount reaching the maximum at 440°C. Chlorine present in Illinois coal is bonded as chloride ions to amine-ion sites associated with the organic matter on the inner walls of micropores in the coal. Emission of gaseous sulfur species occurs mainly between 250°C and 650°C during pyrolysis and combustion of the coal. H2S is a major product during pyrolysis, SO2 is a major product in combustion and COS is observed in both cases.

2. Removal of chlorine from high-chlorine coal by the grinding-washing process will affect its reactivity. Behavior of chlorine and sulfur in leached Illinois coal during combustion is significantly different from that of the parent coal. The emission of chlorine during the leached coal combustion occurs as HCl in relatively lower temperature range 250-550°C with three peak maxima at different temperatures, compared with the parent coal. The release of gaseous sulfur species (SO2 and COS) during the leached-coal combustion takes place earlier than that during the parent-coal combustion.
3. Addition of 5% Ca\((OH)\_2\) or 6% CaCO\(_3\) to high-chlorine and low-sulfur coal will reduce the release of the gaseous chlorine and sulfur species during coal combustion. Ca\((OH)\_2\) is a more reactive sorbent than CaCO\(_3\) and captures more HCl and SO\(_2\) during coal combustion.

4. TG/FTIR/IC systems are able to provide qualitative and semi-quantitative results for gas evolution during coal pyrolysis and combustion.

7.2 Recommendations

1. To analyze the sulfur content in the pyrolysis and combustion residues of Illinois coals, leached coals and coal-sorbent mixtures to give a better understanding of the sulfur balance during pyrolysis and/or combustion.

2. To analyze distribution of the particle sizes of the leached coals to understand better the effect of the particle size on the behavior of chlorine and sulfur in the clean coals during combustion.
REFERENCES


64. Attar, A. Fuel 1978, 57, 201-212.
74. Shao, D., Pan, W.-P., Chou, C.-L. and Riley, J.T.  
