

## IN SITU XAFS STUDIES OF SULFUR IN COAL DURING HIGH TEMPERATURE PYROLYSIS AND OXIDATION

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### Abstract:

*In situ* sulfur K-edge XAFS measurements have been performed on Illinois No. 6 and low rank Australian brown coals in order to study the behavior of sulfur forms in coal during pyrolysis and oxidation. The results show that under the relatively slow pyrolysis conditions employed, degradation of organic disulfide starts as low as 200°C while sulfide components degrade at temperatures around 300°C. Pyrrhotite was formed from pyrite during pyrolysis of Illinois No. 6 coal above 400°C. Results obtained during oxidation at temperatures up to 450°C are less well understood. Gradual formation of small amounts of sulfate occurs in both samples, while pyritic sulfur and organic sulfide decrease significantly, with most of the sulfur apparently leaving the sample as SO<sub>2</sub>.

### Introduction

It is well recognized that a full understanding of the behavior of all major forms of sulfur, both inorganic and organic, is essential for the solution of many of the significant research problems involving sulfur in coal. Until very recently, however, information about the different organic forms of sulfur in coal could not be obtained directly, but had to be based on indirect methods involving pyrolysis of the coal. Such pyrolysis techniques include the temperature-programmed reduction ("kinetogram") methods advanced by Attar<sup>[1]</sup>, the flash pyrolysis ("pyroprobe") developed by Calkins<sup>[2,3]</sup>, and a variety of pyrolysis/mass-spectroscopy and gas chromatographic/mass-spectroscopy techniques<sup>[4,5]</sup> that are usually performed on extracts and volatile fractions of the coal, rather than the bulk coal itself. Such pyrolysis methods have provided much useful information about sulfur in coal, but because they do not provide information on the sulfur remaining in the residue materials, the information obtained is not complete.

In the last two years, XAFS spectroscopy has been shown<sup>[6-9]</sup> to be a powerful method for the direct, nondestructive, quantitative determination of all major sulfur forms in coal. In this study, we report some preliminary results from the first *in situ* XAFS spectroscopic investigations of sulfur in coal under conditions of high temperature pyrolysis and oxidation. Emphasis has been given to the quantitative analysis of the various forms of sulfur produced during slow pyrolysis of coal in hydrogen and helium atmospheres as well as oxidation in a helium/oxygen mixture at temperatures up to 600°C.

## Experimental

### *Thermal Analysis:*

The coal samples used in this study were a bituminous Illinois No. 6 coal obtained from Argonne Premium Coal Sample Program Bank and a low rank Australian brown coal (Glencoe). The Illinois No. 6 coal contains 4.83 wt% sulfur of which 2.81 wt% is pyritic sulfur, while the Australian coal contains 5.1% organic sulfur and with very little pyritic sulfur (<0.2 wt%). Some model compounds, such as dibenzylsulfide and dibenzothiophene, have also been examined under similar oxidation conditions.

The X-ray reaction furnace used in this work is modified from the design of Sinfelt and Lytle<sup>[10]</sup>. A chromel-alumel thermocouple is imbedded in a stainless steel backing plate in contact with the sample cell. Temperatures were monitored with a digital voltmeter. Water flow through jackets in the furnace body helps to dissipate heat and prevent the mylar windows of the fluorescent detector from melting. Reactant gases were flowed through the samples which were packed into the cell.

XAFS spectra of samples were obtained while flowing a gas stream of helium or hydrogen in pyrolysis and mixture of 95% helium, 5% oxygen in oxidation at temperatures up to 600°C. Since each spectrum takes approximately 30 minutes to complete, these are considered slow pyrolysis and oxidation processes.

### *XAFS Analysis:*

The XAFS measurements were performed at beam line X19-A at the National Synchrotron Light Source in Brookhaven National Laboratory. Experimental procedure are discussed elsewhere<sup>[6]</sup>.

The least squares method for analysis of X-ray absorption near edge structure (XANES) of the sulfur K-edge spectra is based on the concept that the experimental spectrum can be modelled as the sum of an arctangent function representing the edge step and a number of absorption peaks which arise from 1s→3p electronic transitions of the major forms of sulfur in the coal. The shape of the absorption peaks is modelled as a function of energy by a combined 50:50 Lorentzian:Gaussian function. An example of least-squares curve fitting of the sulfur K-edge XANES spectrum of the Illinois No. 6 coal is shown in Figure 1. This spectrum is fit by one-step arctangent function representing the edge step, six peaks of 50% Gaussian - 50% Lorentzian shape representing three different forms of sulfur, both organic and inorganic, and several scattering resonance peaks<sup>[6]</sup>.

To convert the measurement of relative peak areas to wt% sulfur in the different forms, the calibration method described elsewhere<sup>[8]</sup> was utilized. It has been observed that the 1s→3p transition probability increases with increasing sulfur valence. Therefore, calibration constants for converting XANES peak area percentages to sulfur weight percentages have been experimentally determined for the functional forms of sulfur that occur in coal<sup>[9]</sup>. For this work an additional calibration constant had to be determined for pyrrhotite, which was formed from the degradation of pyrite during pyrolysis. The error in the resulting sulfur percentages is approximately ± 5 - 10%.

## Results and Discussion

*In situ* sulfur XANES spectra obtained during pyrolysis of Illinois No.6 coal are shown in Figure 2. The effect of pyrolysis on different forms of sulfur in this coal as a function of temperature is illustrated in bar-graph form shown in Figure 3. It is evident that between 250°C and 600°C, the organic sulfide component decreases from 19% of total sulfur to about 10%. Simultaneously, pyrite begins to transform to pyrrhotite; this transformation continues as the temperature is raised and appears to be more or less completed at 600°C. No significant differences were observed between the pyrolysis in helium and that in hydrogen.

The results of *in situ* XANES measurements for pyrolysis of Australian (Glencoe) coal under H<sub>2</sub> and He atmospheres are shown in Figures 4 and 5, respectively. It is seen that disulfide compounds start to degrade at about 200°C while sulfide components decrease when the temperature reaches around 400°C. Growth of a peak with a negative valence state was observed as a function of temperature during the pyrolysis of Australian coal in both He and H<sub>2</sub> atmospheres. Since this coal contains virtually no iron (<0.05 wt%) the appearance of this peak may indicate the formation of organic compounds such as thioketones or similar functional groups during the course of experiments. A similar peak was observed during the thermal oxidation of a mixture of 50:50 wt% of dibenzothiophene and dibenzylsulfide.

The changes that occur in the sulfur forms of the Glencoe coal during oxidation under a mixture of 95% He-5% O<sub>2</sub> flowing gas are illustrated in bar-graph form in Figure 6. Decomposition of organic sulfide component occurs at the same temperature as for pyrolysis (above 400°C). The only significant changes during the oxidation of this coal are a gradual increase in the sulfate component and a decrease in the sulfide component. Since the Australian coal is one that contains no pyrite, the sulfate is believed to be either an organic sulfate or possibly CaSO<sub>4</sub>. The latter could result from the reaction of SO<sub>2</sub> released from sulfide groups with carboxyl-bound calcium in the coal macerals. At the conclusion of the experiment, the sample contained 4.2 wt.% sulfur, indicating that about 1 wt.% of the sulfur had left the sample as SO<sub>2</sub> formed by oxidation of the organic sulfides.

Figure 7 shows the percentage of different sulfur forms in Illinois No. 6 coal under oxidation in a mixture of 95% helium - 5% oxygen. Pyrite was partially removed from this sample by centrifugation in carbon tetrachloride prior to the oxidation experiment. The initial sulfur content of the sample was 3.6 wt.%, with a pyritic sulfur content of approximately 1.6 wt.% according to the XANES results. The principal change during oxidation is a significant decrease in pyritic sulfur and a small, gradual increase in sulfate. It should be mentioned that the sample was heated to 500°C, but a spectrum was not obtained because of a loss of the X-ray beam at that temperature. The final bar graph obtained at room temperature therefore is from a sample that had experienced oxidation up to 500°C. Pyrite has disappeared and a small peak from elemental sulfur is observed. Since the final sulfur content of the sample was 1.7%, most of the pyritic sulfur leaves the sample as SO<sub>2</sub>.

## Conclusions

Based on the *in situ* XAFS measurements of the sulfur K-edge of the coal samples reported in this research, the following conclusions can be made:

- *In situ* XAFS high temperature measurements can provide insight into the behavior of sulfur compounds during thermal reactions.
- During pyrolysis, the degradation of disulfide starts to occur at about 200°C, while the organic sulfide decomposes at above 400°C. The conversion of pyrite to pyrrhotite in Illinois No. 6 coal was observed above 400°C.
- During oxidation of an Illinois No. 6 coal at temperatures up to 500°C, pyritic sulfur decreases markedly, while a small and gradual formation of sulfate is observed. A minor amount of elemental sulfur was also formed.
- During oxidation of a brown coal containing no pyrite at temperatures up to 450°C, organic sulfides decreased approximately 50% and a gradual increase of sulfate was observed.

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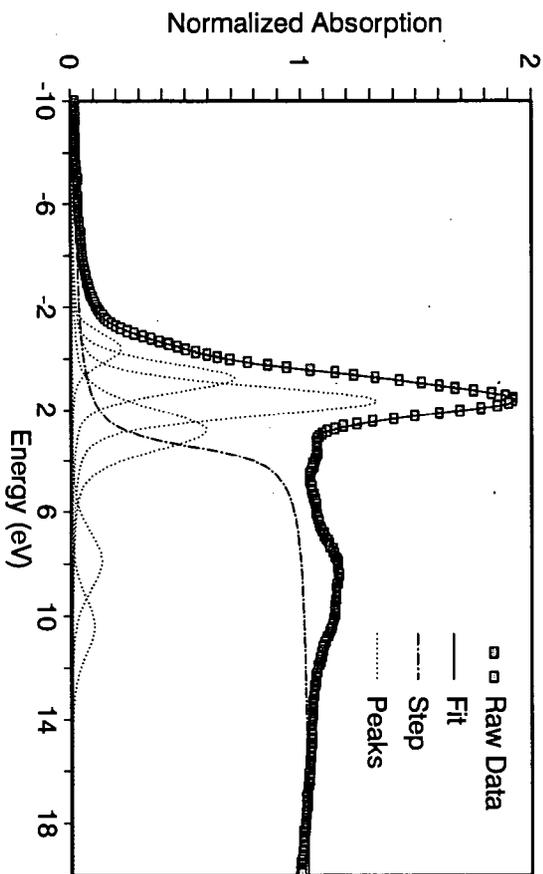


Figure 1. Example of least-squares fitting of the sulfur K-edge XANES spectrum of the Illinois No. 6 coal. The spectrum is fit by one-step arctangent function and a number of peaks of 50% Gaussian - 50% Lorentzian shape.

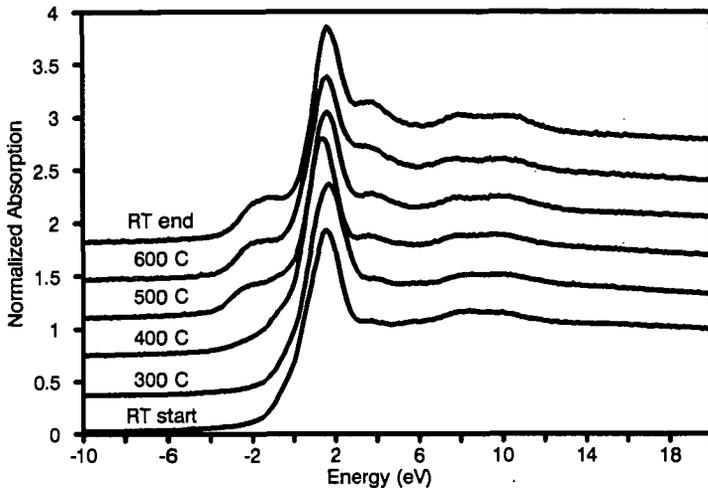


Figure 2. Sequence of sulfur K-edge XANES spectra from Illinois No. 6 at indicated temperatures during pyrolysis in helium.

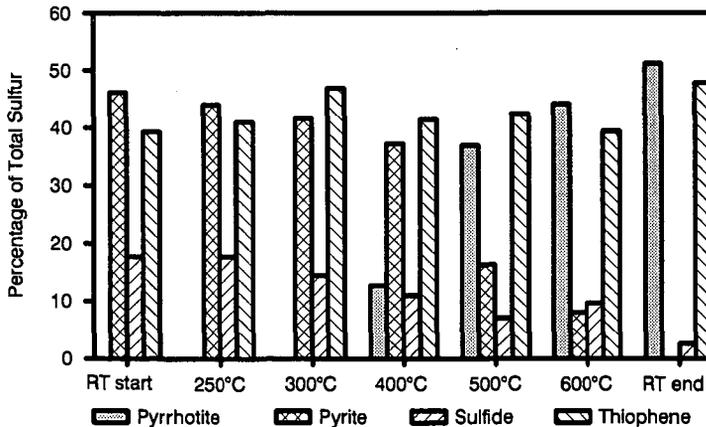


Figure 3. Percentage of different sulfur forms in Illinois No. 6 under pyrolysis in helium obtained by least-squares analysis of the XANES spectra shown in Figure 2.

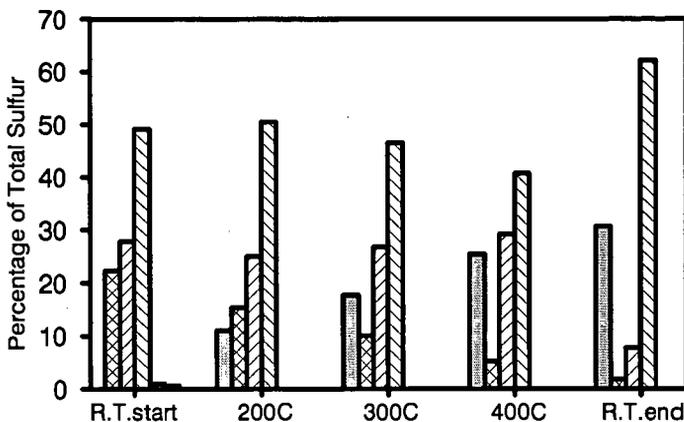


Figure 4. Percentage of different sulfur forms in Australian brown coal (Glencoe) under pyrolysis in hydrogen.

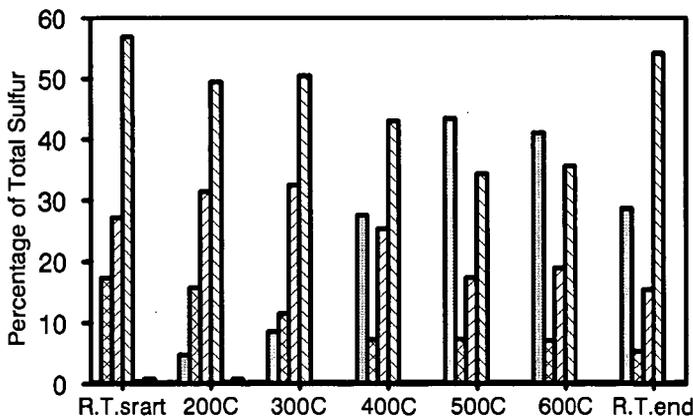


Figure 5. Percentage of different sulfur forms in Australian brown coal (Glencoe) under pyrolysis in helium.

See Text	Disulfide	Sulfide
Thiophene	Sulfone	Sulfate

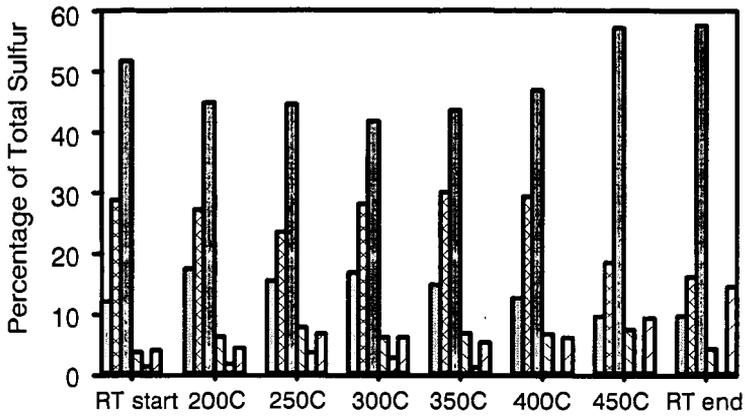


Figure 6. Percentage of different sulfur forms in Australian coal (Glenceo) under oxidation in 95% helium + 5% oxygen.

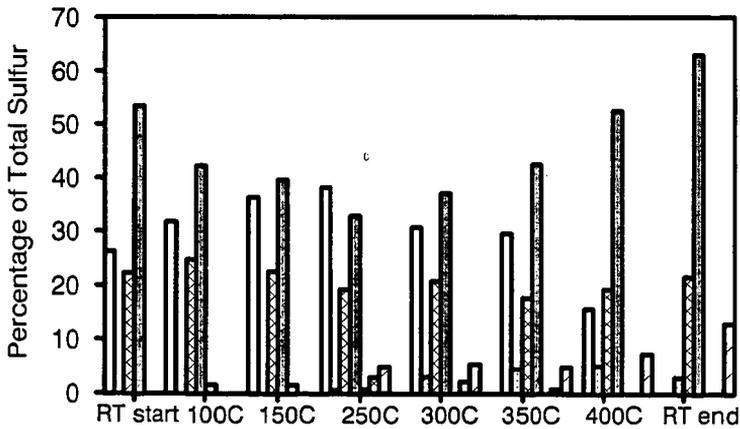


Figure 7. Percentage of different sulfur forms in Illinois No. 6 coal under oxidation in 95% helium + 5% oxygen.

Disulfide  
  Pyrite  
  Elemental Sulfur  
  Sulfide  
 Thiophene  
  Sulfoxide  
  Sulfone  
  Sulfate