

## QUANTITATIVE ANALYSIS OF SULFUR FUNCTIONAL FORMS AND REACTIONS BY XAFS SPECTROSCOPY

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### INTRODUCTION

Recently, significant progress has been made in quantifying the measurement of different functional forms of sulfur in coal using X-ray absorption fine structure (XAFS) spectroscopy. As discussed in detail elsewhere, three methods of analyzing the X-ray absorption near edge structure (XANES) have been proposed.<sup>[1-6]</sup> In the current paper, we will briefly review the method developed by our group, which consists of direct least squares analysis of the XANES and conversion of the photoelectron  $s \Rightarrow p$  transition peak areas into sulfur percentages using empirically determined calibration constants.<sup>[3]</sup> A number of applications of this method will be briefly summarized, including investigation of sulfur forms as a function of rank,<sup>[3]</sup> in situ studies of sulfur transformations during pyrolysis and oxidation,<sup>[7-9]</sup> and chemical and biological reactions of sulfur in coal.<sup>[10]</sup>

### EXPERIMENTAL PROCEDURES

Experimental details are discussed elsewhere.<sup>[1-3,7-10]</sup> All XAFS experiments were conducted in the x-ray fluorescent mode<sup>[11]</sup> at beamline X-19A at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. The in situ experiments were carried using an XAFS compatible high temperature cell with the sample under flowing helium, hydrogen, or helium-5% oxygen at temperatures ranging from 200 to 600°C.<sup>[7-9]</sup> An XAFS spectrum was acquired at each temperature, making the pyrolysis and oxidation treatments fairly slow.

The suite of coals examined have included the Argonne Premium Coal Sample Bank (APCSB) coals, numerous additional whole coals, a suite of maceral separates, and a variety of chemically and biologically treated samples.

### RESULTS AND DISCUSSION

Typical least squares analyzed XANES spectra are shown in Figure 1. The lower spectra in Figure 1 are room temperature spectra of an APCS Illinois No. 6 coal and a low-rank Victorian brown coal (Glencoe). The upper half of Figure 1 shows high temperature spectra obtained in situ during oxidation of the Glencoe coal at 450°C and pyrolysis of the APCS Illinois No. 6 coal at 600°C. As discussed elsewhere,<sup>[3]</sup> the least squares analysis method fits the XANES spectra to a series of photoelectron  $s \Rightarrow p$  transition peaks using 50:50 Lorentzian:Gaussian peak shapes, and to one or two arctangent step functions representing the photoelectron transition to the continuum. Because the major sulfur forms in coal and coal derivatives have characteristic  $s \Rightarrow p$  transition energies, the  $s \Rightarrow p$  peak associated with each sulfur form can be identified. It is found that the  $s \Rightarrow p$  transition energy increases with valence, as follows: pyrrhotite, -1.5 eV; pyrite, -0.5 eV; elemental sulfur, 0.0 eV; organic disulfide, 0.2 eV;

organic sulfide, 0.7 eV; thiophenic sulfur, 1.3 - 1.8 eV; sulfoxide, 3.4 eV; sulfone, 7.5 eV; and sulfate, 9.9 - 10.1 eV.<sup>1</sup> Once the  $s \Rightarrow p$  peak areas have been determined from the least squares fit, empirically determined calibration constants are used to convert them to sulfur percentages.<sup>(3)</sup>

The results for the APCS coal and a number of additional whole coals are summarized in Table 1. A number of points are worth noting. First, the only APCS coal that exhibits significant sulfur oxidation is the Beulah (ND) lignite, which contains a sulfate component believed to be gypsum. Second, the pyritic sulfur percentages derived from XANES agree reasonably well with those derived from Mössbauer spectroscopy.<sup>(11,12)</sup> Third, the percentage of organic sulfur that is sulfidic increases with decreasing rank as shown in Figure 2, although thiophenic sulfur was the dominant organic sulfur form for all coals examined. The thiophenic and sulfidic percentages determined for the APCS coals agree fairly well with those determined by Gorbaty et al.<sup>(5)</sup> using a third derivative method of analyzing the XANES spectra.

We have also completed XANES analysis of a suite of maceral separates, and find that the sulfidic content of exinite is consistently higher than that of vitrinite or inertinite.<sup>(3)</sup> Additionally, it is found that the inertinite separates frequently contain fairly high percentages of pyrite, indicating that coal particles containing fine included pyrite are often incorporated into the specific gravity range corresponding to inertinite during density gradient centrifugation.

Several coals have been investigated by high temperature in situ XAFS spectroscopy conducted during pyrolysis and oxidation. The results, which are discussed in more detail elsewhere,<sup>(7-9)</sup> are summarized in Figure 3. Briefly, the organic sulfide component decreases above approximately 300°C, under both pyrolysis and oxidation conditions, with the sulfide percentage falling to about half of its initial value on reaching 500 to 600°C. The disulfide percentage for the Australian brown coal begins to decrease between 200 and 300°C, reaching approximately one fourth of its original value at 500 to 600°C. The Illinois #6 data shows that pyrite transforms to pyrrhotite during pyrolysis and to pyrrhotite and sulfate during oxidation, above approximately 400°C. During oxidation of the Glencoe coal, a sulfate phase is also formed, but it is unlikely to be an iron sulfate since the coal contains no pyrite and very little iron. Either an organic sulfate or calcium sulfate are possibilities. During pyrolysis of the Glencoe coal, a negative valence ( $\sim -2$ ) sulfur species is observed to form and increase to approximately 40% of the total sulfur at 500°C. A double-bonded C-S compound, such as a thioetone, or calcium sulfide, are possible candidates.

There is considerable interest in the effects of various chemical and biological reactions on sulfur in coal. We have examined the effects of several such treatments on a number of coals using XANES spectroscopy. A more detailed summary of the results is available in a forthcoming paper [10]. For the current article we will summarize some recent data obtained on the use of perchloroethylene (PCE) for removal of sulfur from coal. In this treatment,<sup>(13)</sup> coal is treated with a five-fold excess of PCE at close to its boiling point (125°C) for no more than 30 minutes, in which time a significant reduction (up to 50%) in the organic sulfur is claimed to occur. The exact mechanism has not yet been clarified, but the observation has been made<sup>(13)</sup> that the sulfur removed from the coal by PCE can be readily extracted in the form of elemental sulfur. However, this focus on elemental sulfur has lead others<sup>(14,15)</sup> to criticize this method by claiming the PCE is only removing the elemental sulfur already present in the coal. As

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<sup>1</sup>The energy of the elemental sulfur  $s \Rightarrow p$  transition, which is actually approximately 2472 eV, is chosen to be 0, and all other energies are measured relative to that standard.

oxidation of pyrite is the principal and possibly only method by which elemental sulfur can come to be present in the coal,<sup>(14,16,17)</sup> it has been postulated that the PCE method will only be effective with oxidized coals.

A number of samples before and after treatment with PCE have now been examined with both XAFS and Mössbauer spectroscopies. The Mössbauer results<sup>(10)</sup> show that the amounts of pyrite in these samples are basically unaltered by the PCE treatment. Hence, the pyritic sulfur in these coals is *not* affected by the PCE treatment.

The sulfur K-edge XANES data for the Upper Freeport coal before and after PCE treatment are shown in Figure 4 and the results on the sulfur forms derived from the least-squares fitting are summarized in Table 2. The XANES results for Freeport coal clearly show a major reduction in at least one form of sulfur. Based on the peak position (0.3 eV) of the peak that disappears, it is difficult to reconcile it with an organic sulfide, the peaks of which occur typically at around 0.7 eV. After the PCE treatment, there is a peak located at 0.7 eV, which is approximately 30% of the intensity of the peak present before PCE treatment. This peak position is compatible with an organic sulfide. Hence we interpret the large peak present in the XANES spectrum of the sample before PCE treatment as a composite peak consisting of contributions from both elemental sulfur and organic sulfide. This would also account for its position intermediate between that for sulfide (0.7 eV) and elemental sulfur (0.0 eV). Such an interpretation strongly suggests that the peak removed is due primarily to elemental sulfur, and based on the XANES analysis, we estimate that about 0.6 - 0.7 wt% sulfur is removed in this form. The value was later confirmed independently by D. Buchanan (E. Illinois University).

It should also be noted that there appears also to be some decrease in the amount of thiophenic sulfur ( $\approx 0.15$  wt%) based on the total sulfur value estimated for the coal (3.2 wt%) after elemental sulfur removal. However, this amount is within the experimental uncertainty of the technique and may not be significant.

A sample of Indiana #5 coal also exhibited distinct changes with the 30-minute boiling PCE treatment. The organic sulfur forms, calculated from the peak areas in the XANES spectrum and identified on the basis of their peak position, are summarized in Table 2. It would appear that the sulfur species in the Indiana #5 that are reduced by the PCE treatment are elemental sulfur and, to a lesser extent, possibly also the organic sulfide species. However, such a small change is within the estimated experimental errors of the XANES measurement.

A number of other coals subjected to treatment with boiling PCE exhibit essentially the same spectrum after treatment as before and therefore do not show any significant preferential removal of different sulfur forms. Such coals investigated to date include an Ohio #5/#6 coal, an unoxidized Illinois #6 coal from the Argonne Premium sample bank, an oxidized Illinois coal obtained from Prof. D. Buchanan (E. Illinois University), and high sulfur (5.7 wt%) Australian brown coal (Glencoe) that contained a large organic sulfide content and virtually no pyritic sulfur (<0.2 wt.%).

## SUMMARY AND CONCLUSIONS

Least squares analysis of sulfur K-edge XANES spectra is a powerful method for quantitative analysis of the functional forms of sulfur in coal and related materials. Thiophenic sulfur is the dominant organic sulfur form observed in all of the coals we have examined, but sulfidic sulfur increases significantly with decreasing rank. Sulfidic sulfur is higher in exinite

maceral separates than in vitrinite or inertinite. Pyritic sulfur measured by XANES agrees with that determined by Mössbauer spectroscopy.

The reactions of different sulfur forms during chemical, biological, or thermal treatment can be quantitatively followed using XANES spectroscopy. Quantitative in situ XANES measurements during coal pyrolysis and oxidation have been carried out at temperatures up to 600°C.

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TABLE 1: Derived percentages for forms of sulfur in Argonne Premium coals and several additional coals.

Argonne Premium Coal Sample	Wt% Total Sulfur	Sulfur Forms, %					
		Pyrite	Sulfide	Thioph.	Sulfox.	Sulfone	Sulfate
Pocahontas #3, VA	0.66	24	0	75	0	1	0
Upp. Freeport, PA	2.32	62	6	33	0	1	0
Pittsburgh #8, PA <sup>1</sup>	2.19	52	13	35	0	1	0
Lewis.-Stock., WV	0.71	26	16	56	1	1	0
Blind Canyon, UT	0.62	40	15	46	0	0	0
Illinois #6, IL	4.83	48	19	33	0	0	0
Wyodak-Anders., WY	0.63	24	29	46	0	0	0
Beulah, ND (fresh)	0.80	29	28	30	2	0	12
Beulah, ND (2nd.)	0.80 <sup>1</sup>	37	24	30	2	0	7
Additional Coals							
Illinois #6, IBC-101	3.08	34	21	38	3	4	1
Wyodak (micronized)	n.r.	27	25	45	0	0	3
Texas Lignite	n.r.	49	18	30	0	1	2
Glencoe brown coal	5.73	0	44*	55	0	0	1

\*Sulfide contribution is 27%; disulfide ( $\pm$  polysulfide) contribution is 17%.

TABLE 2: Derived percentages for forms of sulfur in coals treated with PCE.

Coal Sample treated with PCE	Wt% Total Sulfur	Sulfur Forms, %					
		Pyrite	Sulfur	Sulfide	Thioph.	Sulfone	Sulfate
Freeport, before	3.75	1.8	0.65	0.25	0.85	0.0	0.2
Freeport, after	3.10*	1.9	0.0	0.25	0.7	0.0	0.25
Indiana #5, before	2.50	0.85	0.35	0.4	0.4	0.05	0.45
Indiana #5, in situ	(2.25)	(0.85)	0.2	0.3	0.4	0.05	0.45
Indiana #5, after	1.90	0.85	0.0	0.25	0.4	0.05	0.35

Pyritic sulfur values from Mössbauer spectroscopy.

\*Total sulfur estimated as (Total sulfur of coal before - sulfur removed)

Values in ( ) are estimated values, assuming no change in pyritic sulfur.

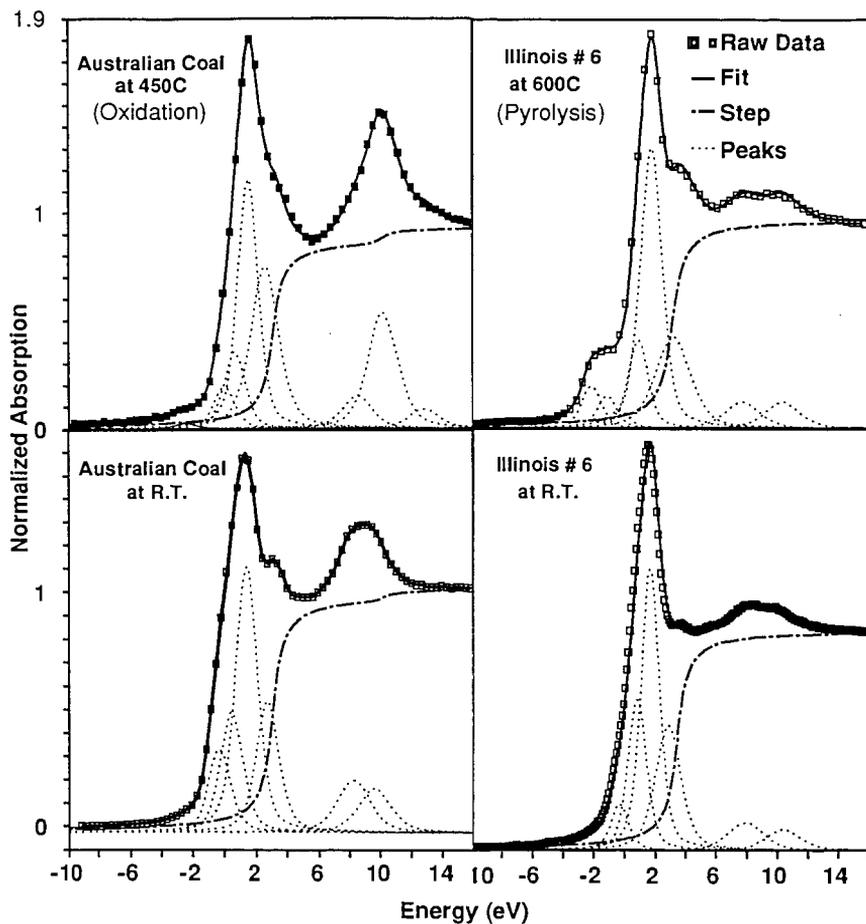


Figure 1. (Right) Fitted XANES spectra of the Illinois # 6 coal obtained at room temperature and at 600C in helium. (Left) Fitted XANES of Australian brown coal at room temperature and at 450C in a helium-oxygen mixture.

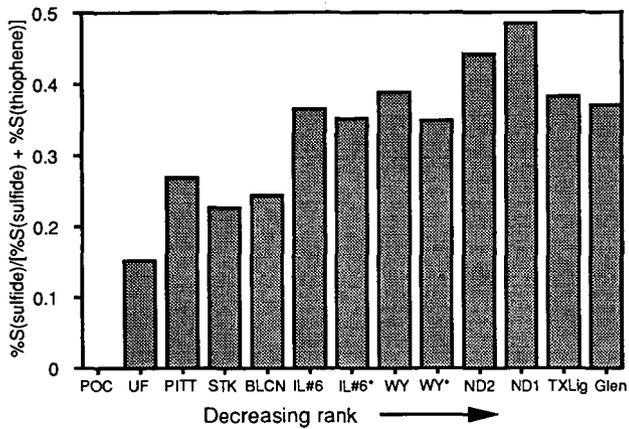


Figure 2: %S(sulfide)/[%S(sulfide)+%S(thiophene)] ratio plotted as a function of rank for the Argonne Premium Coal samples and a number of additional coals. The samples marked with a \* are float samples of Illinois #6 and Wyodak coal obtained from Southern Illinois University. Results for two samples of APCS Beulah-Zap, ND1 and ND2, are also shown.

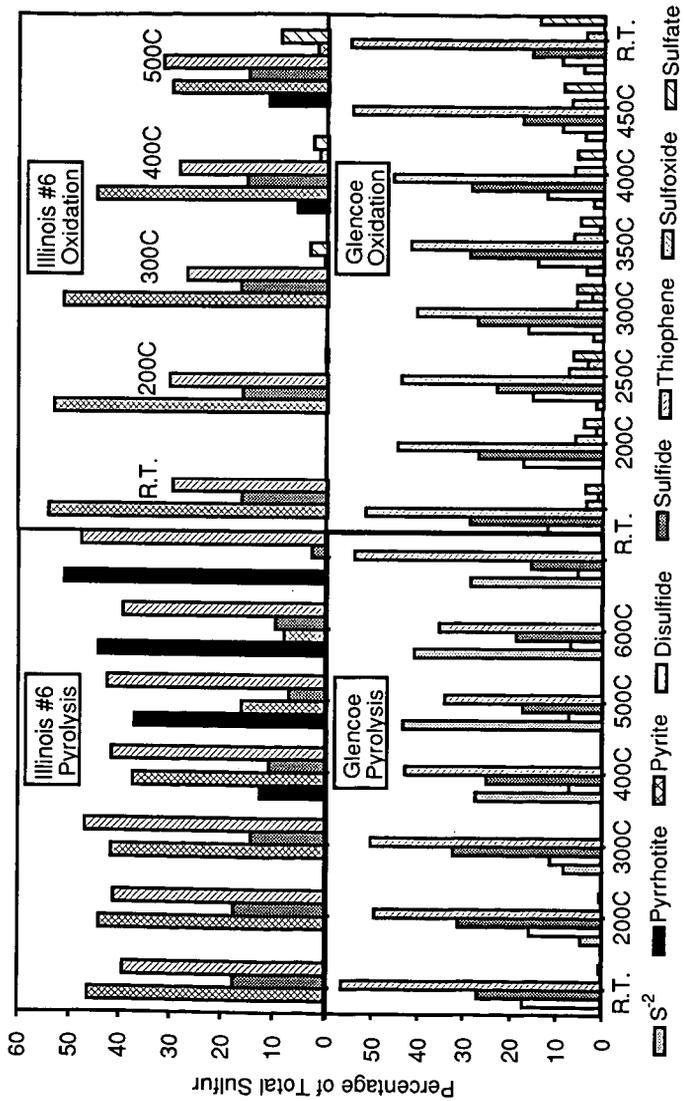


Figure 3. Percentage of sulfur in various functional forms determined by in situ XAFS spectroscopy as a function of temperature for: Illinois # 6-Pyrolysis (upper left); Illinois # 6-oxidation (upper right); Glencoe-Pyrolysis (lower left); Glencoe-oxidation (lower right).

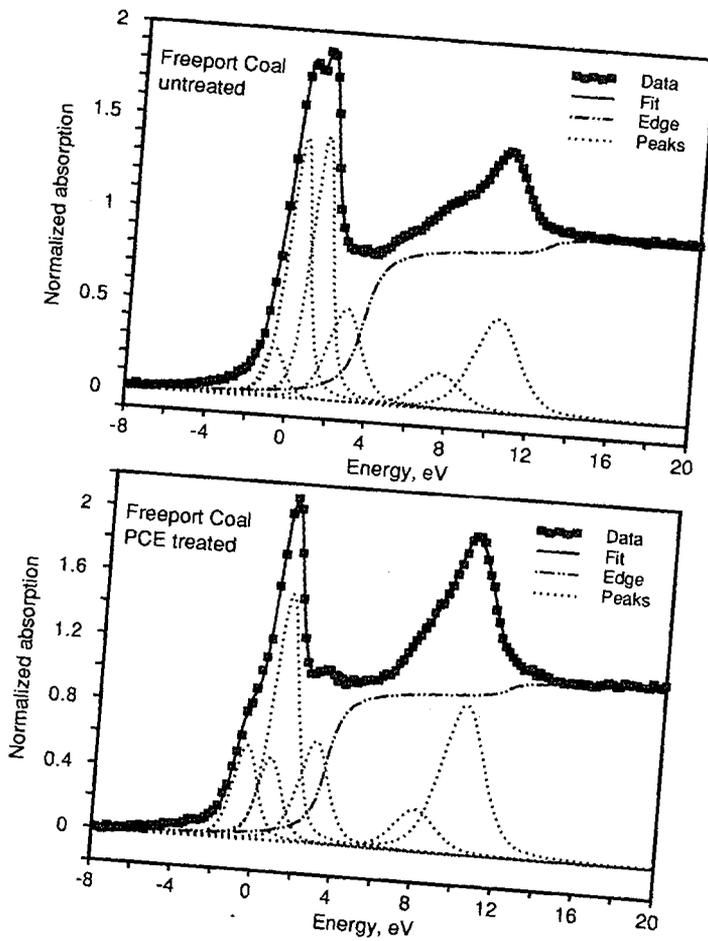


Figure 4: Least-squares fitted sulfur K-edge XANES spectra of Freeport coal before and after treatment with perchloroethylene (PCE).