

## FORMS OF OCCURRENCE OF ARSENIC IN COAL AND THEIR BEHAVIOR DURING COAL COMBUSTION

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### ABSTRACT

New information from XAFS spectroscopy on the occurrence of arsenic in U.S. bituminous coals shows that arsenic may be present in one or more of three distinct forms: (i) arsenical pyrite; (ii) arsenopyrite (FeAsS); and (iii) arsenate ( $\text{AsO}_4^{3-}$ ), most probably as a result of oxidation. In ash samples analyzed to date by XAFS spectroscopy the arsenic is present predominantly as arsenate species. Some preliminary data on arsenic capture efficiency during combustion suggest that the presence of arsenate in the coal may facilitate the retention of arsenic in combustion solids.

### INTRODUCTION:

A recent comprehensive study of ash formation during combustion of U.S. coals [1] has indicated the importance of the form-of-occurrence of an element in the coal for determining the behavior of major elements during pulverized coal combustion. Similarly, information regarding the forms of occurrence of minor and trace elements in coal and ash must also be obtained to understand their behavior during combustion and to assess whether or not the release of these elements during combustion poses a significant environmental hazard. One of the more critical trace elements in this regard is arsenic as its behavior can be variable. For example, large variations (from <1% to >50% of the total arsenic flux) were reported for arsenic concentrations in the vapor phase at a U.S. power station [2]; and, in trace-element mass balance studies at commercial power plants, arsenic in bottom ash has been shown to vary from as little as 0.5% to as much as 10% of the total arsenic, with the balance in fly ash, except for a very small fraction (<0.5%) that escapes in the flue gas [3]. It is likely that one of the more important factors that might influence the behavior of arsenic during combustion is the form of occurrence of arsenic in the coal.

In his comprehensive review of trace elements in coal, Swaine [4] lists the probable major forms of occurrence of arsenic as arsenical pyrite and arsenopyrite (FeAsS) based on observations (and speculations) made on various coals from around the world. In the U.S., there have been a few direct observations made on the forms of occurrence of arsenic in coal: such observations have been made using scanning electron microscopy [5,6], the electron microprobe [7,8], and other less direct methods [9]. These findings by and large confirmed the occurrence of arsenic as arsenical pyrite in most U.S. coals. In recent work [10,11], we have demonstrated the potential of XAFS spectroscopy as a direct and nondestructive probe for forms-of-occurrence information about trace elements in coal and ash down to concentration levels as low as 10 ppm. In this study, we will present new data on arsenic occurrences in various U.S. coals and derived ash materials.

## EXPERIMENTAL:

Samples: Various coals from the Argonne Premium coal sample bank (APCSB), from the Department of Energy Coal Sample (DECS) bank administered by D. Glick and A. Davis (Pennsylvania State University), and from miscellaneous sources were used in this study. Ash samples were prepared from some of these coals in a drop-tube furnace at PSI Technology (PSIT) Company or in a larger-scale combustion unit at the University of Arizona (UAZ). The drop-tube furnace was run at 1750 K and an oxygen content in the furnace atmosphere of either 7% or 10.5%. Ash samples were collected on filters; in the case of the UAZ combustion unit, an Anderson impactor was used to segregate the ash particulate matter by size. Arsenic contents of the coals were determined by either instrumental neutron activation analysis (INAA) or by proton induced x-ray emission (PIXE), although we have relied on published INAA analyses [12] for the arsenic contents of the APCSB coals. The same techniques were also used to determine the arsenic contents of ash samples.

XAFS Spectroscopy: XAFS spectroscopy was performed at beam-line X-19A at the National Synchrotron Light Source, Brookhaven National Laboratory. For arsenic in coals and ash samples, the absorption of X-rays was measured over the spectral range from 11.75 keV to as high as 13.0 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 [13] that detected the fluorescent X-rays only in a specified tunable energy window that corresponded to the energy of the arsenic fluorescent  $K_{\alpha}$  X-rays. 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. Other details of XAFS experimentation for trace element studies are given elsewhere [10,11].

## RESULTS AND DISCUSSION:

### Arsenic in Coal:

Preliminary XAFS work on the speciation of arsenic in coal [10,11] has shown that it is relatively easy to distinguish among the different arsenic oxidation states likely to be found in coals and other geological materials. This work showed that arsenic was present either in association with iron as in arsenical pyrite, in which arsenic substitutes for sulfur in the pyrite structure, or as an arsenate ( $AsO_4^{3-}$ ) species, presumably formed as a result of oxidation.

However, it is also essential for speciation studies of arsenic in coal to be able to distinguish between the discrete arsenic mineral, arsenopyrite ( $FeAsS$ ), and arsenical pyrite ( $FeS_2$ ). These two forms-of-occurrence of arsenic have been postulated to be the likely major forms of arsenic in coal [4]. The As K-edge XAFS spectra of arsenopyrite and arsenical pyrite are quite similar, but there are subtle differences that can be used to discriminate successfully between these alternatives in both the XANES and EXAFS regions of the spectra. Figure 1 compares the XANES and radial structure function (derived by Fourier transform of the EXAFS function,  $k^2 \cdot CHI$ ) spectra from the two materials. There are clearly more distinctive features, in both magnitude and structure, in the radial structure function (RSF), which is the most processed of these spectra. But even in the XANES spectra there are sufficient differences to discriminate between arsenopyrite and arsenical pyrite simply by inspection.

Such distinctions can be seen in arsenic XANES spectra of coals down to at least 10 ppm. Figure 2 shows the normalized XANES spectra of arsenic in three coals that vary in arsenic content from 17 ppm to 434 ppm. Of these coals, the Pittsburgh seam coal is unique in that its XANES spectrum is closely similar to that of arsenopyrite, whereas the remainder of the coals have features consistent with As in solid solution in pyrite. For the two coals richest in arsenic,

the radial structure functions are shown in Figure 3 and, upon comparison with the RSFs shown in Figure 1, the RSF spectra confirm the inferences based on the XANES spectra. As indicated by the extra white-line peak in the XANES spectrum and also by the peak at about 1.4 Å in the RSF, the Jefferson coal contains a significant fraction of its arsenic as arsenate. Even with this complication, it is clear that remainder of the arsenic in this coal is present in substitutional form for sulfur in pyrite.

XAFS spectra of arsenic were reported previously [10,11] from a suite of float/sink fractions from newly opened vials of the APCSB Upper Freeport coal and showed that the dominant arsenic form-of-occurrence was arsenical pyrite. Similar XAFS spectra were also obtained from the same samples after a three month interval, during which time the samples were stored in glass (not air-tight) vials, and from previously opened vials that had been opened for a number of months. The spectra of these samples were found to be significantly different from those obtained previously. As can be seen from Figure 4, the arsenate contents of these Upper Freeport coal fractions are significantly higher after just three months' storage at room temperature in closed glass vials. These observations confirm that the oxidation of arsenical pyrite to arsenate can occur extremely rapidly, even during storage at room temperature.

The data presented here and in previous preliminary studies show that there are at least three forms of occurrence of arsenic that may be found in laboratory samples of U.S. coals. Based on the limited number of samples examined to date, arsenical pyrite appears to be the most common of these forms, with arsenate as the next most common (although it is conceivable that this form is only formed as a result of oxidation during processing and storage), and arsenopyrite as the least common.

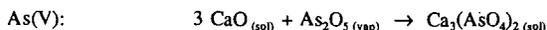
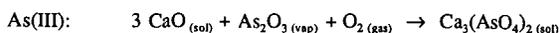
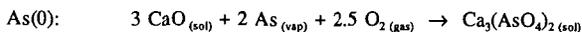
#### Arsenic in Ash:

The conversion of arsenic forms in coal to arsenic forms in ash as a result of combustion has been investigated for a number of ash samples prepared in the drop-tube furnace at PSIT Company or the combustion unit at UAZ. All of the ash samples derived from coal combustion that have been examined to date by XAFS spectroscopy contain arsenic predominantly, if not entirely, in the form of arsenate ( $\text{AsO}_4^{3-}$ ) complexes. Such complexes are readily recognized by the strong white line absorption at about 3 - 4 eV and the broad low intensity peak that is a maximum in the range 80 - 90 eV in the As XANES spectrum, and by the major peak at about 1.3 - 1.4 Å in the RSF of samples rich in arsenic. Figure 5 shows the As K-edge XANES spectra for the bottom ash collected in the UAZ combustion unit from combustion of Kentucky #9 coal and of the fly-ash samples collected in the same unit on an Anderson impactor, during combustion of Beulah (ND) lignite. In comparison to arsenate complexes of known crystal structure, the arsenic K-edge XANES spectra of this and similar bottom ash samples are relatively featureless: the white-line peak is relatively broad and there are no minor peaks in the 10 - 30 eV range and no obvious shoulders or inflection points on the broad peak in the range 50 - 100 eV. Such a lack of features is consistent with a mixture of different structural environments for arsenate complexes in these materials, such as those that might be expected if the arsenate complexes were assimilated in amorphous or glassy materials.

The spectra of the fly-ash samples collected in the UAZ combustion unit on an Anderson impactor, during combustion of Beulah (ND) lignite, begin to deviate from this pattern, particularly for the finer of the two fractions. In the spectrum of the fine fraction, the width of the white line is narrower and there is the obvious presence of a minor peak at about 20 eV in comparison to the coarse fraction. These observations are interpreted as indicating a significantly higher fraction of a crystalline arsenate occurrence in the finer fly-ash fraction than in the coarse fly-ash fraction.

Recent observations and theories on ash particulate formation involving major elements during pulverized coal combustion [1] have invoked two main mechanisms for ash particle formation: (1) evaporation of volatile species and condensation of phases from the vapor, and (2) partial or total fusion and agglomeration of mineral particles. The first mechanism commonly results in the formation of small particles of relatively well defined composition and crystallinity, such as alkali and alkaline-earth sulfates. The second mechanism results in the formation of partially molten aluminosilicate particles that incorporate varied amounts of basic elements. These latter particles tend to be much larger and are generally at least partially amorphous (glass) upon quenching. In such partially molten deposits, it is likely that  $AsO_4^{3-}$  species would be incorporated as a network former in aluminosilicate melts, in much the same way as phosphate anionic species ( $PO_4^{3-}$ ) are incorporated in such melts.

Alkaline-earth orthoarsenates are relatively stable compounds (calcium orthoarsenate melts only at temperatures above 1450°C and magnesium orthoarsenate would be expected to be almost as refractory) and consequently they are prime candidates as condensates from vapor phase arsenic species during combustion, especially of low-rank coals. Under combustion conditions, decomposition of arsenical pyrite or arsenopyrite will be rapid and release arsenic vapor, which should then readily oxidize to vaporous arsenic oxides. In the presence of oxygen, the following solid-vapor reactions will lead to the condensation of calcium orthoarsenate, depending on the oxidation state of arsenic in the vapor phase:



It is apparent that these reactions become simpler and involve fewer molecular species with increasing oxidation state of the arsenic. In particular, regardless of whether the transitory species in the vapor phase is the oxide,  $As_2O_5$ , or the anion species,  $AsO_4^{3-}$ , no additional oxygen is necessary in reactions involving the As(V) oxidation state as a reactant. Hence, the presence of arsenate in the coal might be expected to facilitate the formation of arsenate compounds during combustion and its capture on particulate matter. Furthermore, arsenate mineral species that are not associated with pyrite or arsenopyrite particles in the coal need not undergo vaporization, but may remain as discrete particles or be assimilated by partial fusion into other particles during combustion.

Comparison of the arsenic retention during combustion for the two DECS coals in the PSIT drop-tube experiments is tabulated below:

Coal	As (coal)	As (ash)	Wt% Ash	As cap. eff. <sup>1</sup>
Pittsburgh	70	31	10.0	0.04
Illinois #6	10	21	14.5	0.30

<sup>1</sup>Arsenic capture efficiency is defined as:  $As(ash)/(As(coal)/Wt\text{ fn. ash})$

It can be seen from this table that relatively little of the arsenic is captured on the filter and it is probable that arsenic in both vapor and submicron microparticulate matter may have avoided

the filter sampling process. From this tabulation, it would appear that the arsenic is captured more efficiently in the case of the Illinois #6 (DECS-2) coal than the Pittsburgh (DECS-12) coal. Although this would appear to be consistent with anticipated trends based on the forms of occurrence of arsenic in the original coals (the Pittsburgh coal contains virtually all arsenic as arsenopyrite, whereas about 40-50% of the arsenic in the Illinois #6 coal is oxidized to arsenate), it may be fortuitous because other factors in the combustion experiment and sampling process that might influence arsenic capture have not been considered.

#### CONCLUSIONS:

XAFS spectroscopy has identified three distinct arsenic occurrences in U.S. bituminous coals: (i) arsenical pyrite; (ii) arsenopyrite; and (iii) arsenate species, which may have formed from the other two forms by oxidation. This technique also indicates that, regardless of the original form of occurrence of arsenic in coal, all arsenic forms are oxidized to arsenate forms during combustion of coal. The presence of arsenate forms in the original coal may facilitate the retention of arsenic in ash; however, more work needs to be done to prove this point adequately.

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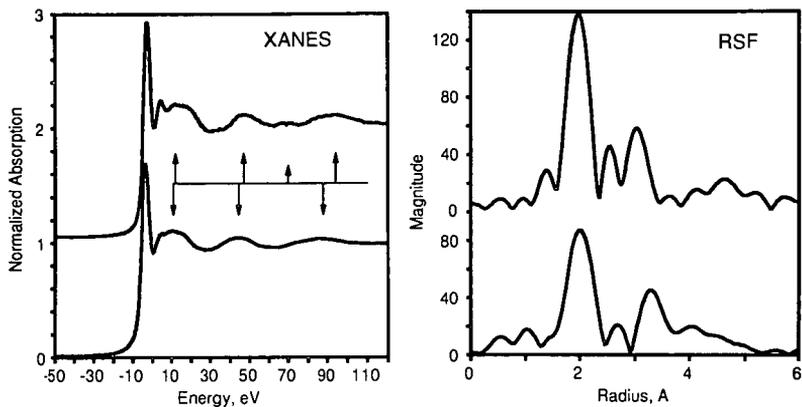


Figure 1: Comparison of XANES and RSF spectra for arsenic in arsenical pyrite (top) and arsenopyrite (bottom).

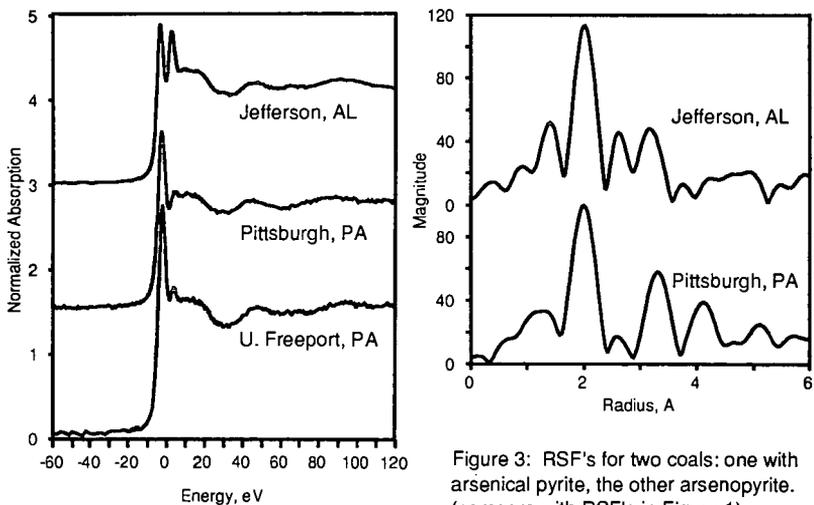


Figure 2: Arsenic K-edge XANES spectra for three U.S. bituminous coals

Figure 3: RSF's for two coals: one with arsenical pyrite, the other arsenopyrite. (compare with RSF's in Figure 1).

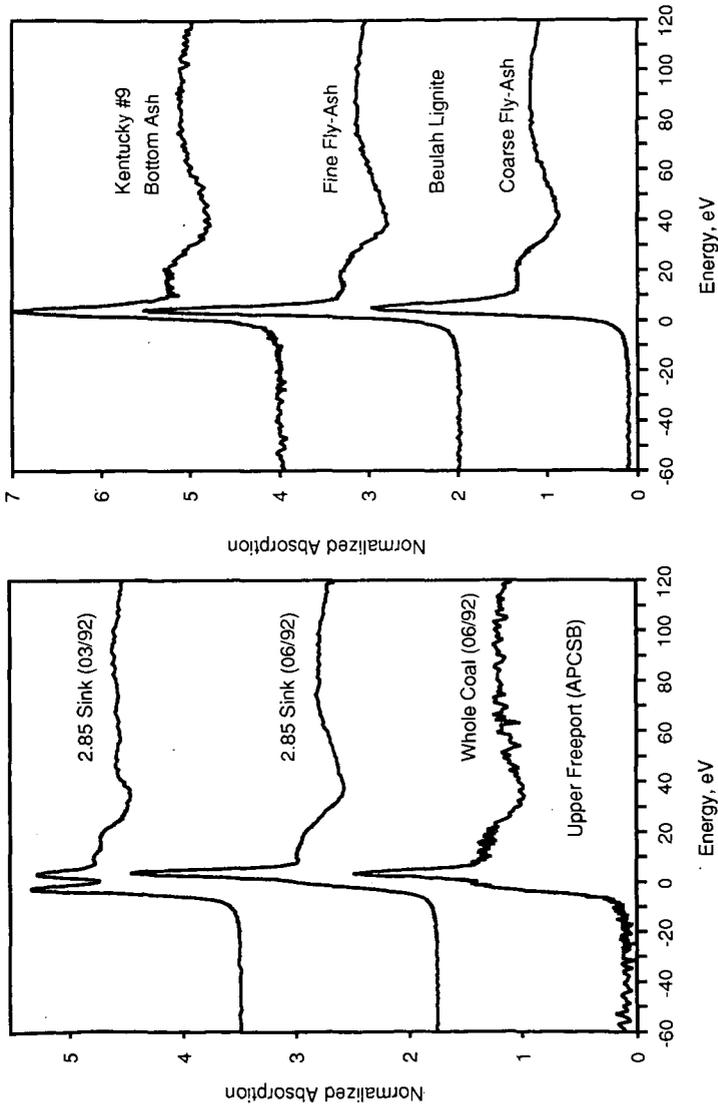


Figure 4: Arsenic K-edge XANES spectra for oxidized coals. (compare bottom spectra with that in Fig. 2)

Figure 5: Arsenic K-edge XANES spectra for ash samples collected in the University of Arizona combustion unit.