

A FUNDAMENTAL INVESTIGATION OF TOXIC SUBSTANCES FROM COAL COMBUSTION

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INTRODUCTION

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. For this reason PSI Technologies, under the support of the U.S. DOE, the Electric Power Research Institute (EPRI), and the Technical Research of Finland (VTT), has teamed with researchers from the USGS and several leading universities to determine the dominant mechanisms that control trace element partitioning in combustion systems. The final objective of this program will be to develop a broadly applicable emissions model useful to regulators and utility planners.

This paper describes the need for this type of fundamentally based emissions model, and some of the important data required to develop such a model. Some of these data include the elemental modes of occurrence in coal of important trace elements, and how these modes of occurrence may control the partitioning of these elements in combustion systems. The current program to study these issues is presented, as are the results obtained to date. Four coals have been selected for their diversity in mineralogy and trace element composition. After a description of the rationale for the approach, preliminary data on coal composition and on modes of occurrence of trace elements in the coals are presented.

RATIONALE

Current understanding about toxic species transformations and partitioning in coal-fired combustion systems points to gaps in data that need to be filled in order to produce a model that will be useful for both new and existing combustion sources. The large amount of data accumulated from field and laboratory tests has defined the general behavior of toxic and trace species during coal combustion. One of the major efforts to collect field data is the Power Plant Integrated Systems Chemical Emissions Study (PISCES) led by EPRI. Within PISCES, EPRI performed an extensive literature search on the partitioning of toxic and trace species into the various output streams of power plants. Detailed field measurements were also made of the concentrations of 22 species in the effluent streams of power plants.¹ This effort has resulted in a large database of emissions of trace and toxic species.² Organic toxins may also be emitted from coal-fired systems. Field studies suggested that emissions of organic species from coal-fired plants are tied to the combustion efficiency and are typically much lower than emissions of inorganic species.³⁻⁵

There appears to be a consensus of opinion that the four most critical trace elements for coal combustion are Hg, As, Cr, and Se. Ni, Mn, and Pb are of lesser concern, while the remaining elements (Sb, Be, Co, Cd) appear to present little cause for concern for coal utilization because of their low abundance in coal and their insignificant contribution to pollution of the atmosphere in comparison to non-coal source.⁶ Chlorine and the other halogens are also of concern. Chlorine, in particular, can be found at concentrations in excess of 1000 ppm in some bituminous coals. Thus for some power plants, either HCl or Cl₂ may exceed the 10 ton/y CAAA limit. Also chlorine may play a key role in determining the volatility of mercury.⁷

Messerole and Chow⁸, using PISCES data, found that several elements, including As, Cd, Hg, and Se, typically vaporize in utility boilers. Some of these condense on flyash particles and are removed by pollution control devices. Others such as Hg, F, and Cl are emitted predominantly as vapors. However, significant variations in trace element behavior were noted, possibly caused by interactions with other minerals or differences in modes of occurrence in the parent coal. This was emphasized by Meij⁷, who observed large differences in Hg and As partitioning as coal type was varied in one utility boiler unit. These differences were attributable to differences in the mode of occurrence and the combustion transformations of these metals. If the fundamental mechanisms that govern the behavior of these species were understood, the utility industry could better predict emission rates.

This need increases in importance when unique fuels, equipment configurations, and operating conditions are considered.

Other investigators have studied the behavior of trace elements in laboratory combustion systems as reviewed in recent papers.¹⁰⁻¹² Despite these efforts, mechanistic information is generally lacking. For example, Linak and Wendi¹¹ presented the results from several laboratory and field studies on the enrichment of trace elements in the submicron ash. Although the data set is not entirely consistent for all species, it does show enrichment of several elements in the submicron ash which is most likely to escape from particulate control devices. These elements include Sb, As, Cd, Cr, Pb, Hg, Ni, and Se. Other elements such as Cl were found to remain in the vapor phase.

Previous mineral matter transformation work has demonstrated the critical importance of the *forms* or *modes* of occurrence of trace elements in coal on their behavior during combustion.^{12,13} The mode of occurrence of an element is important because of the tremendous diversity in which an element can be found in coal.^{14,15} An element can be completely dispersed throughout the coal macerals or can exist within its own discrete mineral phase. Organically associated metals such as sodium typically vaporize during combustion. Metals contained in clays, on the other hand, typically do not vaporize. Bool and Helble showed that the volatility of a number of trace metals is dependent on elemental form in the coal.¹² Quann et al. noted the importance of form in a systematic study of twenty different coals burned under well-characterized conditions.¹⁷

One of the first methods developed for estimating emissions from power plants was the use of empirical emissions factors.^{10,18} For example, based on data from five boilers, Brooks reports an average emission factor of 684 lb/10¹² Btu for arsenic in uncontrolled dry-bottom pulverized coal boilers.¹⁰ Although emissions factors are useful for preliminary calculations, they are clearly inappropriate for use in determining regulatory compliance or in predicting the effect of fuel and boiler modifications on partitioning and emissions. A more complex model to predict trace species partitioning, based on the PISCES database, has been developed by Rubin and co-workers.^{18,19} This model uses a probabilistic analysis to predict the partitioning of a given element into the various output streams of a coal-fired utility boiler. Boiler configuration inputs are combined with trace element partitioning data from the PISCES database. The model predicts a range of emission values based on the uncertainties of the inputs (i.e., species concentrations in the coal). The model has been shown to predict emissions of several species for specific power plants with a reasonable degree of accuracy.²⁰ Use of the model is best suited to well-defined configurations for which partitioning data are available. Since the PISCES project covered less than 5% of the approximately 1,750 utility boilers in the U.S., many existing facilities fall "outside" the data base. For novel fuels and boiler configurations, the uncertainty in predicted toxic species emission will be high.

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. Concentrations of toxic elements have been measured for many coals. A broad variation in elemental form has been reported for many elements with major data gaps existing. 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 Hg, As, Cr, and Se. Halogens, particularly Cl, 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.

TECHNICAL APPROACH

The discussion in the preceding section illustrates the need to perform a comprehensive program to determine how the form of occurrence of an element in coal and the combustion conditions control the partitioning of that element in combustion system. This information, if obtained as part of carefully planned combustion experimentation, will be crucial to better understand the partitioning data collected in full scale units, and to develop a model applicable to all types of coal fired combustion systems. With this objective, the PSIT-led team 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, USGS, and VTT. The following section describes many of the tools that will be used, and the combustion facilities that will be used, to address these issues.

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 (Ti-Sn) with abundances in excess of 5 to 10 ppm.¹⁹ 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 ToPEM. 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 from DoE or 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.

COAL CHARACTERIZATION

Four coals have been 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 Seam (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).

Preliminary work on the mode of occurrence of arsenic in two bituminous coals, Pittsburgh and Elkhorn/Hazard, has been completed. The form of occurrence of As in coal may have an effect on the vaporization behavior during combustion. Most As in U.S. coals is associated with the sulfide phase (i.e., pyrite).²¹ 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.²²

Mössbauer spectroscopy was used to assess the oxidation state of iron in the Pittsburgh and Elkhorn/Hazard coals. Virtually all the iron in the Pittsburgh coal is present as pyrite, whereas almost one-third of the iron in the Elkhorn/Hazard coal is present in other forms (clays, siderite, and jarosite). The presence of jarosite 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.

Based on a previous XAFS study of arsenic occurrence in U.S. bituminous coals,²² three forms of As have been identified in these coals. Arsenical pyrite, in which As substitutes for Fe in FeS₂, is the most common. Arsenate compounds (AsO₄³⁻) 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 As was conducted on both coals as well

as on high density fractions (which are predominantly pyrite) separated by a float/sink technique using bromoform (Figure 1). The much better signal/noise ratio obtained in the high density fractions as compared to the raw coals suggests that As is strongly associated with the pyrite. It is also clear that the As 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 the Mössbauer analysis which indicates that a significant amount of the pyrite in the Elkhorn/Hazard coal is oxidized. Combustion experiments are planned which will explore the relationship between forms of As in the coal and As vaporization during combustion.

A previous study of trace element partitioning in two of the program coals,¹² provides an indication of the combustion behavior of trace elements in the Pittsburgh and Wyodak coals. The two coals were subjected to a leaching analysis to determine the forms of selected trace metals (As, Se, Hg, Zn, Sb, Cr). Combustion experiments and equilibrium calculations were used to understand the mechanisms governing the combustion behavior. The form of the element in the coal was shown to have major impact on the combustion behavior. Those elements that were organically bound or associated with the sulfide minerals were shown to vaporize during combustion. Once in the vapor phase, these elements in some cases reacted with minerals present in the ash to form condensed phases. The size distribution of trace elements resulting from combustion was determined by whether or not the element reacted with mineral compounds in the ash.

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REFERENCES

1. Chow, W. and Torrens, I.M., Presented at the *American Power Conference*, Chicago, IL, 1994
2. Wetherhold, R.G. and Chow, W., Presented at the *International Conf. on Managing Hazardous Air Pollutants*, Palo Alto, CA, 1991.
3. Sage, P.W. and Williamson, J., Presented at the *2nd International Conf. on Managing Hazardous Air Pollutants*, Washington, D.C., 1993.
4. Miller, C.A., Sravistava, R.K., and Ryan, J.V., *Env. Sci. Tech.*, **1994**, 28, 6.
5. Chu, P., Nott, B. and Chow, W., Presented at the *2nd International Conf. on Managing Hazardous Air Pollutants*, Washington, D.C, 1993.
6. Clarke, L.B. and Sloss, L.L., Trace Elements - Emissions from Coal Combustion and Gasification, IEA Coal Research Report IEACR/49, 1992.
7. Meij, R., *Fuel Proc. Technol.*, **1994**, 39, 199.
8. Meserole, F.B. and Chow, W., Presented at the *International Conf. on Managing Hazardous Air Pollutants*, Palo Alto, CA, 1991.
9. Meij, R. and van der Kooij, J. Air Pollutant Emissions from Coal-Fired Power Stations, *KEMA Sci. Tech. Rep.* **1986**, 6, 4.
10. Brooks, G., Estimating Air Toxics Emissions from Coal and Oil Combustion Sources, EPA Report PB89-194229, 1989.
11. Linak, W.P. and Wendt, J.O.L., *Prog. Energy Comb. Sci.*, **1993**, 19, 145.
12. Bool, L.E. and Helble, J.J., *Energy & Fuels*, **1995**, 9, 880.
13. Zygarlicke et al., Combustion Inorganic Transformations, University of North Dakota Energy and Environmental Research Center Final Report on Contract DE-FC21-86MC10637, 1991.
14. Swaine, D.J., *Trace Elements in Coal*, Butterworths, London, 1990.
15. Huggins, F.E., Zhao, J., Shah, N., and Huffman, G.P., Presented at *International Conf. on Coal Science*, Banff, Alberta, 1993.
16. Helble, J.J., *Fuel Proc. Technol.*, **1994**, 39, 159.
17. Quann, R.J. and Sarofim, A.F., *Comb. Sci. Technol.*, **1990**, 74.
18. Edwards, L.O., Muelah, C.A., Sawyer, R.E., Thompson, C.M., Williams, D.H., and Delleny, R.D., Trace Metals and Stationary Conventional Combustion Processes, EPA Report No. EPA-600/s7-80-155, 1981.
19. Rubin, E.S., Berkenpas, M.B., and Chow, W., Presented at the *Ninth Annual Pittsburgh Coal Conference*, Pittsburgh, PA, 1992.
20. Rubin, E.S., Berkenpas, M.B., Freu, H.C., and Toole-O'Neil, B. Presented at the *2nd International Conf. on Managing Hazardous Air Pollutants*, Washington, D.C, 1993.
21. Finkelman, R.B., Palmer, C.A., Krasnow, M.R., Aruscavage, P.J., Sellers, G.A., and Dulong, F.T, *Energy & Fuels*, **1990**, 4, 755.
22. Huggins, F.E., Helble, J.J., Shah, N., Zhao, J., Srinivasachar, S., Morency, J.R., Lu, F., and Huffman, G.P., *Preprints of ACS Div. Fuel Chem.*, **1993**, 38.

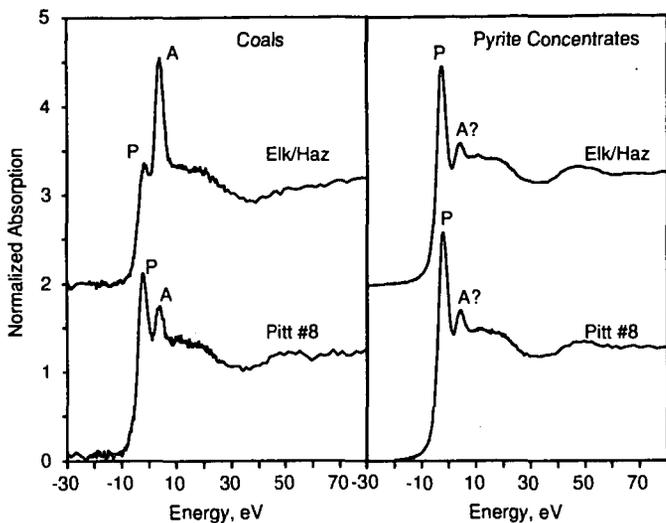


Figure 1. XANES spectra for arsenic: Pittsburgh and Elkhorn/Hazard coals and high density fractions. Peaks corresponding to arsenate (A) and pyrite-associated (P) species are indicated.