

SULFUR SPECIATION STUDIES IN COAL AND OTHER FOSSIL ENERGY MATERIALS BY S K-EDGE XANES SPECTROSCOPY

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Keywords: sulfur speciation, XANES, XAFS, rubber, resids, coal.

ABSTRACT

Sulfur K-edge XANES spectroscopy has been shown to be an excellent technique for quantitative speciation of sulfur in fossil fuels. Earlier studies focused on establishing the method and applying it to sulfur speciation in coal. More recently, it has been applied to a variety of additional problems, including investigation of coal desulfurization processes, and speciation of sulfur in such materials as asphalts, kerogens/asphaltenes, coal liquefaction resids, and rubber. Some of the more interesting results from this research will be presented. Additionally, a comparison will be made of sulfur K-edge and L-edge XANES results for the same coal.

INTRODUCTION

Sulfur K-edge x-ray absorption fine structure (XAFS) spectroscopy has been shown to be an excellent method of speciating the sulfur in coal and related materials. Two methods have developed for sulfur speciation which involve analysis of the x-ray absorption near-edge structure (XANES) region of the XAFS spectrum. The method developed by Gorbaty and coworkers[1-3] analyzes the XANES by a third derivative method, which yields peaks whose heights are proportional to the percentages of sulfidic and thiophenic sulfur. In the method developed by our group[4-6], a direct least squares analysis of the XANES is carried out by fitting it to a series of mixed Lorentzian-Gaussian peaks. The peak areas are then used to determine the percentages of different sulfur forms present, using empirically determined calibration constants.

In the current article, we will briefly review some recent applications of this technique. These include speciation of sulfur in desulfurized coals, asphalts, coal liquefaction resids, and rubber. A comparison will also be made of sulfur speciation by sulfur K-edge and L-edge XANES spectroscopy for one coal.

RESULTS AND DISCUSSION

The experimental procedures used in these experiments have been discussed in detail elsewhere[3-6]. We will merely note that all experiments were carried out on beamline X-19A at the National Synchrotron Light Source (NSLS) in the fluorescent XAFS mode, using a Si(111) double crystal monochromator and a Lytle detector.

Desulfurization studies: XANES results for coals desulfurized by a number of methods have been summarized in recent papers[7,8]. Here we will briefly the principal results for different desulfurization methods.

Perchloroethylene(PCE) treated samples: Results have been obtained for a fairly large number of samples before and after extraction with boiling PCE. For the samples investigated to date, it is concluded that the primary effect of the treatment is to remove elemental sulfur. The samples which show elemental sulfur before treatment normally also exhibit a significant amount of sulfate, indicative of oxidation. Fresh coals are unaffected by PCE treatment, suggesting that an oxidative step is required to produce the elemental sulfur that is removed by PCE. These results are discussed in detail in reference 8.

Treatment with single electron transfer(SET) and basic reagents: Chatterjee and Stock have discussed the removal of organic sulfur by treatment with SET[9] and basic reagents[10]. A suite of these desulfurized coals have been investigated by XANES spectroscopy using both the third derivative method of Gorbaty et al.[11] and the least squares analysis method[7]. The results for the raw coal, an Illinois #6 from the Argonne Premium Coal Sample Bank, are similar to those reported earlier[4]. After treatment with lithium aluminum hydride(LAH), all of the pyrite is removed, and the percentage of organic sulfide appears to have decreased somewhat relative to thiophenic sulfur. Following SET treatment, the thiophenic sulfur percentage is significantly decreased, while the BASE treatment produces a substantial decrease in sulfidic sulfur, exactly as proposed by Stock and Chatterjee[9,10]. The results are obscured somewhat, however, by the appearance of an unidentified sulfide peak in the spectra of the treated coals, which is believed to be due to potassium sulfide.

Biological desulfurization: XANES has been used to investigate two samples of Illinois #6 coal before and after biodesulfurization using the microbe *Rhodococcus rhodochrous* by Kilbane[12]. Pyrite was removed from the coal before biotreatment, leaving a sulfur distribution that consisted of approximately 48% thiophenic sulfur, 31% sulfidic sulfur, 10% sulfate and minor amounts of other components. Following biotreatment, the organic sulfur content was reduced by approximately 2 wt.% and 1 wt.% for two separate samples. The relative percentages of the various sulfur functional forms, however, was unchanged within the error of the measurement(\pm 5%), indicating that the biotreatment does not discriminate between different sulfur forms.

Molten caustic leaching: A molten caustic leaching process has been developed by TRW Corporation for the removal of sulfur and ash from coal[13]. The results obtained by least squares analysis of the XANES for a Kentucky #9 and a Pittsburgh #8 coal subjected to this process establish that the forms of sulfur are drastically changed and reduced[7]. Specifically, no pyrite or organic sulfide remain, and thiophenic sulfur, which is the dominant organic sulfur form in the original coals is reduced to only about 0.1% in the treated coals. Elemental sulfur, sulfone, and sulfate are the dominant sulfur species remaining at levels of approximately 0.2%, indicating rather severe oxidation.

Sulfur speciation in asphalts: The sulfur functional groups present in a

number of asphalt samples were determined by least-squares analysis of their sulfur K-edge XANES spectra[14]. In unoxidized asphalts, oxidized sulfur forms are generally absent, and the principal sulfur form observed is thiophenic. Thiophenic sulfur varied from 54% to 78% of the total sulfur, with the balance being primarily sulfidic. Oxidation tests aimed at mimicing asphalt ageing were carried out at the Western Research Institute. Comparison of the sulfur forms before and after oxidation shows that only the aliphatic sulfur oxidizes to sulfoxide.

Sulfur speciation in rubber: Recently, we completed an XANES analysis of the sulfur forms in rubber tread material provided by Michelin. This is the same rubber used by Farcasiu and Smith in experiments on the coliquefaction of rubber and coal[15]. The XANES spectrum of this rubber is shown in Figure 1. As seen, the major feature of the spectrum can be deconvoluted into the $s \rightarrow p$ transition peaks of polysulfide(0.0 eV), monosulfide(0.8 eV), and thiophenic sulfur(1.5eV). The conversion of peak area percentages into sulfur percentages gives the following results: polysulfides - 38%; sulfides - 29%; thiophenes - 27%; and sulfoxides - 5%. The polysulfides, and possibly the sulfides, are believed to be the sulfur chains formed between polymer chains during vulcanization. A more detailed summary of this work will be prepared for publication elsewhere.

Sulfur speciation in coal liquefaction resids: Sulfur speciation has been carried out on THF soluble extracts from a series of coal liquefaction resids from Wilsonville and on the resids themselves. In the resids, pyrrhotite derived from added iron catalyst is the dominant sulfur form. In the extracts, thiophenic sulfur is dominant, sulfidic sulfur is low relative to the original coals, and most samples exhibit some oxidized sulfur, principally sulfoxide and sulfone.

Comparison of sulfur K-edge and L-edge results: Recently, Brown et al.[15] have examined the sulfur in coal by sulfur L-edge XANES spectroscopy. Analysis of the sulfur forms in Mequinenza lignite[16] by L-edge XANES gave the following results: 40% thiophenic(4.0 wt%), 20% aryl sulfide, 20% aliphatic sulfide, and 20% disulfide(2.0 wt.% for each sulfide form). The K-edge spectrum of this sample is shown in Figure 2. The major white line component was fitted to three peaks that correspond, with increasing energy, to di/polysulfide, organic sulfide, and thiophenic sulfur. Minor amounts of sulfoxide and sulfate are also observed. The results for the percentages of total sulfur and the wt.% of sulfur in each sulfur form identified are summarized in Table 1. Generally speaking, the results for sulfur speciation by K-edge and L-edge spectroscopy agree within the error of the measurements if the aryl and aliphatic sulfide categories of the L-edge measurement are combined for comparison to the K-edge organic sulfide category.

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Table 1
Results of Least-Squares Fitting of
Sulfur K-edge Spectrum of Mequinenza Lignite

<u>Sulfur Form</u>	<u>% of Total Sulfur</u>	<u>Wt% S in Lignite¹</u>
Pyritic Sulfur	nd	(<0.5)
Di-sulfide	10	1.0
Sulfide	33	3.3
Thiophenic	42	4.2
Sulfoxide	9	0.9
Sulfone	0	0.0
Sulfate	5	0.5

¹Based on 10.0 wt% (dry) non-pyritic sulfur in lignite. nd - Not determined

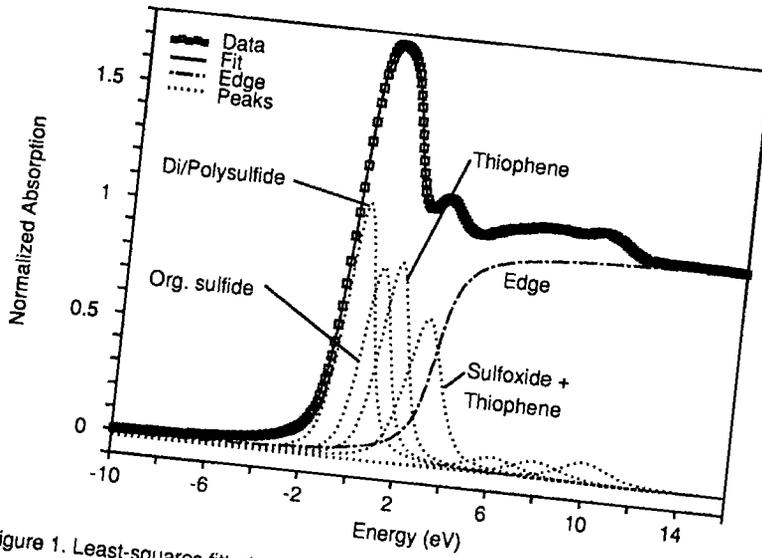


Figure 1. Least-squares fitted sulfur K-edge XANES spectrum of rubber tread material.

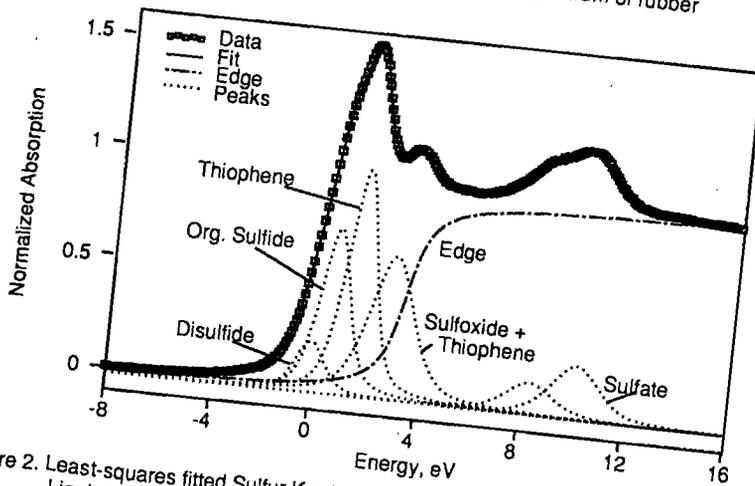


Figure 2. Least-squares fitted Sulfur K-edge XANES spectrum of Mequinenza Lignite