

# A STUDY OF ON-LINE ANALYSIS OF CHLORINE DURING COAL COMBUSTION

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## ABSTRACT

The behavior of chlorine during the combustion of coal was studied using TG-FTIR and TG-MS systems. Parameters of the coal samples studied included variations in chlorine content, rank, and mesh size. The identification of evolved gases at different temperatures indicated three mechanisms of HCl release. The first evolution of HCl was due to thermal effects, and corresponds to the release of HCl absorbed on pore walls of the coal. The second evolution of HCl is a function of coal rank, and represents a more tightly bound chlorine associated with the hydrated coal matrix. The third evolution of HCl is a result of inorganic chlorides in the coal.

## INTRODUCTION

The presence of chlorine in coal is a concern for end users of coal. This concern, if the chlorine in coals causes corrosion, has tremendous impact on the marketability of the coal. The extent of boiler corrosion due to chlorine may not be directly related to the amount of chlorine in the coal. However, it may be related to how the chlorine occurs in the coal or to other factors. During the combustion of coals of various types, the mechanisms of the release of chlorine species are influenced by many factors, such as the forms of chlorine in the coal, coal rank, and experimental conditions.

The main forms of chlorine present in coal that have been proposed are:<sup>1</sup>

- inorganic chlorides
- chlorine ions in brine and other water associated with the coal.

Edgecomb<sup>2</sup> examined the release of chlorine as HCl in the heating of twenty-nine British coals (0.2-1.0% Cl) in dry air at 200°C for twenty-four hours. His studies showed that more than half of the chlorine is liberated as HCl at this temperature. However, Daybell suggested that chlorine in some British coals give off 97% of their chlorine as HCl in oxygen-free nitrogen at 258°C.<sup>3</sup> Gibb observed that most of the chlorine in British coals evolved under mild conditions.<sup>4</sup> Several Illinois coals were studied by Hackley and Chou using a high temperature furnace-quadrupole gas analyzer (HF-QGA) technique. They determined that the evolution of HCl from their coals began around 250°C, peaked at 495°C, and leveled off close to 600°C.<sup>5</sup> Muchmore and coworkers investigated chlorine removal from an Illinois high-chlorine coal with thermal treatment followed by analysis using an electrode technique. It was concluded that 84.3% of the total chlorine in the coal was removed by preheating in nitrogen at a lower temperature prior to a six minute reaction at 385°C.<sup>6</sup>

These studies, reporting different coals having different chlorine release temperatures under different conditions, may provide some insight into the question concerning boiler corrosion and chlorine content. In the work reported in this paper the behavior of chlorine during combustion is investigated using relatively new techniques. The effect of chlorine content as well as rank and mesh size of coal on the evolution of chlorine species was investigated.

## EXPERIMENTAL

This study used ten coal samples ranging in chlorine content (0.03-0.88%), mesh sizes (400, 200, and 60 mesh), and chemical composition as listed in Table 1. Combustion of the samples took place in an air atmosphere under either of two heating methods. The dynamic heating method, a steady increase in temperature with time, enables a view of the complete combustion process. The second, an isothermal heating method, allowed for the isolation and separation of HCl emission mechanisms. The isothermal method consists of steadily heating the sample to a certain temperature, holding at the temperature for a designated amount of time, followed by a continuation of the temperature increase.

Analyses of the combustion process and evolved gases were obtained utilizing TG-FTIR and TG-MS systems. The thermogravimetric (TG) studies gave combustion profiles in terms of weight loss and rate of weight loss and were done with either a DuPont 951 or a TA Hi-Res TGA 2950 thermogravimetric analyzer. By coupling the instruments with a VG Thermolab Quadrupole Mass Spectrometer (MS) one can identify and quantify evolved gases by their molecular weights. Interfacing a TG with a Perkin

Elmer 1650 Fourier Transform Infrared Spectrometer (FTIR) allows one to confirm the identified gases and distinguish between gases of the same molecular weights.

## RESULTS AND DISCUSSION

Figure 1 is a typical thermogram showing the analysis of the combustion of a coal sample using the dynamic heating method. One can follow the transitions through the combustion process by noticing changes in both the TG curve showing weight loss and the DTG curve showing rate of weight loss. Points of interest on the DTG curve are the changes in weight loss rate at 300°C, 400°C, and 447°C. The region containing these points in order show: (1) a devolatilization zone, (2) an overlapping weight loss due to the initial combustion of the fixed carbon at the 400°C inflection point, and (3) a weight loss, due to combustion, with a maximum at 447°C (DTG peak maximum).

Mass spectroscopic profiles given in Figure 2 show the evolution of SO<sub>2</sub> (64), H<sub>2</sub>O (18), CO<sub>2</sub> (44), HCl (36), and either acetic acid (60) or COS (60) during dynamic heating. The peak maximum for rate of weight loss in the TG curve corresponds to the peak maxima of CO<sub>2</sub> and SO<sub>2</sub> emissions at 447°C. The m/z = 60 peak follows the HCl and water curves by 10°C. FTIR on-line analysis shows the first peak in the m/z = 60 curve to be due to the evolution of acetic acid while the second peak is due to COS.

The emission of HCl and H<sub>2</sub>O begins at 200°C, peaks at 300°C, and subsides. Their second peaks appear at 400°C with a maximum at 440°C before leveling off around 500°C. This indicates two mechanisms of chlorine release involving water. Expansion of the HCl curve shows a small third peak occurring at 700-800°C.

Employment of the isothermal heating method revealed HCl and water emissions as the temperature approached 300°C, as illustrated in Figure 3. At that point (30 min, 300°C) the temperature was held constant for one hour with no emissions occurring. Continuation of the temperature increase produced the second emission of HCl and water confirming two separate mechanisms, thus illustrating two different structures of chlorine bonding in the coal.

The first HCl peak is due to thermal effects and consistently peaks around 300°C for all coals. Due to the greater amount of energy needed to break the bonds, the second peak represents a more tightly bound chlorine released during the oxidation of the coal. The second peak is a function of coal rank due to its direct relationship with coal DTG maxima as is illustrated in Figure 4. DTG analyses of the coals indicate higher ranking coals having higher maximum rates of combustion. The higher temperature DTG peaks and higher ranking coals correspond to higher temperature maxima for the second HCl emissions.

A quantitative study of the evolution of HCl and SO<sub>2</sub> versus the content of the chlorine and sulfur in the coal was obtained by integrating the area under the HCl peaks in the mass spectra. A good agreement ( $R^2 = 0.997$  for chloride and  $R^2 = 0.942$  for sulfur) was obtained between the chlorine content and the total amount of HCl evolved, as is illustrated in Figure 5. This figure also provides evidence that most of chlorine in coal is released in the form of HCl during combustion. The slightly lower coefficient obtained for the sulfur is due to the limitation of TG systems. The TG system can only be heated to 1000°C. According to ASTM Method D 4239, the coal should be heated to 1400°C to identify the sulfate species. Thus, the temperature difference may cause the slightly lower correlation coefficient.

Mesh size also played a role in determining the temperature of HCl evolution. The smaller mesh coal produced emissions at a lower temperature. Smaller particle size, such as 400 mesh, has a higher surface-to-volume ratio allowing less hindrance to the devolatilization of the chlorine attached to the coal pores and surface.

## CONCLUSIONS

Thermal analytical techniques reveal there are three HCl evolution peaks, indicating three different types of chlorine bonding to the coal. The first HCl evolution peak, due to thermal effects, is the release of HCl normally absorbed on pore walls. The second peak, a function of the coal rank, represents a more tightly bound chlorine associated with the hydrated coal matrix. A third peak is a result of inorganic chlorides in the coal.

Thermal analytical and mass spectral data indicate a good correlation between chlorine content in the coal and the total amount of HCl evolved. Results also show the smaller particle sizes of the coal cause HCl evolution to occur at a lower temperature.

## ACKNOWLEDGEMENTS

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## REFERENCES

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Table 1. Ultimate Analysis Data (Dry Basis) for Coals Studied

Coal	Cl	C	H	O	N	S	Ash
A	0.88	79.75	5.37	8.20	1.55	0.94	3.23
B	0.39	63.95	4.21	6.31	1.29	1.31	22.24
C	0.38	70.34	4.25	6.55	1.54	1.02	16.10
D	0.26	75.40	4.92	6.70	1.50	2.94	8.17
E	0.16	72.29	4.99	7.13	1.27	4.47	9.71
F	0.20	86.71	4.23	2.17	1.27	0.66	4.77
G	0.13	66.20	4.21	7.10	1.25	0.71	19.84
H	0.04	65.85	4.36	18.19	1.25	0.80	9.72
I	0.03	68.43	4.88	16.24	1.02	0.63	8.77
J	0.03	76.89	5.49	10.76	1.50	0.62	4.71

Sample: COAL 33501 P-8#10-5  
 Size: 20.4480 g  
 Method: COAL  
 Comment: IT-100C HT-15V MV-1638 MSFILE=ICCI607 70EV HT TEST

# TGA

File: C:ICCI607  
 Operator: PAN 10C/MIN TO 890  
 Run Date: 28-Mar-95 02:55

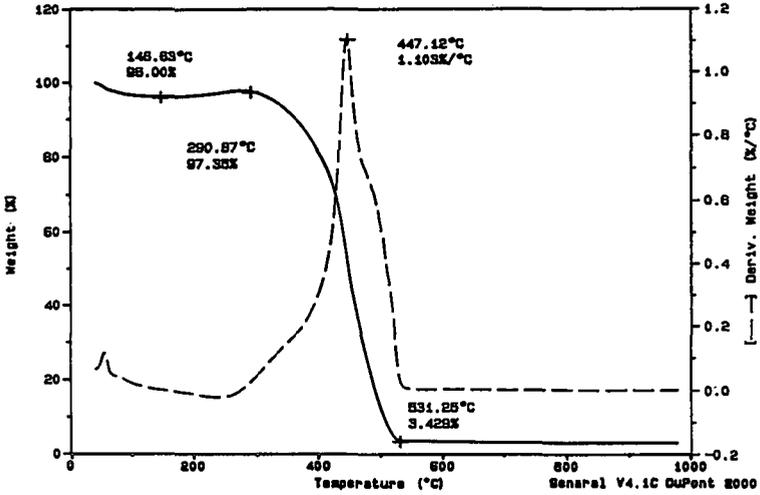


Figure 1. TG curve for the combustion of coal A in air.

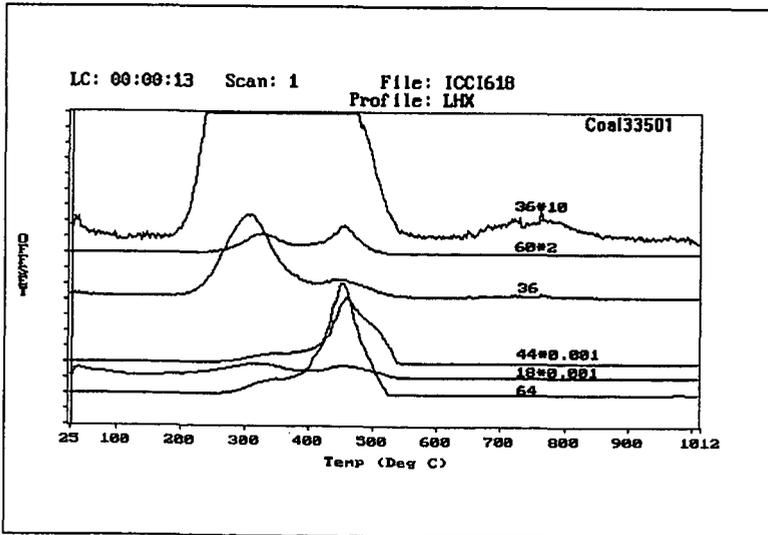


Figure 2. Mass spectrometric evolved gas profiles for the combustion of coal A.

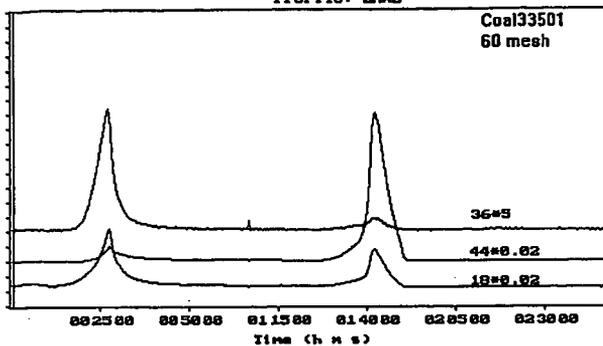


Figure 3. Mass spectrometric evolved gas profiles for combustion of coal A under isothermal conditions.

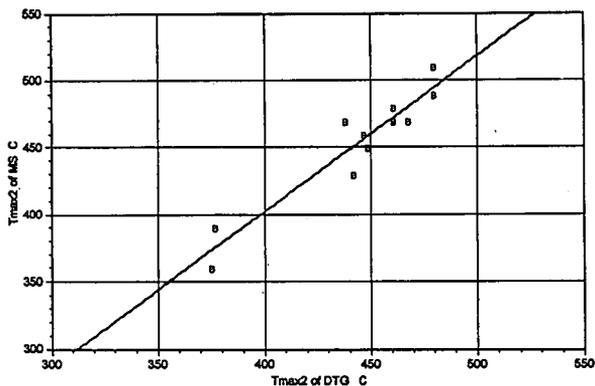


Figure 4.  $T_{max2}$  values from DTG curves versus  $T_{max2}$  values from mass spectra.

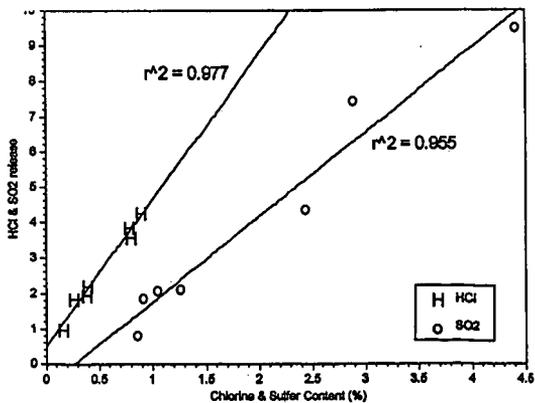


Figure 5. HCl and SO<sub>2</sub> release versus chlorine and sulfur content in coals.