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DOE/PC/92521--T168

TECHNICAL REPORT
March 1, 1994 through May 31, 1994

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

DOE Grant Number:	DE-FC22-92PC92521 (Year 2)
ICCI Project Number:	93-1/6.1B-1P
Principal Investigator:	M.-I.M. Chou, (217) 244-0312, Illinois State Geological Survey (ISGS), 615 E. Peabody Drive, Champaign, IL 61820
Other Investigators:	J.M. Lytle, R.R. Ruch, and C.-L. Chou, (ISGS); J.L. Margrave, C.J. Chu, and B.H. Hauge, Rice University (RU); G.P. Huffman and F.E. Huggins, University of Kentucky (UK); W.P. Pan and L. Liu, Western Kentucky University (WKU).
Project Manager:	Ken K. Ho, ICCI

ABSTRACT

Limited literature and use history data have suggested that some high-chlorine Illinois coals do not cause boiler corrosion while extensive data developed by the British correlate corrosion with chlorine content and other parameters related to the coal and boiler. The differences in corrosivity in coals may be due to the coal properties, to blending of coals, or to the boiler parameters in which they were burned. The goals of this study focus on coal properties.

In this quarter, both destructive temperature-programmed Thermogravimetry with Fourier transform infrared (TGA-FTIR) and non-destructive X-ray absorption near-edge structure (XANES) techniques were used to examine the forms and the evolution characteristics of chlorine in coals. The TGA-FTIR results indicate that under oxidation condition, both British and Illinois coals release hydrogen chloride gas. Illinois coals release the gas at high temperature with maximum evolution temperature ranged between 410 and 450°C, whereas, British coals release chlorine at low temperature with maximum evolution temperature ranged between 210 and 280°C. The XANES results indicate that chlorine in coal exists in ionic forms including a solid salt form. The solid NaCl salt form, however, is observed only in some of the British coals and none of the Illinois coals. These results combined with TGA-FTIR results suggest that the chlorine ions in Illinois coals are different from the chlorine ions in British coals.

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U.S. DOE Patent Clearance is not required prior to the publication of this document.

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EXECUTIVE SUMMARY

The question of whether or not chlorine in Illinois coals really causes corrosion has had an impact on the marketability of the coal. Literature and use history have suggested that some high-chlorine Illinois coals do not cause boiler corrosion. On the other hand, extensive data developed by the British correlate corrosion with chlorine content and other parameters of coals and the type of boiler. Although methods such as blending coals of low and high chlorine content have been used in Britain to control corrosion, the presence of chlorine in Illinois coals, because of this extensive data and other literature, has been a concern for the end users and boiler manufacturers. Providing concrete scientific evidence to explain the variations in corrosivity of these high-chlorine coals, should it support the premise that high chlorine Illinois coals do not cause corrosion, will help relieve market concerns and increase the usage of these coals. The differences in the corrosivity of coals may be due to the coal's properties, to the coal blends, or to the parameters of boilers in which they are burned. This study focuses on the effect of coal properties on corrosivity. The goals of this project are (1) to determine the forms of chlorine and other chemical components (mineral, major, minor, and trace elements) in coals which have been reported to behave differently with respect to corrosion problems during combustion; (2) to determine the evolution profiles of chlorine-containing compounds in coals during pyrolysis (the first stage of combustion and gasification) and oxidation; and (3) to examine the behavior of Cl-, S-, N-, O-containing compounds in coal during pyrolysis at the times and temperatures commonly used in gasification. Analysis will focus on Cl-containing compounds. This is a cooperative effort among the ISGS; RU, Houston, TX; UK, Lexington, KY; and WKU, Bowling Green, KY.

Specific objectives are

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

B. To examine chemical composition of coals and to predict coal corrosion potential contributed from ash composition in coals.

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

D. To conduct thermogravimetry with Fourier transform infrared (TGA-FTIR) analyses and to examine the evolution characteristics of chlorine-containing compounds in coals under pyrolysis and oxidation conditions.

E. To carry out flash pyrolysis with multi-surface matrix isolation-Fourier transform infrared (MI-FTIR) analyses and to examine the behavior of heteroatoms (S, O, N, and Cl compounds) that are present in coal during pyrolysis at the times and temperatures commonly used in gasification.

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

In this quarter, both destructive temperature-programmed Thermogravimetry with Fourier transform infrared (TGA-FTIR) and non-destructive X-ray absorption near-edge structure (XANES) techniques were used to examine the forms and the evolution profiles of chlorine-containing compounds in coals. The HCl evolution profiles obtained from oxidation of the four British coal samples were examined. The results indicate that British coals release chlorine gas at lower temperature than Illinois coals. British coals release HCl gas at temperatures from 150 to 450°C with the maximum HCl evolution temperature ranged between 210°C and 280°C. As reported previously, Illinois coals release HCl gas at temperatures from 150 to 600°C with the maximum HCl evolution temperature ranged between 410°C and 450°C.

Coal analysis by the XANES technique indicates that chlorine in coal exists in ionic forms including a solid sodium chloride salt form. The solid NaCl salt form, however, is observed only in some of the British coals and none of the Illinois coals. Comparison of the TGA-FTIR results between the two coal types, along with forms of chlorine in coal by XANES analysis indicates that chlorine ions in the British coal are different from chlorine ions in the Illinois coals.

Overall the results indicate that chlorine in Illinois coal is different from chlorine in British coal. This difference may be due to the difference in the nature of chlorine in coals or the difference in pore size distribution of the coals, which needs further investigation.

Data on the acid-soluble sodium and potassium in coals are currently being obtained, and will be reported in the next quarter. These data, along with ash composition data, will be used to assess a coal's relative corrosion potential.

GOALS AND OBJECTIVES

The goals of this study are (1) to determine the forms of chlorine and other chemical components (mineral, major, minor, and trace elements) in coals which have been reported to behave differently with respect to corrosion problems during combustion; (2) to determine the evolution profiles of chlorine-containing compounds in coals during pyrolysis and oxidation conditions; and (3) to examine the behavior of Cl-, S-, N-, O-containing compounds in coal during pyrolysis at the times and temperatures commonly used in gasification. Analysis will focus on Cl-containing compounds.

Specific objectives are

A. To determine the types of chlorine and sulfur containing compounds in coals by XANES and the total chlorine, total sulfur, and inorganic forms of sulfur by the ASTM methods.

B. To examine chemical composition of coals and to predict coal corrosion potential contributed from ash composition in coals.

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

D. To conduct thermogravimetry with Fourier transform infrared (TGA-FTIR) analyses and to examine the evolution characteristics of chlorine-containing compounds in coals under pyrolysis and oxidation conditions.

E. To carry out flash pyrolysis with multi-surface matrix isolation-Fourier transform infrared (MI-FTIR) analyses and to examine the behavior of heteroatoms (S, O, N, and Cl compounds) that are present in coal during pyrolysis at the times and temperatures commonly used in gasification.

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

INTRODUCTION AND BACKGROUND

Limited literature and use history data have suggested that high-chlorine Illinois coal does not cause boiler corrosion

(Hamling and Haegi, 1984), while extensive data have been developed by the British which attribute the rate of corrosion to the chlorine content as well as other parameters of coal, such as alkaline content, and coal boiler materials (Latham et al, 1991, Oakey et al, 1991, and Bakker et al, 1990). Although methods such as blending coals of low and high chlorine content have been used in Great Britain to control corrosion, the presence of chlorine in Illinois coals has been a concern for end users and boiler manufacturers. Providing concrete scientific evidence to explain the variations in corrosivity of the high-chlorine coals, should it support the premise that high chlorine Illinois coals do not cause corrosion, will help relieve market concerns and increase the use of these coals.

A study of the materials for future fossil fuel fired steam generators was conducted by Bakker et al (1990). They indicated that superheater corrosion, in general, can be attributed to five factors. These factors are (1) the amount of liquid sulfate deposited, (2) the sulfur content of the coal, (3) the chlorine content of the coal, (4) the temperature of the superheater tube wall, and (5) the chemical composition of the alloy. They also indicated that superheater corrosion was most common in the U.K. where it was attributed to the high level of chlorine in the British coals. The total chlorine content in coal has been used in Great Britain for predicting the corrosivity of a coal. It has been indicated, however, that high-chlorine Illinois coals do not create the serious corrosion problems which the British coals have shown during combustion. Since these two studies involve two different coals and two different boilers, it is not clear whether the differences in observed corrosion were due to the properties of coal, or to the boiler parameters. For example, the chemical forms of chlorine, their behavior during combustion, and their interaction with sulfur and other components of coal may play a role in the corrosivity of a coal with high chlorine content. Also, temperatures of the tubes and tube wall materials, or blending coals combined with the properties of the coal may affect boiler corrosion.
This study focuses on the fundamental effects of chlorine, sulfur, and other elements in these two coals, and perhaps other coals with different corrosion potentials. A complete chemical characterization of these two coals is a necessary first step. The results of this study may also provide information useful in the investigation of boiler parameters, relating their effects and those attributable to the properties of the coal with tube corrosion.

The structure of chlorine in coals with varying corrosion potentials may be different. If this variation is confirmed, the extension of the results of this study will be to determine if or how the absence or the appearance of one form

of chlorine compound in a coal contributes to the corrosive or non-corrosive nature of the coal. If the results indicate no differences among the forms of chlorine in coals of different corrosion potentials, but, instead, indicate a variation of the chlorine evolution profiles of the coals, the logical extension of these results will be to examine if, or how, the interaction of chlorine with other species in the coal is taking place.

EXPERIMENTAL

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

This task was completed in the first quarter. The ISGS has acquired and prepared all the coal samples.

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

In this quarter, ASTM analyses for total chlorine, total sulfur, and inorganic forms of sulfur were completed on all coal samples. The forms of chlorine by XANES analysis was completed.

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

Nine coal samples were subjected to high-temperature (1000°C) ashing. The ashed samples were then analyzed by x-ray fluorescence spectroscopy for ash composition in the forms of major oxides. A split of these coal samples was also subjected to HCl acid treatment for atomic absorption spectroscopic analysis of acid-soluble sodium and potassium in coals . The amounts and the distribution of these elements in both the British coals and the Illinois coals will be examined and reported in the next quarter.

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

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

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

During this quarter, temperature programmed thermogravimetry in conjunction with Fourier transform infrared (TGA-FTIR) was used to obtain thermal evolution characteristics of HCl gas from coals under oxidation and pyrolysis conditions. Simultaneous TGA/FTIR techniques based on a combined analytical method in which thermogravimetry (TGA) in conjunction with Fourier Transform Infrared Spectroscopy (FTIR) were used. By using the combined TGA/FTIR instrumental system, the volatile species produced on a Dupont-951 TGA during pyrolysis or combustion of a coal sample were then analyzed by the Perkin Elmer-1650 FTIR spectrometer. The system continuously measured the mass change of the coal sample with the temperature increase at a heating rate of 10°C/min (by TGA) and identified qualitatively and determined quantitatively the individual gaseous species emitted during coal pyrolysis or combustion. The sample chamber in the TGA furnace was connected to the 100x24 mm gas cell in the FTIR spectrometer through a 1-ram teflon tube. Both the teflon line and gas cell were heated by heating coils up to 250°C, and the gas cell was controlled continuously by temperature controllers. The time lag between the sample chamber and the gas cell was one minute with the oxygen-free nitrogen flow at a rate of 50 ml/min during pyrolysis or with an air flow at a rate of 50 ml/min. The FTIR spectrum was taken automatically every minute by using the LabScan software. The data collection was started from 150°C to 600°C for oxidation and from 200°C to 500°C for pyrolysis. A sample size of 300 mg was used for all the experiments. The evolution profiles of HCl under oxidation and pyrolysis condition were examined with respect to their evolution temperatures. Data examination for Illinois and British coal samples was completed and the results were reported.

Task 6. Examine the behavior of heteroatoms (S, O, N, and Cl compounds) that are present in coal during flash pyrolysis at the times and temperatures commonly used in gasification (ISGS/RU).

The equipment for continuous-feed flash-pyrolysis with multi-surface matrix isolation-Fourier transform infrared (MI-FTIR) analysis is not fully functioning. No data were generated in this reporting period.

RESULTS AND DISCUSSION

CHEMICAL ANALYSES

During this quarter, chemical analyses on both Illinois and British coal samples were completed. The proximate, ultimate, and other standard coal analyses data of the British and Illinois coals are shown in Tables 1 and 2. In addition, data on HCl acid soluable sodium and potassium content in coals are currently obtained, and will be reported in the next year. These data will be examined in evaluation of a coal's corrosive potential.

Table 1. Proximate and BTU analyses of coal samples.

Sample ID	Mois (%)	Vol (%)	FxC (%)	Ash (%)	BTU
British Coal					
C-33499	4.55	32.61	52.61	14.79	12466
C-33500	4.16	29.10	48.66	22.24	11319
C-33501	8.84	38.10	58.68	3.23	13893
C-33502	3.21	35.54	61.33	3.13	14383
Illinois Coal					
C-33068	3.52	35.17	59.37	5.46	13603
C-33873	14.97	40.19	50.23	9.58	12653
C-33874	7.86	38.50	50.75	10.74	12685
C-33875	9.31	31.89	52.27	15.83	12120
C-33876	6.16	36.06	55.98	7.96	13238

Table 2. Ultimate and total chlorine analyses of coal samples

Sample ID	H (%)	C (%)	N (%)	O (%)	TotS (%)	TCl (%)
British Coal						
C-33499	4.64	70.07	1.51	6.96	2.04	0.95
C-33500	4.15	64.56	1.43	6.36	1.26	0.61
C-33501	4.90	79.57	1.62	9.81	0.86	1.54
C-33502	5.09	82.36	1.75	6.76	0.91	1.15
Illinois Coal						
C-33068	4.97	77.70	1.71	9.20	0.97	0.54
C-33873	4.96	70.16	1.26	9.63	4.42	0.22
C-33874	4.83	71.37	1.24	8.17	3.66	0.12
C-33875	4.59	68.60	1.38	8.60	1.00	0.44
C-33876	5.01	74.49	1.47	8.12	2.90	0.45

TEMPERATURE-PROGRAMMED THERMOGRAVIMETRY WITH FOURIER TRANSFORM INFRARED (TGA-FTIR)

The HCl evolution profiles for four British coals determined by TGA-FTIR are presented in Figure 1. The results indicate that British coals release HCl gas beginning at 150°C and ending approximately at 450°C. The maximum HCl evolutuion temperature occurs in a range from 210°C to 280°C.

The HCl evolution profiles of five Illinois coals during combustion are shown in Figure 2. The results indicate that Illinois coals release HCl gas beginning at 150°C and ending approximately at 600°C. The maximum HCl evolution temperature occurs in a range from 410 to 450°C.

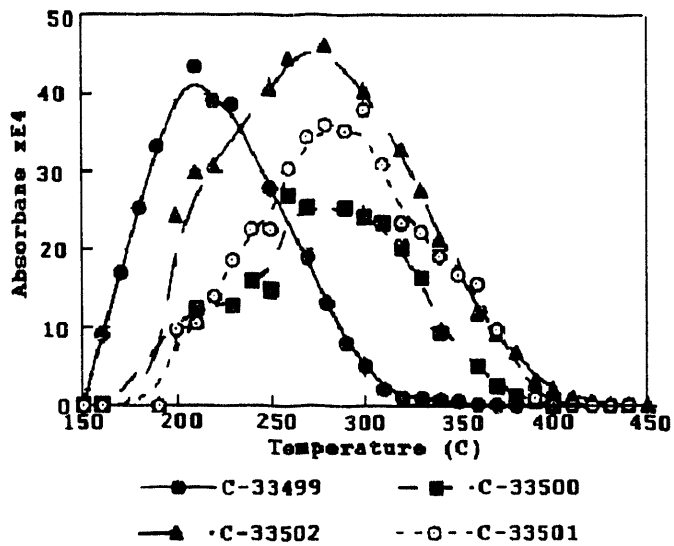

Figure 1: The HCl evolution profiles for British Coal during combustion.

A comparison of the HCl evolution profiles during combustion of Illinois coals and British coals indicates that British coals release gas at lower temperature than Illinois coals. These data indicate that chlorine in Illinois coals is different from chlorine in British coals. This difference may be due to the differences in chemical nature of chlorine in coals or due to the differences in pore size distribution of the coals, which needs further investigation.

THERMOGRAVIMETRY ANALYSIS (TGA)

When TGA was used to determine the mass changes of coal sample during temperature programmed oxidation, both British and Illinois coals show a similarity of three-stage mass

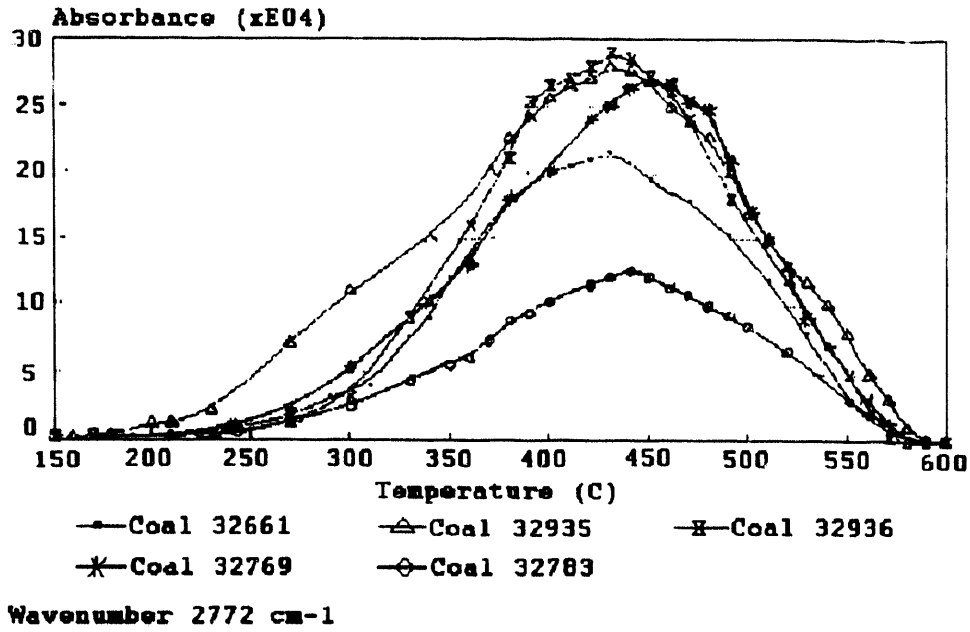

Figure 2: The HCl evolution profiles for Illinois coals under oxidation condition determined by TGA-FTIR.

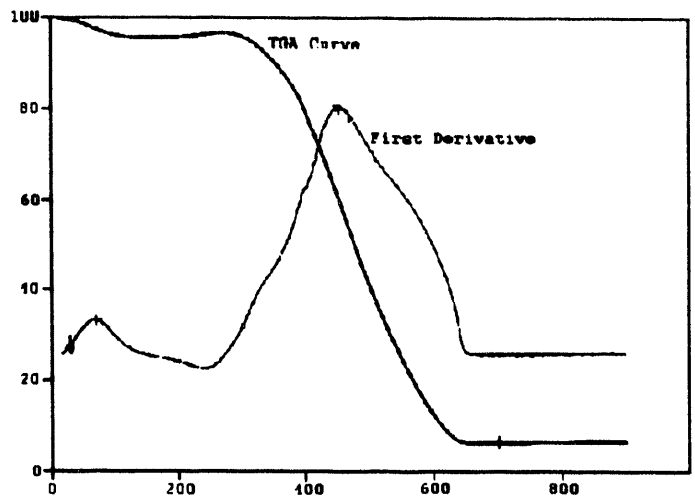

Figure 3: The TGA curve and its first derivative for a typical coal.

variation. At the initial stage of heating, as shown in Figure 1, from ambient to 150°C, the sample weight is slightly reduced. This is attributed to the loss of moisture. Further

heating from 150 to 300°C, the sample weight is slightly increased (1.5 - 2.2 %). This weight gain of the sample may attribute to oxygen being absorbed in coal during mild oxidation of coal. The sample weight is substantially reduced (80 to 95%) by further heating from 300 to 600°C. At this stage, an extensive degradation and combustion of the coal sample have taken place.

When heated under air, both Illinois coals and British coals exhibit similar burning characteristics. They all are burned with maximum mass loss at temperatures around 410°C. When a comparison is made between these mass loss profiles and those previously described chlorine evolution profiles is made, an interesting phenomenon is observed. For the Illinois coals the maximum chlorine evolution occur concurrently with the maximum mass loss, whereas, for British coals the maximum chlorine evolution occurs earlier than the maximum mass loss. This observation may have important implication with respect to the differences in chlorine association in these two types of coals.

X-RAY ABSORPTION NEAR-EDGE STRUCTURE (XANES)

The XANES spectra of the Illinois coals and the British coals analyzed are shown in Figure 2. The minor peak at about 12.5 eV for C-33499 and C-33500 arise because of crystalline NaCl which is absent in the other coals analyzed. The spectra of the Illinois coals are noisier than those for British coals because of the lower concentration of chlorine in Illinois coals.

The XANES results indicate that chlorine in coal exists in ionic forms including a solid sodium chloride salt form. However, the solid sodium chloride salt form is observed in only two of the British coals and none of the Illinois coals.

The XANES result combined with TGA-FTIR results indicate that chlorine ions in the British coals are different from chlorine ions in the Illinois coals. This difference may be due to the differences in chemical nature of chlorine ions in coals or due to the differences in pore size distribution of the coals, which needs further investigation.

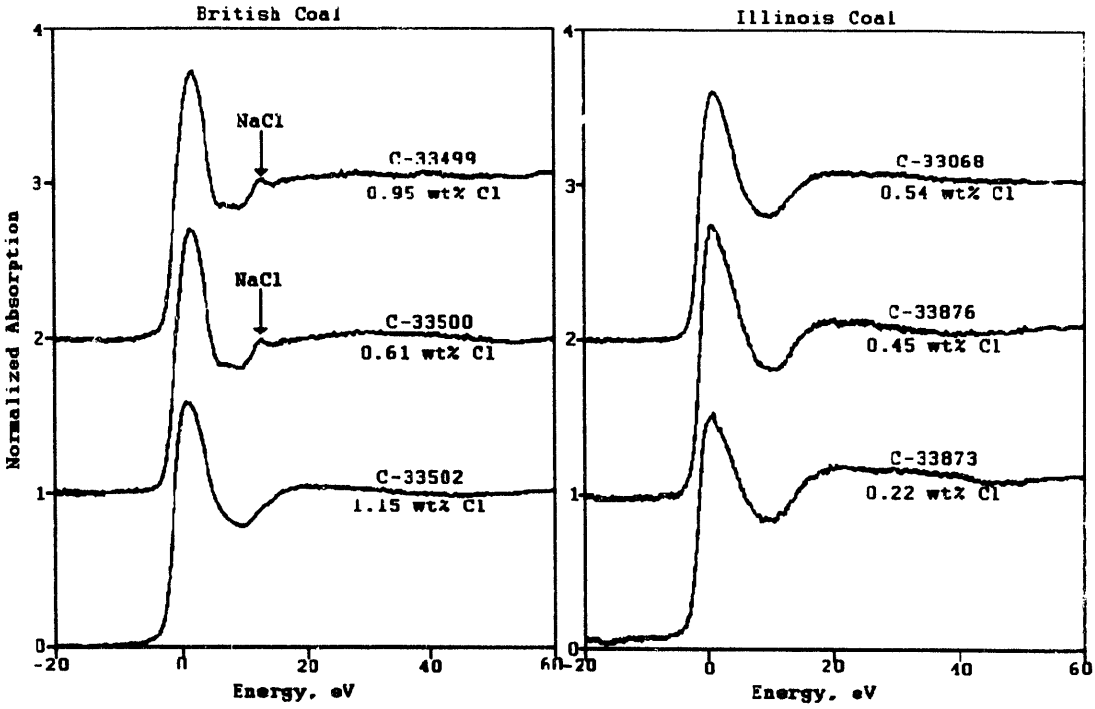

Figure 4: XANES spectra of three British coals and three Illinois coals

SUMMARY AND CONCLUSION

Both Illinois and British coals release hydrogen chlorine gas during combustion. Illinois coals release the gas at temperatures ranging from 150-600°C with the maximum evolution at 410-450°C. On the other hand, British coals release the gas from 150-450°C with the maximum evolution at 210-280°C.

When heated under air, both Illinois coals and British coals exhibit similar burning profiles with a maximum mass loss at around 410°C. This observation may have its important implication with respect to the differences in chlorine association in coals. For the Illinois coal the maximum chlorine evolution occur concurrently with the maximum mass loss, whereas, for British coal the maximum chlorine evolution occurs earlier than the maximum mass loss.

XANES data indicate that chlorine exist in coal in its ionic form. However solid sodium chloride is only observed in some British coals and none of the Illinois coals.

Overall the results indicate that chlorine in Illinois coal is different from chlorine in British coal. This difference may be due to the difference in the chemical association of

chlorine in coals or due to the difference in pore size distribution of the coals, which needs further investigation.

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PROJECT MANAGEMENT REPORT
March 1, 1994 through May 31, 1994

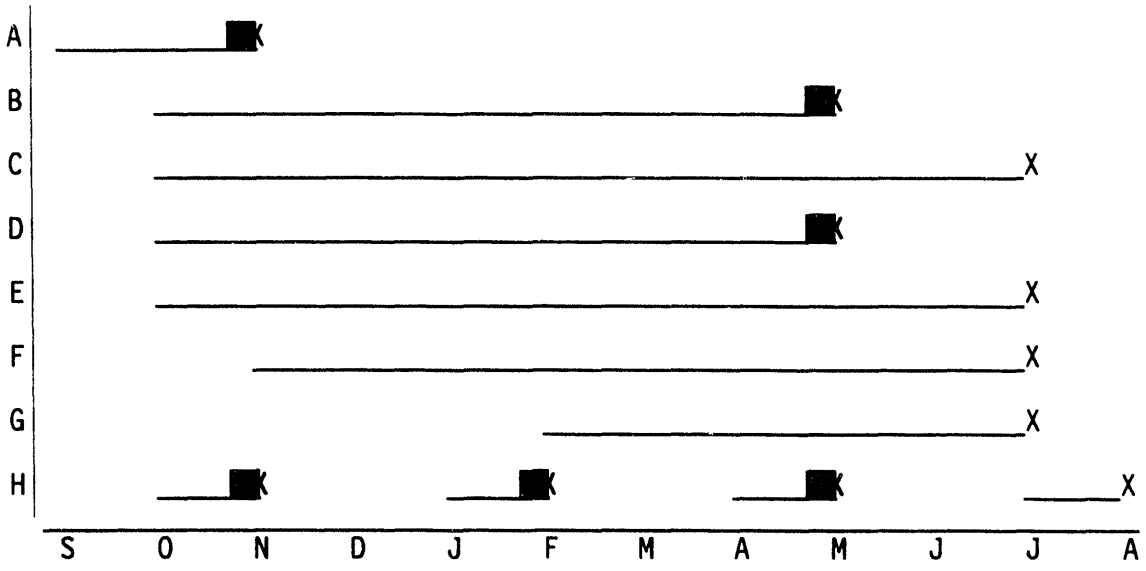
Project Title: CHLORINE IN COAL AND ITS RELATIONSHIP WITH BOILER CORROSION

DOE Grant Number:	DE-FC22-92PC92521 (Year 2)
ICCI Project Number:	93-1/6.1B-1P
Principal Investigator:	M.-I.M. Chou, (217) 244-0312, Illinois State Geological Survey (ISGS), 615 E. Peabody Drive, Champaign, IL 61820
Other Investigators:	J.M. Lytle, R.R. Ruch, and C.-L. Chou, (ISGS); J.L. Margrave, C.J. Chu, and B.H. Hauge, Rice University (RU); G.P. Huffman and F.E. Huggins, University of Kentucky (UK); W.P. Pan and L. Liu, Western Kentucky University (WKU).
Project Manager:	Ken K. Ho, Illinois Clean Coal Institute

COMMENTS

Analyses services from Rice University laboratories have not yet been paid. Payments for these works are made on a cost reimbursement basis after the works are completed.

SCHEDULE OF PROJECT MILESTONES



Milestones:

A. Coal sample preparation (Task 1)
B. XANES and ASTM analyses of coal samples (Task 2)
C. A complete chemical analysis of coal samples (Task 3)
D. XANES data interpretation (Task 4)
E. Characterization of the evolution profiles of Cl-containing compounds in coal (Task 5)
F. Flash pyrolysis analysis (Task 6)
G. Data interpretation (Task 7)
H. Technical project management reports prepared and submitted

EXPENDITURES - EXHIBIT B

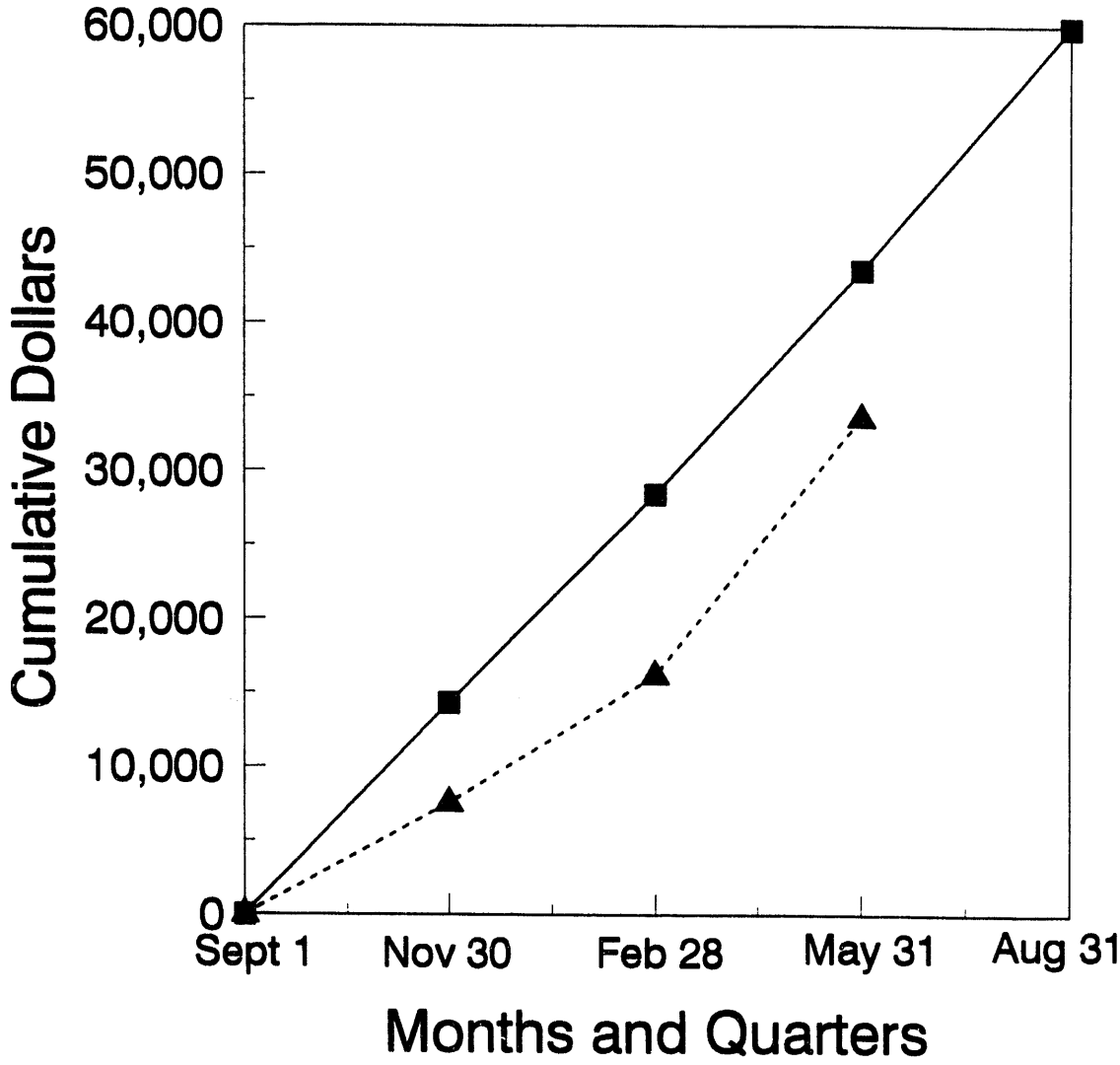
Cumulative Projected and Estimated Expenditures by Quarter

Quarter*	Types of Cost	Direct Labor	Fringe Benefits	Materials and Supplies	Travel	Major Equipment	Other Direct Costs	Indirect Costs	Total
Sep. 1, 1993 to Nov. 30, 1993	Projected	5,978	1,142	500	0	0	5,383	1,316	14,319
	Estimated	4,854	515	542	436	0	783	425	7,555
Sep. 1, 1993 to Feb. 28, 1994	Projected	11,955	2,282	800	0	0	10,766	2,632	28,435
	Estimated	9,707	1,029	1,040	436	0	2,500	1,485	16,197
Sep. 1, 1993 to May 31, 1994	Projected	17,933	3,422	1,200	1,000	0	16,049	3,948	43,552
	Estimated	15,000	2,866	1,043	1,021	0	10,000	3,701	33,631
Sep. 1, 1993 to Aug. 31, 1994	Projected	25,110	4,686	1,500	1,000	0	22,150	5,445	59,891
	Estimated								

*Cumulative by Quarter

COST BY QUARTER - EXHIBIT C

CHLORINE IN COAL AND ITS RELATIONSHIP WITH BOILER CORROSION



Projected Expenditures Actual Expenditures

Total ICCI Award $ 59,891

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