

## APPLICATION OF XAFS SPECTROSCOPY TO THE SPECIATION OF CRITICAL TRACE ELEMENTS IN COAL UTILIZATION

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### ABSTRACT

The environmental impact of specific trace element species in coal utilization and waste disposal depends not only on the abundance, but also on the form(s) of occurrence of the element present in such materials. While there are a number of analytical methods for determining the abundance of trace elements in coal, there are very few methods available for determining the form of occurrence (speciation) of a trace element in coal at abundances as low as 10 ppm. In this report, the potential of XAFS spectroscopy for trace element speciation is demonstrated by means of measurements on two important trace elements, arsenic and chromium, in coal and ash.

### INTRODUCTION:

In the United States in recent years, almost one billion tons of coal have been mined each year, of which 85-90% is used for electrical power generation [1]. Combustion of such huge tonnages of coal has the potential to release vast amounts of undesirable elements into the U.S. environment. For example, for an element such as arsenic that occurs in many U.S. coals only at the 10 - 50 ppm level [2,3], there is the potential for 10,000 - 50,000 tons of arsenic to be released to the environment from coal utilization annually. Some of the arsenic may be removed by coal washing, some will be trapped in the solid products (ash and slag) of coal combustion, some will be collected in fly ash, and some will escape to the environment in combustion gases and fugitive emissions. The collected wastes from coal washing and combustion are often dumped into ash settling ponds, where, due to aqueous leaching of the wastes, there is additional opportunity for arsenic to enter the environment through groundwater. Such a scenario will be followed by many of the eleven trace metal species identified as potentially hazardous to the environment by the 1990 Amendments to the Clean Air Act.

It is clear that the environmental impact and hazard assessment of a specific element in coal combustion is a highly complex issue. For instance, it is apparent that minimization of an element's contribution to degradation of air quality either by coal cleaning prior to combustion or by efficient capture of fly ash and effluent gases in scrubbers after combustion may exacerbate problems with groundwater quality because of the leaching and reactivity characteristics of higher amounts of the element in cleaning or combustion wastes. Moreover, little is known about the forms-of-occurrence of most trace elements in coal, ash and other wastes and how such factors might influence the behavior of the element during combustion and its segregation into various solid and gaseous forms during cleaning, combustion, and waste disposal.

In order to understand the behavior of a given element in coal combustion and waste disposal and perhaps remedy some of the potential problems associated with environmental contamination by hazardous trace elements, it is not enough just to determine the amount of an element in the coal and various waste fractions. It is essential to know also how the element

occurs in the coal and other fractions. The mode or form of occurrence of the element in the coal (i.e., whether the element forms a specific mineral, whether it is dispersed within a particular host mineral or in the coal macerals, with which fraction of the coal the element is associated, in which oxidation state the element occurs in the coal, etc.) controls to a great extent the potential hazard posed by the element to human health and the environment.

There are many different methods of quantitatively determining the amount of an element in coal; such methods include atomic absorption, X-ray fluorescence, instrumental neutron activation analysis, proton induced X-ray or gamma-ray emission, inductively coupled plasma techniques, etc. However, there are very few methods for determining the forms of occurrence of a trace element in materials as complex as coal, ash, slags, and solutions (e.g. leachates). A technique that has excellent demonstrated potential for investigating the forms of occurrence of trace elements in coal and other materials is X-ray absorption fine structure (XAFS) spectroscopy [4-6]. This technique has the ability to focus on a specific element in a material and to provide detailed information relevant to the local bonding and structure of the element in the material, from which the form of occurrence can usually be deduced. Furthermore, this technique is both direct and nondestructive. In this report, the application of XAFS spectroscopy to the speciation of trace element species is demonstrated by a preliminary survey investigation of chromium and arsenic in coal and ash. Both of these elements have been identified as potentially hazardous to the environment in the 1990 Amendments to the Clean Air Act.

#### EXPERIMENTAL:

**Samples:** For this survey study, coal samples were obtained from a variety of sources. Samples unusually high in arsenic (up to 2,000 ppm) were provided by Dr. Leslie Ruppert at the U.S. Geological Survey [7]; the Upper Freeport coal in the Argonne Premium Coal Sample Bank (APCSB), which has an arsenic content of 17 ppm [3], was also investigated as its abundance of arsenic is more typical of that in the majority of U.S. coals. This coal was also subjected to laboratory float/sink tests; a 1.6 float sample, a 1.6 sink - 2.85 float sample, and a 2.85 sink sample were prepared by centrifugation using perchloroethylene ( $C_2Cl_4$ , sp. gr. 1.6) and bromoform ( $CHBr_3$ , sp. gr. 2.85) as the heavy liquid separation media. A raw coal with a typical ( $\approx 20$  ppm) chromium content and the corresponding clean coal after treatment by the spherical oil agglomeration process (SOAP) and the resulting ash samples were obtained from combustion studies performed at Physical Sciences, Inc., by Dr. J. Helble; coals with somewhat higher than average chromium contents (up to 140 ppm) were obtained from the Penn State Coal Bank.

**XAFS Spectroscopy:** XAFS spectroscopy was performed at beam-line X-19A at the National Synchrotron Light Source, Brookhaven National Laboratory. For chromium in coals and ash samples, the absorption of X-rays was measured over the spectral range from 5.9 keV to 6.2 keV; over the X-ray absorption near-edge structure (XANES) region (5.97 to 6.03 keV), absorption data were collected every 0.2 eV. For arsenic in coals and ash samples, the absorption of X-rays was measured over the spectral range from 11.75 keV to 12.0 keV; over the XANES region (11.85 to 11.90 keV), absorption data were collected every 0.25 eV. Absorption of the X-rays was measured by means of a thirteen-element germanium array detector [8] that detected the fluorescent X-rays only in a specified tunable energy window that corresponded to the energy of the chromium or arsenic fluorescent  $K_{\alpha}$  X-rays. In addition, the appropriate 6 $\mu$  vanadium or germanium filter was used to minimize background. Up to ten scans were recorded and summed for the weakest absorbers. The spectral summations, the pulse-height windowing, and the low-energy filtering all contributed to enhance the signal-to-noise ratio of the trace element spectra. For reference standards, conventional ion chambers were used to measure both the fluorescent and absorption XAFS spectra in a single scan. Depending on the amount of arsenic or chromium

in the standard, the standard was diluted in graphite to optimize the absorption spectrum. As is normally done, the chromium or arsenic XAFS spectra were divided into separate XANES and, where feasible, EXAFS regions and standard XAFS analysis methods were employed to analyze the spectral regions. The arsenic K-edge XANES spectra shown in this report are calibrated with respect to a zero energy point (11.867 keV) defined as the position of the white line in the spectrum of  $As_2O_3$  that was run simultaneously with all arsenic spectra. The zero energy point (5.989 keV) for chromium was defined as the first inflection point in the XAFS spectrum of chromium metal foil.

## RESULTS AND DISCUSSION:

Arsenic: Arsenic K-edge XANES spectra for three high arsenic coals from Alabama are shown in Figure 1. It is clear, by inspection, that the spectra are the combination of at least two distinct forms-of-arsenic as the white line features (the prominent peaks near 0 eV) consist of two components. All standards with a single oxidation state of arsenic investigated to date merely give a single component white line, the position of which shifts to higher energy with increasing formal oxidation state of the arsenic atom. Based on comparison of peak positions with standards, the lower-energy component is assigned to arsenic substituting for sulfur in the pyrite structure and the higher-energy component to arsenic in the arsenate anion ( $AsO_4^{3-}$ ). Furthermore, the radial structure functions (RSFs) derived from the EXAFS region for the high-arsenic coals also show two peaks at the appropriate distances for As-O bonds in arsenate anions and for As-Fe(S) bonds in pyrite (Figure 2). The relative heights of the two peaks in the XANES spectra show the same order as the relative heights of the corresponding peaks in the RSFs.

Arsenic K-edge XANES spectra of three Upper Freeport APCS B coal fractions are shown in Figure 3. In comparison to Figure 1, the signal-to-noise ratio is significantly lower, but the spectra are still informative. In the two fresh samples, there is essentially only one white line component, which arises from arsenic associated with pyrite; only a trace amount (<5% of the arsenic) is present in arsenate form, as indicated by the very small peak on the higher energy side of the white line. The arsenic XAFS spectra of these samples were measured just a few days after opening the APCS B vials. Similar measurements made on whole coal and float/sink samples of the Upper Freeport coal from APCS B vials that had been opened six months previously and left exposed to the laboratory atmosphere showed much greater amounts of arsenate, as for example in the spectrum of the oxidized 2.85 sink sample in Fig. 3. An ash sample prepared from an unrelated Upper Freeport coal showed that all of the arsenic was present in the arsenate form (bottom spectrum, Fig. 3)

Chromium: It is a relatively easy matter to discriminate by means of XAFS spectroscopy among the two most common oxidation states of chromium,  $Cr^{3+}$  and  $CrO_4^{2-}$ , found in natural and environmental samples. Chromium XAFS spectra of two chromic oxide and two chromate samples are shown in Figure 4. The chromate oxidation state is characterized by the presence of a large pre-edge feature at about 0 eV that is highly distinctive of first series transition metal  $3d^0$  species in tetrahedral coordination by oxygen anions. In addition, it should be noted that the maximum absorption in the chromate species occurs at about 40 - 50 eV, at which energy a minimum in the absorption occurs for the  $Cr^{3+}$  compounds. These observations appear to be quite general and to apply to all the chromium standards so far examined.

Figures 5 and 6 show chromium XAFS spectra obtained for coal and ash samples. In Figure 5 are shown spectra for the parent Illinois #6 coal and the SOAP cleaned coal. These spectra are virtually identical in appearance and clearly demonstrate that all (>95%) of the chromium is present in the  $Cr^{3+}$  oxidation state. In addition, the abundance of chromium in the two samples is essentially the same. These observations suggest that there is only one significant

chromium form of occurrence and that it is not strongly associated with the mineral matter, otherwise the chromium abundance would have dropped significantly upon cleaning and the XAFS spectrum would have shown significant variation. Chromium in the ash sample is also predominantly  $\text{Cr}^{3+}$ , although the spectral shape differs somewhat from that of the coal samples. The chromium XAFS spectra of the high chromium bituminous coals (Ohio #5 and Illinois #6) shown in Figure 6 are very similar to those shown in Figure 5. The spectrum of the anthracite sample, although similar to those of the bituminous coals, exhibits a somewhat sharper white line peak.

#### CONCLUSIONS:

This survey study demonstrates that XAFS spectroscopy is capable of obtaining significant information on the oxidation state and form of occurrence of trace elements that exist in coal at about the 10 ppm level. This information complements conventional analytical data on trace element abundances and provides additional information for evaluation of the potential environmental hazard of specific elements in coal combustion. For example, of the two oxidation states of chromium considered here, the  $\text{CrO}_4^{2-}$  oxidation state is both toxic and carcinogenic, whereas the  $\text{Cr}^{3+}$  oxidation state at such low concentration levels (<100 ppm) does not pose a significant health risk [9]. If the results of this study can be considered to be general, then the absence of the chromate state in both coal and ash would imply that the hazard posed by chromium in coal utilization is minimal. In contrast, the investigation of arsenic in coal and ash by XAFS reveals significant oxidation of the arsenic associated with pyrite to arsenate ( $\text{AsO}_4^{3-}$ ) species that can be easily leached from coal wastes and which may pose a significant health hazard.

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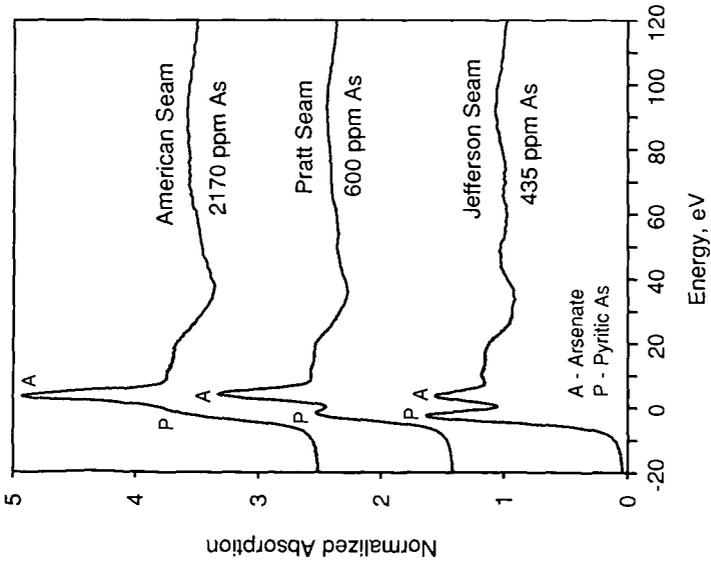


Figure 1: As K-edge XANES spectra of three high arsenic coal fractions from bituminous coal seams in Alabama.

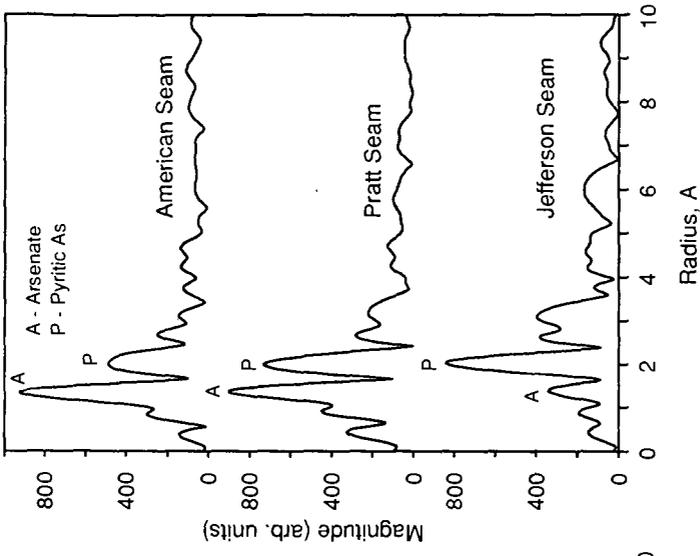


Figure 2: RSFs derived from EXAFS regions of As XAFS spectra for high arsenic coal fractions from Alabama.

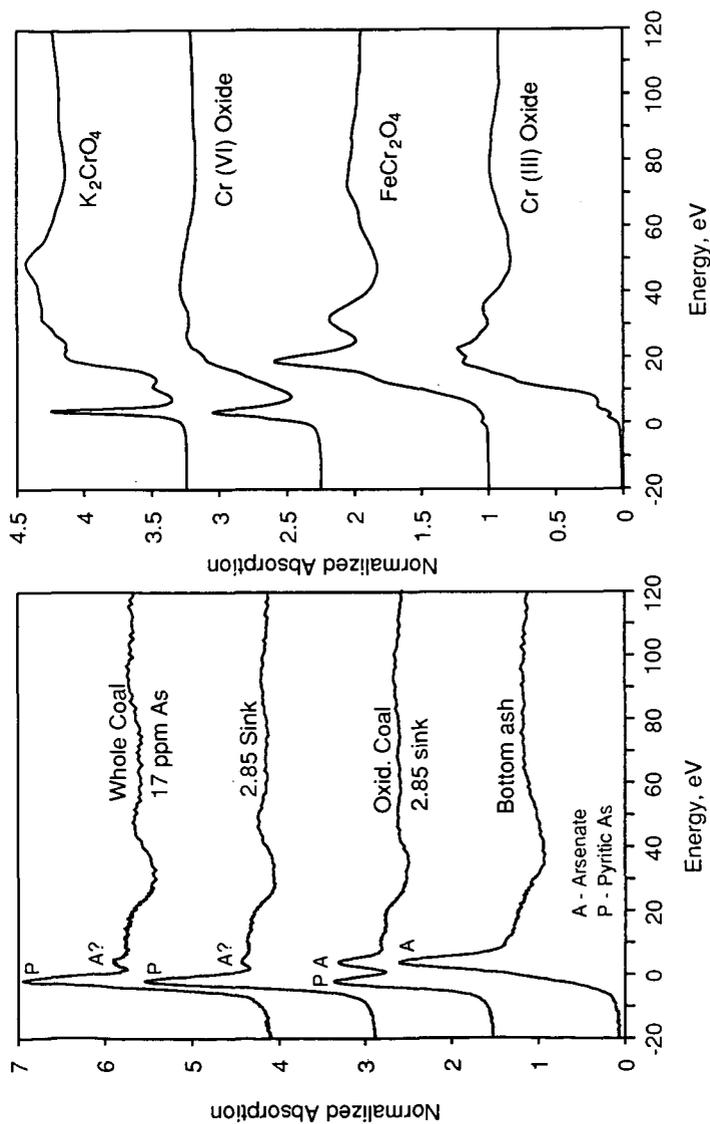


Figure 3: As K-edge XANES spectra of three Upper Freeport coal fractions and an ash sample.

Figure 4: Cr K-edge XANES spectra of two chromic and two chromate oxide reference standards.

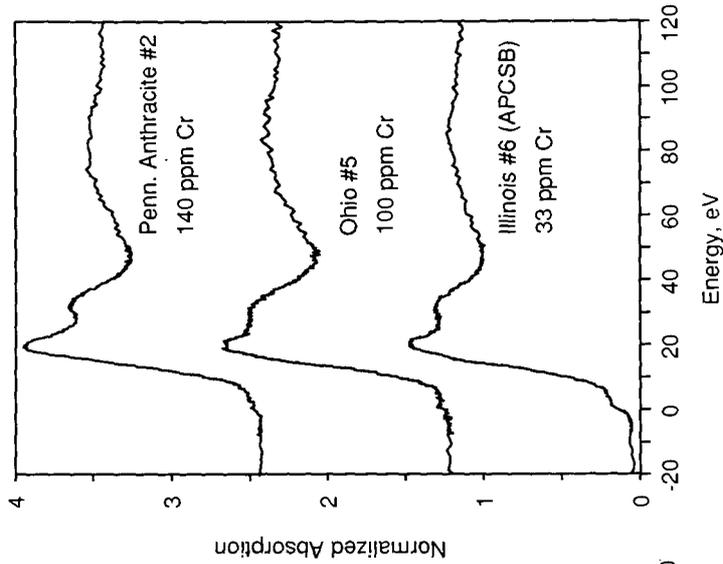


Figure 5: Cr XANES spectra of Illinois #6 parent coal, a cleaned coal, and a derived ash sample.

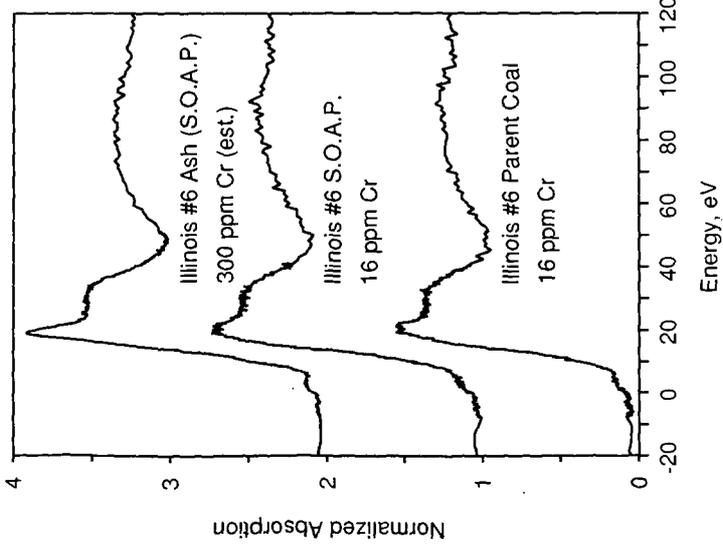


Figure 6: Cr XANES spectra of three high chromium coal samples.