Mode of Occurrence of Arsenic in Feed Coal and its Derivative Fly Ash, Black Warrior Basin, Alabama

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INTRODUCTION

The phase residence and chemical form of arsenic (As) in fly ash influence the rate of As release to the environment and the As-related health risks associated with fly ash utilization and disposal. Arsenic has a strong affinity to concentrate in sulfide minerals and this association is well documented for some coals.[1] In contrast, the mode of occurrence of As in fly ash is less predictable and less understood. A recent study[2] suggested that calcium arsenate $Ca_3(AsO_4)_2$ is a probable host for As in fly ash.

The mode of occurrence of As in fly ash depends upon the composition of the original coal and its derivative fly ash, and on conditions during coal combustion, particularly during cooling. Arsenic is transferred to the gas phase at the temperature of coal combustion, but is mostly deposited on the fly ash particles via a proposed mechanism of surface condensation/adsorption.[3] Compared to other trace elements in fly ash, arsenic shows particularly strong enrichment (5-10X) in the finest (<10 micrometer diameter) size fractions of high surface area.[3,4] Direct observation of arsenic enrichment on surfaces of fly ash particles is analytically challenging because of the low parts-per-million (ppm) concentrations of As and the typically small particle size. Surface enrichment of As is inferred by analogy with observed surface enrichments of elements such as Pb, Cr, and V.[5] Surface enrichment is also suggested by leaching experiments that indicate rapid release of As.[2,6]

Herein we present preliminary observations of As occurrence in a high-As (55 ppm) feed coal from Alabama and its derivative fly ash. Fly ash was produced in a research combustor under controlled conditions designed to simulate commercial operations. Electron microprobe and SEM observations of As-bearing pyrite in feed coal are compared with previous observations of pyrite from coal mine dumps in Alabama.[7] Synchrotron-based x-ray absorption spectroscopy (XAS), laser ablation ICP-MS, and specialized leaching are used to describe the oxidation state, bonding environment, extent of surface residence, and probable solid phase residence of As in fly ash. The implications and general applicability of these findings are briefly discussed.

MATERIALS AND METHODS

Personnel of the Southern Research Institute (SRI), Birmingham, Alabama, graciously provided the bituminous coal (J438) and derivative fly ash used in this study. The Pennsylvanian-aged coal is

from a small surface mine in the Pratt coal bed of the Black Warrior coalfield, central Alabama. Minerals in the coal identified by x-ray diffraction include quartz, kaolinite, muscovite, and minor pyrite. Pulverized coal was combusted in a pilot-scale (3.5 ft X 26 ft) research combustor (2.5% furnace end O_2, 15% overfired air, 1300-1650°C at flame) and its derivative fly ash collected in a baghouse at 150°C. In addition to glass, the fly ash contains quartz, mullite, coal char, and iron oxides.

Total sulfur, forms of sulfur, and moisture, were determined on whole coal by ASTM methods. Mercury and selenium contents in whole coal were determined by cold vapor atomic absorption (CVAA) and hydride-generation atomic absorption (HGAA), respectively. Ash content was determined after heating to 525°C. Other chemical constituents in whole coal were calculated using the measured values in laboratory-ashed (525°C) coal and the ash percent. Major and minor elements and most trace elements were determined on coal ash, fly ash, and leach solutions by inductively coupled plasma-atomic emission spectrometry (ICP-AES) or-mass spectrometry (ICP-MS). Estimated accuracy and precision of all determinations is ±5-10% relative standard deviation (RSD).

A 20 g split of >2.0 mm coal was further crushed to <40 mesh (<0.425 mm) and processed with bromoform ($CHBr_3$) to recover pyrite. A polished grain mount of a dozen representative pyrite fragments (250-400 micrometer) was prepared for SEM observation and wavelength-dispersive analysis and elemental mapping of As, Fe, and S by electron microprobe The detection limit for As point-analyses was approximately 250 ppm.

Large (50-150 micrometer) glassy spheres of J438 fly ash on a polished grain mount were analyzed for As/U ratio by laser ablation ICP-MS. An initial attempt to perform stepwise depth profiling failed to provide the necessary accuracy and precision for confident interpretation. A 100 micrometer beam size provided the required sensitivity for As (~1 ppm), but limited the results to bulk analysis of only the largest spheres. Due to the lack of suitable internal standards of highly homogeneous concentration, signal intensities in counts-per-second were reported rather than concentration. Data for arsenic were normalized to data for U in order to (1) permit comparisons between particles of variable geometry, ablation efficiency, and density and (2) to ratio against an element (U) that is consistently present in a narrow concentration range within the glassy particles of fly ash.[6]

Bulk fly ash was analyzed by XAS at the Stanford Synchrotron Radiation Laboratory. XAS spectra were calibrated on the arsenic foil position of 11,867 eV. Two regions of the x-ray absorption spectrum located near the absorption edge of As were investigated. The XANES (x-ray absorption near-edge structure) region extends from about −10 to +50 electron volts (eV) above the absorption edge and gives information on valence, coordination number, and the general fingerprint of atomic structure in the vicinity of As. The EXAFS (extended x-ray absorption fine structure) region extends from 50 eV to as much as 1000 eV above the absorption edge and gives more specific information about the local (1-2 atom shell) bonding environment such as interatomic distances and the number and type of nearest neighbor atoms. XANES analysis is more sensitive than EXAFS, which generally requires >100 ppm As.

Leaching experiments combined 2 g of solid with 20 ml of leach solution in 50 ml polycarbonate centrifuge tubes. Tubes were capped and shaken in a wrist-action shaker at room temperature for times varying from 10 minutes to two weeks. Recovered slurries were immediately pressure-filtered under nitrogen gas through cellulose acetate filter membranes of 0.45 micrometer opening. The filtered solutions were then acidified to pH<2 with ultrapure nitric acid. Most experiments that were designed to compare the leachability of J438 fly ash and other materials with a variety of solvents were run for 4 hours.

In this study most leaching experiments were designed to operationally extract the readily leachable As present on fly ash surfaces. It is generally recognized that pH is a master controlling variable for fly ash leachability.[8,9] Therefore most leaches were performed at a constant pH of 10.0 in order to ensure a high solubility of arsenic oxyanions and to maximize their long-term stability in solution relative to competing processes such as sorptive uptake on iron or aluminum oxides.[10] The pH was generally controlled with a pH-buffer leach solution of $0.5M$ Na_2CO_3-$0.5M$ $NaHCO_3$ which also acted as an ionic strength buffer. In two experiments conducted with other leachates (H_2O, $1M$ $CaCl_2$) pH was monitored continuously and adjusted to 10.0 by additions of $0.1M$ $NaOH$. A pH of 10 is not alkaline enough to cause significant dissolution of the silicate glass in fly ash or to permit formation of secondary precipitates of ettringite $Ca_6(Al(OH)_6)_2(SO_4)_3$, a well known scavenger of As. The solubility of calcium arsenate $Ca_3(AsO_4)_2$ is enhanced in the presence of dissolved CO_3,[11] but supersaturation of calcium arsenate in the buffer solution is hindered by low dissolved Ca concentrations (<20 ppm). Dissolved Ca in the carbonate-rich buffer solution is limited by solution saturation with calcium carbonate. Dissolved U was compared to As because it is a similar alkali-soluble element that is predominantly contained within the structure of the glass component of fly ash.[6] An elevated concentration of dissolved CO_3 promotes the solubility of uranium through formation of uranyl carbonate complexes.

RESULTS AND DISCUSSION

Coal J438 has moderate total sulfur (1.7 wt.%), moderate ash (17 wt.%), and approximately 50% of sulfur as pyrite (Table 1). Fly ash J438 (Table1) is class F (SiO_2+Al_2O_3+Fe_2O_3>70 wt.%). The ratio of Ca/S in fly ash is <2.5, which predicts an acid pH upon mixing with water. In fact 2 g of the fly ash generates a solution pH of 3.0 when initially mixed with 20 ml of water. Fly ash pH of 3.0 is at the low end of a reported range of 3.3-12.4.[12]

The abundance of As in J438 coal (55 ppm, Table 1) is high compared to the average concentration in U. S. coal of 24±5.5 ppm.[1] The As content of J438 fly ash (225 ppm) is near the middle of a reported range of As in fly ash of 2-440 ppm[13](Table 1). Mass balances of trace elements during combustion were not calculated because bottom ash was not analyzed, but significantly lower concentration of As in fly ash compared to laboratory-ashed coal (525˚C, Table 1) suggests some loss of As in stack gases. Other volatile trace elements such as Hg and Se also show definite deficiencies in the fly ash compared to laboratory-ashed coal (Table 1).

Table 1. Major, minor, and selected trace element composition of J438 coal and its derivative fly ash, Black Warrior Basin, Alabama.

Constituent (wt. %)	Whole Coal	Coal Ash (525˚C)	Fly Ash	Fly ash range[1]
SiO_2	9.0	53.2	55.8	
Al_2O_3	5.9	34.9	28.8	
Na_2O	0.05	0.3	0.3	
K_2O	0.4	2.4	2.7	
CaO	0.2	0.9	0.8	
MgO	0.2	0.9	0.9	
Fe_2O_3	1.4	8.1	10.9	
TiO_2	0.3	1.6	1.4	
P_2O_5	0.03	0.2	0.2	
Total		102.5	101.8	
Ash(750˚C)	17		94	
Moisture	0.64			
$Sulfur_{Total}$ Sulfur Forms	1.7 0.12 sulfate, 0.81 pyrite, 0.78 organic		0.4	0.04-6.44
Constituent (ppm)				
Se*	3.0	17.6	11.5	0.2-130
Hg*	0.3	1.8	0.2	0.01-12
B	20.1	118	126	10-5000
As*	55	324	225	2-440
Cd*	0.1	0.8	0.6	0.1-130
Pb*	12.4	73.1	73.2	3-2100
Sb*	4.4	26.1	27.5	
Be*	3.8	22.3	20.0	
Co*	11.3	66.2	61.4	
Cr*	28.7	169	177	4-900
Ni*	18.5	109	107	2-4300
Mo	3.7	21.5	22.3	1-140
U	2.6	15.5	15.0	

* Hazardous air pollutants, U.S. Clean Air Act.
[1]Mattigod et al., 1990; Eary et al., 1990.

Electron microprobe and SEM of coal

Pyrite in the coal is massive and framboidal. One pyrite grain (#5) in the polished mount was a composite containing massive pyrite and adhered coal. Closer inspection detected the presence of small (10-40 micrometer) spherical pyrite grains in the coal. The SEM indicated that some spheres had a fine grained internal texture characteristic of framboidal pyrite. The fine grained interiors were rimmed by 5-10 micrometer-thick overgrowths of more massive pyrite. Wavelength-dispersive microprobe analysis of the As distribution in a portion of grain 5 (Figure 1) indicated generally higher and more variable concentrations of As in the massive pyrite compared to the spherical framboids. Spot analyses were collected in grain 5 on areas of highest and lowest As concentration and along a vertical and horizontal traverse (Figure 2). Spot analyses were also collected on the framboids of grain 5 and on the 11 other massive pyrites in the mount (Figure 2). Results confirmed the generally lower concentration of As in framboids (<0.2 wt.%) compared to massive pyrite (0.1-0.9 wt.%). The massive pyrite averaged 0.27 wt. % arsenic, which could account for all the As in the coal if pyrite is present in 2 wt.% abundance. Sulfur speciation analysis suggests that the coal contains 0.8 wt.% pyritic sulfur (Table 1), which equates to 1.5 wt.% pyrite. Despite the limitations of this crude mass balance calculation, pyrite clearly accounts for the majority of As in the coal.

Pyrites in J438 coal have similar textures (framboidal, massive), but much lower As concentrations than pyrites from coal mine dumps in the Black Warrior coalfield (0.3-4.5 wt.% As).[7] Arsenic-rich pyrites in the mine dumps usually occurred as discrete grains or as wispy bands in cleat pyrite. The As enrichment was attributed to a period of hydrothermal activity. Fragments of massive pyrite recovered from J438 coal are also likely cleat pyrite, but are apparently less affected by hydrothermal sources of additional As. Discrete, very As-rich pyrite grains are absent in J438 coal or were removed during coal processing.

XAS of coal and fly ash

The XANES spectrum of J438 fly ash has a single large peak that corresponds to the absorption edge position of As(V) (Figure 3). The spectrum for J438 coal has the same As(V) peak and an additional peak at 2-3 eV lower energy that corresponds to the absorption edge position of As(III). These two peak positions are further illustrated by the spectra of some model compounds that contain either As(V) or As(III) as the dominant species (Figure 3). Spectral analysis indicates that the fly ash has at least 95% As(V) and the coal approximately 40% As(V). Similar results reported for coal[14] suggested that the mixed As species are the result of partial oxidation of arsenical pyrite. Comparison of the spectral shape of J438 fly ash to a library of model compounds indicated best fits with the spectra of ferric arsenate (scorodite) $FeAsO_4 \cdot 2H_2O$ or As(V) sorbed on ferrihydrite. Other model compounds considered in this analysis but not plotted included As(V) sorbed on amorphous silica and manganese hydroxides, and crystalline oxides of As. The XANES spectrum of J438 fly ash is clearly different from that of model compound calcium arsenate or the spectra of an As-rich (350 ppm) but highly alkaline fly ash (SOMA) from Turkey.

Preliminary analysis of EXAFS spectra and Fourier transforms of the EXAFS data (Figure 4) generally support the conclusions based on XANES. Comparison of the Fourier transformed data of fly ash J438 with some relevant model compounds indicate a best match with As(V) sorbed on ferrihydrite. More detailed analysis of these spectra indicate strong As-O interactions in the first atom shell and the presence of Fe atoms in the second atom shell. The calculated atomic distances

are very similar to those previously reported for As(V) sorption/coprecipitation on ferrihydrite.[15] In contrast, the relative position and lineshape of the EXAFS spectra of alkaline fly ash (SOMA) from Turkey indicated greatest similarity with calcium arsenate.

Laser ablation ICP-MS of fly ash

The As/U ratio in bulk J438 fly ash is 15.0 (Table 1), but the As/U ratio in 15 large (75-100 micrometer) glassy spheres measured by laser ablation ICP-MS ranged from only 0.57 to 3.57 and averaged 1.43±0.88. For comparison, 23 hollow glassy spheres (cenospheres) obtained from a commercial cenosphere concentrate had very similar As/U ratios ranging from 0.58 to 3.72. The low As/U ratio in large glass particles strongly suggests that arsenic is not highly concentrated <u>within</u> the silicate glass. Any As enriched on the surfaces of these very large particles is apparently too minor to strongly affect the As/U ratio obtained from total particle analysis. Identification of silicate glass as a minor host for As strengthens the argument that As in the smaller size fractions of fly ash is predominantly on the particle surfaces.

Leaching of fly ash

Leaching of As from J438 fly ash with sodium carbonate-bicarbonate buffer (pH=10) was very rapid and efficient. After two weeks 49% of the total As was leached, but most of this leaching occurred within the first four hours (Figure 5). A similar-shaped leaching curve was observed for U but only 7% of the total U was leached in two weeks. The much lower yield of U suggests a very different residence for the majority of U, most probably silicate glass. A duplicate experiment of four hours duration indicated very good reproducibility for dissolved As and U concentration (Figure 5). For comparison, four-hour leaches of crushed and acid-treated commercial cenospheres, and synthetic silicate glass standards doped with As all yielded <1% of total contained As. These results suggest a very alkali-soluble or rapidly exchangeable source of As in the fly ash.

Four-hour leaches of J438 fly ash with different solvents provided some additional insights. A high yield of leachable As with deionized water (42%) was explained by the unusually acidic pH of 3.0 generated in the water. A much lower aqueous leachability of As is predicted with only a minor increase of pH because As is specifically adsorbed to iron and aluminum oxides at pH=4.[8,16,17] Arsenic was less leachable (19%) in water at pH=10, suggesting that As solubility is aided when excess dissolved anions are available to exchange with sorbed arsenate. Very low leachability of As (<1%) in 1M $CaCl_2$ at pH=10 is consistent with precipitation of calcium arsenate.

SUMMARY DISCUSSION

The apparent association of As and Fe(III) in this highly acidic fly ash contrasts with the reported association of As and Ca in alkaline fly ash.[2] These combined results suggest a possible link between fly ash acidity and the residence of As. Possible controls on fly ash acidity include the CaO content of the ash and the SO_2 content of the vapor phase at the time of cooling. Sulfuric acid aerosols are stable below 350°C and may persist as reactive condensates if the fly ash is low in acid-neutralizing free lime (CaO). Reaction of sulfuric acid with fly ash particles can produce Al-sulfate or Fe-sulfate surface coatings that generate acidity when they are first dissolved in water because of hydrolysis of Al or Fe(III).[18] Very acidic (pH<4) slurries of fresh fly ash and water are therefore an indication of excess acidity in the ash/vapor system during cooling. Under highly acidic

condensation conditions gaseous As must associate with phases other than CaO and the most likely candidates are iron compounds. Iron arsenate, iron sulfates, and iron oxides are stable phases at acid pH, whereas calcium arsenate $Ca_3(AsO_4)_2$ is not. At less acidic to mildly alkaline condensation conditions (pH= 4-10) some gaseous As may simply chemisorb to various iron oxides. According to this hypothesis, very alkaline fly ash (pH>10) may be dominated by Ca-As associations whereas fly ashes of moderately alkaline character (pH=7-10) may initially contain a mixture of Fe-As and Ca-As associations. XAS analysis holds promise for estimating the proportions of these two associations in a "mixed" fly ash.

Leaching results for J438 fly ash indicate that a significant fraction (49%) of Fe-associated As is localized on accessible particle surfaces and is readily soluble/exchangeable under alkaline (pH=10) conditions. The XAS results which look at total arsenic, suggest that the majority of unleached As is also associated with iron. Some As may be unavailable for leaching because of mantling or entrapment of iron oxides by other phases. Under the moderately alkaline pH conditions of most ash disposal ponds As should desorb from iron oxides whereas calcium arsenate $Ca_3(AsO_4)_2$ is sparingly soluble and may better retain As during the early stages of fly ash diagenesis.

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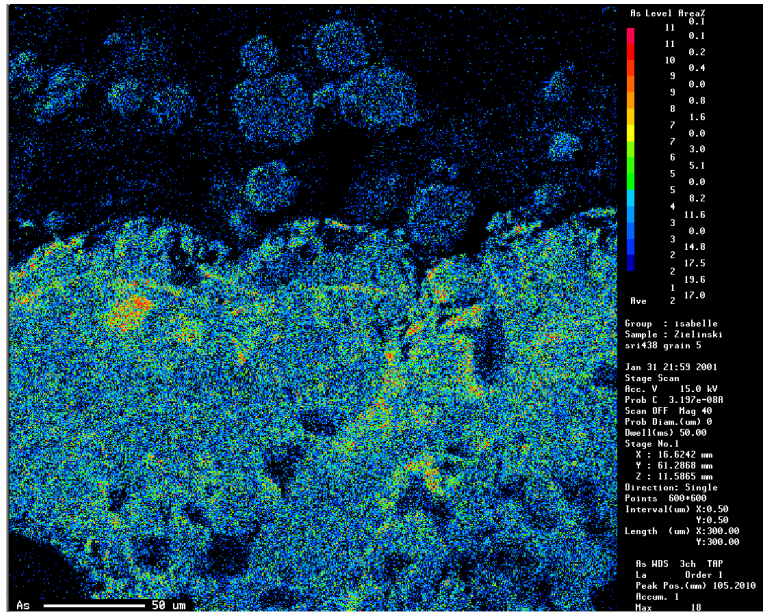   alteration. Fuel, v. 78, p. 187-196.

Figure 1. Electron microprobe map of arsenic distribution in pyrite grain 5, J438 coal.
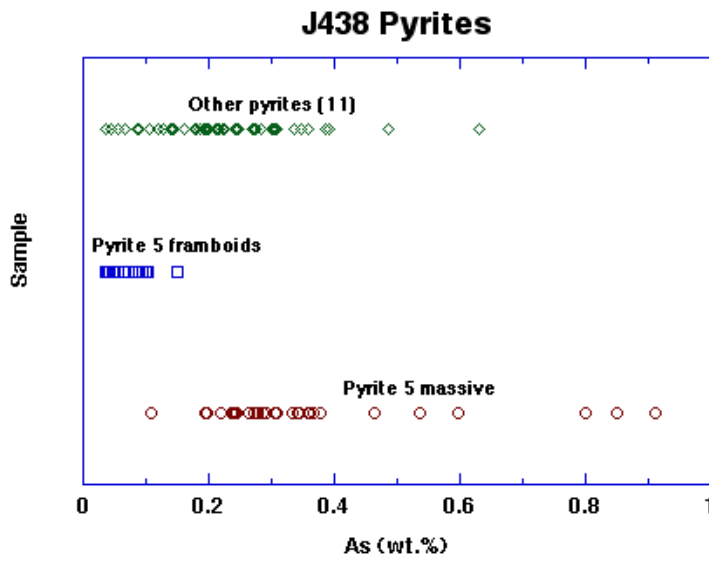

Figure 2. Electron microprobe analyses of arsenic in pyrite grains from J438 coal.
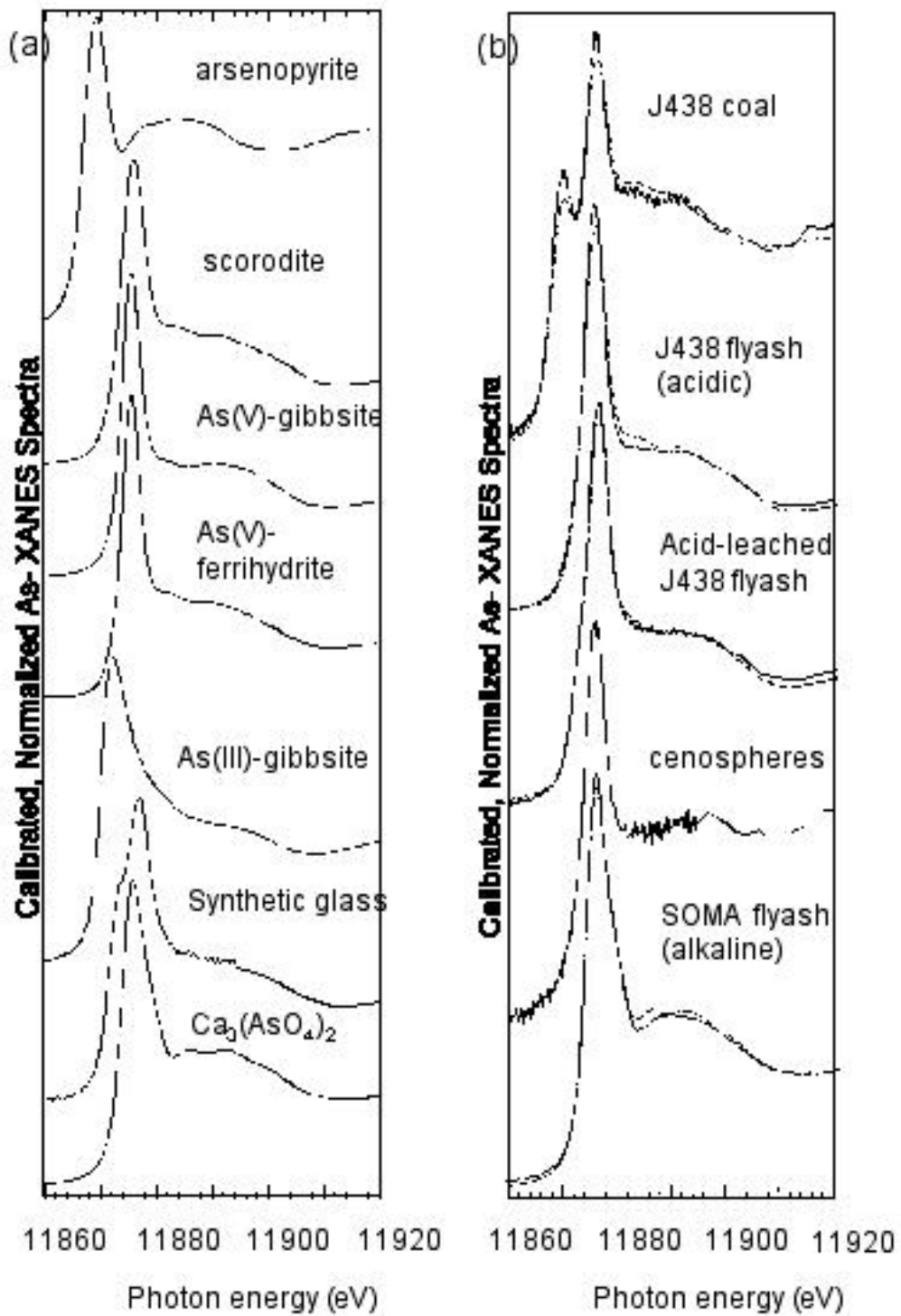
Figure 3. XANES spectra of arsenic in J438 coal, fly ash, and selected model compounds.
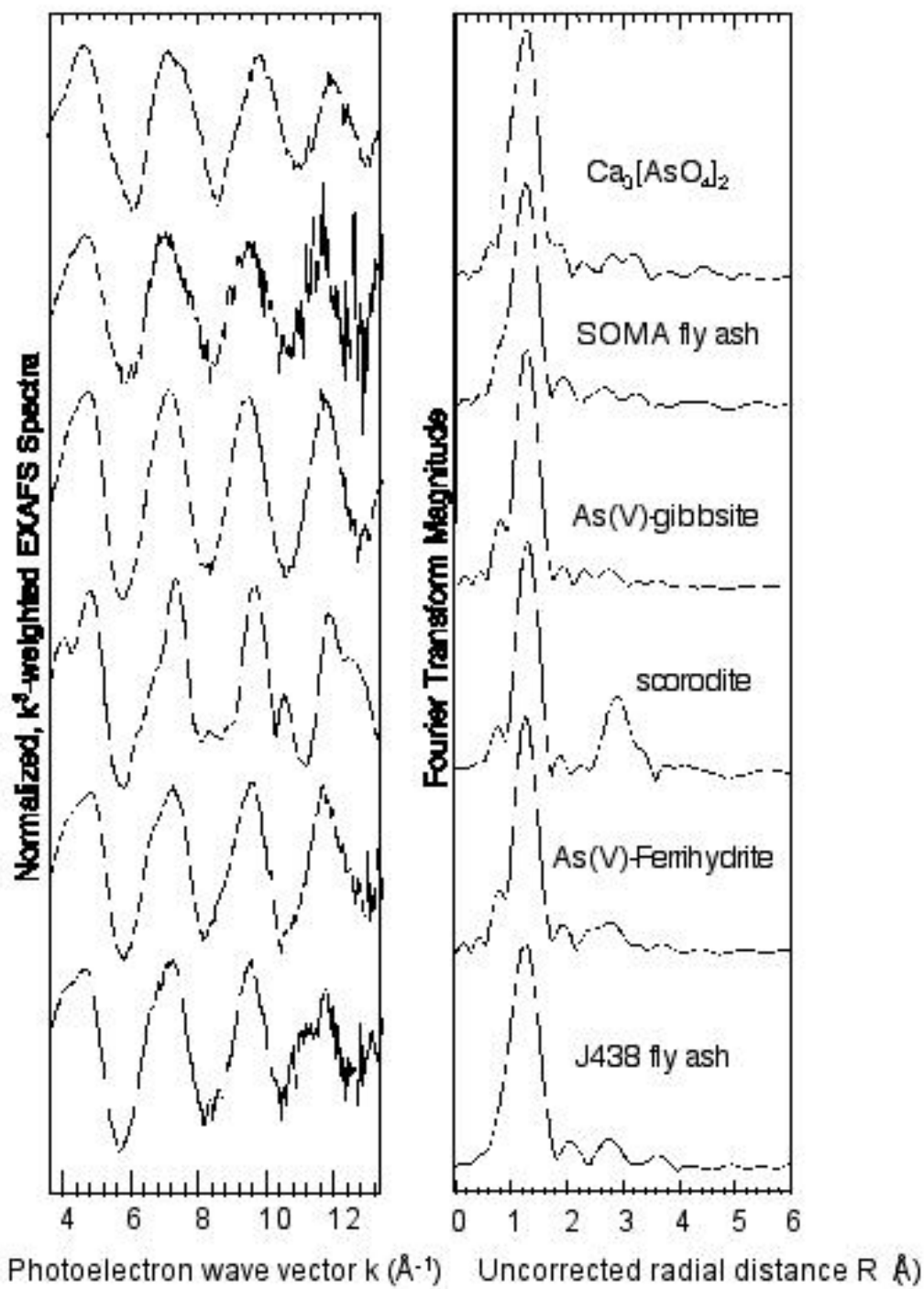
Figure 4. EXAFS spectra (left) and Fourier transforms (right) of J438 fly ash and relevant model compounds.
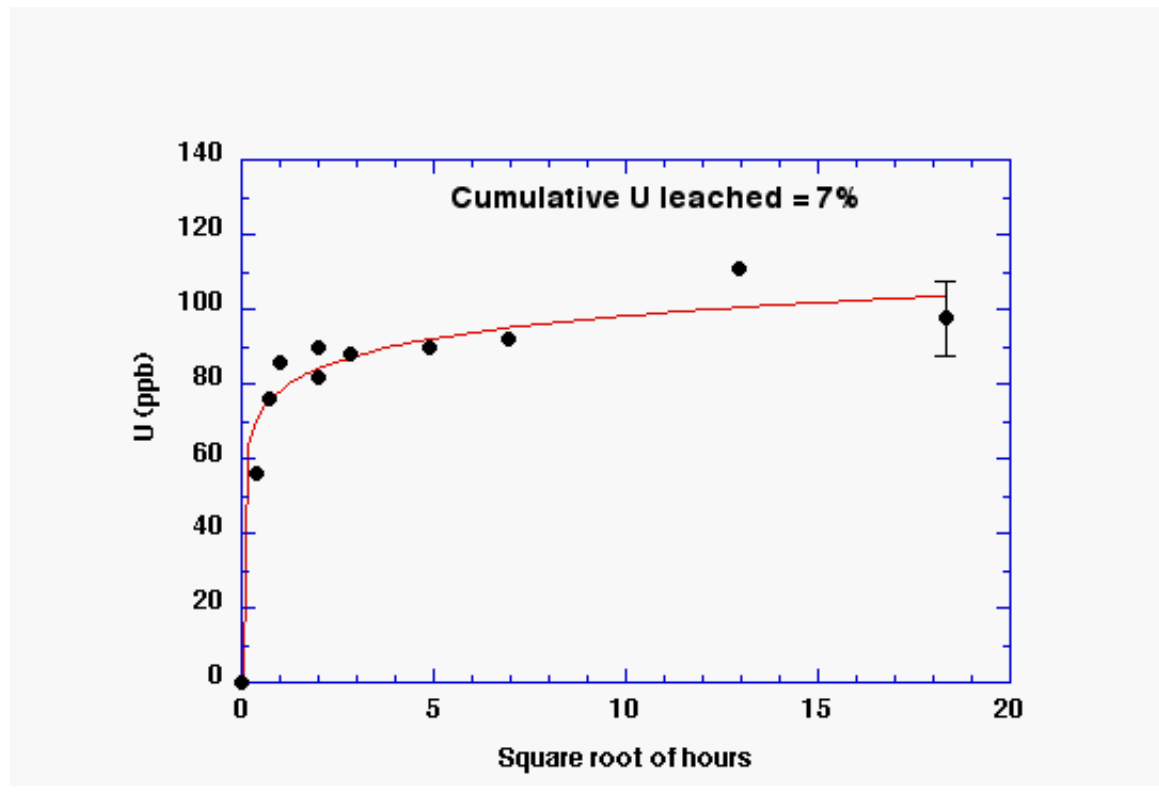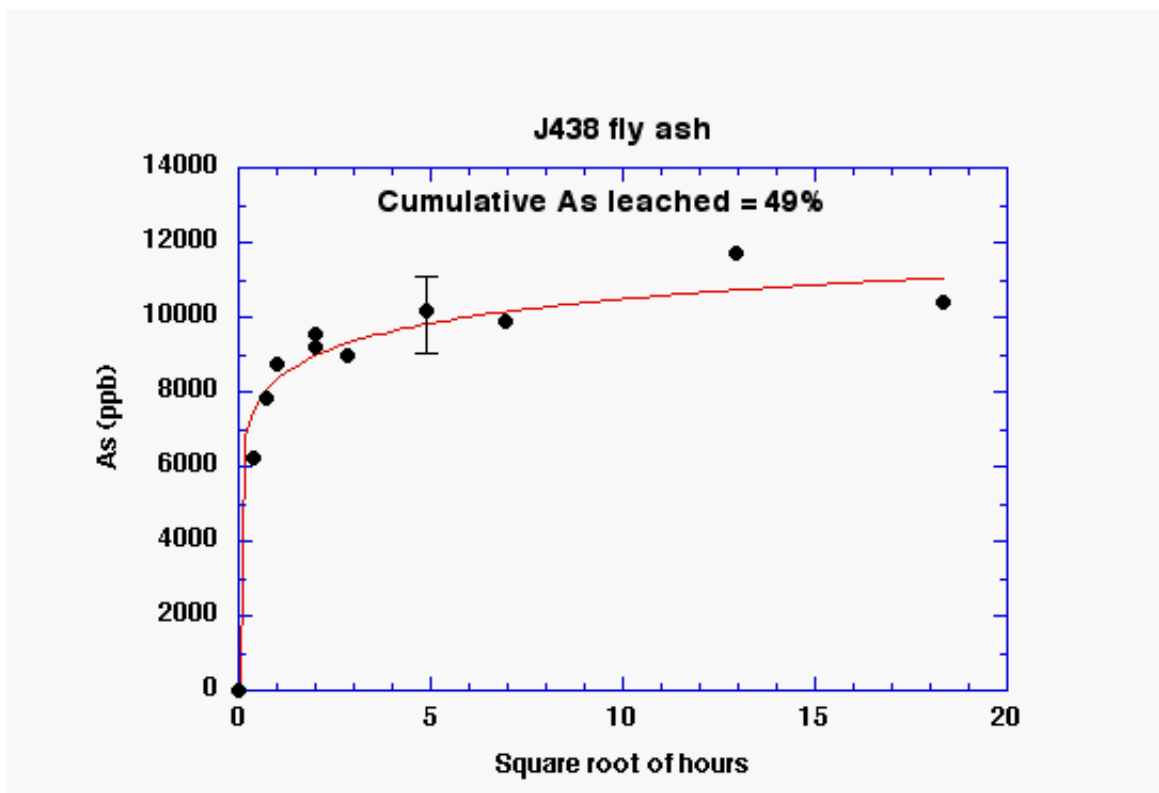
Figure 5. Cumulative leaching of As and U from J438 fly ash as a function of time.