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1. Objectives and Approach

The Clean Air Act Amendments of 1990 identify a number of hazardous air pollutants (HAPs) as candidates for regulation. Should regulations be imposed on HAP emissions from coal-fired power plants, a sound understanding of the fundamental principles controlling the formation and partitioning of toxic species during coal combustion will be needed. With this objective, a team led by PSI Technologies (PSIT) has begun a multi-year program to determine the forms of occurrence in coal, and the effect of the combustion (and post combustion) environment on partitioning of these elements. Participants in the program include researchers from MIT, Princeton University, University of Arizona, University of Connecticut, University of Kentucky, and USGS. Additional support for the program comes from EPRI and VTT (Finland). The final objective of this program will be to develop a broadly applicable emissions model useful to regulators and utility planners.

The large amount of data accumulated from the field and from laboratory tests has defined the general behavior of toxic and trace species during coal combustion. A broad variation in elemental form has been reported for many elements, although major data gaps exist. Very little information on the interactions of trace species with major coal minerals is available. The four most critical trace toxic metals that are emitted to the environment by coal combustion are mercury, arsenic, chromium, and selenium. Halogens, particularly chlorine, are also of key importance. In order to meet the challenges of cleaner power production in the future, a new method is needed to predict emissions of toxic species from a wide range of fuels (and blends) and from many different kinds of combustion systems. The specific approach taken by the team is described below.

Direct identification of the modes of occurrence of trace inorganic species in coal and ash using unique analytical techniques such as XAFS analysis and selective leaching forms a cornerstone of the approach. Elemental modes of occurrence will be established for the key elements using a combined microscopic/spectroscopic approach. XAFS spectroscopy is currently capable of supplying information in the middle of the periodic table (Tl-Sn) with abundances in excess of 5 to 10 ppm. Whereas XAFS spectroscopy will provide a specific signature of all modes of a given element in the coal in a single spectrum, the microscopic-based methods will provide valuable complementary information on the spatial distribution and association of the element. This combined approach, which has not been attempted before, should provide the more information than has been available previously about an element's mode of occurrence in coal. Elemental modes of occurrence will also be determined for trace species using an analytical procedure developed by USGS. This protocol combines low temperature ashing, chemical analysis, x-ray diffraction,

coal segregation via flotation, leaching, electron microbeam measurements, and low and moderate temperature heating tests to elucidate forms of elements in coal.

Combustion testing will be used to determine the importance of each of four fundamental processes that may influence the speciation and partitioning of trace metals during combustion. These processes are (1) vaporization of metallic species, (2) gas-phase transformations of metallic species, (3) condensation of gaseous metallic species, and (4) solid transformations of metallic species. In general all four of these processes can take place simultaneously and in competition with each other.

A unique aspect of the program is an attempt to isolate and study these steps as much as possible while retaining the conditions that are typically present during coal combustion. *Fundamental bench scale studies* will be used to isolate vaporization and condensation of trace metals. Combustion of size and density-classified coal particles will allow a mechanistic interpretation of vaporization. Thermogravimetric studies of metal vapor-solid interactions will provide information on the interactions between gaseous species and ash particles post-combustion. *Integrated combustion experiments* using utility grind coal samples and realistic combustion stoichiometries will allow the evaluation of excluded mineral and combustion effects. *Self-sustained combustion experiments* using a 100,000 Btu/h coal-fired combustor with realistic heating and cooling rates permits the examination of trace metal partitioning when all the important mechanisms are combined.

A critical review of available field data provides guidance for the overall program direction and model validation. An analysis of steady state and transient organic emissions from field data will be conducted to determine whether organic toxic emissions pose a concern and should therefore be included in the model. Inorganic emissions reported from recent comprehensive field sampling campaigns will also be reviewed and one or more sets of model validation data will be selected. Data from EPRI field studies consisting of coal composition, combustion conditions, and concentrations of trace metals in solid and gaseous streams, including the effects of back end conditions on trace metal partitioning. The effect of coal type and combustion conditions on submicron ash morphology will also be assessed using data collected by VTT.

2. Coal Characterization

Four coals have been or will be acquired for the Phase I baseline studies. All coals are currently being used by utilities in the United States and represent a diversity of coal and mineral types. The coals are (1) Illinois 6 (Burning Star No. 4 mine), (2) Washed Pittsburgh Seabrook (Blacksville mine), (3) Eastern Kentucky coal Elkhorn and Hazard seams, and (4) Wyodak subbituminous (Black Thunder mine). All coals will be analyzed for trace element content (Instrumental Neutron Activation Analysis), for iron oxidation state (Mössbauer spectroscopy), mineral distribution (Computer Controlled Scanning Electron Microscopy), and for forms of trace elements (XAFS and selective leaching).

Analysis of the coals has begun with two, the Pittsburgh Elkhorn/Hazard seam coals. Table 1 gives the results of standard analyses. Data on the mineralogy of these coals will be discussed in subsequent papers. Based on the forms of sulfur analysis, it appears that Elkhorn/Hazard coal has little pyrite and that a substantial portion of the pyrite has been oxidized to sulfate. In contrast, the Pittsburgh coal contains much more pyrite, very little of which has oxidized. Since many trace metals in coal, particularly arsenic, are associated with pyrite, the relative amount, size, and oxidation state of this mineral are important as discussed below.

Table 1. Standard Coal Analysis for Pittsburgh and Elkhorn/Hazard Coals

	Pittsburgh	Elkhorn/Hazard
Proximate Analysis(wt%)		
Fixed Carbon	61.99	56.46
Volatile Matter	30.22	33.80
Moisture	1.44	2.33
Ash	7.01	7.41
Ultimate Analysis(wt%, dry)		
Carbon	77.74	76.66
Hydrogen	4.87	4.70
Nitrogen	1.50	1.46
Sulfur	1.66	0.84
Oxygen	7.01	8.48
Chlorine	0.10	0.17
Ash	7.11	7.59
Forms of Sulfur(wt% dry)		
Pyrite	0.91	0.12
Sulfate	0.01	0.03
Organic	1.20	0.72

3. Modes of Occurrence of Trace Elements in Coal

Preliminary work on the mode of occurrence of arsenic in two bituminous coals, Pittsburgh and Elkhorn/Hazard, has been completed. Mossbauer spectroscopy was used to assess the oxidation state of iron in the Pittsburgh and Elkhorn/Hazard coals (Table 2). Virtually all the iron in the Pittsburgh coal is present as pyrite, whereas almost one-third of the iron in Elkhorn/Hazard coal is present in other forms (clays, siderite, and jarosite). The presence of jarosite (an iron sulfate) may be an indication of oxidation of pyrite in the coal. The Elkhorn/Hazard coal showed 12% of the iron as jarosite, while for the Pittsburgh coal only 2% jarosite was detected. Mossbauer data are consistent with the forms of sulfur analysis.

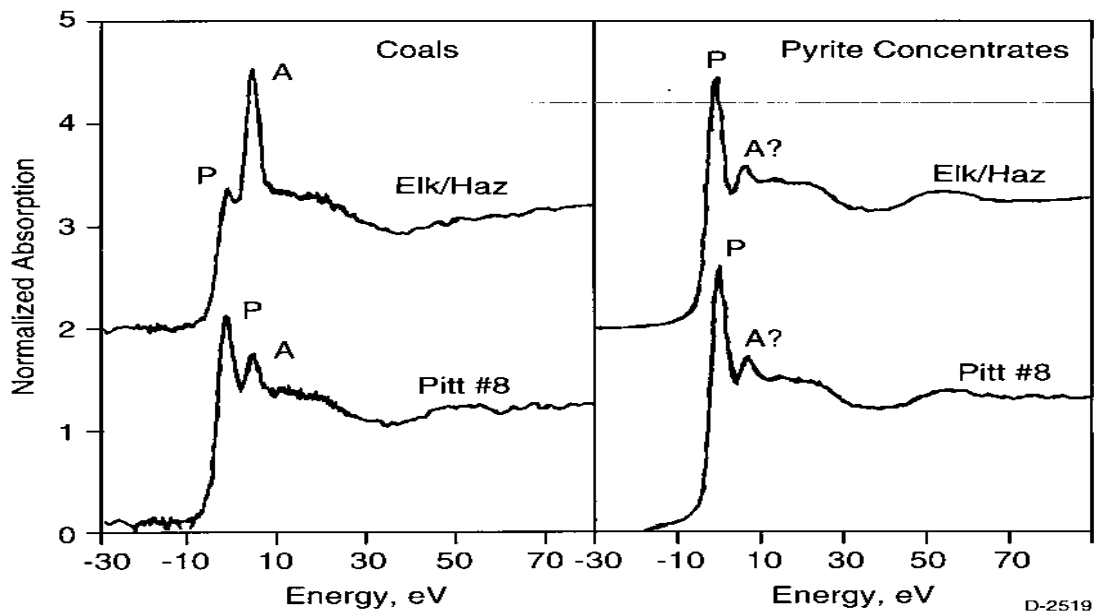
Based on a previous XAFS study of arsenic occurrence in bituminous coals, three forms of arsenic have been identified in these coals. Arsenical pyrite, in which arsenic substitutes for Fe in FeS_2 is the most common. Arsenate compounds (As_2O_5) are the next most common and arsenopyrite ($FeAsS$) is the least common. Oxidation of arsenical pyrite has been shown to produce arsenate compounds. In the present

work XANES spectroscopy for arsenic was conducted on both coals as well as on high density

Table 2. Mossbauer Data for Pittsburgh and Elkhorn/Hazard Coals

Iron-Bearing Mineral	I.S.	Q.S.	%Fe
Pittsburgh			
Pyrite	0.30	0.61	96.5
Fe in clay	1.12	2.66	1.5
Jarosite	0.44	1.08	2.0
Elkhorn/Hazard			
Pyrite	0.31	0.61	57.0
Fe in clay	1.10	2.66	22.0
Siderite	1.22	1.79	9.0
Jarosite	0.43	1.14	12.0

fractions (which are predominantly pyrite) separated by a float/sink technique using bromoform (Figure 1). Note that the raw coal samples of Pittsburgh and Elkhorn/Hazard coals each contain 4 ppm of arsenic.



The much better signal/noise ratio obtained in the high density fractions as compared to the raw coals suggests that arsenic is strongly associated with the pyrite. It is also clear that the arsenic in the Elkhorn/Hazard coal is significantly more oxidized than in the Pittsburgh coal since the arsenate peak (A) is

relatively higher than the pyrite peak (P). This is consistent with Mossbauer analysis which indicates that a significant amount of the pyrite in the Elkhorn/Hazard coal is oxidized.

The form of occurrence of arsenic in coal may have an effect on the vaporization behavior during combustion. Most arsenic in U.S. coals is associated with the sulfide phase (i.e., pyrite). Oxidation of the pyrite in coal will result in the formation of arsenates. Preliminary evidence suggests that arsenic associated with pyrite may volatilize more readily than arsenates. Combustion experiments are planned which will explore the relationship between forms of arsenic in the coal and arsenic vaporization during combustion.

4. Laboratory Study of Trace Element Vaporization

The fundamental mechanisms of toxic species formation and partitioning during combustion will be determined from careful examination of the ash formed under a variety of combustion conditions. Size and density-classified coal samples will be burned in the MIT laminar flow furnace under a range of temperature and oxygen partial pressures. Size-segregated ash samples will be obtained by collecting all the ash through a rapid quench probe and depositing on the plates of an Anderson impactor. The coal samples as well as the ash samples will be analyzed by NAA for total composition. Selected coal and ash samples will be analyzed by XAFS and other techniques.

The Elkhorn/Hazard coal has been size classified into three cuts, < 38 :m, 38 to 75 :m, and > 75 :m. The largest and smallest size cuts were analyzed by NAA to explore variation in trace element concentration with particle size. These data, shown in Table 3, suggest that the concentrations of some elements differ substantially between these two size cuts. For example, iron concentration is significantly higher in the < 38 :m size cut. This suggests that the dominant form of iron, pyrite, is either included (inside the carbon matrix) or found in small excluded particles. The difference in the iron concentration may also explain differences in the concentrations of other elements which are commonly associated with pyrite. For example, concentrations of arsenic and zinc show the same trend in concentration as seen in iron. Therefore, it is likely that the concentration differences between the two size cuts is due largely to differences in the iron-compound concentration. Further analysis by CCSEM, Mossbauer, and selective leaching will be required to fully resolve this issue.

Preliminary combustion experiments were performed on the Pittsburgh coal. First, the coal was segregated into seven size ranges by using standard sieves. Samples of the 45 to 63 :m coal were burned in the laminar flow furnace at a gas temperature of 1700 K using a gas composition of either 20% O₂ or 100% N₂. XAFS analysis of the oxidation state of arsenic in the ash/char shows that under 20% oxygen, virtually all the arsenic is present in the +5 oxidation state. For the samples heated under pure nitrogen, the dominant oxidation state appears to be +3. However, 40% of the arsenic in these samples is in the +5 oxidation state. Whether the +3 reflects oxidized arsenic (arsenate) present in the original coal remains to be demonstrated.

5. Plans

During the second year of this two-year program, detailed experiments with the four program coals are planned using MIT's laminar flow reactor to obtain fundamental information on vaporization kinetics,

Table 3. Trace Element Composition of Elkhorn/Hazard Coal as a Function of Coal Particle Size

Element	Parent Coal,ppm	d _p < 38 :m,ppm	d _p > 75 :m,ppm
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As	4	5.9	1.5
Br	25	14	20
Cd	0.31	0.12	0.28
Co	6.2	6.0	6.3
Cr	20	18	14
Fe	2970	3880	1245
Hg	0.13	0.13	0.15
Na	340	255	175
Sb	1	1.1	0.85
Sc	39	40	36
Se	3.1	3.3	2.1
Sr	120	140	110
Zn	18	17	3.1

using PSIT's entrained flow reactor to evaluate excluded mineral and combustion effects with utility grind coal samples and realistic combustion stoichiometries, and using the University of Arizona's self-sustained combustion facility to examine trace metal partitioning when all the important mechanisms are combined. Critical experiments on post-flame interactions between coal minerals and trace metals will be performed at the University of Arizona utilizing thermogravimetric analyzer. In parallel with experimental work, researchers at MIT, PSIT, and the University of Arizona will begin theoretical examination of chlorine partitioning in post-combustion gases as well as silicate equilibrium thermodynamics. These efforts will lead to definition of the new Toxic Partitioning Engineering Model (TPEM) to be completed in Phase II of the program. An analysis of steady state and transient organic emissions from field data will be conducted to determine whether organic toxic emissions pose a concern and should therefore be included in the model. Recent comprehensive field sampling campaigns will be reviewed and model validation data will be selected.