TECHNICAL REPORT

December 1, 1991 through February 29, 1992

Project Title: Behavior of Sulfur and Chlorine in Coal during Combustion and Boiler Corrosion

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Project Monitor: Ken K. Ho, CRSC

ABSTRACT

The goal of this project is to study the evolution of gaseous sulfur and chlorine species during temperature-controlled pyrolysis and combustion and their effect on boiler corrosion. We have been developing two techniques for determining the gas evolution profiles of sulfur and chlorine during coal pyrolysis and combustion. First, using a pyrolysis-combustion system in combination with a quadrupole gas analyzer, the evolution of sulfur dioxide (SO_2) in combustion gas during temperature-programmed coal pyrolysis-combustion was monitored. When the atmosphere of the combustion chamber was changed to a reducing condition, gaseous COS and H_2S were also detected in the combustion gas. Detection of hydrogen chloride by QGA has been improved by using a larger-diameter ($75\text{ }\mu\text{m}$) capillary tubing. The HCl evolution profile during the pyrolysis of coal IBC-109 was determined by QGA and by a chloride ion selective electrode for quantitative purposes. Second, the technique of thermogravimetry (TG) in conjunction with Fourier transform infrared (FTIR) spectroscopy was used to characterize gaseous species during coal pyrolysis. Gas evolution profiles of sulfur (SO_2 and COS), chlorine (HCl), and nitrogen (NH_3 and HCN) species were determined for coal IBC-109. Similar release profiles of HCl and NH_3 supported an interpretation that chlorine and nitrogen are closely associated in coal. COS may be formed by reaction of CO with H_2S in the gas phase. A mass balance study of chlorine evolution from coal IBC-109 in a TG-FTIR experiment was completed; the chloride dissolved in solutions was determined by an ion chromatographic technique.

MASTER

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EXECUTIVE SUMMARY

Behavior of gaseous sulfur and chlorine species during coal pyrolysis and combustion is related to their retention in boiler deposits and the mechanism of boiler corrosion. Research in this area was hampered previously by the lack of techniques for identification of gaseous sulfur and chlorine species and precise determination of gas evolution profiles. In this project, two techniques are being developed to attack this problem. First, a quadrupole gas analyzer (QGA), which identifies gaseous species based on their molecular masses, was used to monitor gases evolution from coal in a pyrolysis-combustion system. In this system, coal was pyrolyzed under a nitrogen atmosphere and the evolved gas was carried over to an adjoining combustion chamber maintained at 850°C under a flow of oxygen. The sulfur species evolved during pyrolysis were oxidized to SO₂ in the combustion chamber. QGA determination of SO₂ showed that sulfur in coal IBC-109 was evolved primarily between 250°C and 650°C. When the combustion atmosphere was changed to a reducing condition, gaseous COS and H₂S were also detected in the combustion gas.

We have made important progress in developing a method for monitoring HCl gas by QGA. An HCl evolution profile of mass-36 in the combustion chamber under a reducing condition was determined to be from H₂³⁴S, not HCl. In checking the detection of HCl using a standard HCl-N₂ gas (950 ppm HCl) in nitrogen, we found that absorption and desorption of HCl on the wall of capillary tubing posed a problem. Changing capillary tubing to a larger diameter (75 μm) greatly improved the detection of HCl by the QGA. A high chlorine coal (IBC-109) showed a remarkably stronger peak than a low-chlorine coal (IBC-102). A chloride ion selective electrode method was also used to quantitatively monitor the release of HCl during coal pyrolysis.

The second technique to study the behavior of gaseous species during coal pyrolysis and combustion is by integrating thermogravimetry (TG) with Fourier transform infrared spectroscopy (FTIR). Thermogravimetry provides a means for measuring heating condition and weight change. The combined TG-FTIR system has the capability of continuously monitoring the weight change of a coal sample as well as quantitatively determining the evolution of gases. Evolution profiles of sulfur species (SO₂ and COS) released during pyrolysis of coal IBC-109 in a nitrogen atmosphere was determined by TG-FTIR spectroscopy. The profile of SO₂ evolution showed a strong peak between 450°C and 600°C with a maximum at 500°C. This peak corresponds to the major release of organic sulfur. There was a lower temperature peak between 300°C and 400°C with a maximum at 350°C, indicating that there is a fraction of organic sulfur in IBC-109 which is reactive at a low temperature. Sitting on the higher temperature shoulder of the main peak was a peak between 570°C and 700°C, which resulted from decomposition of pyrite. The evolution profile of COS showed a broad peak

between 400°C and 900°C with a maximum at 500°C, resembling that of CO. It is likely that COS is formed by the reaction of CO with a sulfur species in the gas phase. HCl and NH₃ have nearly identical gas evolution profiles: a single peak with a maximum at 500°C, supporting an interpretation that chlorine and nitrogen are closely associated in raw coal. The mass balance of chlorine during coal pyrolysis was studied by heating 2 grams of coal IBC-109 in the combustion chamber of the TGA. The HCl gas was collected in 0.01% sodium carbonate solution at 50°C intervals. The total amount of chloride collected was 7598 µg, which accounts for 90.4% of the total chlorine in raw coal (8400 µg). The TG-FTIR spectroscopy and pyrolysis-combustion-QGA method results are now at a confluence, yielding important insights regarding the behavior of sulfur and chlorine in coal during pyrolysis and combustion.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

OBJECTIVES

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

- Identify gaseous sulfur and chlorine species evolved from coal under various pyrolysis and combustion conditions.
- Determine the rate of release of sulfur and chlorine species during heating in oxidizing and reducing atmospheres.
- Determine the mineralogical and chemical compositions of slag and ash samples from boilers and to relate the chlorine level in coal to boiler corrosion rate.
- Perform simulated corrosion tests to determine the effects of chloride concentration in combustion gas (which is dependent on the chlorine content in coal) on corrosion rate of steels.
- Evaluate pragmatic remedial measures to solve the chlorine-enhanced corrosion problem.

INTRODUCTION AND BACKGROUND

A better understanding of the behavior of sulfur and chlorine during coal combustion is needed for elucidating the mechanism of boiler corrosion. Two methods are used to identify gaseous species and to determine gas evolution profiles of sulfur and chlorine during coal pyrolysis and combustion: temperature-programmed pyrolysis-combustion coupled with quadrupole gas analysis and integrated thermogravimetry-Fourier transform infrared spectroscopy.

The pyrolysis-combustion apparatus used with the QGA to study the release of gases from coal is capable of heating the coal sample in the pyrolysis chamber from the ambient to about 850°C at different heating rates, and the combustion gas is carried to an adjoining combustion chamber maintained at 850°C under a flow of oxygen. The sulfur species evolved in the pyrolysis chamber were oxidized to SO₂ in the combustion chamber. The SO₂ profile showed a small initial release of sulfur between 250° and 400°C followed by a large peak between 400° and 550°C with a maximum at 510°C, followed by a small peak close to 625°C. The main SO₂ peak is associated with the release of volatile matter from the coal. The smaller 625°C peak is probably associated with the release of pyritic sulfur. The low-temperature (250° - 400°C) peak of SO₂

indicates that there is a significant amount of weakly bonded organic sulfur compounds in IBC-109. In some of the experiments, once all oxygen in the pyrolysis system was consumed causing a reducing condition in the combustion chamber, additional sulfur species (COS and H₂S) were also detected between 450°C and 550°C during the major release of volatiles from coal.

We observed the gas evolution profile for species mass-36 when the chamber was under a reducing condition. But this profile appeared to have resulted from hydrogen sulfide (H₂³⁴S, total mass = 36), rather than HCl. Further experiments using standard HCl/N₂ (950 ppm HCl) gas revealed instable HCl detection; the problem appeared to be in the capillary tube and is probably due to adsorption and desorption of HCl on the inside wall of the capillary. Thus, during the second quarter, our effort was focused on improving the detection of HCl using two different approaches: (1) using a larger inner diameter capillary tubing connecting the QGA to the pyrolysis system to increase the volume of gas sampled by the QGA and minimize the effect of adsorption and desorption of capillary walls, and (2) using an ion selective electrode for Cl⁻ detection to monitor the gas release profile and to obtain a mass balance determination.

In Fourier transform infrared spectroscopic studies, we previously obtained an HCl release profile that has a peak between 400° and 650°C with a maximum at 490°C. During this quarter we developed an ion chromatographic analysis procedure to conduct a mass balance study of the chlorine release during pyrolysis and combustion. Gas evolution profiles of sulfur (SO₂ and COS) and nitrogen species (NH₃ and HCN) during coal pyrolysis and combustion were also determined by the TGA-FTIR technique.

EXPERIMENTAL PROCEDURES

Samples

Two coal samples from the Illinois Basin Coal Sample Program were used in the experiments: IBC-109 (1.13% sulfur, 0.42% chlorine), IBC-102 (3.30% sulfur, 0.02% chlorine), and IBC-106 (3.77% sulfur, 0.02% chlorine).

Pyrolysis- quadrupole gas analysis (QGA) experiments

Major components of the pyrolysis-combustion system include a quartz tube reactor, a gas flow controller, two split-tube furnaces, a programmable temperature controller, 50-μm capillary tubing connecting a Dycor QGA to the pyrolysis-combustion system, and a microcomputer. Approximately 0.5 gram of coal is heated (temperature programmed) under a controlled atmosphere in the quartz-tube reactor which consists of two consecutive chambers. The coal is

heated in the first (pyrolysis) chamber under a nitrogen atmosphere, and the volatile products are carried with the nitrogen flow to the second (combustion) chamber maintained at 850°C under a constant flow of oxygen. The gas flowing into the second chamber is combusted. The gaseous products are sampled through a capillary tubing and monitored with a quadrupole gas analyzer. The different gaseous species are identified in the QGA by monitoring the atomic mass associated with different species, such as mass 64 for SO_2 and 44 for CO_2 . The data from the QGA and temperature controller are then transmitted to and stored on a microcomputer.

Much of the first half of the second quarter was spent improving the QGA detection of HCl by changing the capillary size. New experiments were conducted by changing the capillary tubing from a $50\text{-}\mu\text{m}$ to a $75\text{-}\mu\text{m}$ inner diameter. Using the standard HCl/N_2 (950 ppm HCl) gas, a steady HCl peak developed in approximately 30 minutes with the $75\text{-}\mu\text{m}$ capillary, whereas the smaller capillary initially took 2 hours to develop a steady peak. Figure 1 compares two profiles of HCl obtained from pyrolyses of IBC-109 using the smaller diameter capillary and the larger diameter capillary. The profile of HCl obtained from a $75\text{-}\mu\text{m}$ diameter capillary is considerably better than that using a $50\text{-}\mu\text{m}$ diameter capillary. Therefore, additional HCl release profiles were obtained on QGA with a $75\text{-}\mu\text{m}$ diameter tubing for a high-chlorine coal and a low-chlorine coal.

Using a chloride ion-selective electrode technique to determine the amount of chloride in the trapping solution provided an independent supporting method for determining the chloride evolution profile during coal pyrolysis. An Orion pH/volt meter and a chloride ion selective electrode were both available from a previous CRSC contract for studying the removal of chloride from Illinois coal by various leaching techniques. The electrode and voltmeter were calibrated for use with the pyrolysis-combustion system. The efficiency of the chloride electrode for monitoring HCl from the gas phase was tested using a standard $\text{HCl}-\text{N}_2$ gas (950 ppm HCl) whose concentration was checked with a AgNO_3 trap. Of the two different solutions, KNO_3 and Na_2CO_3 , tested with the chloride electrode for trapping HCl out of the gas stream, 10% Na_2CO_3 gave the best results. Initially a glass container with a wide opening to allow room for the electrode, a thermometer and gas inlet tube with a fritted end for dispersing gas bubbles was used to trap the HCl from the gas stream. It was later discovered that a small portion of the trapping solution remained inside the fritted area of the inlet tube and did not mix well with the rest of the solution during the constant gas flow resulting in a significantly low chloride yield. A straight tube with no frit gave much better results, and we were able to achieve 100% recovery of chloride from the $\text{HCl}-\text{N}_2$ gas standard.

Thermal gravimetry (TG)-Fourier transform infrared (FTIR) spectroscopy experimental procedures

The experimental setup is shown in Figure 2. The system consists of a DuPont 951 thermogravimetric (TG) analyzer in conjunction with a Perkin-Elmer 1650 FTIR spectrometer. A coal sample (about 100 mg) is heated in the combustion chamber of the TGA. The gases released from the coal are transported with the carrier gas through the transfer line (1-mm Teflon tubing) to the 100 X 24 mm gas cell of the FTIR spectrometer. Both the Teflon line and the gas cell are heated with a heating coil to 250°C. Thermogravimetry provides a means for measurement of heating condition and weight change. The TG-FTIR system is capable of continuously monitoring the weight change of a coal sample as well as of quantitatively determining the gases evolved (CO, CO₂, SO₂, COS, H₂O, HCl, NH₃, HCN, CH₄, C₂H₂, C₂H₄, and C₃H₄) during pyrolysis and combustion. The FTIR spectrum can be taken every minute, including the time it takes to store the spectrum on the computer. Calibration of the FTIR is made using pure gases or prepared gas mixtures. The pyrolysis was conducted with nitrogen gas (flow rate 25 mL/min) with a heating program from 20°C - 900°C at a rate of 10°C/min. The FTIR scanning period was four seconds.

Mass balance experiments. The sample size of coal was increased to 2 grams, and the coal was heated in a container in the combustion chamber of the TGA. The weight loss was not monitored when the TGA was operated for this purpose because there was too much sample to be placed in the weighing boat. The volatiles (including sulfur and chlorine species) released during programmed heating (20°C to 900°C at a rate of 10°C/min) were transported with the carrier gas (N₂ at a flow rate of 50 mL/min) through a three-stage trap each with 50 mL of 0.1% sodium carbonate solution. The gases were collected at 50°C intervals. The chloride and sulfur contents were then determined using a Shimadzu HIC-6A ion chromatograph.

RESULTS AND DISCUSSION

Pyrolysis-Quadrupole Gas Analysis (QGA) experiments

Using the 75-μm capillary tubing with the QGA, pyrolysis-combustion experiments were performed and mass-36 gas evolution profiles were obtained for a high-chlorine coal (IBC-109, 0.42% chlorine) and a low-chlorine coal (IBC-102, 0.02% chlorine). The intensity of the mass-36 peak for coal IBC-109 was indeed much stronger than that of IBC-102 as a result of much higher chlorine content in the former. Thus, the measured mass-36 peak between 300°C and 550°C was indeed due to HCl gas.

However, during further experiments of HCl release during the pyrolysis of IBC-109, the position of the HCl peak relative to temperature, and the intensity of the HCl peak showed considerable variation even though pyrolysis conditions were kept the same for each run (Figure 4). (The small first peak on curve 38e coincides with a similar fluctuation in the profile of CO₂, and is thus not a concern.) The peaks of other gas profiles (such as CO₂ and SO₂) remained in the same positions with respect to temperature while the HCl peak shifted between approximately 380°C and 480°C. This problem prompted us to pursue the second, independent approach of using an ion selective electrode for detecting chloride.

Initial results using the chloride electrode to monitor HCl released during pyrolysis of IBC-109 coal are shown in Figure 5. The three curves in Figure 5 reflect the cumulative increase of HCl trapped in solution during the three different pyrolysis runs. The last point at the end of each run, plotted at an arbitrary temperature of 810°C, shows the increase in Cl⁻ concentration due to purging (with an aspiration bulb) the inlet tube with the Na₂CO₃ trapping solution. Curve A shows the effect of having the gas inlet tube enter from the top of the solution, which resulted in condensation on the inside of the inlet tube where a significant amount of HCl was absorbed. The trap was redesigned so that the gas inlet tube enters near the base of the container (see the inset of Figure 5), eliminating the submersion of the tube in the trapping solution, and allowing the inlet tube to be wrapped with heating tape. Curves B and C are results obtained from the newly designed trap with heating tape wrapped around the inlet tube up to the point where the gas phase contacts the trapping solution (see the inset of Figure 5). However, it should be noted that during experiment B the heating tape was turned off at approximately 420°C, whereas the heating tape remained on throughout the duration of experiment C. The final recovery of chloride, after purging the inlet tube, from experiments B and C was nearly 100% relative to the chlorine content of coal IBC-109.

TG-FTIR spectroscopy of coal

Thermal gravimetry and differential thermogravimetry of IBC-109. Figure 6 shows the thermogravimetric curves (TG and DTG) for coal IBC-109. The sample was heated in air at a rate of 10°C/min. Weight loss occurred mainly in two temperature ranges: between 20°C and 129°C, and between 274°C and 668°C. The former corresponded to the loss of moisture (4.2%) at a rate of 0.51%/min and the latter the loss of organic matter of coal. The rate of weight loss showed a maximum at 440°C, corresponding to the major loss of volatile matter of coal. The weight loss occurs much more rapidly during combustion in air (Figure 6) than pyrolysis in the nitrogen atmosphere reported in the previous quarterly report (Figure 9 in Chou et al., 1991).

Evolution of sulfur gases during coal pyrolysis. Sulfur species SO_2 and COS are evolved during pyrolysis of coal in a nitrogen atmosphere and during combustion in air. The profile of SO_2 evolution during pyrolysis showed that two major peaks occurred at 350°C and 500°C (figure 7). A major peak occurred between 450°C and 600°C with a maximum at 500°C . This peak results from the release of organic sulfur (Liu *et al.*, 1987) during the major release of volatile matter of coal. A lower temperature peak between 300°C and 400°C with a maximum at 350°C indicated that there is a small fraction of organic sulfur which is reactive at this temperature range. On the higher temperature shoulder of the main peak there is a broad peak between 570°C and 700°C resulted mainly from pyrite decomposition.

The evolution profile of COS during coal pyrolysis showed a broad peak between 400°C and 900°C with a maximum at 500°C (Figure 7). Possible mechanisms for formation of COS during pyrolysis include (Attar, 1978; Oh *et al.*, 1988):

(1) reaction of CO gas with FeS_2 :

(2) reactions of CO or CO_2 with H_2S in the gas phase:

Attar (1983) indicated that reaction [1] is very slow below 800°C . The FTIR spectra showed that the evolution of COS closely follows CO (Figure 7), suggesting that COS is likely formed by reaction in the gas phase.

Evolution of hydrogen chloride and ammonia during pyrolysis. Figure 8 shows the gas release profiles of HCl (2796.0 cm^{-1}), NH_3 (949.0 cm^{-1}), CO_2 (2362.0 cm^{-1}), and CH_4 (1303.8 cm^{-1}). Such similarity between HCl and NH_3 have nearly identical release patterns: a single peak with a maximum at 500°C , which are clearly different from those of CH_4 and CO_2 . Similar behavior of chlorine and nitrogen during coal pyrolysis supports an interpretation that chlorine and nitrogen are closely associated in coal (Chou, 1991). Evolution of another nitrogen species HCN (713 cm^{-1}) occurred between 400°C and 850°C (Figure 7). The peak intensity gradually increases and reaches 710°C . HCN may be produced from pyridine and other nitrogen functional groups in coal (Houser *et al.*, 1980).

Mass balance of chlorine release during pyrolysis. This experiment (R-10) was carried out on 2 grams of coal (IBC-109) with programmed temperature from 20°C to 900°C at a heating rate of $10^\circ\text{C}/\text{min}$ and a carrier gas flow rate of 50

mL/min. The HCl gas was collected in 90 ml of 0.01% sodium carbonate solution. The amount of chloride collected at each 50°C interval is shown in Figure 9. The total amount of chloride collected was 7598 µg, which accounts for 90.4% of the chlorine in the raw coal (8400 µg). The temperature range of highest chloride evolution was between 350°C and 650°C. This range is consistent with our previous TG-FTIR experiments, which showed that chloride was released from coal between 400°C and 650°C with a maximum at 490°C.

CONCLUSIONS AND RECOMMENDATIONS

We were successful in both improving the detection of HCl by the QGA as well as setting up the chloride selective electrode for continuous quantitative monitoring. The ion meter connected to the chloride electrode is equipped with a serial port which will allow data acquisition from the electrode by the same computer that is used to control QGA and temperature data acquisition. Having two independent methods of monitoring chloride release will allow us to determine whether the variations in the HCl peak observed from the QGA data is real or still due to problems within the capillary tube, such as adsorption and desorption of HCl.

Using the TG-FTIR technique, we have determined gas evolution profiles for sulfur, chlorine, and nitrogen species. A mass balance study of HCl evolution during pyrolysis of coal IBC-109 was completed; the temperature range of HCl evolution is consistent with the TG-FTIR results.

REFERENCES

- Attar A. (1978) Chemistry, thermodynamics and kinetics of reactions of sulphur in coal-gas reactions: a review. Fuel 57, 201-212.
- Chou C.-L. (1991) Distribution and forms of chlorine in Illinois Basin coals. In Chlorine in Coal (edited by J. Stringer and D.D. Banerjee), Coal Science and Technology, vol. 17, p. 11-29, Elsevier.
- Chou C.-L., Hackley K.C., Donnals G.L., Ruch R.R., Pan W.-P. and Shao D. (1991) Behavior of sulfur and chlorine in coal during combustion and boiler corrosion. Technical Report, September 1, through November 31, 1991, Illinois Center for Research on Sulfur in Coal, 20 p.
- Houser T.J., Hull M., Alway R.M. and Biftu T. (1980) Kinetics of formation of HCN during pyridine pyrolysis. International Journal of Chemical Kinetics 12, 569-574.

- Liu C.L., Hackley K.C. and Coleman D.D. (1987) Use of stable sulphur isotopes to monitor directly the behaviour of sulphur in coal during thermal desulfurization. Fuel 66, 683-687.
- Oh M.S., Burnham A.K. and Crawford R.W. (1988) Evolution of sulfur gases during coal pyrolysis. ACS Division of Fuel Chemistry. Preprints 33, No. 1, p. 274-282.

Figure 1. Comparison of HCl (mass 36) profiles obtained from quadrupole gas analyzer using a 50- μm diameter and a 75- μm diameter tubing.

Figure 2. Experimental setup for thermogravimetry-Fourier transform infrared spectroscopy.

Figure 3. Comparison of HCl evolution profiles obtained from the QGA for a high-chlorine coal (IBC-109, 0.42% chlorine) and a low chlorine coal (IBC-102, 0.02% chlorine).

Figure 4. Comparison of HCl evolution profiles obtained from the QGA using 75 μ m capillary during five pyrolysis runs for coal IBC-109. The pyrolysis conditions were the same (heating rate = 20 $^{\circ}$ C/min).

Figure 5. Cumulative increase of chloride concentration determined with an ion selective electrode to monitor the HCl release during pyrolysis of coal IBC-109. The different shapes of the three curves are primarily due to the effect of condensation on the inlet tube. The inset shows the trap for HCl gas and the electrode.

Sample: COAL-IBC-109 (0.42% CL; 1.13% S) TGA File: A: IBC10SCB.008
 Size: 99.5690 mg Operator: SHAOON
 Method: SHAO-TG/FTIR/HIC-IBC-CB Run Date: 26-Jan-92 10:01
 Comment: 20-950 C, 10 C/MIN.; AIR-50ML/MIN; TG/DTG CURVES; SAMP WT-100MG

Figure 6. Thermogravimetric (TG and DTG) curves for coal IBC-109.

Figure 7. Gas evolution profiles during pyrolysis of coal IBC-109 in a nitrogen atmosphere determined by the TG-FTIR technique. [4th run, 12/22/91; 109PY04C]

1. TG/FTIR IN N₂, 50 ml/min
 2. Sample Wt. = 1000 mg
 3. 4th Run (12/22/91; 109PY04)

Figure 8. Gas evolution profiles of HCl, NH₃, CO₂, and CH₄ during pyrolysis of coal IBC-109 (0.42% chlorine) in a nitrogen atmosphere.

Figure 9. A mass balance study of chlorine evolution during pyrolysis of 2 grams of coal IBC-109 (0.42% chlorine) with nitrogen carrier gas (50 mL/min). The HCl evolved from the coal was trapped in sodium carbonate solution at 50°C intervals; chloride concentration in solution was determined by ion chromatography. Total chloride trapped in the solution was 7598 µg (90.4%) out of 8400 µg in raw coal. [10th run, 1/20/92; 109PY10(CL)]

PROJECT MANAGEMENT REPORT
December 1, 1991 through February 29, 1992

Project Title: Behavior of Sulfur and Chlorine in Coal during Combustion and Boiler Corrosion

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COMMENTS

The project has proceeded well. The expenditures are in line with the projected amounts.

EXPENDITURES - EXHIBIT B

Projected and Estimated Actual Expenditures by Quarter

Quarter*	Types of Cost	Direct Labor	Materials and Supplies	Travel	Major Equipment	Other Direct Costs	Indirect Costs	Total
Sept. 1, 1991	Projected	4,300	600	500	0	30,000	3,540	38,940
to								
Nov. 30, 1991	Estimated Actual	4,300	769	0	0	29,612	3,468	38,149
Sept. 1, 1991	Projected	8,600	1,200	1,000	200	32,500	4,350	47,850
to								
Feb. 29, 1992	Estimated Actual	8,600	1,134	289	0	30,165	4,019	44,207
Sept. 1, 1991	Projected	12,900	1,800	1,500	200	35,000	5,140	56,540
to								
May 31, 1992	Estimated Actual							
Sept. 1, 1991	Projected	17,234	2,400	2,000	400	39,716	6,175	67,925
to								
Aug. 31, 1992	Estimated Actual							

* Cumulative by quarter

COSTS BY QUARTER - EXHIBIT C

Behavior of sulfur and chlorine in coal during combustion
and boiler corrosion

Months and Quarters

O = Projected Expenditures -----

Δ = Actual Expenditures _____

Total CRSC Award \$ 67,925

Schedule of major milestones

Year 1 (September 1, 1991 - August 31, 1992)

Milestones:

- A. Employ research assistants
- B. Subcontract WKU
- C. Request for and receive samples from the Illinois Basin Coal Sample Program; set up the equipment
- D. Perform kinetic studies of sulfur and chlorine release using temperature-programmed pyrolysis coupled with quadrupole gas analysis (Task 1)
- E. Determine chlorine contents in combustion residues and mass balance
- F. Identify gaseous sulfur and chlorine species in combustion gases, and determine gas release profiles using thermal gravimetric analysis in conjunction with Fourier transform infrared spectroscopy (Task 2, WKU)
- G. Prepare and submit technical reports
- H. Prepare and submit project management reports

END

**DATE
FILMED**

9 / 14 / 92