TOXIC SUBSTANCES FROM COAL COMBUSTION
A Comprehensive Assessment

Quarterly Technical Report

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ABSTRACT

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 support from the Federal Energy Technology Center (FETC), the Electric Power Research Institute, and VTT (Finland), Physical Sciences Inc. (PSI) has teamed with researchers from USGS, MIT, the University of Arizona (UA), the University of Kentucky (UK), the University of Connecticut (UC), the University of Utah (UU) and the University of North Dakota Energy and Environmental Research Center (EERC) to develop a broadly applicable emissions model useful to regulators and utility planners. The new Toxics Partitioning Engineering Model (ToPEM) will be applicable to all combustion conditions including new fuels and coal blends, low-NO_x combustion systems, and new power generation plants. Development of ToPEM will be based on PSI's existing Engineering Model for Ash Formation (EMAF).

This report covers the reporting period from 1 January 1999 to 31 March 1999. During this period, a full Program Review Meeting was held at the University of Arizona. At this meeting, the progress of each group was reviewed, plans for the following 9 month period were discussed, and action items (principally associated with the transfer of samples and reports among the various investigators) were identified.

Also during this reporting period, in the area of coal analysis, USGS leaching procedures have been completed for the three Phase II 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 also been determined. Low temperature ashing has also been completed for the Ohio and Wyodak samples, and these will be followed by XRD determinations. Preliminary leaching results were revised to reflect as-received fractions in the coals. As a result, the fractions leached by ammonium acetate that were reported at the Program Review Meeting were revised downward. XAFS experiments were conducted at both the Stanford University SSRL and the Brookhaven National Synchrotron Light Source (NSLS) during this reporting period. Experiments at the Stanford SSRL examined samples for mercury while experiments at NSLS examined samples for sulfur and chlorine. Interpretation of spectra will be continuing throughout the next reporting period.

Initial experiments to determine the extent of trace metal vaporization during coal devolatilization were conducted at the University of Utah during this reporting period. Samples were devolatilized using procedures outlined in ASTM volatile analysis standards and subsequently sent to MIT for neutron activation analysis. Initial analysis of the resulting compositional data suggested that several metals were vaporizing under these devolatilization conditions. Also during this reporting period, tube furnace experiments were conducted at the University of Connecticut to assess potential chemical reaction between arsenic species and calcium contained within silicates. Preliminary results indicated that calcium contained within calcium silicates is capable of reacting with arsenic to form calcium arsenate under conditions of

idealized contact. Larger scale baseline combustion experiments were also conducted during this reporting period with the Ohio coal at the University of Arizona. Interpretation of experimental results suggests that particle fragmentation may be contributing to the formation of ash particles that are around 1 micron in size, and that vaporization, condensation, and surface reaction processes are contributing to trace element enrichment in the smallest particulate.

Modeling of post-combustion mercury reactions continued during this reporting period at the University of Connecticut. Calculations of mercury oxidation using both global and elementary reaction kinetics were extended to higher temperatures.

SECTION 1
EXECUTIVE SUMMARY

1. EXECUTIVE SUMMARY

The technical objectives of this project are:

- a) To identify the effect of the mode-of-occurrence of toxic elements in coal on the partitioning of these elements among vapor, submicron fume, and fly ash during the combustion of pulverized coal
- b) To identify the mechanisms governing the post-vaporization interaction of toxic elements and major minerals or unburnt char
- c) To determine the effect of combustion environment (i.e., fuel rich or fuel lean) on the partitioning of trace elements among vapor, submicron fume, and fly ash during the combustion of pulverized coal
- d) To model the partitioning of toxic elements among various chemical species in the vapor phase and between the vapor phase and complex aluminosilicate melts
- e) To develop the new Toxics Partitioning Engineering Model (ToPEM), applicable to all combustion conditions including new fuels and coal blends, low-NO_x combustion systems, and new power generation plants.

A description of the work plan for accomplishing these objectives is presented in Section 2.1 of this report.

The work discussed in this report covers the reporting period from 1 January 1999 to 31 March 1999. During this quarter, a Program Review Meeting was held at the University of Arizona. At that meeting progress in the areas of coal characterization, coal combustion experimentation, and modeling of homogeneous gas phase chlorine and mercury chemistry was discussed. These results were reported principally in Quarterly Report 9, covering October 1998 to December 1998, with some additional reporting contained within this report.

During this quarter, leaching procedures were completed for the three Phase II coals by USGS and a portion of the analytical results were 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 also been determined. Low temperature ashing has been completed for the Ohio and Wyodak samples, and these will be followed by XRD determinations. Preliminary leaching results were revised to reflect as-received fractions in the coals. On this basis, none of the trace element content in North Dakota coals was found to be leachable by ammonium acetate, whereas only 10% of the selenium and 5% of the mercury in the Ohio coal were ammonium acetate leachable. HCl leachable fractions ranged from 0 to 35 % for the two coals, and HF leachable fractions ranged from 0 to 50%. In general, the leachable fractions observed for the Ohio coal were much lower

than those observed for the North Dakota coal. Further form-of-occurrence information was derived from electron microprobe analysis of carbonate grains in several program coals. Results indicated that Mg, Fe, Sr, and Mn were commonly present at trace to minor levels in calcite, with measurable concentrations of Pb, Ba, and Zn found in a few cases.

XAFS experiments were conducted by the University of Kentucky at both the Stanford University SSRL and the Brookhaven National Synchrotron Light Source (NSLS) during this reporting period. Experiments at the Stanford SSRL primarily examined samples for mercury while experiments at NSLS primarily examined samples for sulfur and chlorine. Some arsenic analysis was also conducted. A sink fraction of the Ohio coal was found to contain more than 90% of the arsenic as arsenical pyrite, consistent with previous work on bituminous coal fractions.

Mercury analysis of selected sorbent samples provided further evidence that XANES absorption spectra can provide information on the bonding of mercury to the solid sorbent through use of the inflection point difference (IPD). Interpretation of spectra will be continuing throughout the next reporting period.

Initial experiments to determine the extent of trace metal vaporization during coal devolatilization were conducted at the University of Utah. Samples were devolatilized using procedures outlined in ASTM volatile analysis standards and subsequently sent to MIT for neutron activation analysis. Initial analysis of the resulting compositional data suggested that several metals were vaporizing during devolatilization under these conditions. Analysis of the data will be continuing during the next reporting period.

The potential reaction between arsenic and calcium contained within silicate-derived fly ash particles was investigated in tube furnace experiments conducted at the University of Connecticut. The objective was to determine whether calcium contained within silicate particles typical of fly ash could react with arsenic under idealized contacting conditions. Subsequent analysis of these samples by the University of Kentucky using arsenic XAFS demonstrated that As (V) typical of calcium arsenate was obtained in all samples containing calcium. The arsenic XANES spectrum of the SiO₂ sample indicated that the dominant oxidation state was As (III), potentially the result of As₂O₃ formation on the surface of the silica particles. These results suggest that arsenic can react with calcium embedded within silicates under idealized contacting conditions and long residence times.

Larger scale baseline combustion experiments using the Ohio coal were completed at the University of Arizona during the reporting period. Based on these experiments, it was concluded that particle fragmentation may be occurring in the 0.5 to 2.2 res. sec. furnace zone. The majority of the particles generated during this fragmentation are around 1 micron in size. There was also some evidence that vaporization of trace metals occurs in the 0.5 to 2.2 res. sec. furnace zone. A portion of this vaporized material appears to be selenium and antimony-based compounds. Also in the 0.5 to 2.2 res. sec. furnace zone, heterogeneous transformations did not appear to be significant for any of the trace elements evaluated. No correlation was observed between trace element concentration in the fly ash and particle size. It was thus concluded that

at inlet ESP conditions, surface reaction/pore diffusion heterogeneous transformation mechanisms appear to control the transformation of the gas-phase arsenic and cobalt species, whereas condensation appears to control the transformation of gas-phase antimony species for this coal. The lack of surface reaction/pore diffusion controlled heterogeneous transformation in the post-combustion zone for As, Se, and Cd was attributed to the low concentration of calcium present in the Ohio blend coal.

Modeling of post combustion mercury reactions continued during this reporting period at the University of Connecticut. Calculations of mercury oxidation using global reaction kinetics were extended to higher temperatures as a result of suggestions by University of Washington researchers that super-equilibrium concentrations of mercuric chloride had been experimentally observed. Using chlorine species concentration profiles described in the previous quarterly report (October 1998 to December 1998), it was concluded that conversions in the range of the 40 to 80% reported in field data could be obtained if the starting point for mercury oxidation was increased to approximately 950°C at a cooling rate of 200 K s⁻¹. At higher cooling rates representative of the post combustion temperature profile of a small boiler, however, conversion to oxidized species remained below that observed in the field data. Calculations using typical post combustion temperature profiles will be continuing during upcoming reporting periods.

Also during this reporting period, favorable reviews were returned for two papers integrating USGS results and XAFS results, and a third paper describing the modeling of trace element emissions in field data, all submitted to the special issue of *Fuel Processing Technology* devoted to the Phase I study. A third Phase I manuscript, combining USGS results, XAFS results, and analysis size/density separates has recently been submitted for publication in the special issue, and is currently in review. An additional paper describing XAFS investigation of the speciation of mercury and other elements involved in sorption of mercury on activated carbons was published in the January issue of *Energy and Fuels*. A second paper published in the January issue of *Fuel* described an XAFS method for determining quantitatively the chromium oxidation states in ash products from coal combustion.

SECTION 2

INTRODUCTION AND PROGRAM OVERVIEW

2. INTRODUCTION AND PROGRAM OVERVIEW

2.1 Introduction

Before electric utilities can plan or implement emissions minimization strategies for hazardous pollutants, they must have an accurate and site-specific means of predicting emissions in all effluent streams for the broad range of fuels and operating conditions commonly utilized. Development of a broadly applicable emissions model useful to utility planners first requires a sound understanding of the fundamental principles controlling the formation and partitioning of toxic species during coal combustion. PSI and its team members will achieve this objective through the development of an "Engineering Model" that accurately predicts the formation and partitioning of toxic species as a result of coal combustion. The "Toxics Partitioning Engineering Model" (ToPEM) will be applicable to all conditions including new fuels or blends, low-NO_x combustion systems, and new power systems being advanced by DOE in the Combustion 2000 program.

Based on a goal of developing and delivering this ToPEM model, a 5-year research program was proposed. This program is divided into a 2-year Phase I program and a 3-year Phase II program. The objective of the ongoing Phase II program is to develop an experimental and conceptual framework for the behavior of selected trace elements (arsenic, selenium, chromium, and mercury) in combustion systems and incorporate these concepts into a new engineering model. This Phase II objective will be achieved by a team of researchers from USGS, the Massachusetts Institute of Technology (MIT), the University of Arizona (UA), the University of Kentucky (UK), the University of Connecticut (UC), the University of Utah (UU), the University of North Dakota Energy & Environmental Research Center (EERC) and PSI. Model development and commercialization will be carried out by PSI.

2.2 Program Overview

Our general approach to the development of the ToPEM model is to break the process for toxic formation into sub-processes, each of which will be addressed by team members who are experts in the area. Ultimately, this will result in new sub-models which will be added to the existing Engineering Model for Ash Formation (EMAF) to create ToPEM. Table 2-1 describes the work breakdown structure for the Phase II program. Figure 2-1 illustrates the relationship between the elements of the Phase I work breakdown structure and the sub-processes. Each of the areas identified in the figure will be addressed in the Phase II program as described below.

Forms of Occurrence of Trace Elements in Coal

One of the most important questions to be answered in the program as a whole is whether the form of a particular element in the coal affects its form of emission at the end of the process. The answer to this question will determine the shape of the sub-models that must be developed in this program. Thus, a detailed understanding of the forms of individual trace elements in coal

Table 2-1. Task Breakdown

Technical Task	Team Member	Task (WBS) Number
Program management	PSI	1
Coal acquisition, characterization	PSI	2
Coal, ash trace element characterization	PSI	2
Coal (and ash) characterization -- forms of occurrence	UK, USGS	3, 4
Coal, ash trace element characterization and mercury capture and analysis	MIT	5.2
Mechanistic study: dilute bench scale combustion tests plus equilibrium, kinetic modeling	UU	5.1
Large scale tests at 100,000 Btu/h facility	UA	6
Mechanistic study of kinetic rates for gas-phase reactions	UC	10
Mercury-fly ash interactions at bench scale	EERC	11
Fundamental Engineering Model development	PSI	9.1
Inorganic emissions: literature survey and model validation	UC	9.2

provides a foundation for much of the rest of the program. Key issues that will be addressed in Phase II are the specific mineral associations of individual elements and the relationship between trace metal form and “standard” coal analyses.

Because of the importance of elemental form (e.g., sulfate versus silicate mineral) on partitioning, it is critical that coals representing a broad range of elemental forms be examined in this program. In Task 2 we will select and acquire a total of three coals for study in this program. The coals chosen will represent a broad range of elemental forms of occurrence taken from the major coal ranks and commercial coal seams used for pulverized coal power generation in the US. Once selected, fresh coal samples will be acquired and distributed to team members. These samples will be subjected to ultimate, proximate, and ASTM ash analysis. Coal samples will be analyzed for trace element concentrations by Neutron Activation Analysis (NAA) at the MIT Nuclear Reactor Laboratory (Task 5.2).

Advanced analytical techniques such as Mössbauer spectroscopy and Computer-Controlled Scanning Electron Microscopy (CCSEM) will be used by UK (Task 3) to determine the major mineral species present in the program coals and the combustion generated ash. Whole coal samples and density segregated coal samples will be studied. This analysis will provide important insight on the minerals present in the coal, how they interact during the combustion process, and how this interaction may affect the partitioning of toxic elements.

Figure 2-1. Phase II program organization.

Another important issue is the form-of-occurrence of the trace elements in the coal. In this task the mode of occurrence of As, Cr, and Se will be determined by combining XAFS and the Mössbauer/CCSEM derived data discussed above. Hg will also be evaluated where possible. Other less critical trace elements (Mn, Ni, Zn, Pb, U, etc.) may also be evaluated, especially if their abundance is unusually high in any of the program coals. In addition, the form-of-occurrence of Cl and S in coals and chars will be investigated.

As a complement to the XAFS analysis mentioned above, a unique protocol developed by USGS will be used in Task 4 to analyze selected raw coal, and size and density segregated coal, samples for trace element forms of occurrence. This protocol combines low temperature (< 200EC) ashing, chemical analysis, x-ray diffraction, coal segregation via flotation, ammonium acetate and selected acid leaching, electron microbeam measurements, and low and moderate temperature heating tests to determine the forms of elements in coal. Because of the unique combination of existing testing and analytical facilities available at USGS, the work will be conducted at USGS laboratories.

Combustion Zone Transformations

The effect of coal type and combustion conditions on the emission of the toxic trace elements will be investigated using the UU laminar-flow drop tube reactor (Task 5.1). The fundamental mechanisms of toxic species formation and partitioning will be determined from careful examination of the ash formed under a variety of combustion conditions. Measurements will be made of the partitioning of the trace elements in the three coals as a function of temperature and equivalence ratio. These measurements will provide the baseline data on the fraction vaporized. Individual size-segregated ash samples (collected with a cascade impactor) will then be analyzed by NAA for total composition and other analyses as needed, for example, Auger and STEM for surface composition, TEM and SEM for particle morphology, and possibly water washing and/or chemical leaching to determine the solubility of selected trace elements in the ash samples. Samples will also be submitted to UK for chemical species analysis by XAFS and other techniques.

Post-Combustion Transformations

The goal of this task is an increased understanding of the transformations of selected metals as the flue gases cool following the high temperature combustion zone. Bench scale experimentation will be carried out by several organizations as well as large scale combustion measurements. Advanced analytical methods will be used extensively to understand speciation of trace elements in the post-combustion flue gas.

At the UC (Task 10) experiments will focus on determination of trace vapor-ash particle reactions rates in post-combustion gases, including

- Identification of the rate controlling phenomena in the oxidation of arsenic under combustion conditions
- Relative rates of gas-phase reaction of elemental mercury with HCl and Cl₂ under combustion conditions
- Measurement of rates of heterogeneous conversion of HCl to Cl₂ in the presence of coal combustion products such as iron oxide, iron sulfate, and fly ash samples.

Interactions of mercury with ash and ash components at lower temperatures will be the focus of the effort at EERC in Task 11. A bench-scale sorbent evaluation system will be used to increase our understanding of the interactions between gas-phase mercury and coal ash. Experiments will explore the effects of temperature and the interactions between elemental mercury or mercuric chloride and fly ash samples generated under oxidizing conditions, the effect of mercury concentration on the interactions between elemental mercury and fly ash, and the effect of coal combustion conditions on the ash and ultimately on the interaction between mercury and ash.

On a larger scale in Task 6, UA will determine how both coal composition, detailed mineralogy and combustion conditions (including low NO_x conditions) govern the fate of toxic metals under practical time/temperature, self sustained, yet still aerodynamically well defined, pulverized coal combustion conditions. Program coals will be burned in the UA self-sustained combustor under premixed conditions. The baseline tests will employ the naturally occurring temperature profile for each coal at a stoichiometric ratio of 1.2. Samples will be withdrawn at several ports, representing a range of temperatures and residence times. Complete impactor samples will be collected and analyzed for each toxic metal (11 as listed in the CAAA plus U and Th) plus major elements. This will yield the particle size segregated toxic metal composition, which can be compared to data obtained from other tasks of this program. These data will then be examined to determine particle size dependence in order to infer possible mechanisms governing the fate of each metal.

Model Validation

UC will conduct a more in-depth review of the relevant field data on inorganic emissions (Task 9.2). In Phase II we will emphasize use the field data to validate the models we will develop. The Phase II effort focuses on data from the following sources:

- EPRI PISCES
- DOE Program
- VTT (Finland)
- KEMA (Netherlands).

Important issues to be addressed when reviewing these data include mass balance closure, methods of analysis and sample collection, effect of APCD, effect of bulk coal ash chemistry, particle size distribution, and speciation of Hg.

Model Development

In Task 9.1, data obtained from subcontractor and PSI tasks will be combined to create a comprehensive model of the transformations of important inorganic species during combustion. This model, denoted the ToPEM, will be based on an existing model (the PSI Engineering Model for Ash Formation which predicts ash particle size and composition distributions – EMAF). Because the development of this model is strongly dependent on the mechanistic, equilibrium, and kinetic information being developed under the experimental tasks, ToPEM will incorporate information on the mechanisms controlling species behavior, equilibrium modeling where appropriate and kinetic modeling to mimic kinetic constraints on species behavior. During the later stages of the Phase II work, sufficient detailed information will be available to support specific modifications to EMAF in order to describe the combustion transformations of important inorganic trace elements. Based on the experimental studies, equilibrium modeling, and kinetic modeling, it will be clear which modifications are required. Once complete, the model will be validated using a combination of laboratory and field data. As part of the validation effort, coal and size fractionated ash samples collected from operating utility boilers will be provided by Dr. Esko Kauppinen of VTT, Finland. Once validated, the ToPEM will be

used to simulate the behavior of these and other coals under utility boiler conditions. The results from these simulations will then be compared to field data from PISCES obtained through EPRI participation in this program, DOE field sampling campaigns, and other relevant data in the literature. This validation procedure will ensure that the model developed as the result of the proposed research efforts accurately predicts the behavior of toxic metals species from a wide range of coals during the combustion process in any combustion system.

SECTION 3

RESULTS AND DISCUSSION

3. RESULTS AND DISCUSSION

3.1 Program Management (PSI)

A Program Review Meeting was held at the University of Arizona on January 13 and 14, 1999. Action items identified at the meeting were as follows:

- Several drums of the Phase I coals are in storage at Consol (approximately three drums of each coal). These will be shipped to the University of Arizona.
- UNDEERC will be examining mercury testing data obtained the Coal Creek Station (burning North Dakota lignite) and assessing whether it can be used to focus the bench scale experimental effort.
- Chlorine speciation measurements are planned for the next 6 to 12 month period at the U. Utah. Prior to initiating experiments, U. Utah will contact staff at the EPA laboratory to discuss EPA Method 26A for chlorine speciation measurement.
- The USGS will supply U. Utah with a sample of a Chinese high arsenic coal which U. Utah may use to examine arsenic vaporization from coal macerals.
- MIT will be coordinating the use of vapor phase sorbents (for analytical sample collection) with PSI. UConn, U. Utah, and U. Arizona may be interested in using these sorbents for sampling (and speciating) mercury.
- MIT will repeat neutron activation analysis (NAA) of the program coals to determine calcium concentrations.
- DOE FETC will provide PSI with a copy of a contractor report to provide additional data on the assessment of ash particle penetration through ESPs.
- Researchers at U. Utah will develop a list of planned experiments and provide this to MIT to help with the planning of NAA analyses in the coming months.
- Several possible improvements to the chlorine kinetic calculations will be considered, including an examination of the role of surfaces in the removal of Cl radicals, a consideration of low temperature reactions other than chlorine radical recombination, and an examination of the possible existence of other oxidized forms of mercury such as HgO.

Progress in these areas will be presented and discussed at the next Program Review Meeting, tentatively scheduled for September 1999.

3.2 Coal Characterization (UK, USGS)

3.2.1 *Coal Properties*

Basic coal testing at USGS is now complete, as reported in the previous quarterly report (Quarterly 9, October 1998 to December 1998).

3.2.2 *Coal Mineralogical Characterization*

Initial determination of the mineralogy of the three Phase II coals was made by SEM/EDX at USGS, as reported in Quarterly Report 9. Subsequent SEM work will attempt to reconfirm these basic findings and identify additional trace phases that could host the elements of interest in this study.

Low temperature ashing of the Phase II samples has been ongoing in the first quarter of 1999. 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 plasma 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.

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.

3.2.3 *Forms of Occurrence of Trace Elements by Leaching and Microprobe Analysis*

Leaching of the Ohio 5/6/7 and North Dakota samples was completed by USGS 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. We have, however, confirmed our speculation (reported at the Program Review Meeting) that the normality of the HNO₃ 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 have been submitted for analysis. Meanwhile, the leaching procedure has 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 HNO₃ step. Polished mounts of the solid residues have been prepared to confirm that digestion of pyrite and other minerals was complete. To further characterize the leached residues, Frank Huggins at U. Kentucky has agreed to do XAFS determinations on residues from the Wyodak sample.

Preliminary leaching results reported at the Program Review Meeting 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 H₂ 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 3-1. 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 3-1 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 HNO₃ and the unleached fraction cannot be reported due to the problem with the normality of the HNO₃ noted above. Note also that these results will likely be modified as all of the leaching data become available.

Table 3.1 Preliminary Leaching Data (Revised and Corrected to As-Received Basis)
INAA Only (in Percent; Hg by CVAA).

ELEMENT/Coal	CH ₃ COONH ₄	HCl	HF
<u>As (ppm)</u>			
Ohio 16.5	0	20	5
N. Dakota 9.9	0	35	15
<u>Fe (wt. %)</u>			
Ohio 1.43	0	15	5
N. Dakota 0.79	0	55	15
<u>Cr (ppm)</u>			
Ohio 15.0	0	0	25
N. Dakota 11.8	0	15	50
<u>Se (ppm)</u>			
Ohio 1.8	10	0	0
N. Dakota 0.94	0	0	25
<u>Hg (ppm)</u>			
Ohio 0.18	5	0	15
N. Dakota 0.05	0	15	0

Electron microprobe analyses were obtained for a number of pyrite grains in each of the three Phase II coals, as reported in the last quarterly report (October 1998 to December 1998).

Elements determined include Pb, Se, Cu, Cd, As, Ni, Zn, Co, Fe, and S. 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 I Pittsburgh and Illinois #6 samples, the Phase II Ohio sample, and two samples from a previous USGS 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 II Ohio 5/6/7 sample are given in Table 3-2.

Table 3-2. Electron Microprobe Analyses of Calcite in the Phase II Ohio 5/6/7 Sample
(Note: Ideal total for pure stoichiometric calcite is 56.0%)

PSI Phase II 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
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

Review of Phase I results conducted during the hiatus between Phase I and Phase II 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 I 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) reported previously, show that for Se, the nitric acid fraction (20%) did not change, and HNO₃ results for Hg changed from 0% to 20%. Re-leaching results for the remainder of the Phase I elements were returned in the last quarter and are reported in Table 3-3. 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.

As reported in Quarterly Report 9 (October 1998 to December 1998), cold atomic fluorescence development work for Hg analyses is ongoing at USGS 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 to 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 V₂O₅ (30 to 40 parts per trillion (ppt)) versus < 2 ppt for each of the acids. To test this, two new high-purity V₂O₅ reagents (99.99% and 99.995% pure) have recently been obtained, and blank levels for these are currently being evaluated.

Table 3-3. Summary of Results from Re-Leaching Phase I Elkhorn/Hazard Sample (HNO₃ 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

During the last quarter, the issue of moisture was raised in discussions between the USGS and PSI. 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. Constance L. Senior of PSI, 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 that all labs should report elemental results on a dry basis (Appendix 1).

3.2.4 *Forms of Occurrence of Trace Elements by XAFS*

During the last quarter (January-March, 1999), new project-related experiments were run by U. Kentucky researchers during two synchrotron sessions, one at SSRL, Stanford University,

CA, (February 11th -18th, 1999), the other at NSLS, Brookhaven National Laboratory, NY, (March, 10th-15th 1999). Some new directions for XAFS investigation were explored including reactions of As with Ca-rich synthetic ash particles and direct measurement of elements on ash-collection filters, as well as continuation of work on developing new Hg XANES systematics for interpreting the speciation of Hg sorbed on chars, and characterization of elemental speciation in project coal samples by XAFS spectroscopy.

The new 2.88 sink fraction of the Ohio coal, prepared during the previous quarter, was examined by XAFS spectroscopy at the arsenic K edge. As anticipated from previous work on bituminous coal fractions, it was found to contain more than 90% of the arsenic as arsenical pyrite, with a minor fraction of arsenate. Chromium XAFS spectroscopy was attempted on the Wyodak coal sample, but the Cr content of this coal is so low that the signal/noise ratio was very poor and virtually useless for speciation elucidation.

In addition, the feasibility of using XAFS spectroscopy directly on a filter sample of combustion ash was explored. This particular sample was obtained from the combustion of Illinois #6 coal in the combustion unit at the University of Arizona and was provided to U. Kentucky researchers by W. Seames (University of Arizona). Both the As and Cr absorption edges were examined at SSRL and the quality of the XAFS data obtained from such a sample is indicated in Figure 3-1. Although noisy, it is clear that the oxidation states of chromium and arsenic are predominantly, if not entirely, Cr^{3+} and As^{5+} , respectively. However, direct measurements of trace element occurrences do appear feasible from filter samples from combustion systems.

As discussed in detail in Quarterly Report 9¹ (October 1998 to December 1998) and elsewhere,² the IPD parameter, defined as the separation of the two prominent inflection points in mercury XANES spectra, is proving to be a very useful probe of the chemistry and structure of the local environment around Hg atoms sorbed onto various materials. Also, we have demonstrated that a simulation of mixtures of the XANES spectra of Hg metal and HgCl_2 could reproduce fairly well the observed spectral data trends defined by the IPD parameter and the relative peak-height ratio for mercury captured on char samples. During the last quarter, new XAFS measurements on mercury sulfide, mercuric chloride, and mercury metal have been made at U. Kentucky, and the simulation trends are in the process of being re-evaluated and revised. Moreover, a mathematical simulation is being developed assuming that the first derivative of the mercury XANES spectra can be approximated by Lorentzian-shaped peaks. Both the experimental and theoretical simulation approaches to the data trends observed for the sorption experiments carried out at the University of Arizona are looking promising.

Also during the reporting period, XAFS experiments were conducted at SSRL for mercury and at NSLS for sulfur and chlorine on the following samples: three lignite activated carbon (LAC) sorbents used for Hg capture from different formulations of the synthetic flue gas

Figure 3-1. Chromium and arsenic XANES spectra obtained directly from a filter used to collect fly-ash from the combustion of Illinois #6 coal in the University of Arizona. combustion unit.

in the experimental rig at the Energy and Environmental Research Center (EERC) at the University of North Dakota (prepared by Grant Dunham and Stan Miller, EERC) and a baghouse-hopper ash sample from the Cherokee power plant that had been impregnated with Hg at ADA Technologies (received from Jason Albiston and Sheila Haythornthwaite, ADA Technologies).

As shown in Figure 3-2, there are some significant differences in the appearance of the Hg LIII absorption edge that must relate to differences in how the mercury is bound to the different sorbent matrices. The parameters derived from the XANES spectra are shown in Table 3-4 for each sorbent. The ADA baghouse-hopper ash has the highest value for the IPD parameter and is comparable or greater than the value for HgCl_2 . However, the ash contains virtually no chlorine; hence, the value may represent an average value for different components in the ash. Table 3-5 summarizes data on the mercury, sulfur and chlorine step-heights for the LAC sorbent exposed to different flue gas formulations. The step-height is an approximate measure of the elemental concentration.

No absorption edge was observed for chlorine in the XAFS spectrum of the ADA baghouse-hopper ash, confirming that the ash is essentially devoid of chlorine. This observation reinforces the speculation that the IPD value does not arise from a Hg-Cl complex, but rather represents an average value for two (or more) different mercury components in the ash. To explore this possibility further, the Cherokee ash sample was submitted to J. K. Neathery (UK CAER) for separation using triboelectrostatic technology into carbon-rich and carbon-poor

Figure 3-2. Mercury LIII XANES spectra of mercury captured on the ADA Cherokee baghouse-hopper ash and on three samples of a lignite-activated carbon (LAC) under different flue-gas formulations.

Table 3-4. Mercury XAFS systematics for ADA and EERC Sorbent Samples

Sample	IPD (eV)	Mean Position (eV)	RSF Peak A	Peak Height Ratio
ADA Cherokee baghouse-hopper ash	8.6	4.5	1.91	1.25
LAC #1	6.8	2.8	1.98	0.95
LAC #2	7.0	3.2	1.95	1.00
LAC #3	7.9	3.8	1.91	1.05

Table 3-5. Hg, S and Cl Step-Height Data for Hg Sorbent Samples

Sample	Relative Step-Height Mercury	Relative Step-Height Sulfur	Relative Step-Height Chlorine
LAC #1	1.2	0.5	12
LAC #2	1.0	1	1
LAC #3	0.9	3.5	0.2

samples. A good separation was achieved and the resulting samples have been submitted to the Analytical Laboratory at UK CAER for determination of both the Hg contents and the carbon contents. XAFS investigations of the mercury, sulfur, chlorine and possibly other elements are planned for these fractions during synchrotron sessions scheduled for later this summer. In addition, a second, larger sample of the Hg-impregnated ash from the Cherokee station will be supplied to us by personnel at ADA for more detailed investigation.

The step-height data given in Table 3-5 indicate that there are significant differences in the sulfur and chlorine contents of the lignite activated carbon (LAC) samples after exposure to the different formulations of the simulated flue gas. Sample LAC #1 has clearly adsorbed significant chlorine and furthermore the chlorine XANES spectra show (Figure 3-3) that the form of chlorine adsorbed is in the form of HCl, whereas the Cl XANES spectra of samples LAC #2 and LAC #3 clearly show the presence of organochlorine species. There are also significant differences among the three samples in sulfur contents, but the spectral differences are less marked. All three samples contained predominantly sulfate sulfur with small fractions (<10%) of the sulfur as elemental sulfur (Figure 3-4). The fraction of sulfur in elemental form decreased as the step-height increased, indicating that sulfur was being adsorbed in a sulfate form. The ADA Cherokee ash also had significant sulfate sulfur, but with a very minor fraction of organic (thiophene) sulfur present rather than elemental sulfur.

Figure 3-3. Chlorine K-edge XANES spectra of the three LAC sorbent samples.

Figure 3-4. Sulfur K-edge XANES spectra of the ADA Cherokee baghouse-hopper ash and the three LAC sorbent samples.

3.3 Combustion Zone Transformations (UU, MIT)

3.3.1 *Metal Vaporization at Devolatilization Temperatures*

The objective of this task is to determine whether metal vaporization occurs at the temperatures normally associated with coal devolatilization. Seven coals were studied at the University of Utah, the six project coals and a Utah bituminous for which the University of Utah has extensive data from other projects. The coals were converted to fixed carbon using the ASTM volatile analysis procedure. Samples of the parent coal and of the fixed carbon and samples of NIST trace elements in coal fly ash standard reference material were sent to MIT for elemental analysis by INAA. Table 3-6 presents a summary of the current data. Overall, the results suggest significant metal vaporization has occurred. However, many of the data are suspect and are subject to revision.

Tests for data consistence and accuracy include comparison of the NIST standard material analysis to published values and agreement between replicate values within counting uncertainty. One of three standard samples showed large differences from published values. Many of the values in Table 3-6 show poor agreement between replicate determinations. In some cases the element could not be quantified in one or more of the samples and a limit of detection without a $\pm$ value was reported. Discussions regarding these data problems are underway and reanalysis of samples is anticipated.

In the table the composition of the parent coals (p-sample numbers) and fixed carbon (c-sample numbers) are listed along with the $\pm$ value reported. These values are then averaged. The expected value is the parent coal content of that element divided by the fixed carbon and is the concentration obtained by material balance assuming no loss of the element. The next two columns compare the measured concentration in the fixed carbon to the expected value. Differences less than twice the pooled uncertainty should not be considered statistically significant. The last column shows the apparent loss of the element as a percentage of the expected value.

3.3.3 *Measurement of Gas-Phase Mercury and Other Trace Metals*

Attempts to develop an alternative to the Ontario Hydro method for speciated Hg sampling are continuing, but as yet are still unsuccessful. Collection of HgCl_2 by ion exchange methods have been unrepeatable and, at least for the present, have been set aside. The Rand TRIS/EDTA method is being tested, but may not offer much of an advantage over the Ontario Hydro method.

Table 3-6. Metal Concentrations (Dry Basis) for Parent and Devolatilized Coals from U.Utah Experiments

Coal Name:	North Dakota Lignite														
	Volatile Matter														
	Sample #2	Avg	Avg fixed carbon												
Sample # 1	0.4275	0.4275	0.5725												
μg/g									Pooled ±	Dried Avg	Fixed C Avg	Expected	M-E/ StDev	(M-E)/E	Δ %
Sample ID	D14p1	±	D14p2	±	D14c3	±	D19c4	±							
Na	3800	260	3400	230	5600	380	6500	440	327.50	3600	6050.00	6288.21	-0.73	-0.04	-3.79
Mg	5200	1100	5200	970	8200	1500	8600	1700	1317.50	5200	8400.00	9082.97	-0.52	-0.08	-7.52
Al	8700	360	7800	320	12000	480	13000	530	422.50	8250	12500.00	14410.48	-4.52	-0.13	-13.26
Cl	81	18	53	14	57	17	110	26	18.75	67	83.50	117.03	-1.79	-0.29	-28.65
K	2500	770	1500	480	1800	480	3000	640	592.50	2000	2400.00	3493.45	-1.85	-0.31	-31.30
Sc	1.8	0.12	1.7	0.11	3.3	0.21	3.1	0.2	0.16	1.75	3.20	3.06	0.90	0.05	4.69
Ti	580	86	350	57	610	88	610	91	80.50	465	610.00	812.23	-2.51	-0.25	-24.90
V	17	1.3	18		24	1.6	29	1.7	1.53	17.5	26.50	30.57	-2.65	-0.13	-13.31
Cr	9.3	1.1	20	1	18	0.8	23	0.65	0.89	14.65	20.50	25.59	-5.73	-0.20	-19.89
Mn	67	1.1	65	1.1	100	1.7	120	1.8	1.43	66	110.00	115.28	-3.71	-0.05	-4.58
Fe	8900	470	8300	380	13000	540	16000	620	502.50	8600	14500.00	15021.83	-1.04	-0.03	-3.47
Co	9	0.71	7.8	0.5	13	0.72	14	0.74	0.67	8.4	13.50	14.67	-1.76	-0.08	-7.99
Zn	13		28	7.5	40	6.6	40	5.9	6.67	20.5	40.00	35.81	0.63	0.12	11.71
Ga	8.6		4.3	3.5	8.1	6.5	2.6		5.00	6.45	5.35	11.27	-1.18	-0.53	-52.51
As	12	1.2	11	1.1	16	1.6	17	1.7	1.40	11.5	16.50	20.09	-2.56	-0.18	-17.86

Table 3-6. Metal Concentrations (Dry Basis) for Parent and Devolatilized Coals from U.Utah Experiments (Continued)

μg/g									Pooled ±	Dried Avg	Fixed C Avg	Expected	M-E/ StDev	(M-E)/E	Δ %
Sample ID	D14p1	`±	D14p2	`±	D14c3	`±	D19c4	`±							
Se	2.1	1.4	1.3	1.1	1.9	0.87	1	0.48	0.96	1.7	1.45	2.97	-1.58	-0.51	-51.17
Br	3.3	0.91	2.7	0.76	3.6	0.96	9.3	2.5	1.28	3	6.45	5.24	0.94	0.23	23.09
Rb	32		8.8	5.8	12		12	2.8	4.30	20.4	12.00	35.63	-5.50	-0.66	-66.32
Sr	370	55	320	46	670	91	630	79	67.75	345	650.00	602.62	0.70	0.08	7.86
Mo	2.4	0.61	2.6	0.69	4.2	0.93	3.4	0.76	0.75	2.5	3.80	4.37	-0.76	-0.13	-12.98
Cd	0.22		0.54	0.51	110		0.18	0.14	0.33	0.38	55.09	0.66	167.47	82.00	8199.74
In	44	42	21	20	23		78	58	40.00	32.5	50.50	56.77	-0.16	-0.11	-11.04
Sb	0.79	0.068	0.65	0.06	1.4	0.1	1.4	0.11	0.08	0.72	1.40	1.26	1.68	0.11	11.32
Cs	190		0.64	0.16	0.73	0.18	0.88	0.15	0.16	95.32	0.81	166.50	-1014.45	-1.00	-99.52
Ba	690	53	620	48	820	61	890	62	56.00	655	855.00	1144.10	-5.16	-0.25	-25.27
La	4	0.25	4.2	0.27	6.9	0.44	6.5	0.41	0.34	4.1	6.70	7.16	-1.35	-0.06	-6.45
Ce	6	0.59	7.2	0.49	13	0.69	12	0.61	0.60	6.6	12.50	11.53	1.63	0.08	8.43
Nd	1.5	0.67	2.4	0.51	6.4	0.97	5.6	0.71	0.72	1.95	6.00	3.41	3.63	0.76	76.15
Sm	0.66	0.057	0.66	0.058	1.1	0.098	1.1	0.094	0.08	0.66	1.10	1.15	-0.69	-0.05	-4.58
Eu	0.36		0.18	0.062	0.2	0.053	0.31	0.056	0.06	0.27	0.26	0.47	-3.80	-0.46	-45.93
Yb	0.43	0.089	0.48	0.094	1	0.16	0.89	0.15	0.12	0.455	0.95	0.79	1.22	0.19	18.90
Lu	0.061	0.014	0.07	0.016	0.2	0.033	0.15	0.032	0.02	0.0655	0.18	0.11	2.55	0.53	52.96
Au	0.0024	0.001	0.003	0.002	0.0027	0.001	0.0055	0.0028	0.00	0.0027	0.00	0.00	-0.36	-0.13	-13.06
Hg	0.075	0.025	0.11	0.035	0.012		0.055	0.021	0.03	0.0925	0.03	0.16	-4.74	-0.79	-79.27
Th	1.4	0.15	1.7	0.13	2.7	0.17	3.1	0.18	0.16	1.55	2.90	2.71	1.22	0.07	7.11
U	1.2	0.076	1.2	0.089	2.5	0.11	3.9	0.13	0.10	1.2	3.20	2.10	10.90	0.53	52.67

Table 3-6. Metal Concentrations (Dry Basis) for Parent and Devolatilized Coals from U.Utah Experiments (Continued)

Coal Name:	Wyodak Subbituminous														
	Volatile Matter														
Sample # 1	0.4413	Avg.	Avg fixed carbon												
Sample # 2	0.4463	0.4438	0.5562												
μg/g									Pooled ±	Dried Avg	Fixed C Avg	Expected	M-E/ StDev	(M-E)/E	Δ %
Sample ID	D14p1	±	D14p2	±	D14c3	±	D19c4	±							
Na	980	70	830	57	1600	110	1500	100	84.25	905	1550.00	1627.11	-0.92	-0.05	-4.74
Mg	2200	510	1500	250	4000	780	3300	680	555.00	1850	3650.00	3326.14	0.58	0.10	9.74
Al	5600	230	6000	250	13000	530	11000	440	362.50	5800	12000.00	10427.90	4.34	0.15	15.08
Cl	51	30	39	8.1	41	11	47	13	15.53	45	44.00	80.91	-2.38	-0.46	-45.62
K	1400		370		200		180		0.00	885	190.00	1591.15	—	-0.88	-88.06
Sc	2.2	0.15	1.8	0.11	3.1	0.2	3.5	0.23	0.17	2	3.30	3.60	-1.71	-0.08	-8.23
Ti	650	87	690	79	1300	130	1100	110	101.50	670	1200.00	1204.60	-0.05	0.00	-0.38
V	18	1.1	16	0.9	34	1.9	28	1.6	1.38	17	31.00	30.56	0.32	0.01	1.42
Cr	17	3.6	8.8	0.42	14	0.52	22	1.3	1.46	12.9	18.00	23.19	-3.56	-0.22	-22.39
Mn	11	0.31	9.2	0.21	18	0.36	17	0.34	0.31	10.1	17.50	18.16	-2.16	-0.04	-3.63
Fe	4400	340	3400	150	5900	240	6300	300	257.50	3900	6100.00	7011.87	-3.54	-0.13	-13.00
Co	7.9	1.1	4.9	0.3	8.8	0.5	10	0.62	0.63	6.4	9.40	11.51	-3.34	-0.18	-18.31
Zn	40	12	34	5.5	35	5.5	32	5.6	7.15	37	33.50	66.52	-4.62	-0.50	-49.64
Ga	4.9	2.8	4.3		5.2		2.3	1.8	1.15	4.6	3.75	8.27	-3.93	-0.55	-54.66
As	3.2	0.4	1.7	0.17	3	0.32	3.3	0.37	0.32	2.45	3.15	4.40	-3.98	-0.28	-28.49

Table 3-6. Metal Concentrations (Dry Basis) for Parent and Devolatilized Coals from U.Utah Experiments (Continued)

Se	1.1	0.81	0.98	0.35	1.2	0.38	2.2	1.5	0.76	1.04	1.70	1.87	-0.22	-0.09	-9.08
Br	1.8	0.56	1.2	0.34	2	0.55	1.6	0.47	0.48	1.5	1.80	2.70	-1.87	-0.33	-33.26
Rb	12		2.1	1.2	0.84	0.71	12		0.48	7.05	6.42	12.68	-13.10	-0.49	-49.35
Sr	170	30	310	42	380	47	540	66	46.25	240	460.00	431.50	0.62	0.07	6.61
Mo	1.6	0.89	1.8	0.42	2.3	0.52	1.7	0.56	0.60	1.7	2.00	3.06	-1.77	-0.35	-34.56
Cd	0.24		0.21	0.15	0.083		0.45		0.04	0.225	0.27	0.40	-3.68	-0.34	-34.12
In	12		9.8		33	27	31	27	13.50	10.9	32.00	19.60	0.92	0.63	63.29
Sb	0.37	0.067	0.2	0.02	0.39	0.035	0.44	0.047	0.04	0.285	0.42	0.51	-2.31	-0.19	-19.01
Cs	0.48	0.35	0.095	0.051	0.15	0.051	0.63		0.11	0.2875	0.39	0.52	-1.12	-0.25	-24.55
Ba	570	41	510	36	990	65	930	61	50.75	540	960.00	970.87	-0.21	-0.01	-1.12
La	6.7	0.43	4.9	0.31	8.7	0.55	9.8	0.63	0.48	5.8	9.25	10.43	-2.45	-0.11	-11.30
Ce	11	1.3	8.6	0.45	15	0.74	17	0.99	0.87	9.8	16.00	17.62	-1.86	-0.09	-9.19
Nd	2.3	1.6	4.2	0.59	5.9	0.73	7.2	1.4	1.08	3.25	6.55	5.84	0.65	0.12	12.10
Sm	1	0.088	0.77	0.067	1.4	0.12	1.7	0.14	0.10	0.885	1.55	1.59	-0.40	-0.03	-2.59
Eu	0.5	0.16	0.18	0.036	0.31	0.046	0.24	0.077	0.08	0.34	0.28	0.61	-4.22	-0.55	-55.01
Yb	0.29	0.11	0.39	0.068	0.68	0.11	0.76	0.14	0.11	0.34	0.72	0.61	1.02	0.18	17.78
Lu	0.11	0.032	0.06	0.013	0.1	0.022	0.13	0.028	0.02	0.085	0.12	0.15	-1.59	-0.25	-24.75
Au	0.0081	0.004	0.0019	0	0.0022	0.001	0.0024	0.0012	0.00	0.005	0.00	0.01	-3.65	-0.74	-74.41
Hg	0.37	0.072	0.11	0.017	0.021	0.011	0.072	0.044	0.04	0.24	0.05	0.43	-10.69	-0.89	-89.22
Th	2.4	0.3	1.9	0.12	3.4	0.2	3.9	0.25	0.22	2.15	3.65	3.87	-0.99	-0.06	-5.58
U	0.64	0.19	0.7	0.038	1.2	0.058	1.4	0.11	0.10	0.67	1.30	1.20	0.96	0.08	7.92

Table 3-6. Metal Concentrations (Dry Basis) for Parent and Devolatilized Coals from U.Utah Experiments (Continued)

Coal name:	Pittsburgh														
	Volatile Matter														
Sample # 1	0.3761	Avg	Avg fixed carbon												
Sample #2	0.3755	0.3758	0.6242												
μg/g									Pooled ±	Dried Avg	Fixed C Avg	Expected	M-E/ StDev	(M-E)/E	Δ %
Sample ID	D15p9	`±	D15p10	`±	D16c20	`±	D18c26	`±							
Na	730	52	650	45	1200	84	940	65	61.50	690	1070.00	1105.41	-0.58	-0.03	-3.20
Mg	540	190	340	140	900	310	1300	340	245.00	440	1100.00	704.90	1.61	0.56	56.05
Al	9300	390	8800	360	17000	700	11000	450	475.00	9050	14000.00	14498.56	-1.05	-0.03	-3.44
Cl	880	62	940	63	300	26	320	25	44.00	910	310.00	1457.87	-26.09	-0.79	-78.74
K	1000	320	680	290	990	370	1400	320	325.00	840	1195.00	1345.72	-0.46	-0.11	-11.20
Sc	1.9	0.12	1.8	0.12	3.1	0.2	0.02	0.0024	0.11	1.85	1.56	2.96	-12.69	-0.47	-47.36
Ti	490	77	410	75	880	110	580	78	85.00	450	730.00	720.92	0.11	0.01	1.26
V	15	1.2	12	0.82	26	1.7	19	1.3	1.26	13.5	22.50	21.63	0.70	0.04	4.03
Cr	14	0.95	13	2.2	19	0.68	0.32	0.2	1.01	13.5	9.66	21.63	-11.88	-0.55	-55.34
Mn	16	0.34	14	0.28	30	0.53	27	0.99	0.54	15	28.50	24.03	8.35	0.19	18.60
Fe	9800	420	10000	550	16000	640	120	23	408.25	9900	8060.00	15860.30	-19.11	-0.49	-49.18
Co	3.1	0.27	4	0.61	4.4	0.25	0.84	0.06	0.30	3.55	2.62	5.69	-10.31	-0.54	-53.93
Zn	51	12	39	30	37	4.8	8.6	1.3	12.03	45	22.80	72.09	-4.10	-0.68	-68.37
Ga	1.9	1.4	43		360		2		1.40	22.45	181.00	35.97	103.60	4.03	403.25
As	4.5	0.46	3.8	0.38	6.8	0.71	11		0.52	4.15	8.90	6.65	4.36	0.34	33.86

Table 3-6. Metal Concentrations (Dry Basis) for Parent and Devolatilized Coals from U.Utah Experiments (Continued)

μg/g									Pooled ±	Dried Avg	Fixed C Avg	Expected	M-E/ StDev	(M-E)/E	Δ %
Sample ID	D15p9	`±	D15p10	`±	D16c20	`±	D18c26	`±							
Se	0.76	0.62	3.8	1.9	1.4	0.57	0.13		1.03	2.28	0.77	3.65	-2.80	-0.79	-79.06
Br	17	4.4	16	4.2	11	2.9	390		3.83	16.5	200.50	26.43	45.41	6.59	658.50
Rb	3	2.9	27		10	2.2	2.3	1.4	2.17	15	6.15	24.03	-8.25	-0.74	-74.41
Sr	110	22	110	25	190	29	250	36	28.00	110	220.00	176.23	1.56	0.25	24.84
Mo	1.4	0.41	1.2	0.38	1.2	0.34	27		0.38	1.3	14.10	2.08	31.90	5.77	577.02
Cd	0.27		0.51		0.11		68		—	0.39	34.06	0.62	—	53.51	5350.55
In	54	40	23		37	32	12		36.00	38.5	24.50	61.68	-1.03	-0.60	-60.28
Sb	0.24	0.031	0.2	0.034	0.38	0.037	1.4		0.03	0.22	0.89	0.35	15.81	1.53	152.52
Cs	0.56	0.17	0.77	0.31	0.8	0.13	0.16	0.043	0.16	0.665	0.48	1.07	-3.59	-0.55	-54.95
Ba	110	16	150	17	250	22	220	20	18.75	130	235.00	208.27	1.43	0.13	12.84
La	4.8	0.31	4.8	0.31	7.7	0.49	18		0.37	4.8	12.85	7.69	13.95	0.67	67.10
Ce	11	0.58	9.8	0.77	15	0.74	0.11		0.70	10.4	7.56	16.66	-13.07	-0.55	-54.66
Nd	4.4	0.73	8.1	1.4	8.9	1.2	4.5	0.87	1.05	6.25	6.70	10.01	-3.16	-0.33	-33.09
Sm	0.79	0.069	0.79	0.068	1.3	0.11	1.5		0.08	0.79	1.40	1.27	1.63	0.11	10.62
Eu	0.21	0.058	0.34	0.15	0.27	0.041	0.014	0.009	0.06	0.275	0.14	0.44	-4.63	-0.68	-67.77
Yb	0.37	0.074	0.26	0.074	0.69	0.12	0.42	0.24	0.13	0.315	0.56	0.50	0.40	0.10	9.98
Lu	0.071	0.016	0.046	0.012	0.099	0.021	0.023		0.02	0.0585	0.06	0.09	-2.00	-0.35	-34.91
Au	0.0015	0	0.0021	0.001	0.0046	0.002	0.0016	0	0.00	0.0018	0.00	0.00	0.21	0.08	7.50
Hg	0.095	0.028	0.12	0.031	0.14	0.026	0.049		0.03	0.1075	0.09	0.17	-2.74	-0.45	-45.13
Th	1.4	0.11	1.4	0.17	2.1	0.13	12		0.14	1.4	7.05	2.24	35.17	2.14	214.33
U	0.27	0.047	0.36	0.034	0.43	0.067	12		0.05	0.315	6.22	0.50	115.75	11.32	1131.56

Table 3-6. Metal Concentrations (Dry Basis) for Parent and Devolatilized Coals from U.Utah Experiments (Continued)

Coal Name:	Illinois #6														
	Volatile Matter														
Sample # 1	0.3927	Avg	Avg fixed carbon												
Sample #2	0.3963	0.3945	0.6055												
μg/g									Pooled ±	Dried Avg	Fixed C Avg	Expected	M-E/ StDev	(M-E)/E	Δ %
Sample ID	D15p11	±	D15p12	±	D16c19	±	D18c29	±							
Na	430	31	460	32	610	43	600	43	37.25	445	605.00	734.93	-3.49	-0.18	-17.68
Mg	620	170	510	160	1300	160	1500	410	225.00	565	1400.00	933.11	2.08	0.50	50.04
Al	9700	410	11000	430	16000	690	15000	63	398.25	10350	15500.00	17093.31	-4.00	-0.09	-9.32
Cl	420	31	450	32	56	12	61	15	22.50	435	58.50	718.41	-29.33	-0.92	-91.86
K	2300	440	1800	390	2800	460	2600	540	457.50	2050	2700.00	3385.63	-1.50	-0.20	-20.25
Sc	2.2	0.14	2.4	0.16	3.1	0.2	4.2	0.27	0.19	2.3	3.65	3.80	-0.77	-0.04	-3.91
Ti	730	90	710	90	1100	110	990	100	97.50	720	1045.00	1189.10	-1.48	-0.12	-12.12
V	27	1.8	26	1.5	39	2.5	35	2.3	2.03	26.5	37.00	43.77	-3.34	-0.15	-15.46
Cr	18	0.67	20	1.4	28	1.5	36	0.77	1.09	19	32.00	31.38	0.57	0.02	1.98
Mn	31	0.55	33	0.58	54	0.86	51	0.87	0.72	32	52.50	52.85	-0.49	-0.01	-0.66
Fe	14000	580	16000	710	5800	300	26000	1000	647.50	15000	15900.00	24772.91	-13.70	-0.36	-35.82
Co	3.4	0.21	4.1	0.48	2.1	0.28	5.8	0.31	0.32	3.75	3.95	6.19	-7.01	-0.36	-36.22
Zn	48	7.2	74	16	23	6.5	66	6.8	9.13	61	44.50	100.74	-6.16	-0.56	-55.83
Ga	8.4		43		4.6	3.2	8.8	4.5	3.85	25.7	6.70	42.44	-9.28	-0.84	-84.21
As	2.3		2.3	0.23	1.4	0.2	3.6	0.38	0.27	2.3	2.50	3.80	-4.81	-0.34	-34.18

Table 3-6. Metal Concentrations (Dry Basis) for Parent and Devolatilized Coals from U.Utah Experiments (Continued)

μg/g									Pooled ±	Dried Avg	Fixed C Avg	Expected	M-E/ StDev	(M-E)/E	Δ %
Sample ID	D15p11	`±	D15p12	`±	D16c19	`±	D18c29	`±							
Se	2.2	0.89	3.8	1.9	3.1	1.2	2.9	0.56	1.14	3	3.00	4.95	-1.72	-0.39	-39.45
Br	6.6	1.8	5.2	1.4	1.8	0.53	1.3	0.37	1.03	5.9	1.55	9.74	-7.99	-0.84	-84.09
Rb	13	2.6	21	7.3	4.4		25	2.8	4.23	17	14.70	28.08	-3.16	-0.48	-47.64
Sr	24	16	39		40	19	50	18	17.67	31.5	45.00	52.02	-0.40	-0.14	-13.50
Mo	5.4	1.2	4.9	1.1	2	0.54	7.3	1.6	1.11	5.15	4.65	8.51	-3.47	-0.45	-45.33
Cd	0.29		0.097		0.11		0.16		—	0.1935	0.14	0.32	—	-0.58	-57.76
In	13	12	52	40	37	25	30	21	24.50	32.5	33.50	53.67	-0.82	-0.38	-37.59
Sb	0.41	0.035	0.43	0.041	0.29	0.043	0.67	0.53	0.16	0.42	0.48	0.69	-1.32	-0.31	-30.80
Cs	0.99	0.15	0.95	0.3	0.77	0.25	19	0.21	0.23	0.97	9.89	1.60	36.41	5.17	517.05
Ba	48	14	48	15	90	12	57	15	14.00	48	73.50	79.27	-0.41	-0.07	-7.28
La	4.4	0.28	4.5	0.29	12	0.77	7.8	0.5	0.46	4.45	9.90	7.35	5.55	0.35	34.71
Ce	9.1	0.46	9.3	0.67	19	1.1	16	0.77	0.75	9.2	17.50	15.19	3.07	0.15	15.18
Nd	3.7	0.5	2.4	0.73	4.5	0.75	7.2	0.83	0.70	3.05	5.85	5.04	1.16	0.16	16.14
Sm	0.86	0.074	0.87	0.076	1.6	0.14	1.7	0.14	0.11	0.865	1.65	1.43	2.06	0.16	15.50
Eu	0.25	0.043	0.2	0.086	0.45	0.13	0.37	0.16	0.10	0.225	0.41	0.37	0.37	0.10	10.34
Yb	0.52	0.089	0.6	0.11	0.81	0.15	0.98	0.16	0.13	0.56	0.90	0.92	-0.23	-0.03	-3.23
Lu	0.093	0.02	0.11	0.025	0.16	0.034	0.17	0.037	0.03	0.1015	0.17	0.17	-0.09	-0.02	-1.57
Au	0.0025	0.001	0.0043	0.002	0.0027	0.001	0.0016	0.001	0.00	0.0034	0.00	0.01	-2.52	-0.62	-61.71
Hg	0.13	0.018	0.096	0.031	0.15	0.05	0.023	0.014	0.03	0.113	0.09	0.19	-3.54	-0.54	-53.65
Th	1.6	0.1	2.4	0.21	3.6	0.23	3.2	0.19	0.18	2	3.40	3.30	0.53	0.03	2.94
U	0.97	0.04	2.9	0.11	1.6	0.14	5.5	0.17	0.12	1.935	3.55	3.20	3.08	0.11	11.09

Table 3-6. Metal Concentrations (Dry Basis) for Parent and Devolatilized Coals from U.Utah Experiments (Continued)

Coal Name:	Elkhorn / Hazard														
	Volatile Matter														
Sample # 1	0.3728		Avg fixed carbon	Std											
Sample #2	0.3752	0.374	0.626												
µg/g									Pooled ±	dried avg	fixed C avg	Expected	M-E/ StDev	(M-E)/E	Δ %
Sample ID	D15p13	±	D15p14	±	D16c21	±	D18c28	±							
Na	400	32	470	35	550	38	510	35	35.00	435	530.00	694.89	-4.71	-0.24	-23.73
Mg	250	160	610	210	650	200	580	170	185.00	430	615.00	686.90	-0.39	-0.10	-10.47
Al	15000	650	16000	680	22000	910	17000	690	732.50	15500	19500.00	24760.38	-7.18	-0.21	-21.25
Cl	1800	120	1700	120	410	29	360	25	73.50	1750	385.00	2795.53	-32.80	-0.86	-86.23
K	960	480	850	310	1700	340	1000	390	380.00	905	1350.00	1445.69	-0.25	-0.07	-6.62
Sc	3.9	0.25	3.9	0.25	5.6	0.36	6.3	0.43	0.32	3.9	5.95	6.23	-0.87	-0.04	-4.49
Ti	880	99	990	110	1500	150	1200	100	114.75	935	1350.00	1493.61	-1.25	-0.10	-9.62
V	26	1.9	27	1.7	39	2.4	32	1.6	1.90	26.5	35.50	42.33	-3.60	-0.16	-16.14
Cr	21	4.7	18	0.66	23	0.83	33	7.3	3.37	19.5	28.00	31.15	-0.93	-0.10	-10.11
Mn	17	0.37	16	0.33	25	0.46	23	0.42	0.40	16.5	24.00	26.36	-5.97	-0.09	-8.95
Fe	3400	280	3000	130	4700	200	5400	470	270.00	3200	5050.00	5111.82	-0.23	-0.01	-1.21
Co	8.3	1.1	7.1	0.41	9.1	0.52	14	1.8	0.96	7.7	11.55	12.30	-0.78	-0.06	-6.10
Zn	19	7.6	32	4.23	25	4.1	20	8.7	6.16	25.5	22.50	40.73	-2.96	-0.45	-44.76
Ga	5.6		2.8	1.7	4.3		14	6.2	3.95	4.2	9.15	6.71	0.62	0.36	36.38
As	4.4	0.49	3.8	0.38	4.1	0.54	6.3	0.66	0.52	4.1	5.20	6.55	-2.61	-0.21	-20.60

Table 3-6. Metal Concentrations (Dry Basis) for Parent and Devolatilized Coals from U.Utah Experiments (Continued)

μg/g									Pooled ±	dried avg	fixed C avg	Expected	M-E/ StDev	(M-E)/E	Δ %
Sample ID	D15p13	`±	D15p14	`±	D16c21	`±	D18c28	`±							
Se	1.3		2.4	0.85	3	0.9	1.1		0.88	1.85	2.05	2.96	-1.03	-0.31	-30.63
Br	28	7.9	21	5.5	11	3.1	13	3.7	5.05	24.5	12.00	39.14	-5.37	-0.69	-69.34
Rb	12		5.4	1.7	7.6	2	12		1.85	8.7	9.80	13.90	-2.22	-0.29	-29.49
Sr	150	25	140	27	210	34	140	21	26.75	145	175.00	231.63	-2.12	-0.24	-24.45
Mo	3.5	1.3	2.8	0.65	5.6	1.3	7.3	2.6	1.46	3.15	6.45	5.03	0.97	0.28	28.18
Cd	0.092		0.047		0.49	0.45	0.3		0.45	0.0695	0.40	0.11	0.63	2.56	255.78
In	70	50	28		27		23	21	35.50	49	25.00	78.27	-1.50	-0.68	-68.06
Sb	0.89	0.095	0.86	0.067	1.4	0.11	1.4	0.15	0.11	0.875	1.40	1.40	0.02	0.00	0.16
Cs	1.1	0.66	0.51	0.11	0.6	0.11	1.6		0.29	0.805	1.10	1.29	-0.63	-0.14	-14.46
Ba	150	20	150	15	200	22	150	16	18.25	150	175.00	239.62	-3.54	-0.27	-26.97
La	16	1	14	0.9	19	1.2	22	1.4	1.13	15	20.50	23.96	-3.08	-0.14	-14.45
Ce	31	3.6	28	1.4	40	1.9	44	5.2	3.03	29.5	42.00	47.12	-1.69	-0.11	-10.87
Nd	18	5.8	13	1.6	17	2	19	6.3	3.93	15.5	18.00	24.76	-1.72	-0.27	-27.30
Sm	2.8	0.24	2.5	0.22	3.8	0.33	4.1	0.35	0.29	2.65	3.95	4.23	-0.99	-0.07	-6.69
Eu	0.43	0.2	0.34	0.057	0.52	0.077	0.76	0.35	0.17	0.385	0.64	0.62	0.15	0.04	4.06
Yb	1.1	0.23	1.5	0.25	1.9	0.32	1.9	0.41	0.30	1.3	1.90	2.08	-0.58	-0.09	-8.51
Lu	0.29	0.07	0.23	0.049	0.31	0.067	0.46	0.11	0.07	0.26	0.39	0.42	-0.41	-0.07	-7.30
Au	0.0026	0.001	0.0037	0.002	0.0014	0	0.0033	0.0016	0.00	0.0032	0.00	0.01	-1.98	-0.53	-53.30
Hg	0.28	0.082	0.11	0.023	0.11	0.038	0.28	0.096	0.06	0.195	0.20	0.31	-1.95	-0.37	-37.40
Th	5.2	0.59	4.2	0.25	6.1	0.37	6.8	0.79	0.50	4.7	6.45	7.51	-2.12	-0.14	-14.09
U	2.4	0.29	1.4	0.064	3	0.13	4.2	0.47	0.24	1.9	3.60	3.04	2.37	0.19	18.61

Table 3-6. Metal Concentrations (Dry Basis) for Parent and Devolatilized Coals from U.Utah Experiments (Continued)

Coal name:	Utah - Wasatch Plateau															
	Volatile Matter															
Sample # 1	0.4383	Avg	Avg fixed carbon	Std												
Sample #2	0.4383	0.4383	0.5617	#REF!												
μg/g									Pooled ±	Dried Avg	Fixed C Avg	Expected	M-E/ StDev	(M-E)/E	Δ%	
Sample ID	D16p17	`±	D16p18	`±	D17c24	`±	D17c25	`±								
Na	3000	200	3300	220	4400	290	4400	300	252.50	3150	4400.00	5607.98	-4.78	-0.22	-21.54	
Mg	1500	350	1300	250	1700	330	2500	500	357.50	1400	2100.00	2492.43	-1.10	-0.16	-15.75	
Al	12000	510	9900	400	18000	740	18000	730	595.00	10950	18000.00	19494.39	-2.51	-0.08	-7.67	
Cl	230	23	240	18	90	15	97	13	17.25	235	93.50	418.37	-18.83	-0.78	-77.65	
K	930	240	1200	310	1400	360	950	380	322.50	1065	1175.00	1896.03	-2.24	-0.38	-38.03	
Sc	1.8	0.12	2	0.15	2.9	0.18	2.9	0.18	0.16	1.9	2.90	3.38	-3.06	-0.14	-14.27	
Ti	780	110	630	57	1000	120	1100	110	99.25	705	1050.00	1255.12	-2.07	-0.16	-16.34	
V	14	1.3	10	0.61	20	1.4	18	1.3	1.15	12	19.00	21.36	-2.05	-0.11	-11.06	
Cr	8.9	1.1	9.8	5.3	18	0.67	17	0.63	1.93	9.35	17.50	16.65	0.44	0.05	5.13	
Mn	6.4	0.2	7.8	0.18	9.5	0.24	11	0.24	0.22	7.1	10.25	12.64	-11.12	-0.19	-18.91	
Fe	2200	240	2500	620	5500	230	5600	230	330.00	2350	5550.00	4183.73	4.14	0.33	32.66	
Co	2.2	0.31	2.6	2	3.8	0.23	2.1	0.15	0.67	2.4	2.95	4.27	-1.97	-0.31	-30.96	
Zn	32	19	42	21	17	2.9	30	5	11.98	37	23.50	65.87	-3.54	-0.64	-64.32	
Ga	3.7	2.6	8.4		4.3		3.8	3.7	3.15	6.05	4.05	10.77	-2.13	-0.62	-62.40	
As	720	84	810	130	0.88	0.18	1.1	0.14	53.58	765	0.99	1361.94	-25.40	-1.00	-99.93	

Table 3-6. Metal Concentrations (Dry Basis) for Parent and Devolatilized Coals from U.Utah Experiments (Continued)

μg/g									Pooled ±	Dried Avg	Fixed C Avg	Expected	M-E/ StDev	(M-E)/E	Δ%
Sample ID	D16p17	`±	D16p18	`±	D17c24	`±	D17c25	`±							
Se	1.2		2.3		1.9	0.79	2.2	0.76	0.78	1.75	2.05	3.12	-1.37	-0.34	-34.20
Br	2.4	0.66	2.4	0.7	1.1	0.33	1.7	0.46	0.54	2.4	1.40	4.27	-5.34	-0.67	-67.23
Rb	27		12		7.1	1.5	8.7	2.3	1.90	19.5	7.90	34.72	-14.11	-0.77	-77.24
Sr	53	20	63	13	85	50	140	28	27.75	58	112.50	103.26	0.33	0.09	8.95
Mo	1.7	0.46	1.4	0.96	3.5	0.8	2.7	0.62	0.71	1.55	3.10	2.76	0.48	0.12	12.34
Cd	1		0.89		0.35		230	180	180.00	0.945	115.18	1.68	0.63	67.46	6745.90
In	25		37		75		17	16	16.00	31	46.00	55.19	-0.57	-0.17	-16.65
Sb	0.54	0.049	0.19	0.09	0.28	0.027	280	25	6.29	0.365	140.14	0.65	22.17	214.66	21466.20
Cs	1		3.3		0.83	0.12	730	120	60.06	2.15	365.42	3.83	6.02	94.47	9446.68
Ba	91	14	110	13	170	22	180	17	16.50	100.5	175.00	178.92	-0.24	-0.02	-2.19
La	7.5	0.48	8.4	0.54	12	0.79	12	0.75	0.64	7.95	12.00	14.15	-3.36	-0.15	-15.22
Ce	12	0.75	12	2.1	19	0.94	21	1	1.20	12	20.00	21.36	-1.14	-0.06	-6.38
Nd	2	0.73	10		8.1	0.98	7.5	0.93	0.88	6	7.80	10.68	-3.27	-0.27	-26.98
Sm	0.9	0.078	1	0.089	1.5	0.13	1.4	0.12	0.10	0.95	1.45	1.69	-2.31	-0.14	-14.27
Eu	0.4		0.61		0.36	0.056	0.26	0.046	0.05	0.505	0.31	0.90	-11.55	-0.66	-65.52
Yb	0.48	0.097	0.64		0.8	0.13	0.69	0.12	0.12	0.56	0.75	1.00	-2.18	-0.25	-25.27
Lu	0.055	0.013	0.11		0.13	0.029	0.13	0.028	0.02	0.0825	0.13	0.15	-0.72	-0.11	-11.49
Au	0.0017	0	0.0012	0	0.001	0	0.0032	0.0016	0.00	0.0015	0.00	0.00	-0.63	-0.21	-21.36
Hg	0.087	0.023	0.25	0.073	0.025	0.014	0.035	0.018	0.03	0.1685	0.03	0.30	-8.44	-0.90	-90.00
Th	2	0.2	1.8	0.45	3.4	0.2	3.5	0.21	0.27	1.9	3.45	3.38	0.25	0.02	1.99
U	0.51	0.033	0.98	0.2	0.81	0.036	1.5	0.06	0.08	0.745	1.16	1.33	-2.08	-0.13	-12.92

Table 3-6. Metal Concentrations (Dry Basis) for Parent and Devolatilized Coals from U.Utah Experiments (Continued)

Coal Name:	Ohio															
	Volatile Matter															
Sample # 1	0.4002	Avg	Avg fixed carbon	Std												
Sample #2	0.4017	0.40095	0.59905													
µg/g									Pooled ±	Dried Avg	Fixed C Avg	Expected	M-E/StDev	(M-E)/E	Δ%	
Sample ID	D16p15	±	D16p16	±	D17c22	±	D18c27	±								
Na	310	23	390	28	450	31	530	37	29.75	350	490.00	584.26	-3.17	-0.16	-16.13	
Mg	340	110	270	81	800	190	640	210	147.75	305	720.00	509.14	1.43	0.41	41.42	
Al	12000	500	9600	390	15000	600	19000	780	567.50	10800	17000.00	18028.55	-1.81	-0.06	-5.71	
Cl	950	64	920	58	130	11	140	16	37.25	935	135.00	1560.80	-38.28	-0.91	-91.35	
K	1900	400	2100	380	3200	430	3500	620	457.50	2000	3350.00	3338.62	0.02	0.00	0.34	
Sc	3.6	0.23	4.5	0.29	6	0.39	6.7	4.3	1.30	4.05	6.35	6.76	-0.32	-0.06	-6.07	
Ti	730	100	600	51	1100	70	1200	120	85.25	665	1150.00	1110.09	0.47	0.04	3.60	
V	25	1.7	21	1	35	1.7	42	1.2	1.40	23	38.50	38.39	0.08	0.00	0.28	
Cr	20	0.86	30	5.7	31	6.9	45	1.6	3.77	25	38.00	41.73	-0.99	-0.09	-8.94	
Mn	21	0.4	28	0.45	33	0.5	38	0.66	0.50	24.5	35.50	40.90	-10.74	-0.13	-13.20	
Fe	19000	760	17000	1200	33000	2200	30000	1200	1340.00	18000	31500.00	30047.58	1.08	0.05	4.83	
Co	5.1	0.33	6.6	0.96	10	1.3	8.5	0.5	0.77	5.85	9.25	9.77	-0.67	-0.05	-5.28	
Zn	37	6.6	19	6.8	22	9.2	41	6.3	7.23	28	31.50	46.74	-2.11	-0.33	-32.61	
Ga	9.1	4.3	6.1	3	34	11	43		6.10	7.6	38.50	12.69	4.23	2.03	203.47	
As	25	2.5	31	3.1	32	3.2	34	3.3	3.03	28	33.00	46.74	-4.54	-0.29	-29.40	

Table 3-6. Metal Concentrations (Dry Basis) for Parent and Devolatilized Coals from U.Utah Experiments (Continued)

μg/g									Pooled ±	Dried Avg	Fixed C Avg	Expected	M-E/ StDev	(M-E)/E	Δ%
Sample ID	D16p15	`±	D16p16	`±	D17c22	`±	D18c27	`±							
Se	1.7	0.73	0.82		1.9		2.3	0.97	0.85	1.26	2.10	2.10	0.00	0.00	-0.16
Br	16	4.3	18	4.9	6.5	1.9	6.2	1.7	3.20	17	6.35	28.38	-6.88	-0.78	-77.62
Rb	13	3	12		12		20	3.9	3.45	12.5	16.00	20.87	-1.41	-0.23	-23.32
Sr	120	24	95	15	100	14	130	25	19.50	107.5	115.00	179.45	-3.31	-0.36	-35.92
Mo	5.1	1.1	4.5	1.3	7.4	2.4	8.9	1.9	1.68	4.8	8.15	8.01	0.08	0.02	1.71
Cd	0.66		0.42		0.21		0.36		—	0.54	0.29	0.90	—	-0.68	-68.38
In	12		33	28	30	23	68		25.50	22.5	49.00	37.56	0.45	0.30	30.46
Sb	2	0.15	2.4	0.22	3.1	0.29	3.5	0.27	0.23	2.2	3.30	3.67	-1.60	-0.10	-10.14
Cs	0.62	0.14	0.79	0.44	35	4.1	1.3	0.2	1.22	0.705	18.15	1.18	13.91	14.42	1442.24
Ba	90	12	110	11	83	9.1	150	18	12.53	100	116.50	166.93	-4.03	-0.30	-30.21
La	8.7	0.55	11	0.69	15	0.94	16	1	0.80	9.85	15.50	16.44	-1.19	-0.06	-5.73
Ce	19	0.95	21	2	35	4.1	33	1.6	2.16	20	34.00	33.39	0.28	0.02	1.84
Nd	0.63		7.5	2.5	14	4.6	16	1.9	3.00	4.065	15.00	6.79	2.74	1.21	121.05
Sm	1.8	0.15	2.3	0.2	3.1	0.27	3.4	0.3	0.23	2.05	3.25	3.42	-0.75	-0.05	-5.03
Eu	0.51	0.086	0.5	0.17	0.81	0.56	0.79	0.12	0.23	0.505	0.80	0.84	-0.18	-0.05	-5.10
Yb	1.1	0.18	1.2	0.25	1.4	0.3	2	0.33	0.27	1.15	1.70	1.92	-0.83	-0.11	-11.44
Lu	0.19	0.04	0.25	0.064	0.37	0.089	330	70	17.55	0.22	165.19	0.37	9.39	448.79	44879.12
Au	0.0016	0	0.002	0.001	0.0015	0	0.001	0.001	0.00	0.0018	0.00	0.00	-2.29	-0.58	-58.40
Hg	0.2	0.023	0.23	0.051	0.1	0.051	0.029		0.04	0.215	0.06	0.36	-7.07	-0.82	-82.03
Th	2.1	0.14	2.7	0.35	4.1	0.51	3.9	0.23	0.31	2.4	4.00	4.01	-0.02	0.00	-0.16
U	0.83	0.034	1.6	0.17	2.5	0.27	1.5	0.05	0.13	1.215	2.00	2.03	-0.22	-0.01	-1.39

3.4 Post-Combustion Transformations (UA, UC, UU)

3.4.1 *Bench Scale Experimental Studies*

To provide a reference point for potential interactions between arsenic species and calcium compounds in fly ash, tube furnace experiments were conducted at the University of Connecticut utilizing organic arsenic solutions, calcium compounds, and model silica ash particles produced by sol-gel methods. The objective was to determine whether calcium contained within silicate particles typical of fly ash could react with arsenic under idealized contacting conditions. If no reaction were observed, further study in the flat flame burner would be deemed unnecessary. If reaction were observed, the additional study of arsenic - silicate reactions in the flat flame would be warranted. In these experiments, cacodylic acid, an organic arsenic containing compound, was prepared in aqueous solution and placed in a small alumina combustion boat. One of the following compounds were then added to the solution in the combustion boat: (1) nominal 1 μm diameter spherical silica particles produced by sol-gel reactions of tetraethyl orthosilicate (TEOS) in ethanol; (2) commercial calcium silicate particles (Ca_2SiO_4); (3) water-soluble calcium acetate crystals; or (4) laboratory derived calcium-containing silica, produced by heat treating a mixture of calcium acetate crystals and sol-gel silica particles at 800°C for 1 hour, cooling to room temperature, and water-washing to remove any unreacted calcium acetate. Combustion boat samples were then placed in a tube furnace under flowing air, heated to 800°C , held at temperature for 15 minutes, cooled to room temperature, removed, and shipped to the U. Kentucky for subsequent As XAFS analysis.

Arsenic XAFS spectra obtained by U. Kentucky for cacodylic acid crystals as well as for the four reaction samples are provided in Figure 3-5. As the spectra indicated, all three calcium compounds (Ca_2SiO_4 -pure, Ca_2SiO_4 - II, and Ca acetate) after reaction exhibited virtually identical As XANES and RSFs. All ($>95\%$) of the arsenic was present as As(V), in a form similar to that found in arsenates, and it would appear that the same calcium arsenate form is present in all three materials. The arsenic XANES spectrum of the sol-gel SiO_2 sample indicates that the dominant oxidation state of arsenic was trivalent, potentially the result of As_2O_3 formation on the surface of the silica particles. The XANES spectrum of the cacodylic acid sample also differed from those of the calcium arsenates. The RSFs are also consistent with these observations, as the RSFs for the Ca-based materials are closely similar with the main peak occurring at $1.31 \pm 0.02 \text{ \AA}$, whereas the RSF for the SiO_2 material is rather different and the main peak occurs at $1.37 \pm 0.02 \text{ \AA}$.

As a result of these initial screening experiments, additional study of the Ca-Si-As system in the flat flame burner is planned.

Figure 3-5. Arsenic XANES (top) and RSFs (lower) of products following the reaction of various compounds with arsenic species under combustion-like conditions.

3.4.2 *Large Scale Integrated Combustion Studies*

The University of Arizona's pilot-scale downflow laboratory combustion furnace was used to test the partitioning of toxic metals in the Phase II baseline experiments for the Ohio 5/6/7 blend coal. The objectives of these experiments were:

1. To obtain toxic metal partitioning data under test conditions which simulate the time/temperature combustion and post-combustion conditions of commercial scale utility boilers at 20% excess oxygen.
2. To investigate the differences in toxic metal partitioning from samples collected immediately after char burnout compared to samples collected near the furnace exit and to samples collected at the entrance to the baghouse.

A detailed description of the furnace and sampling systems is given in the Phase I final report. A Berner low pressure impactor (BLPI) was used for particulate sample collection in all of the experiments performed.

Sample collection media for the BLPI consisted of polycarbonate membranes sprayed with a high purity grease. The membranes were dried in a vacuum dessicator for a minimum of 3 hours. One and a half milliliter PVC sample vials were used to contain the particulate-laden membranes. The vials were weighed with and without the particulate-laden membranes on a microbalance and stored in zip-loc sealed polyethylene bags. The dried sample media were also weighed on the microbalance just prior to loading into the BLPI. All microbalance weights were repeated. Two readings with a deviation of less than 0.00003 g were required before the weight data were accepted as accurate.

A total of 16 sets of particulate samples were collected during 9 test runs. Seven sets of particulate samples were collected from Port 4 of the furnace which is located after the majority of the char burnout has been completed, that is, approximately 0.5 seconds residence time relative to the burner and at a gas temperature of about 1350 K. This port is at approximately the same location as Port 4B used in the Phase I experiments. Five sets of particulate samples were collected from Port 14 which is located near the bottom of the furnace and represents a snapshot of the flue gas in the post combustion zone that is, at approximately 2.2 seconds residence time relative to the burner and at a gas temperature of about 1100 K. This port is at approximately the same location as Port 12 used in the Phase I experiments,. These five sample sets were taken immediately after one of the sample sets from Port 4 so that matched sample sets could be selected for analysis. Four sample sets were taken from the inlet to the baghouse and represent hot-side ESP sampling conditions, a gas temperature of approximately 600 K. The baghouse samples are taken after partial segregation of large particles in an ash trap and a small particle trap. Therefore, it was found that a single collection test, performed without the BLPI inlet cyclone, could be used to collect all eleven size-segregated samples from the BLPI. This was performed for sample set 16 only.

The following information obtained during these experiments was reported in Quarterly Report 9 (October 1998 to December 1998):

1. A description of the experiments performed and the sample sets obtained
2. The sampling conditions for the most important sample sets
3. The typical steady-state temperature profile from these tests

Using the size-segregated ash weights collected in the BLPI in each test, particle size distributions (PSDs) were determined. Typical fly ash PSDs, developed following the method described by Markowski and Ensor (Markowski, 1977), are shown in Figure 3-6. Figures 3-7 through 3-9 show PSDs for individual sample sets at each of the three sampling locations. These figures provide insight into the variability in the PSDs shown in Figure 3-6. At all three sample locations, a typical bi-modal PSD is observed. The submicron fume maximum occurs at around 0.1 microns. It should be noted that the large-size particle distribution for the hot-side ESP sample is artificially depressed because a majority of the large-size particles drop out of the gas phase prior to this sample collection point.

In order to compare the results at each sampling location, the PSDs can be normalized by calculating an enrichment factor, $E_{fa,x}$, defined as the ratio of the ash mass collected on a given plate to the average ash mass collected over the entire impactor (Haynes, 1982):

$$E_{fa,x} = \text{ash on plate } x \text{ (mg)} / \text{average ash on all plates (mg)} \quad (1)$$

A comparison of the PSD, normalized as a set of efficiency factors, for each sampling location is shown in Figure 3-10. This normalization removes the effect of sample condition upon the mass concentrations.

Figure 3-6. A comparison of the fly ash particle size distribution in Ohio baseline tests.

Figure 3-7. Fly ash particle size distribution in Ohio baseline tests at 0.5 seconds residence time.

Figure 3-8. Fly ash particle size distribution in Ohio baseline tests at 2.2 seconds residence time.

Figure 3-9. Fly ash particle size distribution in Ohio baseline tests at hot-side ESP conditions.

Figure 3-10. A comparison of total fly ash enrichment factors for Ohio baseline experiments (compared to the corresponding average fly ash concentration).

Comparing $E_{fa,x}$ at 2.2 seconds residence time to $E_{fa,x}$ at 0.5 seconds residence time provides insight into partitioning behavior in the post combustion zone. Similarly, comparing $E_{fa,x}$ at the hot-side ESP condition to $E_{fa,x}$ at 2.2 seconds residence time provides insight into partitioning behavior between the boiler and the ESP.

$$DE_{fa,x,2.2-0.5} = E_{fa,x,2.2} - E_{fa,x,0.5} \quad (2)$$

$$DE_{fa,x,ESP-2.2} = E_{fa,x,ESP} - E_{fa,x,2.2} \quad (3)$$

This comparison is shown in Figures 3-11 and 3-12. Looking at the super-micron portion of Figure 3-11, it appears that post-combustion particle fragmentation may be occurring for particles in the 5 to 10 micron size range. The majority of the particles generated are around 1 micron in size.

Figure 3-12 provides an expanded vertical axis scale to allow resolution of the submicron fume regime. Due to the sampling method employed, the smallest particle sizes (below about 0.1 microns) in the profile represent vapor-phase material that nucleates in the sample probe. There is an increase in this size range during the 0.5 to 2.2 seconds residence time region in the furnace zone (~1350 to ~1100 K), indicating that post-combustion vaporization may be occurring. Particle sizes in the 0.1 to 0.8-micron size range represent the homogeneous transformation region. The results indicate that there is no significant homogeneous nucleation occurring in the 0.5 to 2.2 seconds residence time region in the furnace zone. However, homogeneous nucleation appears to be present at the cooler temperatures encountered prior to the ESP entrance.

Figure 3-11. Residence time-dependent enrichment (depletion) for Ohio baseline experiments.

Figure 3-12. Residence time-dependent enrichment (depletion) for Ohio baseline experiments (expanded scale for submicron fume).

One representative sample set from the 0.5 second sample location (sample 6) and the corresponding sample set from the 2.2 seconds sample location (run 7) were selected for analysis of size-segregated particle metal content at MIT by NAA. Two representative sample sets from the 0.5 seconds sample location, (runs 9 and 11) and the corresponding sample sets from the 2.2 seconds sample location, (runs 10 and 12) plus one sample set from the baghouse inlet (run 16) sampling location (representing the hot-side ESP conditions) were selected for analysis of size-segregated particle metal content at the University of Arizona by AA/GFAA. Tables 3-7 through 3-9 summarize the analytical results for 11 inorganic elements at 0.5 seconds, 2.2 seconds, and hot-sided ESP conditions, respectively. To obtain the typical concentrations, we looked for consistency within the element, consistency across elements, and consistency at plates 6/6c where we had duplication of the cyclone and no cyclone runs. There was a tendency to choose AA/GFAA results when there was a difference in order to have some consistency with the hot-side ESP sample (which was only analyzed by AA/GFAA) and because typically there were multiple results from two samples rather than a single result from one sample. However, in some cases, the typical concentration was the average of a GFAA and a NAA result.

There was more difficulty in obtaining relevant analytical results for Ohio fly ash than for the Phase I fly ash samples we analyzed (Illinois #6 and Pittsburgh seam coal fly ash). This difficulty is reflected in the total mass fraction row at the bottom of each table where values of 25 to 40 wt% are typical. It was particularly difficult to analyze for calcium, selenium, and antimony. In addition, the cadmium results appear to be out of the expected range. We believe this is due to contamination of the fly ash from cadmium desorbing from the furnace walls. Experiments

Table 3-7. Summary of Analytical Results for 0.5 Seconds Residence Time Samples

	Concentrations (ppmw)										
Plate	11	10	9	8	7	6	5	4	3	2	1
Silica											
0.5 Seconds/AA (sample 9)	191394	235193	227125	168192	97070	24180	21750	19209	2952	33499	84386
0.5 Seconds/AA (sample 11)	219015	212466	189502	226842	172542	184430	92259	115370	49148	43085	22110
Typical Concentration	205204	223829	208313	197517	134806	104305	57005	67290	26050	38292	53248
Calcium											
0.5 Seconds/NAA	315	1493	453	287	349	5009	3249	981	1019	1456	3003
0.5 Seconds/AA (sample 9)	6260	5633	6565	7484	9356	2381	5106	-56	-56	-56	20516
0.5 Seconds/AA (sample 11)	4744	5526	6884	12917	10853	8736	10611	8833	-56	-56	-56
Typical Concentration	5502	5579	6725	10200	10105	5009	3249	981	1019	1456	3003
Sodium											
0.5 Seconds/NAA	154	381	129	100	53	1395	1100	845	2266	1247	2838
0.5 Seconds/AA (sample 9)	20441	6209	12389	18155	20515	5170	11809	6805	15025	8399	14895
0.5 Seconds/AA (sample 11)	8769	4274	6055	8080	6173	8601	13320	15217	6209	7457	11088
Typical Concentration	14605	5242	9222	13117	13344	6885	12565	11011	10617	7928	12992
Magnesium											
0.5 Seconds/NAA	0	425	251	54	31	1543	520	315	1136	593	1841
0.5 Seconds/AA (sample 9)	56477	6035	4600	10944	27870	17909	5441	-365	10223	37530	-365
0.5 Seconds/AA (sample 11)	21235	14705	20454	6932	48726	-365	-365	12968	-365	-365	11438
Typical Concentration	38856	10370	12527	8938	38298	1543	520	315	1136	593	1841

Table 3-7. Summary of Analytical Results for 0.5 Seconds Residence Time (Continued)

	Concentrations (ppmw)										
Plate	11	10	9	8	7	6	5	4	3	2	1
Iron											
0.5 Seconds/NAA	3825	19157	3296	1702	902	12743	7625	3760	5787	5274	14608
0.5 Seconds/AA (sample 9)	283396	371836	344667	464515	229238	134340	238371	248509	110022	121712	918224
0.5 Seconds/AA (sample 11)	203481	353174	138189	404108	611626	215103	537525	186710	73081	99722	70523
Typical Concentration	243439	362505	241428	434311	420432	174721	387948	217610	91551	110717	494373
Arsenic											
0.5 Seconds/NAA	11	22	12	11	8	472	659	1266	2312	1833	2857
0.5 Seconds/GFAA (sample 9)	387	245	391	632	634	492	3709	1953	1227	1356	379
0.5 Res. Sec./GFAA (sample 11)	182	136	216	331	309	1571	1375	1670	2179	3075	2454
Typical Concentration	284	190	304	481	472	482	1914	1630	1906	2088	1897
Selenium											
0.5 Seconds/NAA	2	4	2	2	1	40	52	108	175	143	228
0.5 Seconds/GFAA (sample 9)	22	18	23	42	44	64	79	231	312	301	263
0.5 Seconds/GFAA (sample 11)	21	15	28	37	38	403	656	1300	2608	3924	3227
Typical Concentration	21	16	26	40	41	52	66	169	243	222	245

Table 3-7. Summary of Analytical Results for 0.5 Seconds Residence Time Samples (Continued)

	Concentrations (ppmw)										
Plate	11	10	9	8	7	6	5	4	3	2	1
Cadmium											
0.5 Seconds/NAA	34	34	54	17	10	175	79	14	15	17	25
0.5 Seconds/GFAA (sample 9)	113	255	337	542	522	131	149	364	425	439	395
0.5 Seconds/GFAA (sample 11)	174	157	131	77	259	52	117	699	907	131	1069
Typical Concentration	143	206	234	310	390	91	133	531	666	285	732
Cobalt											
0.5 Seconds/NAA	6	8	2	2	1	26	18	7	11	10	34
0.5 Seconds/GFAA (sample 9)	18	18	51	42	36	47	196	363	119	335	1195
Typical Concentration	18	18	51	42	36	47	196	363	119	335	1195
Antimony											
0.5 Seconds/NAA	2	3	1	1	1	31	39	100	178	133	210
0.5 Seconds/GFAA (sample 9)	340	19	43	31	28	63	162	56	148	166	267
0.5 Seconds/GFAA (sample 11)	35	30	31	49	53	1024	504	1176	2671	4024	3226
Typical Concentration	35	24	37	40	40	373	235	444	999	1441	1234
Chromium											
0.5 Seconds/NAA	168	260	178	70	53	477	301	253	476	405	2447
0.5 Seconds/GFAA (sample 9)											
0.5 Seconds/GFAA (sample 11)											
Typical Concentration	168	260	178	70	53	477	301	253	476	405	2447
Totals (Wt. Fraction)	0.508	0.608	0.479	0.665	0.618	0.294	0.464	0.301	0.135	0.164	0.573

Table 3-8. Summary of Analytical Results for 2.2 Seconds Residence Time Samples

	Concentrations (ppmw)										
Plate	11	10	9	8	7	6	5	4	3	2	1
Silica											
2.2 Seconds/AA (sample 10)	119815	168565	170364	20947	1413148	1478333	140767	22926	15073	8923	18080
2.2 Seconds/AA (sample 12)	176179	221880	252153	235370	41148	239815	69815	55200	19015	101353	21884
Typical Concentration	147997	195223	211259	128159	727148	859074	105291	39063	17044	55138	19982
Calcium											
2.2 Seconds/NAA	0	658	484	229	250	24508	18417	2381	3398	2456	1442
2.2 Seconds/AA (sample 10)	11373	7444	5219	2963	-56	8833	22801	-56	1181	1421	-56
2.2 Seconds/AA (sample 12)	1763	6796	7109	6611	3944	-56	29944	18406	19144	18406	71668
Typical Concentration	6568	7120	6164	4787	3944	24508	18417	2381	3398	2456	1442
Sodium											
2.2 Seconds/NAA	154	381	129	100	53	1395	1100	845	2266	1247	2838
2.2 Seconds/AA (sample 10)	12762	8059	12996	3975	149143	10032	25333	8432	2696	1212	5581
2.2 Seconds/AA (sample 12)	5537	2107	2914	4106	23143	41143	146809	5348	8129	5348	93051
Typical Concentration	9149	5083	7955	4040	86143	25587	86071	6890	5413	3280	2838
Magnesium											
2.2 Seconds/NAA	0	425	251	54	31	1543	520	315	1136	593	1841
2.2 Seconds/AA (sample 10)	16778	22135	47107	2352	479635	19635	33921	-365	5202	4066	6210
2.2 Seconds/AA (sample 12)	11908	1448	17545	12968	53635	-365	89635	82712	57235	27327	74118
Typical Concentration	14343	11792	32326	7660	266635	9635	61778	41173	31218	15696	40164

Table 3-8. Summary of Analytical Results for 2.2 Seconds Residence Time Samples (Continued)

	Concentrations (ppmw)										
Plate	11	10	9	8	7	6	5	4	3	2	1
Iron											
2.2 Seconds/NAA	3825	19157	3296	1702	902	12743	7625	3760	5787	5274	14608
2.2 Seconds/AA (sample 10)	136128	417081	92026	68930	1117081	237081	576128	159747	52338	26865	152697
2.2 Seconds/AA (sample 12)	64353	2799700	126036	148192	149081	357081	537081	329388	157081	163234	168115
Typical Concentration	100241	1608390	109031	108561	633081	297081	556604	244568	104710	95050	160406
Arsenic											
2.2 Seconds/NAA	11	22	12	11	8	472	659	1266	2312	1833	2857
2.2 Seconds/GFAA (sample 10)	667	365	434	176	8399	672	3702	1519	125	547	574
2.2 Res. Sec./GFAA (sample 12)	104	93	63	77	102	519	359	251	443	694	389
Typical Concentration	386	229	248	126	4251	554	1573	1012	960	1025	1273
Selenium											
2.2 Seconds/NAA	2	4	2	2	1	40	52	108	175	143	228
2.2 Seconds/GFAA (sample 10)	0	0	0	0	0	178	297	368	421	103	335
2.2 Seconds/GFAA (sample 12)	0	0	0	0	0	0	0	0	0	0	0
Typical Concentration	2	4	2	2	1	109	175	238	298	123	281
Cadmium											
2.2 Seconds/NAA	34	34	54	17	10	175	79	14	15	17	25
2.2 Seconds/GFAA (sample 10)	147	382	1487	54	3519	176	275	44	16	19	32
2.2 Seconds/GFAA (sample 12)	57	59	188	184	195	1977	1206	381	755	227	468
Typical Concentration	79	158	576	85	1242	776	520	146	262	88	175

Table 3-8. Summary of Analytical Results for 2.2 Residence Second Samples (Continued)

	Concentrations (ppmw)										
Plate	11	10	9	8	7	6	5	4	3	2	1
Cobalt											
2.2 Seconds/NAA	6	8	2	2	1	26	18	7	11	10	34
2.2 Seconds/GFAA (sample 10)	34	276	46	6	497	79	55	15	12	8	7
2.2 Seconds/GFAA (sample 12)	54	68	79	107	145	926	702	343	261	154	90
Typical Concentration	31	117	42	39	215	344	258	121	95	58	43
Antimony											
2.2 Seconds/NAA	2	3	1	1	1	31	39	100	178	133	210
2.2 Seconds/GFAA (sample 10)	88	263	4710	2632	2079	55	148	56	1097	277	186
2.2 Seconds/GFAA (sample 12)	-1	-1	-1	-1	-1	213	3029	-1	-1	-1	-1
Typical Concentration	2	3	1	1	1	43	94	78	638	205	198
Chromium											
2.2 Seconds/NAA	584	159	230	123	241	2733	5625	1342	485	366	1914
2.2 Seconds/GFAA (sample 10)											
2.2 Seconds/GFAA (sample 12)	54	68	79	107	145	926	702	343	261	154	90
Typical Concentration	584	159	230	123	241	2733	5625	1342	485	366	1914
Totals (Wt. Fraction)	0.279	1.828	0.368	0.254	1.723	1.220	0.836	0.337	0.165	0.173	0.229

Table 3-9. Summary of Analytical Results for Hot-Side ESP Condition Samples

	Concentrations (ppmw)										
Plate	11	10	9	8	7	6	5	4	3	2	1
Silica											
Hot-Side ESP/AA (sample 16)	222919	200991	155691	197048	175749	124070	83883	55467	12329	102672	0
Calcium											
Hot-Side ESP/AA (sample 16)	6051	5238	5718	2963	5256	10157	8080	-56	-56	-56	0
Sodium											
Hot-Side ESP/AA (sample 16)	2741	2545	5912	5344	7046	8320	18521	7635	2759	35619	0
Magnesium											
Hot-Side ESP/AA (sample 16)	8795	4929	3346	1899	11585	-365	109465	46591	-365	-365	0
Iron											
Hot-Side ESP/AA (sample 16)	193722	118845	117493	111798	132516	237081	224877	144907	46243	195176	0
Arsenic											
Hot-Side ESP/GFAA (sample 16)	708	217	351	660	755	933	1109	1282	2235	8605	0
Selenium											
Hot-Side ESP/GFAA (sample 16)	4	7	12	11	10	29	103	205	260	3657	0
Cadmium											
Hot-Side ESP/GFAA (sample 16)	66	133	272	488	498	153	184	304	357	5005	0
Cobalt											
Hot-Side ESP/GFAA (sample 16)	29	27	32	59	72	125	40	30	12	55	0
Antimony											
Hot-Side ESP/GFAA (sample 16)	64	9	128	72	81	78	65	103	103	504	0
Chromium											
Hot-Side ESP/GFAA (sample 16)											
Totals (Wt. Fraction)	0.435	0.333	0.289	0.320	0.334	0.381	0.446	0.256	0.064	0.351	0.000

performed using the furnace immediately prior to the Ohio baseline tests involved doping methane flames with high concentrations of cadmium, lead, and cesium.

Of the major species analyzed, iron and silica dominate followed by magnesium and sodium. The calcium concentration of Ohio coal is low compared to other program coals and is on the order of the concentration of arsenic and chromium.

The typical concentration values from Tables 3-7 through 3-9 were used to generate individual element distribution profiles (Markowski, 1977) which were subsequently normalized using the enrichment factor (E_{fa}) method (Haynes, 1982). Profiles for Arsenic are shown in Figures 3-13 and 3-14, for selenium are shown in Figures 3-15 and 3-16, for cadmium are shown in Figures 3-17 and 3-18, for cobalt are shown in Figures 3-19 and 3-20, and for antimony are shown in Figures 3-21 and 3-22. Comparisons of the normalized elemental distributions (E_{fa}) are shown in Figures 3-23 and 3-24 for the conditions at 0.5 and 2.2 seconds residence time, respectively.

Comparing E_{fa} at 2.2 seconds to E_{fa} at 0.5 seconds provides insight into partitioning behavior in the post-combustion zone. This comparison is shown in Figures 3-25 and 3-26.

Figure 3-13. Typical arsenic distribution in Ohio baseline fly ash.

Figure 3-14. A comparison of arsenic enrichment factors for Ohio baseline experiments (compared to the corresponding average fly ash concentration).

Figure 3-15. Typical selenium distribution in Ohio baseline fly ash.

Figure 3-16. A comparison of selenium enrichment factors for Ohio baseline experiments (compared to the corresponding average fly ash concentration).

Figure 3-17. Typical cadmium distribution in Ohio baseline fly ash.

Figure 3-18. A comparison of cadmium enrichment factors for Ohio baseline experiments (compared to the corresponding average fly ash concentration).

Figure 3-19. Typical cobalt distribution in Ohio baseline fly ash.

Figure 3-20. A comparison of cobalt enrichment factors for Ohio baseline experiments (compared to the corresponding average fly ash concentration).

Figure 3-21. Typical antimony distribution in Ohio baseline fly ash.

Figure 3-22. A comparison of antimony enrichment factors for Ohio baseline experiments (compared to the corresponding average fly ash concentration).

Figure 3-25 implies that significant vaporization occurs in the 0.5 to 2.2 seconds furnace zone (~1350 K to ~1100 K) for selenium. However, this conclusion must be tempered by the fact that the actual selenium concentrations are very low and a relatively small increase in concentration will generate a large enrichment factor. Figure 3-25 also implies that there is little or no vaporization for cobalt, chromium, and arsenic in the 0.5 to 2.2 seconds furnace zone. It is unclear from Figures 3-25 and 3-26 whether there is significant vaporization of antimony in the 0.5 to 2.2 seconds furnace zone. Like Se, Sb concentrations are relatively low in this fly ash.

For particles between 0.1 and 0.5 μm , there appears to be homogeneous nucleation of those containing Se and Sb in the 0.5 to 2.2 seconds furnace zone. By contrast, small particles containing As, Co, and Cd or vapor-phase molecules generated in the combustion zone appear to undergo coagulation/ agglomeration into larger particles as shown by depletion in this size range.

For particles between 0.5 and 1 micron, the coagulation/agglomeration of the small particles containing As, Co, and Cd shows up as enrichment in this size range. We also see enrichment of Se, Co, and Cr in this size range, implying coagulation/agglomeration of these elements.

Note that Figures 3-14, 3-16, 3-18, 3-20, and 3-22 do not include the hot-side ESP samples. Element distribution profiles cannot be normalized to the average elemental fly ash concentration (E_{fa}) because of the removal of the majority of the large particles prior to this sampling location. However, an alternate normalization method can be used. This method

Figure 3-23. Enrichment of elements in size-segregated fly ash particles compared to the average fly ash concentrations at 0.5 seconds residence time.

Figure 3-24. Enrichment of elements in size-segregated fly ash particles compared to the average fly ash concentrations at 2.2 seconds residence time.

Figure 3-25. Elemental residence time-dependent enrichment (depletion) for Ohio baseline experiments in the post-combustion zone (2.2 seconds to 0.5 seconds).

Figure 3-26. Elemental residence time-dependent enrichment (depletion) for Ohio baseline experiments in the post-combustion zone (2.2 seconds to 0.5 seconds). Expanded scale.

(Gladney, 1976) ratios the elemental concentration on a given plate to the average concentration, E_c , in the coal prior to combustion.

$$E_{c,M,x} = \text{conc. element M on plate x (ppmw)} / \text{conc. element M in feed coal (ppmw)} \quad (4)$$

A comparison of the elemental distributions normalized as $E_{c,M,x}$ is shown in Figures 3-27 to 3-29 for all three sample locations.

We can now compare $E_{c,M,x}$ at hot-side ESP conditions to $E_{c,M,x}$ at 2.2 seconds (see Eq. (3), above) and evaluate partitioning behavior between the boiler post-combustion zone and the ESP inlet. This comparison is shown in Figures 3-30 and 3-31. When considering particles < 0.1 micron, it is likely that the observed enrichment of Cd is due to contamination from the walls at the bottom of the furnace. The selenium enrichment values most likely result from analytical limitations. The values used in these calculations were obtained near the detection limits of analysis due to the very low concentrations of selenium in these samples. For particles between 0.1 to 0.5 micron in size, continued coagulation/agglomeration of the very small particles containing As and Cd is observed. Particles in this size range are depleted in Se, Cd, and Co, indicating that the coagulation/agglomeration of particles from this size range (to larger sizes) exceeds the rate of coagulation/agglomeration of the very small particles into this size range. Finally, for particles between 0.5 and 1 micron, the expected growth of particles is observed. Note that data above around 5 microns cannot be used in evaluation since a majority of these particles are removed from the gas stream prior to the sampling location.

Figure 3-27. Enrichment of elements in size-segregated fly ash particles compared to the initial coal concentration at 0.5 seconds residence time.

Figure 3-28. Enrichment of elements in size-segregated fly ash particles compared to the initial coal concentration at 2.2 seconds residence time.

Figure 3-29. Enrichment of elements in size segregated fly ash particles compared to the initial coal concentration at hot-side ESP conditions.

Figure 3-30. Elemental residence time-dependent enrichment (depletion) for the Ohio baseline experiments in the ESP entrance region (hot-side ESP - 2.2 seconds).

Figure 3-31. Elemental residence time-dependent enrichment (depletion) for the Ohio baseline experiments in the ESP entrance region (hot-side ESP - 2.2 seconds). Expanded scale.

Heterogeneous partitioning mechanisms include condensation of metal vapor upon existing particles and reaction of metal vapor with other chemical species on the surface or within the pores of a particle. The rate of transformation by reaction may be limited by diffusion of the metal vapor through the gas film surrounding the particle, diffusion into the pores of the particle, by the reaction rate on the exterior surface of a nonporous particle, or by the reaction rate on the internal surface within a porous particle. Log-log plots of elemental concentration versus particle size can provide some insight into these heterogeneous partitioning mechanisms.

A $1/d_p$ (particle diameter) dependence indicates that, in the continuum regime, exterior surface reaction or pore diffusion may be the dominant formation mechanism (Linak, 1994). A $1/d_p^2$ dependence indicates that gas film transfer is the controlling rate process; which is true for condensation in the continuum regime or for infinitely fast surface reaction (Linak, 1994).

Log-log plots of elemental concentration versus particle size (for impactor plates of greater than 0.8 micron 50% cutoff diameter) are shown in Figures 3-32 through 3-36 for As, Se, Cd, Co, and Sb, respectively for all three sampling locations.

Arsenic (Figure 3-32). A $1/d_p$ dependence occurs at the 0.5 seconds sample, indicating that redeposition of arsenic in the combustion zone may be controlled by exterior surface/pore diffusion mechanisms. This dependence is not evident in the 2.2 seconds results.

Figure 3-32. Particle size dependence for As in Ohio fly ash.

Selenium (Figure 3-33). It is difficult to draw any conclusions from selenium since there is so little selenium present in the fly ash samples collected. There appears to be a $1/d_p$ dependence at the 0.5 seconds sample and no correlation of concentration to particle size for the 2.2 seconds and hot-side ESP results. Figure 3-16 implies that homogeneous mechanisms are the most significant for this element in the post-combustion and ESP inlet zones.

Figure 3-33. Particle size dependence for Se in Ohio fly ash.

Cadmium (Figure 3-34). These results must be considered suspect due to the contamination problem during the experiments. The results in Figure 3-34 are analogous to those for arsenic.

Figure 3-34. Particle size dependence for Cd in Ohio fly ash.

Cobalt (Figure 3-35). There is no definitive correlation between concentration and particle size for any of the sample locations. There appears to be very little cobalt in the vapor-phase after the combustion zone.

Figure 3-35. Particle size dependence for Co in Ohio fly ash.

Antimony (Figure 3-36). No correlation of concentration to particle size is observed for the 0.5 seconds and 2.2 seconds results. The hot-side ESP results show a $1/d_p^2$ dependent which imply that condensation may be important for this element at ESP inlet conditions.

Figure 3-36. Particle size dependence for Sb in Ohio fly ash.

Based on the results presented above, the following preliminary conclusions can be drawn for the combustion of Ohio coal under baseline conditions:

1. Particle fragmentation may be occurring for particles in the 5 to 10 micron size range in the 0.5 to 2.2 seconds furnace zone. The majority of the particles generated during this fragmentation are around 1 micron in size.
2. There is some evidence that vaporization occurs in the 0.5 to 2.2 seconds furnace zone. A portion of this vaporization appears to be selenium and antimony-based compounds.
3. Homogeneous nucleation of the material present in the gas phase after 0.5 seconds primarily occurs at the ESP inlet conditions rather than in the 0.5 to 2.2 seconds zone of the furnace. There is evidence that some of the gas-phase Se and Sb transforms to the solid phase by homogeneous nucleation in the 0.5 to 2.2 seconds zone. However, these elements are present at very low concentrations.
4. In the 0.5 to 2.2 seconds furnace zone, heterogeneous transformation is not significant for any of the trace elements evaluated. No correlation was observed between elemental concentration and particle size.
5. At inlet ESP conditions, surface reaction/pore diffusion heterogeneous transformation mechanisms appear to control the transformation of the gas-phase arsenic and cobalt species whereas condensation appears to control the transformation of gas-phase antimony species.
6. It is postulated that the lack of surface reaction/pore diffusion controlled heterogeneous transformation in the post-combustion zone for As, Se, and Cd is due to the low concentration of calcium present in the Ohio blend coal.

3.4.3 *Modeling of Post-Combustion Mercury Reactions*

In Quarterly Report 9 (October 1998 to December 1998), we reported the results of initial calculations conducted to assess the importance of reaction kinetics in determining the extent of mercury oxidation. In this initial work, two different kinetic models were considered. Here we extend these calculations to higher temperatures, based upon data reported by Hall et al. (1990) and Kramlich et al. (1997) suggesting that super-equilibrium concentrations of HgCl_2 were possible at temperatures greater than 900 K.

To briefly review the approach outlined previously, global kinetics were derived from the studies of Hall et al. (1990) and Gaspar et al. (1997). To assess the importance of atomic Cl, further kinetic calculations were conducted using elementary reactions as described by Kramlich and co-workers (Kramlich et al., 1997). Specifically, Hall et al. report data flow reactor studies that were used to derive a rate constant of $k = 1.07 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 500°C for the global reaction

For the global reaction with HCl,

Gaspar et al. report a rate constant of $k = 2.20 \times 10^7 \exp(-3460/T)$ liters $\text{mol}^{-1} \text{s}^{-1}$ over the temperature range 400 to 900°C. For the elementary pathway, studies by Kramlich et al. suggest that the key oxidizing species is atomic Cl through a homogeneous pathway, governed by two principal steps,

and note that super-equilibrium concentrations of Cl are required to account for observed HgCl_2 concentrations. The consumption of elementary mercury in the mechanism proposed by Kramlich et al. proceeds by Reaction (3). An average rate constant for this reaction is $1.5 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

To extend these calculations to higher initial temperatures, Cl, HCl, and Cl_2 profiles reported previously (October 1998 to December 1998, Quarterly Report 9) were used. Using linear and nonlinear regression, characteristic equations were fitted for each compound in order to have a function of Cl compound concentration versus elapsed time of reaction. It should be noted that it would be preferable to examine the chlorine and mercury chemistry in a combined reaction set, a task which is planned for the later stages in this project.

Table 3-10 summarizes the calculations conducted during this quarter. Calculations using the combined global reaction mechanism were conducted at initial temperatures of 1500 and 1200 K at a cooling rate of -200K/s, and at initial temperatures of 1520 K and 1220 at a cooling rate of -500K/s. The slight difference in initial temperatures was due to a desire to match the output of the chlorine calculations at the starting point.

Table 3-10. Initial Conditions and Temperatures for Mercury Kinetic Calculations

Mechanism	[Hg], ppm	[Cl ₂] _o , ppm	[HCl] _o , ppm	dT/dt	T range, K
Global Kinetics	0.01	0.0001	31	-200 K/s	1500 to 300
Global Kinetics	0.01	0.0009	32	-200 K/s	1200 to 300
Global Kinetics	0.01	0.0001	31	-500 K/s	1520 to 300
Global Kinetics	0.01	0.001	32	-500 K/s	1220 to 300

Results of these calculations are shown in Figure 3-37 and Figure 3-38. In Figure 3-37, conversions of 50% to 80% were achieved after 2 seconds, corresponding to a cooling rate of -200 K/s and initial temperatures of 1500 and 1200 K, respectively. In Figure 3-38, conversions of 30% and 50% can be seen after 1 second, with initial temperatures of 1520 K and 1220 K and a cooling rate of -500 K/s. respectively. The final temperature is 300K in all cases.

Figure 3-37. High temperature mercury oxidation at -200 K s⁻¹.

Figure 3-38. High temperature mercury oxidation at -500 K s⁻¹.

Comparing these results with those reported previously (October 1998 to December 1998, Quarterly Report 9), conversions are in general much higher, not surprising given the higher initial starting temperature. Conversions to oxidized mercury are also observed to be within the

range observed in field measurements (40 to 80% oxidation) when these higher starting temperatures are considered. Although global kinetic expressions were used to derive these results, it is instructive to note that chlorine atom concentrations are four times higher at 1520 K than at 970 K. The mechanistic assessment of the importance of chlorine atom in the oxidation of mercury is thus consistent with this finding, but it must be emphasized that it remains to be determined whether super-equilibrium concentrations of mercuric chloride can form at temperatures above approximately 1000 K, where equilibrium indicates that mercury should be present entirely as Hg(0) vapor.

Additional calculations were conducted using a cooling rate calculated from the specifications for a small industrial boiler provided by PSI. The specifications and cooling rates derived from this calculation are provided in Table 3-11. Although the temperatures will be lower and the residence times in most sections shorter than those obtained in a large utility boiler, the shape of the temperature profile is representative of that encountered in a coal-fired utility boiler and thus can provide insight into the role of boiler temperature profile in mercury oxidation.

Global kinetics and elementary kinetics were both used to determine mercury conversions attained at the end of the boiler using the temperature profile reported in Figure 3-39. The corresponding cooling rates are shown in Figure 3-40. Total Hg conversions are achieved within 0.2 seconds or less. The results are very similar to the ones observed at lower temperatures (see Quarterly Report 9, October 1998 to December 1998). Figures 3-41 and 3-42 show conversions similar to the Hg global reaction modeling done starting at 960 K and 970 K reported previously. The conversions achieved were 23% for an initial temperature of 1370 K, and 13% for an initial temperature of 970 K. The sequences were run for 1.66 seconds and 1.38 seconds, respectively. Note that the final observed conversions are below the 40 to 80% conversion reported in field measurements.

Table 3-11. Boiler Temperature Profile Used in Kinetic Calculations

Location	T _{in} (K)	T _{out} (K)	T-avg	Res. Time (s)	Cooling Rate (K/s)
Screen Tubes	1368	1322	1345	0.025	-1840
Superheater	1322	1147	1231	0.151	-1160
Boiler Bank	1147	711	903	1.162	-1670
Rear cavity	711	708	709	1.162	-3
Economizer	708	602	653	0.060	-1770
Air Heater	602	390	485	0.252	-840

Figure 3-39. Calculated boiler temperature profile used in kinetic calculations.

Figure 3-40. Calculated cooling rates for boiler temperature profile.

Figure 3-41. Conversion of Hg to HgCl₂ using boiler temperature profiles for calculations begun at 1370 K.

Figure 3-42. Conversion of Hg to HgCl₂ using boiler temperature profiles for calculations begun at 970 K.

SECTION 4

SUMMARY AND FUTURE PLANS

4. SUMMARY AND FUTURE PLANS

4.1 Summary

The first full Program Review Meeting was held at the University of Arizona in January 1999. At this meeting, the progress of each group was reviewed, and action items were identified. Important near term actions identified at this meeting included:

- Shipment of remaining samples of Phase I coals from Consol to the University of Arizona
- Shipment of a sample of a Chinese coal containing high arsenic concentrations from the USGS to the University of Utah. The coal may then be used in an examination of arsenic vaporization.
- Neutron activation analysis of the program coals will be repeated with an emphasis on obtaining more accurate calcium concentration data.
- Modifications to the chlorine kinetic calculations will be explored.

In the area of coal analysis, leaching procedures have been completed for the three Phase II coals by USGS 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 also been determined. Low temperature ashing has been completed for the Ohio and Wyodak samples, and these will be followed by XRD determinations. Preliminary leaching results were revised to reflect as-received fractions in the coals. As a result, the fractions leached by ammonium acetate that were reported at the Program Review Meeting were revised downward.

XAFS experiments were conducted at both the Stanford University SSRL and the Brookhaven National Synchrotron Light Source (NSLS) during this reporting period. Experiments at the Stanford SSRL examined samples for mercury while experiments at NSLS examined samples for sulfur and chlorine. Mercury analysis of selected sorbent samples provided further evidence that XANES absorption spectra can provide information on the bonding of mercury to the solid sorbent. Interpretation of spectra will be continuing throughout the next reporting period.

Initial experiments to determine the extent of trace metal vaporization during coal devolatilization were conducted at the University of Utah. Samples were devolatilized using procedures outlined in ASTM volatile analysis standards and subsequently sent to MIT for neutron activation analysis. Initial analysis of the resulting compositional data suggested that several metals were vaporizing during devolatilization under these conditions. Analysis of the data will be continuing during the next reporting period.

To provide a reference point for potential interactions between arsenic species and calcium compounds in fly ash, tube furnace experiments were conducted at the University of Connecticut utilizing organic arsenic solutions, calcium compounds, and model silica ash particles produced by sol-gel methods. The objective was to determine whether calcium contained within silicate particles typical of fly ash could react with arsenic under idealized contacting conditions. In these experiments, aqueous solutions of cacodylic acid were added to silica, calcium acetate (expected to form calcium oxide), or calcium silicate particle samples and allowed to react 800°C for 10 to 15 min under flowing air. Subsequent analysis of these samples by the University of Kentucky using arsenic XAFS demonstrated that As (V) typical of calcium arsenate was obtained in all samples containing calcium. The arsenic XANES spectrum of the SiO₂ sample indicated that the dominant oxidation state was As (III), potentially the result of As₂O₃ formation on the surface of the silica particles. These results suggest that arsenic can react with calcium embedded within silicates under idealized contacting conditions and long residence times. Experiments in the next several reporting periods will extend these experiments to conditions closer to post combustion conditions encountered by fly ash particles to determine whether arsenic vapors can form As(V) compounds by reaction with calcium embedded within silicate particles.

Modeling of post combustion mercury reactions continued during this reporting period at the University of Connecticut. Calculations of mercury oxidation using global reaction kinetics were extended to higher temperatures as a result of suggestions by University of Washington researchers that super-equilibrium concentrations of mercuric chloride had been experimentally observed. Using chlorine species concentration profiles described in the previous Quarterly Report, it was concluded that conversions in the range of the 40 to 80% reported in field data could be obtained if the starting point for mercury oxidation was increased to approximately 950°C at a cooling rate of 200 K s⁻¹. At higher cooling rates that are more representative of much of the post combustion boiler temperature profile, however, conversion to oxidized species remained below that observed in the field data. Calculations using typical post combustion temperature profiles will be continuing during upcoming reporting periods.

Larger scale baseline combustion experiments using the Ohio coal were completed at the University of Arizona during the reporting period. Based on these experiments, the following preliminary conclusions were drawn:

1. Particle fragmentation may be occurring for particles in the 5 to 10 micron range in the 0.5 to 2.2 res. sec. furnace zone. The majority of the particles generated during this fragmentation are around 1 micron in size.
2. There is some evidence that vaporization of trace metals occurs in the 0.5 to 2.2 res. sec. furnace zone. A portion of this vaporized material appears to be selenium and antimony-based compounds.
3. Homogeneous nucleation of the material present in the gas phase after 0.5 residence seconds primarily occurs at ESP inlet conditions rather than in the 0.5 to 2.2 residence second zone of the furnace. There is evidence that some of the gas-phase Se and Sb

transforms to the solid phase by homogeneous nucleation in the 0.5 to 2.2 res. sec. zone. However, these elements are present at very low concentrations.

4. In the 0.5 to 2.2 res. sec. furnace zone, heterogeneous transformation is not significant for any of the trace elements evaluated. No correlation was observed between elemental concentration and particle size.
5. At inlet ESP conditions, surface reaction/pore diffusion heterogeneous transformation mechanisms appear to control the transformation of the gas-phase arsenic and cobalt species whereas condensation appears to control the transformation of gas-phase antimony species.
6. It is postulated that the lack of surface reaction/pore diffusion controlled heterogeneous transformation in the post-combustion zone for As, Se, and Cd is due to the low concentration of calcium present in the Ohio blend coal.

Also during the reporting period, favorable reviews were returned for two papers integrating USGS results and XAFS results, and a third paper describing the modeling of trace element emissions in field data, all submitted to the special issue of Fuel Processing Technology devoted to the Phase I study. 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 I 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. An additional paper describing XAFS investigation of the speciation of mercury and other elements involved in sorption of mercury on activated carbons was published in the January issue of *Energy and Fuels*.³ A second paper published in the January issue of *Fuel*⁴ described an XAFS method for determining quantitatively the chromium oxidation states in ash products from coal combustion. The contribution on chromium speciation in Phase I project coals for the Air-Toxics special issue of Fuel Processing Technology was revised and has been re-submitted.⁵

4.2 Future Plans

In March, 1999 it was learned that the USGS proposal to use a new state-of-the-art SHRIMP-RG ion microprobe run jointly by the USGS and Stanford University has been approved. The initial SHRIMP-RG session is being planned for the summer of 1999 and will focus on studies of pyrite and illite grains, and organic portions of the coals. 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.

No new XAFS experimental sessions are currently scheduled for the next quarter and as a result, the University of Kentucky will concentrate on the detailed analysis of the data newly obtained at SSRL and NSLS. In addition, the mercury XANES trend simulations should be completed. Data and samples should be available for the Cherokee station ash sample supplied

by personnel at ADA Technologies. Late in the quarter, in anticipation of beam-time in the following quarter, fractionated samples of the project coals should be provided to the University of Kentucky by the USGS. These samples will have been prepared according to the USGS leaching protocol. XAFS examination of these fractions prepared at USGS should be mutually beneficial for interpretation of the XANES spectra on the one hand and for understanding of the leaching chemistry on the other.

Combustion experiments will be continuing at the University of Utah and the University of Arizona during the upcoming reporting period. Samples produced in these experiments will be sent to MIT for neutron activation analysis with the hope of generating compositional data prior to the next Program Review Meeting scheduled for early fall 1999.

SECTION 5

REFERENCES

5. REFERENCES

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APPENDIX A

Text of Correspondence Between USGS and PSI on Moisture Corrections in Project Samples

To: Dr. Connie Senior
PSI, Inc.
Andover, MA

From: Curtis A. Palmer
USGS Energy Resources Program
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 kept in a desiccator in a dry state until weighing for analysis. The ash generally is not as hygroscopic 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