

THE FORMS OF TRACE METALS IN AN ILLINOIS BASIN COAL BY X-RAY ABSORPTION FINE STRUCTURE SPECTROSCOPY

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Abstract

Utilities burning Illinois coals currently do not consider trace elements in their flue gas emissions. After the US EPA completes an investigation on trace elements, however, this may change and flue gas emission standards may be established. The mode of occurrence of a trace element may determine its cleanability and flue gas emission potential. X-ray Absorption Fine Structure (XAFS) is a spectroscopic technique that can differentiate the mode of occurrence of an element, even at the low concentrations that trace elements are found in coal. This is principally accomplished by comparing the XAFS spectra of a coal to a database of reference sample spectra. This study evaluated the technique as a potential tool to examine six trace elements in an Illinois #6 coal. For the elements As and Zn, the present database provides a definitive interpretation on their mode of occurrence. For the elements Ti, V, Cr, and Mn the database of XAFS spectra of trace elements in coal was still too limited to allow a definitive interpretation. The data obtained on these elements, however, was sufficient to rule out several of the mineralogical possibilities that have been suggested previously. The results indicate that XAFS is a promising technique for the study of trace elements in coal.

Introduction

Currently, Illinois utilities are exempt from having to consider their trace element flue gas emission; however, this may eventually change after the U. S. EPA completes its risk analyses and establishes emission standards. The mode of occurrence of a trace element may determine its cleanability and flue gas emission potential. Trace elements associated with clays and minerals can be reduced by cleaning and those minerals highly dispersed in the coal may be further reduced by advanced cleaning techniques. Also, the volatility of trace elements associated with the organic matrix is different than the volatility of trace elements associated with the inorganic fraction of the coal.

From previous studies of specific gravity testing, many trace elements (such as As, Cd, Mn, Th, and Zn) were shown to have predominantly inorganic/mineral association¹. Some elements (such as Be and B) exhibit an organic/maceral association while others (such as Co, Ni, Cu, Cr, and Se) indicate a mixed behavior resulting from different compounds or possibly being highly disseminated in the coal¹. Recently, a database of trace element concentrations in a set of 34 commercially utilized coals from the Illinois Basin, which included the Illinois #6 coal used in this investigation, was established². These data on cleaned and washed samples were compared with those on a set of 222 channel or equivalent samples in the Illinois State Geological Survey records, which represented coal in-place prior to mining and cleaning. A comparison of results indicated that with the exception of uranium (U) and vanadium (V), all other trace elements are reduced in the washed samples as a result of coal cleaning. This phenomenon could suggest that most trace elements may be associated with mineral matter and the U and V in coal may be associated with the organic portion of the coals.

The possibility of misleading results from previous investigations for organic/inorganic association of trace elements in coal was indicated by many investigators. For example, Finkelman stated that most studies so far offer "little beyond the very rudimentary, and possibly misleading, organic/inorganic affinity of an element" in coal³. Clarke and Sloss in their review stated that "Genuine organic affinity (organic bonding) has been overestimated in the past, and simple classifications based on rudimentary organic or inorganic affinities may be misleading⁴." It is important to verify previous results with a direct method of determination. This study was conducted to evaluate XAFS techniques as a direct, nondestructive method to determine the mode of occurrence (organic/inorganic affinity) of trace elements in coal.

Experimental

X-ray Absorption Fine Structures (XAFS) spectroscopy, a synchrotron-based technique, is direct and nondestructive. XAFS spectra for Ti and V were obtained at beam-line X19A of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory, and the XAFS spectra for Cr, Mn, Zn, and As were obtained at beam-line IV3 of the Stanford Synchrotron Radiation Laboratory. Essentially identical experimental procedure was carried out at the two synchrotron facilities. Samples of the coal were exposed to monochromatic X-rays and the fluorescent radiation emitted in response to the X-ray absorption process was detected in a 13 Ge-element solid-state detector. Normally, a scan was made from about 100 eV below the K absorption edge of the element of interest to as much as 1,000 eV above the K-edge. The individual signals recorded in each channel of the 13 Ge-element detector were combined into a single spectral scan. In addition, multiple scans were made for most elements and these scans were also combined to provide a single spectrum for each element. Hence, for most elements, the spectra shown in this paper represent 3 to 5 hours of spectral accumulation time. All spectra were collected and stored on a computer and were transferred electronically to a similar computer at the University of Kentucky for analysis.

The XAFS spectra obtained from different elements in the coal sample were divided into two separate regions: the X-ray Absorption Near-Edge Structure (XANES) region (from -20 to 100 eV of the absorption edge) and the Extended XAFS (EXAFS) region (from 30-50 eV above the edge to the high-energy limit). The XANES region was used directly as a fingerprint, whereas the EXAFS region was mathematically manipulated further to obtain a radial structure function (RSF) which provided information on the coordination environment of the element. For trace elements, the EXAFS structure is usually only useful if the element is somewhat concentrated (>50 ppm) or if the element is surrounded by heavy elements. Hence, as a consequence of this and other complications, the interpretation of the elemental mode of occurrence was based solely on the XANES region in many cases.

Results

Using the data previously obtained on average concentrations of trace elements in coal, a representative Illinois #6 coal sample was chosen for this study². XAFS/XANES spectra were interpreted by comparing them to the spectra of standard compounds. Also, Ti and Mn XAFS spectra of an Argonne #3 coal sample (an Illinois #6 coal from the Argonne Premium Coal Sample) and the Zn XAFS spectra of coals previously studied¹ were compared with those in this study. The data obtained for the six trace elements in the coal are described as follows:

Arsenic: The Illinois #6 coal as well as its extensively oxidized sample was examined (Figure 1). In both spectra, two distinct peaks were observed, indicating two different forms of arsenic present in these samples. The peak to the negative side of 0 eV arose from arsenic in pyrite (FeAsS), while the higher energy peak arose from an arsenate (AsO_4^{3-}) phase, formed by oxidation of the arsenic in pyrite^{6,7}. These assignments were confirmed by examining the RSF derived from the EXAFS region. Although the noise level was high for the arsenic XAFS spectrum of this sample, the RSFs for the two spectra did correctly locate the major peak for the dominant forms at about 2.05 Å for arsenic in pyrite and at about 1.30 Å for the arsenate anion (Figure 2).

Zinc: The spectrum for zinc in the Illinois #6 coal (Figure 3) was strong and was clearly derived largely from zinc sulfide (ZnS). The spectrum was consistent with that seen for other coals from the same seam¹. The RSF derived from the EXAFS region for Zn was examined and found to be very similar to that from a ZnS standard (not shown).

Titanium: The titanium spectrum had a relatively weak pre-edge peak at about 3 eV and a broad main peak between 20 and 30 eV that consists of two components (Figure 4). The form of Ti cannot be identified. The spectrum was very similar to that from Ti in Argonne #3 that was examined previously¹. Also, because no sharp minor features were discernable in the spectrum, and because the small pre-edge peak did not exhibit any apparent splitting, virtually all common minerals (rutile, anatase, sphene, Ti-illite, etc.) can be eliminated as being a major contributor to this spectrum.

Vanadium: The University of Kentucky has no database to draw upon to interpret V XAFS/XANES spectrum obtained; however, a V rich Kentucky #9 was extensively studied by Maylotte et al^{8,9}. The spectrum of Illinois coal (Figure 5) had a sharp pre-edge feature at about 4 eV which was indicative of either a highly distorted V^{3+} environment or an unusual V^{4+} compound. This was followed by a two broad peaks from 10 to 30 eV. The spectra of the Illinois #6 coal was similar to the spectra of the float fraction of a Kentucky #9 coal reported by Maylotte et al^{8,9}.

Chromium: A very weak pre-edge peak at about 2 eV above the K-edge calibration zero-point indicates that all (>95%) of the chromium was present as Cr³⁺; there was no evidence for the more toxic Cr⁶⁺ oxidation state (Figure 6). The detection limit was about 5% for Cr⁶⁺ for this technique. The Cr spectrum for the Illinois #6 coal was similar to those for Cr in most bituminous coals^{6,7}. Such a spectrum of the Illinois coal was tentatively identified as being derived from a chromium oxyhydroxide (CrOOH) phase.

Manganese: The spectrum from the Illinois #6 coal used in this study (Figure 7) was quite different from that from Argonne #3⁵ and, except for a weak feature at about 17 eV, appeared to have a profile that was more similar to that of Mn in a lignite (Beulah lignite, ND)⁵. Additional study using a simulated sample which composed of calcite, illite, and carboxyl material was conducted. The results (Figure 7) suggested its mineral association of calcite and illite and its organic association of carboxyl material.

Summary and Conclusions

For the elements As and Zn, the present XAFS data provided a definitive interpretation of the predominant mode of occurrence in the specific sample of Illinois #6 coal investigated. The Zn in this coal was predominately ZnS. The As occurs as either pyritic arsenic or arsenate, and predominately in the arsenate form after extensive oxidation.

For the elements Ti, V, Cr, and Mn; the database of XAFS spectra of trace elements in coal was still too limited to allow definitive interpretations; however, the data obtained on some of these elements were sufficient to make preliminary interpretations. For Ti, the XANES spectrum was sufficient to rule out the minerals suggested previously¹⁰. The fact that the V XAFS spectra for the Illinois #6 coal was similar to the float fraction of the Kentucky #9 coal may indicate that V was associated with the organic fraction of coal. Most of the Cr in this coal was tentatively identified from coming from a CrOOH phase, but more importantly, the more toxic Cr⁶⁺ oxidation state was ruled out from being present in this coal (<5%). The Mn in coal appears to be associated with both mineral (calcite and illite) and organic (carboxyl) phases.

In general, XAFS is a promising technique to determine the mode of occurrence of trace elements in coals. However, more investigations on various coals and standard compounds to produce a larger database should be helpful in drawing solid conclusions for spectrum interpretation. Also, greater understanding of the modes of occurrence of trace elements may help control there flue gas emission.

Acknowledgment & disclaimer

This study was supported, in part, by grants made possible by U.S. department of Energy (DOE) Cooperative Agreement Number DEFC22-PC92521 and the Illinois Coal Development Board (ICDB) and the Illinois Clean Coal Institute (ICCI). Neither authors nor any of the subcontractors nor the U.S. DOE, ISGS, ICDB, ICCI, nor any person acting on behalf of either assumes any liabilities with respect to the use of, or for damages resulting from the use of, any information disclosed in this paper.

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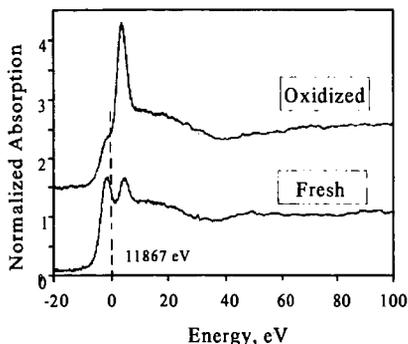


Figure 1: The As XANES spectrum of the fresh and oxidized Illinois #6 coal.

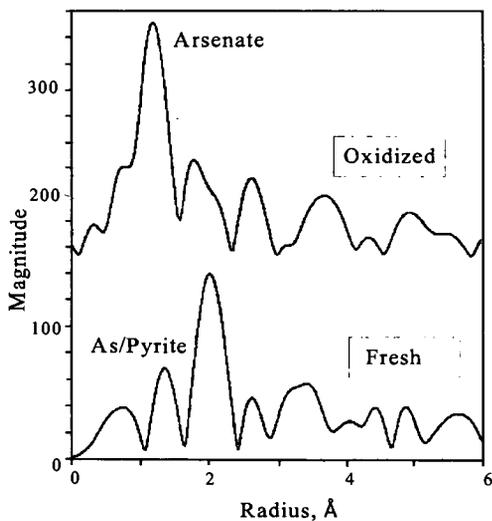


Figure 2: The radial structure functions for the fresh and oxidized coal from their As EXAFS spectrum.

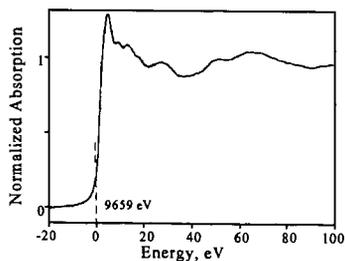


Figure 3: The Zn XANES spectrum.

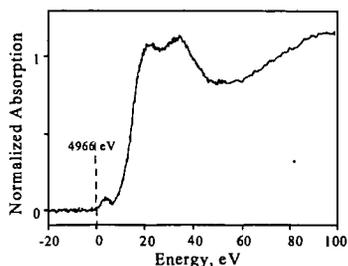


Figure 4: The Ti XANES spectrum.

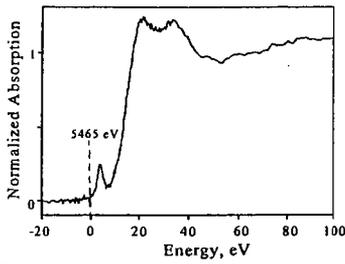


Figure 5: The V XANES spectrum

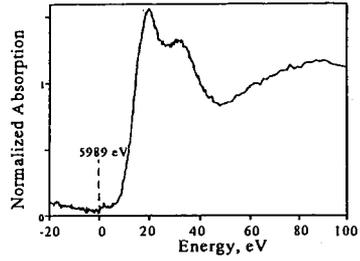


Figure 6: The Cr XANES spectrum.

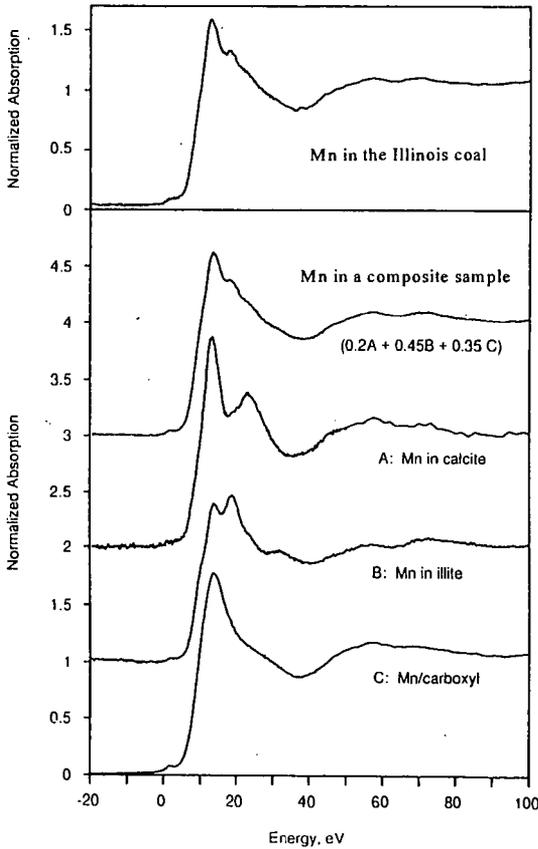


Figure 7: The Mn XANES spectra of the Illinois coal, a composite sample and samples of calcite, illite and carboxyl material.