DEPARTMENT OF ENERGY SUPPORT FOR USGS TOXIC SUBSTANCES FROM COAL COMBUSTION-FORMS OF OCCURRENCE ANALYSIS

Semiannual Report

Submitted to the U.S. Department of Energy

By

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Phase II

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Introduction

Detailed information on trace-element modes of occurrence in coal is essential to understanding and predicting trace-element transformations taking place during coal combustion. The USGS has developed quantitative and semi-quantitative methods for determining the mode of occurrence of trace elements in coal. This information is needed to generate predictive models for trace-element behavior, the ultimate goal of DOE contract DE-AC22-95PC95101 “Toxic Substances From Coal Combustion- A Comprehensive Assessment” awarded to PSI, Inc. USGS activities in support of this contract have a direct bearing on the predictive equations being developed as the primary product of the PSI program.

USGS Procedures

The USGS procedure uses an iterative selective leaching protocol on whole coals in combination with a range of complementary studies. The sequence of leaching steps, and the intended results, are as follows: 1) exchangeable cations, and a fraction of the carbonate-hosted cations are removed by ammonium acetate; 2) cations primarily associated with carbonates and monosulfides such as galena, sphalerite and chalcopyrite are removed by hydrochloric acid; 3) silicate-associated cations are removed by hydrofluoric acid; and 4) elements associated with di-sulfides (pyrite and marcasite) are removed by nitric acid. The amount of an element leached by a given reagent is compared to concentrations of that element in the whole coal to obtain the fraction of an element having the indicated residence. Elements not leached by any of the four reagents may be present in the organic portions of the coal, or in insoluble phases such as zircon or titanium dioxides. Additionally, where mineral grains are completely encased by the organic matrix, these “shielded” grains may not be completely digested. As an internal check, leaching results are obtained for both the solid residues (by INAA) and leachates (by ICP-MS and ICP-AES). Element-specific methods are used for Se (hydride generation) and Hg analysis (cold vapor atomic absorption or atomic fluorescence). Quantitative results are obtained by interpreting the leaching data together with the results obtained by complementary techniques such as electron microprobe analysis.

The electron microprobe is used to determine minor and trace elements on a grain scale, on points selected by the operator. This technique is especially useful for pyrite grains, as many of the HAP’s elements of interest are present at concentration levels about the minimum detection limit of about 100 ppm. Other essential components of the USGS procedure include semi-quantitative determination of mineralogy by X-ray diffraction (XRD) analysis of low temperature ash (LTA), and confirmation of mineralogy for operator-selected grains using a scanning electron microscope (SEM) equipped with an energy-dispersive X-ray analyser (EDX).

The USGS approach complements results obtained by X-ray absorption fine structure (XAFS) by our colleagues at the University of Kentucky. The USGS technique also provides data for elements such as Se and Hg, whose concentrations are commonly too low to obtain XAFS spectra, and for elements with atomic numbers beyond the current XAFS atomic number range of about 20 to 42 (Ca to Mo). For elements that are common to the two approaches, such as As and Cr, comparison of results obtained by the USGS and by XAFS provides an important confirmation of our results.

Phase II Work Scheduled and Accomplishments

Conventional Coal Testing

Two of the Phase 2 coal samples, the Ohio 5/6/7 and North Dakota lignite, were received in June, 1998, and the remaining sample, the Wyodak, was received in August of 1998. Splits of these coals were sent to Geochemical Testing, Inc. of Somerset, PA, for Proximate, Ultimate, BTU, FSI, Ash Fusion, Sulfur Forms and Air Dry Loss testing. Results of these tests are given in Appendix 1, which includes results for the Wyodak sample, not available at the time of the previous semiannual report.

Leaching Studies

Leaching of the Ohio 5/6/7 and North Dakota samples was initiated during the last reporting period, and completed during the fall of 1998. Preliminary leaching results for these samples were reported at the review meeting in Tucson in January, 1999. These results were based only on the INAA data for solid residues, and CVAA data for Hg, as ICP-MS and ICP-AES data for the leachates had not been returned at that time. The ICP-MS data have since been returned, but ICP-AES data are still unavailable. As suspected in January, we have confirmed that the normality of the HNO_3 used to leach the Ohio and North Dakota samples was too low, resulting in incomplete digestion of pyrite. As a result, the entire leaching procedure has been repeated for these samples. Leachates and solid residues for this repeat procedure will be submitted for analysis shortly. Meanwhile, the leaching procedure has also been completed for the Wyodak sample, and we are awaiting the initial (INAA) results. Leaching of the Wyodak sample proceeded without problem, using the correct normality for the HNO_3 step. Polished mounts of the solid residues are being prepared to confirm that digestion of pyrite and other minerals was complete. To further characterize the leached residues, Frank Huggins has agreed to do XAFS determinations on residues from the Wyodak sample.

Preliminary leaching results reported in Tucson indicated unusually high ammonium acetate leachable fractions for As (35%), Fe (35%), Cr (35%) and Se (20%) in the North Dakota sample. We now recognize that this is due to the fact that the reference whole coal was dried before INAA analysis (to prevent production of H_2 gas when the sample is irradiated), whereas the leaching splits were taken from the as-received coal having a moisture content of 35.9%. The large ammonium acetate-leachable fractions reported in Tucson result from this difference in basis. Revised preliminary leaching results, corrected to an as-received basis are given in Table 1. Note that correction for moisture content of samples is routinely taken into account in the calculations as the leaching process progresses, but the correction was omitted in this case. Results in Table 1 are for the ammonium acetate, HCl and HF leaching steps only, for the elements As, Fe, Cr, Se, and Hg. Because of its low moisture content (2.3%), the preliminary results for the Ohio sample are unchanged. Results for HNO_3 and the unleached fraction cannot be reported due to the problem with the normality of the HNO_3 noted above. Note also that these results will likely be modified as all of the leaching data become available.

Table 1. PRELIMINARY LEACHING DATA (revised)

INAA ONLY (in percent; Hg by CVAA)

ELEMENT/Coal	*CH_3COONH_4*	*HCl*	*HF*
As (ppm)			
Ohio 16.5	0	20	5
N. Dakota 9.9	0	35	15
Fe (wt. %)			
Ohio 1.43	0	15	5
N. Dakota 0.79	0	55	15
Cr (ppm)			
Ohio 15.0	0	0	25
N. Dakota 11.8	0	15	50
Se (ppm)			
Ohio 1.8	10	0	0
N. Dakota 0.94	0	0	25
Hg (ppm)			
Ohio 0.18	5	0	15
N. Dakota 0.05	0	15	0

SEM

Initial determination of the mineralogy of the three Phase 2 coals was made by SEM/EDX and is summarized in Appendix 2. The Ohio 5/6/7 coal contains all of the 5 most common major phases: quartz, illitic clay, kaolinitic clay, pyrite and calcite. The illite grains in this sample are large (some larger than 50 micrometers) and well formed, and may be appropriate for follow-up studies on Cr distribution using the ion probe (see below). Based on this preliminary work, the North Dakota sample appears to lack both kaolinite and calcite, and the Wyodak sample appears to lack calcite.

The minor or trace phases found, and their compositions are shown in the lower part of Appendix 2. Each of the 3 samples contains a TiO_2 phase (probably rutile), monazite (REE phosphate) and sphalerite (ZnS). Barite ($BaSO_4$) and an iron-oxide or hydroxide phase are common in both the North Dakota and Wyodak samples. An interesting suite of accessory silicates is present in the North Dakota sample, including epidote, chlorite, and probable, alkali-feldspar. The presence of these phases is suggestive of a metamorphic contribution to the coal basin. Subsequent SEM work will attempt to reconfirm the basic findings presented here, and identify additional trace phases that could host the elements of interest in this study.

LTA

Low temperature ashing of the Ohio and Wyodak coal samples is complete. Ashing of the North Dakota sample is continuing. The excessive ashing time for this sample is probably due to its low rank. Lignites tend to have a high concentration of cations associated with carboxyl groups. These cations tend to neutralize the oxygen plamsa during ashing thus significantly reducing the rate of ashing. An additional problem with lignites is that the fixation of sulfur as sulfate is much higher than with bituminous coals. As the ashing progresses this fixed sulfate coats the remaining particles, which shields the surfaces from the oxygen plasma, further hampering the ashing process. The increased sulfates also may obscure the X-ray diffractogram making it difficult to interpret. As a result, the North Dakota sample will be re-ashed following an ammonium acetate leach which should remove the carboxyl-bound cations, and prevent fixation of the organic sulfur as sulfate.

XRD

X-ray diffraction studies of the Wyodak coal and Ohio are commencing. These results will provide semi-quantitative estimates of the modal proportions of minerals present in the coal, to be used in conjunction with the SEM data. XRD studies of the North Dakota sample will commence when ashing of this sample is completed.

Microprobe

Electron microprobe analyses were obtained for a number of pyrite grains in each of the three Phase 2 coals. Elements determined include Pb, Se, Cu, Cd, As, Ni, Zn, Co, Fe, and S. Analytical methods are similar to those used in Phase 1, except that Pb has been added to the procedure. Each of the analyses plotted represents a ~3 micrometer spot, and individual pyrite grains are represented by 1 to 6 spot analyses. The most commonly encountered pyrite forms include subhedral, irregular, and framboidal. The data are not sufficient to make generalizations about trace-element differences among the various pyrite forms, or to approximate average concentrations of these elements in pyrite for each sample. Additional data for pyrite will be obtained in subsequent probe sessions.

The largest pyrite grains, up to nearly 200 micrometers in maximum dimension, occur in the Ohio sample, but as shown by Figure 1, these grains appear to be among the lowest in As. Some of the smaller pyrite grains in this sample have higher As contents, but in no case does this exceed about 0.35 weight percent. Pyrite grains in the North Dakota and Wyodak coals are generally small (<5 to about 75 micrometers) and show a range of As contents below about 0.25 weight percent [note: grain sizes represent grains chosen for microprobe analysis and are not the result of a systematic grain-size analysis].

An electron microprobe session devoted to carbonates was also completed. The following elements were determined (as oxides)- Mn, Mg, Pb, Ca, Sr, Ba, and Zn. Five samples were investigated including the Phase 1 Pittsburgh and Illinois #6 samples, the Phase 2 Ohio sample, and two samples from our previous PRDA project with CQ, Inc.- an Eastern Interior, and a Northern Appalachian coal. Calcite is a common constituent in each of these samples. The results confirm that Mg, Fe, Sr, and Mn are commonly present at trace to minor element levels in calcite, and measurable concentrations of Ba, Pb, and Zn were found in a few cases. Results for calcite in the Phase 2 Ohio 5/6/7 sample are given in Table 2.

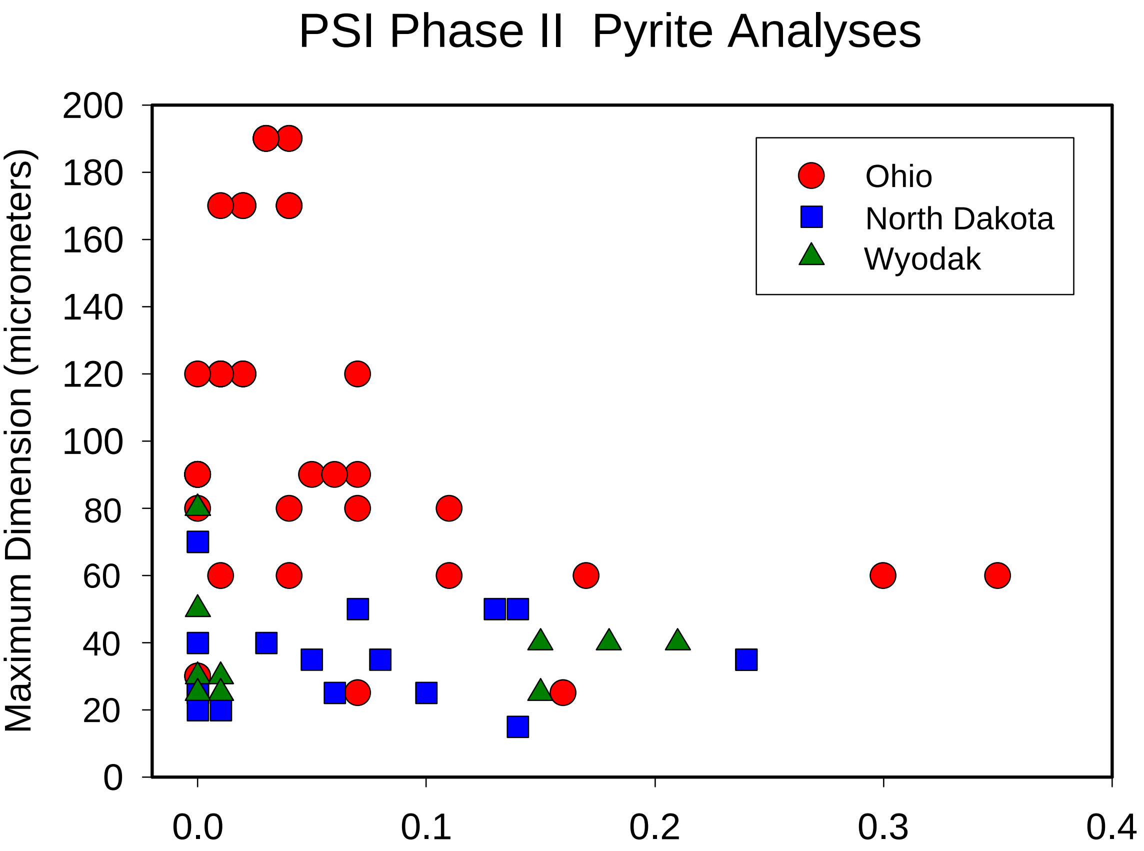

Figure 1. Plot of arsenic weight percent vs. maximum dimension of analyzed pyrite grains in the 3 Phase 2 coals.

Table 2. Electron microprobe analyses of calcite in the Phase 2 Ohio 5/6/7 Sample [note: ideal total for pure stoichiometric calcite is 56.0%].

				PSI PHASE 2		OHIO			
MnO	MgO	PbO	CaO	FeO	SrO	BaO	ZnO	Total	Analysis
0.39	0.38	0.03	55.71	0.37	0.20	0.06	n.d.	57.14	clc1.1
0.47	0.47	0.00	55.53	0.49	0.30	0.00	n.d.	57.26	clc1.2
0.81	0.21	0.00	57.66	1.53	0.02	0.04	n.d.	60.27	clc2.1
0.67	0.22	0.03	58.02	1.67	0.07	0.00	n.d.	60.67	clc2.2
0.80	0.19	0.01	57.01	1.37	0.02	0.00	n.d.	59.40	clc2.3
0.50	0.23	0.01	54.35	0.86	0.08	0.04	0.01	56.08	clc2.4
0.54	0.20	0.01	51.13	0.89	0.05	0.00	0.00	52.81	clc2.5
0.00	0.39	0.01	59.16	2.05	0.06	0.00	n.d.	61.66	clc4.1
0.03	0.63	0.03	56.74	1.89	0.06	0.00	n.d.	59.37	clc4.2

PSI PHASE 2 OHIO Continued

MnO	MgO	PbO	CaO	FeO	SrO	BaO	ZnO	Total	Analysis
0.32	0.41	0.00	56.88	1.04	0.17	0.00	n.d.	58.82	clc5.1
0.32	0.43	0.00	56.32	1.25	0.20	0.00	n.d.	58.52	clc5.2
0.29	0.43	0.02	56.76	1.30	0.22	0.00	n.d.	59.01	clc5.3
0.22	0.49	0.00	55.86	1.23	0.19	0.05	n.d.	58.03	clc5.4
0.26	0.40	0.00	54.67	0.75	0.28	0.00	0.00	56.35	clc5.5
0.32	0.35	0.03	54.64	0.85	0.20	0.00	0.00	56.38	clc5.6

Ion Probe

In keeping with our goal of developing new quantitative methods for direct determination of trace element concentrations in coal components, we began exploratory work during Phase 1 using the Cameca 4f Secondary Ion Mass Spectrometer (Ion Probe) at the National Institute of Standards and Technology, and the Cameca 6f ion probe at the Carnegie Institution of Washington. Based on our experience with these “smaller” ion probe facilities, in December, 1998, we developed a proposal to use a new state-of-the-art SHRIMP-RG ion microprobe run jointly by the USGS and Stanford University (Appendix 3). The proposal addresses the following elements: 1) distribution of arsenic on the surface of fly ash particles; 2) distribution of mercury in sulfides in coal; 3) distribution of Cr in illite in coal, and 4) distribution of trace elements in coal macerals. As of March, 1999 we have learned that this proposal has been approved, and we are planning the initial SHRIMP-RG session during the summer of 1999.

Priorities for upcoming work

New procedures in Phase II

Development of new procedures for Hg. Cold vapor atomic fluorescence (CVAF) development work for Hg analyses is ongoing in Denver. Trials indicate that the minimum detection limit by this method is limited by a total analytical blank level in the 0.01 to 0.02 ppm (10-20 ppb) range, similar to the detection limit for the cold vapor atomic absorption (CVAA) method used previously. Reagents used in this procedure include nitric acid, sulfuric acid, and vanadium pentoxide (99.5% pure). It appears that the blank is controlled by V_2O_5 (30-40 parts per **trillion**) vs. <2 ppt for each of the acids. Two new high-purity V_2O_5 reagents (99.99% and 99.995% pure) are currently being evaluated. As an interim step, Hg analyses will be done by CVAA, in parallel with CVAF development. Once an acceptable CVAF blank level is attained, the analyses will be repeated as necessary.

SEM examination of solid residues after leaching. Another procedural change in Phase 2 involves routine SEM examination of residues after leaching, to insure that mineral matter, especially pyrite, is completely digested. Polished mounts of these residues are currently being prepared, and these will be examined when they are available.

Revision and Clarification of Phase I Results

Elkhorn/Hazard sample

Review of Phase I results conducted during the hiatus between Phase 1 and Phase 2 primarily concerned the Elkhorn/Hazard sample, in which pyrite digestion during the nitric acid leaching step was found to be incomplete. As a result, in our revised Phase 1 Final Report, the fraction of arsenic in pyrite determined (20%) was adjusted to the maximum value (65%), assuming that all of the unleached arsenic in this sample (45%) occurred in pyrite. The actual value for percent arsenic in pyrite must be somewhere between 20% and 65%. Re-leaching of the Elkhorn/Hazard sample was completed and SEM examination of the re-leached solid residue shows that all of the pyrite was digested. Re-leaching results for the element-specific techniques (Se and Hg) were reported in the last semi-annual report, showing that for Se, the nitric acid fraction (20%) did not change, and HNO_3 results for Hg changed from 0% to 20%. Re-leaching results for the remainder of the Phase 1 elements were returned in the last quarter and are reported in Appendix 4. The data show that significant additional amounts of Fe (15%), As (15%) and Ni (35%) were obtained, consistent with the occurrence of these elements in pyrite.

Phase I Publications

Three papers involving USGS authors have been submitted to the special issue of Fuel Processing Technology, devoted to the Phase 1 study. These include two papers integrating USGS results and XAFS results for 1) chromium (Huggins et al.), and 2) arsenic (Kolker et al.) in the four Phase I coals. Abstracts of these two papers were given in the previous semiannual report. Favorable reviews have been returned for both manuscripts. Based on the reviewers comments, a revised version of the chromium manuscript has been submitted, and revisions of the arsenic manuscript are in progress. A third Phase 1 manuscript, combining USGS results, XAFS results, and analysis size/density separates (Senior et al.) has recently been submitted for publication in the special issue, and is currently in review.

Other Issues

Moisture correction

During the last quarter, the issue of moisture was raised in discussions between the USGS and PSI, Inc. Because of the high moisture content of the North Dakota and Wyodak samples, it is very important that chemical results be reported on a uniform basis. According to Dr. Connie Senior, some labs are currently reporting on an as received basis while others are reporting on a dry basis. This makes it very difficult to compare results. We have expressed our view to Connie that all labs should report elemental results on a dry basis (Appendix 5).

Summary

Leaching procedures have been completed for the three Phase 2 coals and a portion of the analytical results have been returned. A problem with the nitric acid concentration necessitated re-leaching the Ohio and North Dakota samples and these procedures have been completed as well. Initial SEM and electron microprobe results have been determined, and these results are summarized here. Low temperature ashing has been completed for the Ohio and Wyodak samples, and these will be followed by XRD determinations. A proposal to use the USGS-Stanford University SHRIMP-RG ion microprobe for trace-element studies of pyrite and illite grains, and organic portions of the coals has been approved by the USGS selection committee, and time on the instrument is being scheduled.

References

Huggins, F. E., Shah, N., Huffman, G. P., Kolker, A., Crowley, S, Palmer, C. A., and R. B. Finkelman, R. B, Mode of occurrence of chromium in four U.S. coals: Submitted to Fuel Processing Technology.

Kolker, A., Palmer, C. A., Crowley, S., Finkelman, R. B., Huggins, F. E., Shah, N.and Huffman, G. P., Mode of occurrence of arsenic in four U.S. coals: Submitted to Fuel Processing Technology.

Senior, C. L., Sarofim, A. F., Olmez, I., Ames, M. R., Zeng, T., Huffman, G. P., Huggins, F. E., Kolker, A., Finkelman, R. B., Palmer, C. A., and Mroczkowski, S., Chemical form and physical distribution of trace elements in selected U.S. coals: Submitted to Fuel Processing Technology.

APPENDICES

Appendix 1. Summary of coal test results for the Ohio 5/6/7, North Dakota and Wyodak samples (as received basis).

	OHIO 5/6/7	NORTH DAKOTA	WYODAK
PROXIMATE ANALYSIS			
Moisture	2.33	35.88	25.81
Ash	9.70	9.38	6.03
Volatile Matter	39.19	28.15	34.85
Fixed Carbon	48.78	26.59	33.31
TOTAL	100.00	100.00	100.00
ULTIMATE ANALYSIS			
Hydrogen	5.07	6.59	6.51
Carbon	71.07	38.57	51.19
Nitrogen	1.37	0.42	0.72
Sulfur	2.62	0.63	0.32
Oxygen	10.17	44.41	35.23
Ash	9.70	9.38	6.03
TOTAL	100.00	100.00	100.00
FORMS OF SULFUR			
Sulfate	0.02	0.09	0.01
Pyritic Sulfur	1.39	0.18	0.04
Organic Sulfur	1.21	0.36	0.27
HEATING VALUE (BTU/lb)	12865	6392	8869

Appendix 2. Preliminary Mineralogy- PSI Phase II Coals (SEM Only)

		Ohio	**North Dakota**	**Wyodak**
Major Phases				
Quartz		X	X	X
Illite		X	X	X
Kaolinite		X		X
Pyrite		X	X	X
Calcite		X		
Minor or Trace Phases				
Epidote	*Fe-Mg-Ca-Al silicate*		X	
Chlorite	*Fe-Mg-Al silicate*		X	
Alkali-feldspar	*K-Al-silicate*		X	
Zircon	$ZrSiO_4$			X
Barite	$BaSO_4$		X	X
Fe-O(OH) phase			X	X
TiO_2 phase		X	X	X
Apatite	*Ca-phosphate*	X	X	
Crandellite	*Ca-Al phosphate*			X
Goyazite	*Sr-Al-REE phosphate*		X	
Monazite	*REE phosphate*	X	X	X
Sphalerite	ZnS	X	X	X
Chalcopyrite	$CuFeS_2$			X

Appendix 3. Proposal to USGS SHRIMP-RG Facility Committee for machine-time on this instrument.

Stanford – USGS Ion Microprobe Research Project Proposal
Toxic Elements in Coal and Coal Combustion Products

Principal Investigator: Allan Kolker, Energy Resources Team, Eastern Region
Co-Principal Investigators: Harvey E. Belkin, Eastern Energy Resources Team and Office of the Eastern Regional Geologist; Robert A. Zielinski, Energy Resources Team, Central Region

P.I 's experience with beam instruments and mass spectrometry: The PI has been a hands-on user of the following: 1) Synchrotron X-Ray fluorescence microprobe, beamline X-26, National Synchrotron Light Source, Brookhaven National Lab; 2) VG-PlasmaQuad ICP-MS (University of Nebraska); 3) Shields (NBS)-type mass spectrometers (SUNY-Stony Brook) 4) Electron microprobe, including ETEC Autoprobe, ARL-EMX, Cameca Camebax, and JEOL 8900 5) SEM, including ETEC Autoscan and JEOL 840.

Description: Understanding the occurrence of potentially toxic elements is necessary for making environmentally sound decisions about coal utilization and predicting the dispersion of unwanted substances during coal combustion and disposal of combustion wastes. In this context, four specific studies are proposed for the SHRIMP-RG, including: 1) determination of arsenic, selenium, and mercury contents and distribution in fly ash; 2) determination of mercury contents and distribution in pyrite in coal; 3) determination of chromium contents in illitic clays, in coal; and 4) providing in-situ measurements of the concentrations of organically-bound elements in coal macerals.

The first study is prompted by indications that volatile elements such as As, Se, and Hg condense on the surface of fly ash particles as they cool, leading to surface enrichments of these elements that may be leached into the environment (EPRI, 1998). This surface enrichment phenomenon has been demonstrated for a range of minor and trace elements (Linton et al., 1977), but attempts to determine the distribution of As, Se and Hg have been inconclusive, due in large part to difficulties in determining concentrations of these elements on particle surfaces. Evidence for volatilization-condensation of As and Se on fly ash is largely based on extreme enrichments of these elements in bulk samples of very fine particle fractions (Davidson et al., 1974), and not on direct measurements of surface coatings. In preliminary studies, we investigated fly ash samples using a time of flight (pulsed) SIMS instrument, and a Cameca IMS 4f at NIST, and a Cameca IMS 6f instrument at the Department of Terrestrial Magnetism, Carnegie Institution of Washington. In all cases, we could not resolve ^{75}As from a range of possible interferences. We believe that the superior mass resolution of the SHRIMP-RG, together with its depth-profiling capability, will be required to address the question of As, Se, and to the extent possible, Hg deposition on fly ash surfaces.

The second proposed study follows from coal leaching studies conducted in our labs (Palmer et al., 1998) showing that elements such as As, Se and Hg occur primarily in pyrite. The presence of As (and Se) in pyrite is confirmed by electron microprobe, but Hg concentrations are below the microprobe detection limit. The detection limits of a SIMS instrument are needed to determine these Hg contents. We also wish to distinguish possible epitaxial Hg, from Hg in solid solution in pyrite, again requiring elemental depth profiles. In preliminary studies, we investigated mercury in arsenic-rich pyrite using the Cameca 6f SIMS, but found that there was not sufficient ionization of ^{202}Hg to obtain meaningful results. Mercury is especially important in light of current interest in this issue, resulting from the likelihood for legislative mandates of Hg emissions from coal-burning power plants.

The issue of chromium in the environment is of interest because the hexavalent form of the element is a known carcinogen. Coal leaching studies show that fractions of Cr are removed by HF, indicating an aluminosilicate association. We have tentatively assigned this Cr fraction to the clay mineral illite, one of the most common minerals in coal. Electron microprobe analyses indicate that Cr is present in illite at concentrations near the detection limit, but precision at these levels (100-200 ppm) is very poor. Ion probe data are needed to help refine our understanding of the distribution of Cr in coal.

Understanding the distribution of toxic elements in organic portions of coal is important because this is the largest fraction of coal, it is consumed in power generation, and by definition, it cannot be removed in coal cleaning procedures. Much of what is known about the elemental distribution of coal macerals is based on bulk studies, some of which are contradictory and method-dependent. In coal leaching studies, the organic association of elements can only be inferred, as this generally represents the fraction remaining in the solid residue. The proposed SIMS investigation of coal macerals follows from preliminary results by Kolker (1989; published in Kolker and Finkelman,1998), Lyons et al. (1989) and others, showing concentrations of As, Se, and other elements at the 1-10 ppm level, and measurable concentrations of Hg in the organic fraction of coal.

Quantification of results with the SHRIMP-RG will require appropriate standards. NIST glasses SRM 610 and 611 may provide an acceptable matrix match for the fly ash samples. Arsenic is present in these glasses, but its concentration must be defined independently. For the chromium in illite study, USGS microprobe standard MBST (Stillwater biotite), having 2.15 wt. % Cr_2O_3 should be of use. Mercury-bearing sulfide standards, such as cinnabar, will be used in analysis of mercury in pyrite. Standards and procedures for the analysis of organic portions of coal have yet to be determined.

Each of the proposed study elements has important environmental implications, and none is routine, even for the SHRIMP-RG. Our studies require good spacial resolution for fine grained samples such as clays, high mass resolution to resolve interferences, and depth profiling capability, to determine enrichments on grain surfaces. While third-generation synchrotron sources offer comparable detection limits and spot sizes, penetration depths are typically much greater, and are not a function of time. Only the SHRIMP-RG offers all of the features needed for the proposed investigations.

Analysis time: A minimum of 1 machine-day, exclusive of pump-down and beam change-over time, will be required for an initial evaluation of each of the 4 proposal elements (4 days total). This study would not commence until both the O^- and the Cs^+ ion sources are available in order to optimize instrument conditions for the task at hand.

Funding sources: Funding for portions of the proposed work is available from DOE contract DE-AC22-95PC95101 to PSI, Inc., “Toxic Elements from Coal Combustion- A Comprehensive Assessment”, and SIR project “Environmental Impact of Coal Utilization”.

Relevant publications:

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Electric Power Research Institute (EPRI), 1998, Identification of arsenic species in coal-ash particles, EPRI Report TR-109002, Palo Alto, CA, 227 p.

Linton, R. W., Williams, Peter, Evans, C. A., Jr., and Natusch, D. F. S., 1977, Determination of the surface predominance of toxic elements in airborne particles by ion microprobe mass spectrometry and auger electron spectrometry: Analytical Chemistry, v. 49, no. 11, p. 1514-1521.

Lyons, P. C., Palmer, C. A., Bostick, N. H., Fletcher, J. D., Dulong, F. T., Brown, Z. A., Krasnow, M. R., and Romankiw, 1989, Chemistry and origin of minor and trace elements in vitrinite concentrates from a rank series from the eastern United States, England, and Australia: International Journal of Coal Geology, v. 13, p. 481-527.

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Kolker, Allan, and Koeppen, R. P. 1998, Arsenic variation in pyrite in coal: Proceedings of the Fifteenth Pittsburgh Coal Conference, 10 p. (CD-ROM).

Kolker, Allan and Finkelman, R. B., 1998, Potentially hazardous elements in coal: Modes of occurrence and summary of concentration data for coal components: Coal Preparation, v. 19, p. 133-157.

Appendix 4. Summary of results from re-leaching Phase 1 Elkhorn/Hazard sample (HNO_3 only- other leaching steps are unchanged).

Element	Previous Result (HNO_3 % leached)	Additional % Leached	Revised Result (HNO_3 % leached)	Total % leached
Fe	15	15	30	90
As	20	15	35	70
Cr	10	0	10	45
Ni	5	35	40	70
Hg	0	20	20	70
Se	5	0	5	50

Appendix 5. Text of correspondence on moisture corrections in project samples.

To: Dr. Connie Senior	From: Curtis A. Palmer
PSI, Inc.	USGS Energy Resources Program
Andover, MA	Reston, VA

Connie:

We also have a serious concern about moisture in low rank coals. We have in the past always reported values on an as received or as determined basis. Recently we have become convinced that the only consistent way to report values is on a dry basis. The best way to deal with low rank coals is on an equilibrium basis which means that you allow the coal to equilibrate with room conditions for 1 to 2 hours prior to weighing, then weigh all whole coal moisture and chemical analysis sample splits as quickly as possible. This reduces the change in moisture during weighing and allows one to calculate values on a dry basis.

For whole coal techniques, once the weight has been taken, changes in weight due to moisture changes will not affect the analysis. For samples, determined on the ash, losses during ashing need to be corrected for the amount of moisture at the time of ashing to determine the dry basis. Generally, the ash is keep in a desiccator in a dry state until weighing for analysis. The ash generally is not as hydroscopic as the low rank coals.

In the future we will report all whole coal values on a dry basis and we suggest that this should be done for all your labs.

Curtis A. Palmer
Research Chemist