**TOXIC SUBSTANCES FROM COAL COMBUSTION --
A COMPREHENSIVE ASSESSMENT**

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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, the Lignite Research Council, 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 July 1998 through 30 September 1998. During this period distribution of all three Phase II coals was completed. Standard analyses for the whole coal samples were also completed. Mössbauer analysis of all project coals and fractions received to date has been completed in order to obtain details of the iron mineralogy. The analyses of arsenic XAFS data for two of the project coals and for some high arsenic coals have been completed. Duplicate splits of the Ohio 5,6,7 and North Dakota lignite samples were taken through all four steps of the selective leaching procedure. Leaching analysis of the Wyodak coal has recently commenced. Preparation of polished coal/epoxy pellets for probe/SEM studies is underway. Some exploratory mercury L_{III} XAFS work was carried out during August at the Advanced Photon Source (APS), the new synchrotron facility at Argonne National Laboratory, Chicago, IL. Further analysis of small-scale combustion experiments conducted at PSI in Phase I was completed this quarter. The results of these experiments for the first time suggest almost complete vaporization of certain trace elements (Se, Zn) from coal combustion in the flame zone, in accordance with theoretical equilibrium predictions. Other elements (As, Sb, Cr) appeared considerably less volatile and may react with constituents in the bulk ash at combustion temperatures. The combustion section of the University of Arizona's Downflow Combustor was completely rebuilt. The University of Utah worked on setting up EPA Method 26A to give the capability to measure chlorine in flue gas. The chlorine kinetic calculations performed as part of the Phase I program were found to have an error in the initial conditions. Therefore, the calculations were re-done this quarter with the correct starting conditions. Development of a quasi-empirical emissions model based on reported emissions of particulate matter from field measurements was continued this quarter. As a first step in developing the ToPEM, we developed a sub-model that calculates the evaporation of major elements (Na, K, Fe, Si, Al, Ca and Mg) from both inherent and extraneous minerals of coal. During this quarter, this sub-model was included into EMAF, which formed the ToPEM. Experimental data from the Phase I program were used to test and modify the sub-model and the ToPEM.

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 between vapor, submicron fume, and fly ash during the combustion of pulverized coal
- d) To model the partitioning of toxic elements between 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 Subsection 2.1 of this report.

The work discussed in this report covers the reporting period from 1 July 1998 through 30 September 1998. During this quarter, distribution of all three Phase II coals was completed. Standard analyses for the whole coal samples were also completed. Mössbauer analysis of all project coals and fractions received to date has been completed in order to obtain details of the iron mineralogy.

The analyses of arsenic XAFS data for two of the project coals and for some high arsenic coals have been completed. The reason for studying the high-As coals is to try and get a better understanding of the oxidation behavior of arsenic, which is prevalent in virtually all coals that we have examined with the XAFS technique. In addition, complementary Mössbauer analyses of the high-As coals have also been completed. As in Phase I bituminous coals, both As/pyrite and arsenate forms are readily apparent in the spectra of the Ohio bituminous coal and fractions. Half of the arsenic in the North Dakota lignite is found as arsenate; the rest is either in pyrite or as arsenite. Some exploratory mercury L_{III} XAFS work was carried out during August at the Advanced Photon Source (APS), the new synchrotron facility at Argonne National Laboratory, Chicago, IL. Comparable quality data were obtained for mercury in carbonaceous systems using a Lytle detector at APS to that obtained at SSRL using a more sensitive 13-element germanium detector. However, for mercury in an aluminosilicate matrix (zeolite), the quality of the data from SSRL was superior because of the effectiveness of the 13-element germanium detector in reducing the background signal.

During the reporting period, duplicate splits of the Ohio 5,6,7 and North Dakota lignite samples were taken through all four steps of the selective leaching procedure. Results for whole-coal splits are not available. Leaching analysis of the Wyodak coal has recently commenced. Preparation of polished coal/epoxy pellets for probe/SEM studies is underway.

Further analysis of small-scale combustion experiments conducted at PSI in Phase I was completed this quarter. Good mass balance closure (90 to 140%) was obtained overall for ash in the sampling system. More refractory elements had good mass balance closure with the exception of chromium. High chromium mass balance closure may have been due to contamination. The volatile elements As, Sb, Se, and Zn showed mass balance closures significantly less than 100%. The results of these experiments for the first time suggest almost complete vaporization of certain trace elements (Se, Zn) from coal combustion in the flame zone, in accordance with theoretical equilibrium predictions. Other elements (As, Sb, Cr) appeared considerably less volatile and may react with constituents in the bulk ash at combustion temperatures. Confirmation of these experiment results will require gas-phase sampling in addition to aerosol sampling in order to close the mass balance for the volatile elements.

The combustion section of the University of Arizona's Downflow Combustor was completely rebuilt. Concurrently, an air preheater was constructed and commissioned. The University of Utah worked on setting up EPA Method 26A to give the capability to measure chlorine in flue gas. In the next few months calibration of the impinger train will be finished and it will be connected to the 100,000 Btu/hr furnace running with coal.

The chlorine kinetic calculations performed as part of the Phase I program were found to have an error in the initial conditions. The results reported in the Phase I Final Report had 1/10 the amount of hydrogen typically found in coal. Therefore, the calculations were re-done this quarter with the correct starting conditions.

Development of a quasi-empirical emission model based on reported emissions of particulate matter from field measurements was continued this quarter. The emission model predicts stack emissions of selected trace elements based on the penetration of fly ash particles through the particulate collection device and on an overall degree of vaporization. The latter quantity is derived from a best fit of field data. In the future, the emission model can be coupled to TOPEM to provide a fundamental method for calculating trace element emissions.

As a first step in developing the ToPEM, we developed a sub-model that calculates the evaporation of major elements (Na, K, Fe, Si, Al, Ca and Mg) from both inherent and extraneous minerals of coal. During this quarter, this sub-model was included into EMAF, which formed the ToPEM. Experimental data from the Phase I program were used to test and modify the sub-model and the ToPEM.

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 (< 200°C) 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 discussion was held to discuss analysis of trace metals in coal and ash samples via XAFS using the Advanced Photon Source (APS) at Argonne National Laboratory. Participants were Gene Dalverny (DOE FETC), Jerry Huffman and Frank Huggins (University of Kentucky), Ken Kemner (Environmental Research Division, Argonne National Laboratory), and Connie Senior (Physical Sciences Inc.). We hope that use of the APS would allow us to improve our detection limits for mercury down to 1 ppm. We would also like to be able to do X-ray imaging and micro-XAFS of ash samples. This would provide better insight into the association of trace elements in flyash with major ash constituents. Kentucky personnel worked with Ken Kemner to obtain some preliminary data on mercury sorbent samples during a beam run at APS.

PSI talked with Professor Robert Brown and Dr. Glenn Norton from Iowa State University. They will start a three year UCR program in September. In this program, they will look at the role of flyash in the conversion of Hg^0 to Hg^{+2} in flue gas. They will look at factors such as unburned carbon content, mineral phases, and trace mineral content of the flyash as well as the effects of flue gas composition. They will do lab scale experiments and larger scale pc combustion.

Information on the Phase I program was sent to Dr. John Munthe at IVL in Sweden. Dr. Munthe has a program on mercury measurement and emissions from combustion. In this program, they have performed a measurement campaign in a pressurized fluidized bed combustor and are working on a simple flue gas model for Hg transformations. He promised to provide more detail on his program after a review meeting in September.

This quarter papers were prepared for a special issue of *Fuel Processing Technology*. Eight papers covering all aspects of the Phase I program are in preparation.

3.2 Coal Characterization (UK, USGS, MIT, PSI)

3.2.1 *Coal Selection*

We chose three coals for detailed study in Phase II. The coals were chosen in an attempt to (1) represent a broad range of elemental forms of occurrence and (2) represent the major coal ranks and commercial coal seams used for pulverized coal power generation in the U.S. The list of Phase II coals includes the Wyodak coal from Phase I and two new coals.

A bituminous coal from Ohio coal was selected for study. The particular coal sample was a blend of three seams: Ohio 5, Ohio 6, and Ohio 7. This blend was made for testing at McDermott Technologies Clean Environment Development Facility (CEDF). The CEDF test

program, also sponsored by DOE, is intended to study mercury emissions from coal-fired combustion systems and the interactions of mercury and air pollution control devices such as scrubbers. A similar coal, a blend of Ohio 5 and 6 seams, is burned at a full scale power plant which is currently being sampled for trace element emissions in another DOE-sponsored program.

The second new coal in Phase II is a lignite from North Dakota (Hagel Bed). This coal is burned at a mine-mouth utility power plant in North Dakota. While lignites are not major steam producing coals throughout the United States, they are important regionally. The mineralogy of lignites from this seam is different from other coals. A pulverized sample was obtained from EERC. This coal is burned at a full scale power plant which will be sampled for trace element emissions in another DOE-sponsored program.

The Wyodak coal will continue to be studied in the Phase II program. This is a sub-bituminous coal from the Powder River Basin and is an important steam coal. More experimental work, particularly large scale combustion studies, remains to be completed for this coal. The Phase I Wyodak sample was obtained through ABB. Since there was not enough of the Phase I material left for Phase II, a fresh sample was procured from a power plant which burns this coal. Both Phase I and Phase II samples came from the same mine, although the samples were mined approximately two years apart. Approximately 1.5 tons of coal were shipped from the power plant to EERC. The coal was pulverized this quarter and shipped to the University of Arizona.

3.2.2 *Coal Composition*

Tables 3-1 through 3-3 summarize the coal composition analyses. The coal particle size distribution is shown in Table 3-4. The Ohio coal has a moderate sulfur content (2.6 wt%) which is intermediate between the Phase I Illinois and Pittsburgh coals. The ash is lower in iron than the Illinois and Pittsburgh coals. The North Dakota lignite has a substantial amount of water as well as a moderately high (~10%) ash content. The lignite has more sulfur than the Wyodak coal and about 1/3rd of the sulfur is pyritic, indicating that this coal will have a significant amount of pyrite. This can also be seen from the ash analysis since the ash has a moderate amount of iron oxide. The ash is also high in calcium, magnesium, and sodium. These are probably organically associated to some degree. The Wyodak sample contained more moisture, as received, than the Phase I sample. The ash contains somewhat less calcium than the Phase I sample.

The chlorine contents of the Wyodak coal and the North Dakota lignite are low, 26 ppmw and 36 ppmw, respectively. The Ohio bituminous coal, on the other hand, has a chlorine content of 974 ppmw which is in the range of values for US bituminous coals.

Table 3-1. Coal Properties Phase II Program Coals (As-received basis)

	Wyodak	Ohio 5,6,7	ND Lignite
Proximate, wt%			
Moisture	25.81	2.33	35.88
Volatile matter	34.85	39.19	28.15
Fixed carbon	33.31	48.78	26.59
Ash	6.03	9.70	9.38
Heating value, Btu/lb	8,869	12,865	6,392
Ultimate, wt%			
Hydrogen	6.51	5.07	6.59
Carbon	51.19	71.07	38.57
Nitrogen	0.72	1.37	0.42
Sulfur	0.32	2.62	0.63
Chlorine	0.0026	0.0974	0.0036
Oxygen	35.23	10.17	44.41
Ash	6.03	9.7	9.38

Table 3-2. Coal Ash Composition (wt%, sulfur-free basis)

	Wyodak	Ohio 5,6,7	ND Lignite
SiO ₂	43.28	38.09	22.00
Al ₂ O ₃	17.17	39.41	20.38
Fe ₂ O ₃	6.32	13.03	11.75
TiO ₂	1.38	2.04	0.50
P ₂ O ₅	1.78	0.51	0.13
CaO	22.74	2.24	30.25
MgO	4.03	1.02	8.00
Na ₂ O	1.67	0.92	5.12
K ₂ O	0.45	2.55	1.38
BaO	0.68	0.20	0.50
SrO	0.49		

Table 3-3. Forms of Sulfur in Phase II Coals (wt%, as-received basis)

	Wyodak	Ohio 5,6,7	ND Lignite
Sulfate	0.01	0.02	0.09
Pyritic	0.04	1.39	0.18
Organic	0.27	1.21	0.36

Table 3-4. Coal Particle Size Distribution for Phase II Coals (in wt%)

Size Range (microns)	Wyodak	Ohio 5,6,7	North Dakota Lignite
2.2 to 2.6	1.7	0.6	0.3
2.6 to 3.0	1.7	0.8	1.0
3.0 to 3.4	1.8	1.2	1.2
3.4 to 4.0	1.6	1.4	1.3
4.0 to 4.6	1.9	1.1	0.9
4.6 to 5.3	2.7	1.1	0.9
5.3 to 6.2	3.7	1.2	1.5
6.2 to 7.2	4.4	1.8	2.2
7.2 to 8.3	4.4	3.1	2.9
8.3 to 9.6	3.9	3.3	3.4
9.6 to 11	3.6	2.5	3.1
11 to 13	4.1	2.2	2.9
13 to 15	4.9	3.2	3.1
15 to 17	5.5	5.0	4.6
17 to 20	5.7	6.4	6.9
20 to 23	5.3	6.6	7.7
23 to 27	3.9	4.7	5.7
27 to 37	3.0	4.0	4.6
31 to 36	3.1	5.2	5.6

Table 3-4. Coal Particle Size Distribution for Phase II Coals (in wt%) (continued)

Size Range (microns)	Wyodak	Ohio 5,6,7	North Dakota Lignite
36 to 42	3.7	6.9	7.2
42 to 49	4.3	7.8	7.8
49 to 57	5.0	7.9	7.4
57 to 66	5.5	7.1	6.3
66 to 76	5.4	6.1	5.0
76 to 88	4.7	4.7	3.7
88 to 102	3.3	3.1	2.3
102 to 118	1.3	1.1	0.8

3.2.3 *Coal Mineralogy*

Analysis was conducted on the as-received coal samples as well as on density-fractional samples. A portion of each coal sample was separated into float (or concentrate) and tailings fractions using a flotation method. The as-received coal sample is denoted as the raw sample. Mössbauer analysis of all project coals and fractions received to date has been completed in order to obtain details of the iron mineralogy. The spectra are shown in Figures 3-1 and 3-2 and the results of the computerized analyses are summarized in Table 3-5. The dominant iron-bearing phase in all samples is pyrite, but the lower sulfur, low-rank coals also contain appreciable iron as clays, sulfates, or carbonates, as well. Pyritic sulfur contents, calculated as described elsewhere,¹ are also listed in Table 3-5. These data will be used in conjunction with the CCSEM data to be obtained on the project coals to provide detailed mineralogical descriptions of the coals, as well as for understanding aspects of the occurrence of pyrite-associated trace elements

3.2.4 *Trace Elements in Coal*

Table 3-6 presents the elemental composition of the raw coal samples as measured by neutron activation analysis (NAA) at MIT. The analysis was conducted twice; the second analysis was optimized for mercury detection in order to reduce the error in the mercury measurement. The Wyodak coal is generally similar to the Phase I sample in terms of trace element concentrations. Zn and Co are noted to be higher than in the Phase I sample. The new coals (Ohio 5,6,7 and North Dakota lignite) show similar trace element concentrations to the previously studied coals with a few exceptions. Both coals have higher arsenic levels than any others studied in the program. The Ohio coal has the highest arsenic concentration, 19 ppmw. All three Phase II coals show mercury concentrations of about 0.13 ppmw.

Table 3-5. Mössbauer Results for Phase II Project Coals

Coal Sample	Iron-Bearing Mineral	I.S., Q.S. mm/s	%Fe	Pyritic Sulfur wt % of coal
North Dakota Lignite	Pyrite	0.30, 0.60	68	0.23
	Jarosite	0.39, 1.03	20	
	Clay	1.10, 2.69	12	
Wyodak	Pyrite	0.30, 0.59	67	0.05
	Jarosite	0.38, 1.08	22	
	Siderite	1.19, 1.92	11	
Ohio, raw	Pyrite	0.29, 0.60	88	1.14
	Jarosite	0.36, 1.00	6	
	Clay/Szom.	1.21, 2.70	6	
Ohio, tailings	Pyrite	0.29, 0.60	90	8.8
	Jarosite	0.37, 1.03	6	
	Clay	1.16, 2.64	4	
Ohio, concentrate	Pyrite	0.29, 0.60	91	0.99
	Jarosite	0.36, 1.01	5	
	Clay/Szom	1.20, 2.68	4	

3.2.5 *Forms of Occurrence of Trace Elements in Coal via XAFS*

The analysis of arsenic XAFS data for two of the project coals and for some high arsenic coals obtained from colleagues (R.B. Finkelman, H.E. Belkin) at the USGS have been completed. Some of these spectra were obtained during the current quarter in July during a brief session at NSLS. The reason for studying the high-As coals is to try to get a better understanding of the oxidation behavior of arsenic, which is so prevalent in virtually all coals that we have examined with the XAFS technique. In addition, complementary Mössbauer analyses of the high-As coals have also been completed.

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Figure 3-1. ^{57}Fe Mössbauer spectra of Ohio raw bituminous coal and the North Dakota lignite.

Figure 3-2. ^{57}Fe Mössbauer spectra of Wyodak sub-bituminous coal.

Table 3-6. Trace Element Concentrations in Phase II Coals by Neutron Activation Analysis

Element ($\mu\text{g/g}$)	Wyodak	+/-	Ohio 5,6,7	+/-	ND Lignite	+/-
Na	660	60	350	43	2400	180
Mg	1700	540	760	450	3100	950
Al	5400	400	11100	390	5400	400
Cl	62	26	880	120	170	55
K	2300	1800	2500	780	3200	
Sc	1.40	0.09	3.90	0.25	1.20	0.09
Ti	530	160	670	190	330	120
V	14.0	1.8	23.0	2.5	11.0	1.5
Cr	7.3	0.6	19.0	1.7	8.5	1.1
Mn	8.2	0.4	19.0	0.7	44.0	1.6
Fe	2300	170	15100	650	5300	350
Co	5.1	0.4	5.8	0.5	6.4	0.6

Table 3-6. Trace Element Concentrations in Phase II Coals by Neutron Activation Analysis
(continued)

Element ($\mu\text{g/g}$)	Wyodak	+/-	Ohio 5,6,7	+/-	ND Lignite	+/-
Zn	52	13	39	9	57	14
Ga	9.7	5.2	11.0	5.4	17.0	
As	1.4	0.2	19.0	1.9	8.1	0.8
Se	1.08	0.75	1.40	0.77	1.50	1.40
Br	1.2	0.3	23.0	6.2	1.9	0.5
Rb	20.0		21.0	8.6	32.0	7.8
Sr	100	37	100	38	120	50
Mo	1.5	0.4	7.6	1.8	0.7	0.3
Cd	0.24	0.20	0.40	0.30	0.21	0.20
In	0.07	0.04	0.06	0.07	0.12	0.12
Sb	0.40	0.03	2.30	0.18	0.91	0.08
Cs	2.50	0.50	0.63	0.30	0.50	0.36
Ba	380	53	102	43	420	75
La	4.00	0.25	9.40	0.60	3.10	0.33
Ce	7.4	0.5	14.0	0.8	4.3	0.6
Nd	2.6	0.6	11.0	2.1	1.8	0.6
Sm	0.60	0.05	2.00	0.17	0.50	0.04
Eu	0.25	0.08	0.38	0.15	0.27	0.08
Yb	0.30	0.06	1.10	0.20	0.40	0.10
Lu	0.04	0.01	0.22	0.05	0.04	0.01
Au (ng/g)	5.0	2.7	3.0	2.0	1.7	0.9
Hg	0.13	0.01	0.15	0.01	0.13	0.01
Th	1.30	0.10	2.70	0.26	1.20	0.14
U	0.70	0.05			0.80	0.06

Project Coals. The arsenic XANES spectra of two of the project coals (Ohio bituminous and North Dakota lignite) are shown in Figure 3-3. The spectrum of the Ohio raw bituminous coal was recorded at both SSRL (05/98) and NSLS (07/98), about 2 months apart. As can be seen the quality of the data at SSRL is somewhat better, but the difference is not that marked. The As spectra of the fractions were also obtained at NSLS in July. As with the investigation into As in Phase I bituminous coals, both As/pyrite and arsenate forms are readily apparent in the spectra of the Ohio bituminous coal and fractions. Using the procedure previously described,² quantitative estimates of the two major As forms in these coals have been made and are summarized in Table 3-7. The difference in relative peak heights between the spectra of the raw Ohio coal taken two months apart indicates on-going oxidation of arsenical pyrite to arsenate.

Figure 3-3. Arsenic XANES spectra of Ohio bituminous coal and fractions and of the North Dakota lignite.

Table 3-7: As XANES Results of Least-squares Fitting - Project Coals

Coal Sample	As/Pyrite	As/Arsenite	As/Arsenate
Ohio raw	84		16
Ohio, concentrate	80		20
Ohio, tailings	86		14
ND Lignite	28	18	54

High-As Coals. The arsenic XAFS spectra of the five high-As coals were divided into separate XANES and EXAFS regions for analysis. The resulting arsenic XANES spectra are shown in Figure 3-4. It is clear by visual inspection that these spectra, with a main peak and an obvious shoulder, indicate the presence of at least two different arsenic forms in each sample, with the possible exception of sample JL-As6-97A. The spectrum of this last sample indicates

Figure 3-4. Arsenic XANES spectra of five high arsenic coals from USGS Reston.

only the presence of significant arsenate (AsO_4^{3-}), based on the peak position of the main peak. The radial structure functions (RSFs) derived from analysis of the EXAFS regions are shown in Figure 3-5. Only a relatively poor quality RSF was obtained from sample JL-As1-97A, owing to the poor signal/noise ratio in the EXAFS region. The RSFs shown in Figure 3-5, especially the top four, are similar; all show one major peak at about 1.25 Å that, as previous work³ has documented, clearly corresponds to the As-O distance in the AsO_4^{3-} anion unit. However, the spectra are slightly different in that the RSF peak at 1.25 Å is more intense for the JL-As6-97A sample and less intense for the JL-As1-97A sample than for the other samples and may therefore indicate somewhat higher and lower relative fractions of arsenic as arsenate, respectively, in these samples. In addition, the top four RSF spectra indicate a small but significant peak at around 2.7 Å (denoted by the dashed line in Figure 3-4). This peak may indicate the presence of a small fraction of arsenic as As_2O_3 , since this oxide has a significant peak at about 2.8 Å (its main peak at 1.35 Å can not be seen as it is hidden by the much larger arsenate peak at about 1.25 Å).

Figure 3-5. Radial structure functions derived from arsenic EXAFS spectra of five high arsenic coals from USGS Reston.

Only one of the RSF spectra (for sample JL-As1-97A) showed any evidence for a peak at

about 1.9 to 2.0 Å that could be attributed to arsenical pyrite. As a result, the mixture of different forms in sample JL-As1-97A (see discussion below and data in Table 3-8) may also have been a contributing factor as to why a relatively poor RSF was obtained with this particular sample.

Table 3-8: Results of Mössbauer and As XANES Spectral Fitting on USGS High-As Coals

Coal Sample	Mössbauer, % Fe			XANES, % As			
	Pyr	Jar	Other	As/Pyr	As/Sulf	As/Oxide	Arsenate
JL-As1-97A	82	11	7**	40	14		46
RBF96-Hz-106	91	9			7	24	69
HZ-Au7-97A	64	29	7**		18	25	57
JL-As6-97A	<5	<10	>90*			12	88
RBF96-As-103	60	40		22		11	67

*superparamagnetic FeOOH; ** unknown

The individual arsenic XANES spectra have been subjected to least-squares fitting in order to identify and quantify the different forms of arsenic in the samples. Initially, two-peak fits were tried; but there was no consistency in the location of the peak at lower energy, although the prominent arsenate peak was fitted precisely each time. It was clear that the behavior is more complicated than that indicated by just two peaks, in agreement with inferences from earlier work.² We next tried a constrained three-peak fit: one peak for the arsenate absorption peak at 3 to 4 eV; and then two peaks for two absorptions among the following three different types of arsenic forms: a peak at about -2.3 eV for arsenical pyrite; a peak at -1.5 eV for arsenic sulfide forms (AsS, As₂S₃) and a peak at 0.0 eV for As³⁺ oxide forms (e.g., As₂O₃) (see Ref. 3. for data on arsenic standard compounds). Fits were tried with all four peaks; but typically one of the peaks would tend to zero height and would then be dropped from the analysis so that the final fit consisted of three peaks, in which the two peaks at lowest energy were constrained to occur at a certain peak positions. Such fitting was reasonably robust and two examples are given in Figure 3-6. The results of such fitting are summarized in Table 3-8.

Also summarized in Table 3-8 are the results of the ⁵⁷Fe Mössbauer analysis for the five samples. Examples of the fitted spectra are shown in Figure 3-7. Except for sample JL-As6-97A, the Mössbauer spectra of all samples were dominated by iron as pyrite, ranging from 60 to 91% of the iron. The sulfate phase, jarosite, is next most common iron-bearing form, ranging from 9 to 40% of the iron. Sample JL-As6-97A exhibits a quite different Mössbauer spectrum to those of the other four samples. No pyrite or jarosite could be identified in this sample and it appears that all of the iron is present as paramagnetic or superparamagnetic goethite (α -FeOOH).

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Figure 3-6. Examples of the least-squares fitting method for arsenic XANES spectra.

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Figure 3-7. Examples of the ^{57}Fe Mössbauer spectra of high-arsenic coals from USGS Reston.

It is clear that there are some significant implications arising from differences between the iron Mössbauer and arsenic XAFS data for these samples. Only for the most oxidized sample (JL-As6-97A), for which both techniques indicate that the iron and arsenic in this sample are almost completely oxidized, is there any apparent agreement between the two methods. For the other four samples, the arsenic XANES results always indicate much less arsenic as arsenical pyrite and much more arsenic in oxidized forms than the corresponding Mössbauer data for iron as pyrite and iron in oxidized forms. Of course, there is no reason to expect a 1:1 correlation between these two measurements and the data clearly indicate that arsenic is much more sensitive to oxidation compared to iron, even though both elements were probably almost certainly present entirely in pyrite in these coal samples prior to the oxidation process. Clearly, the fraction of pyrite that contains arsenic oxidizes more rapidly than those pyrite fractions devoid of arsenic. Whether this is because it is the smallest and easiest to oxidize pyrite grains that contain the arsenic or whether it is the presence of the arsenic itself that promotes the oxidation process in pyrite regardless of particle size remains to be answered. However, in at

least two cases (RBF96-Hz-106 and Hz-Au7-97A), there was no evidence for any arsenical pyrite remaining in the sample, but substantial amounts of iron as pyrite are still present. The fully oxidized arsenic may be incorporated as arsenate in the jarosite phase, as earlier data have suggested for the Kentucky #9 coal,⁴ or it may occur as an independent arsenate phase. The data are compatible with a sequential step-wise oxidation of arsenical pyrite to arsenate via relatively reactive [As-S] and [As³⁺-O] intermediate phases. A similar mechanism has been previously proposed.² The presence of significant [As³⁺-O] noted in the fitted XANES spectra of some of the samples may correspond also with the observation of a small peak near 2.7 Å in the RSF. It is tempting to attribute this RSF peak to the presence of a small fraction of As₂O₃, as this arsenic oxide has a very prominent peak at about this position in its RSF.³ Evidence for the presence of an intermediate [As-S] phase is restricted to the XANES fitting.

Advanced Photon Source. Some exploratory mercury L_{III} XAFS work was carried out during August at the Advanced Photon Source (APS), the new synchrotron facility at Argonne National Laboratory, Chicago, IL. With the expert help of Dr. Ken Kemner (APS), some Hg XAFS spectra were obtained for carbon-based and other sorbents for direct comparison with spectra from the same samples that were investigated at the Stanford Synchrotron Radiation Laboratory (SSRL) in May. Although a full analysis of the data has not been completed, it is clear that comparable quality data were obtained for mercury in carbonaceous systems using a Lytle detector at APS to that obtained at SSRL using a more sensitive 13-element germanium detector. However, for mercury in an aluminosilicate matrix (zeolite), the quality of the data from SSRL was superior because of the effectiveness of the 13-element germanium detector in reducing the background signal.

3.2.6 *Forms of Occurrence of Trace Elements in Coal via Selective Leaching and Microprobe Analysis*

Leaching Studies. During the reporting period, duplicate splits of the Ohio 5,6,7 and North Dakota lignite samples were taken through all four steps of the selective leaching procedure. The solid residues were sent to USGS's Denver laboratory for analysis; results have not yet been returned. In addition, splits of these two samples were sent to Denver to begin determination of the 47-element USGS whole-coal package. The whole-coal determinations utilize a combination of methods including instrumental neutron activation analysis (INAA), inductively-coupled plasma atomic emission spectroscopy (ICP-AES), inductively-coupled plasma mass spectrometry (ICP-MS), and element-specific methods for Se (hydride generation) and Hg (cold vapor atomic fluorescence). Results for whole-coal splits are not available. Leaching analysis of the Wyodak coal has recently commenced.

Probe/SEM and LTA/XRD. Because of the time involved in obtaining results of leaching and whole-coal elemental analyses, first priority was given to these procedures. Now that these studies are underway, supporting studies conducted in-house are commencing. Preparation of polished coal/epoxy pellets for probe/SEM studies is underway. An ASTM procedure is used as discussed in the Phase I Final Report. Once the pellets are available, blocks of microprobe and SEM machine time will be reserved for sample characterization. Preparation of low-temperature ash for XRD analysis is underway.

Ion Probe. In keeping with our goal of developing new quantitative methods for direct determination of trace element concentrations in coal components, we have begun exploratory work using the Cameca 6f Secondary Ion Mass Spectrometer (Ion Probe) at the Carnegie Institution of Washington, Department of Terrestrial Magnetism (DTM). In our initial visit to DTM in March 1998, we concentrated on determining Hg in sulfides. We found that Hg ionization was not sufficient for us to obtain useful results. Ionization of Ni in pyrite was relatively good, suggesting that if necessary, we could measure Ni at concentrations below 100 ppm, the detection limit for the electron microprobe. A second visit is scheduled for early 1999, during which we will concentrate on determining the Cr content of illite, found to be near the detection limit for electron microprobe analysis (~200 ppm) in Phase I.

Our experience with one ion probe session, together with discussion with the DTM staff will result in optimization of sample preparation procedures for ion probe analysis. For example, in the very high vacuum ($\sim 10^{-9}$ torr) of the ion probe, degassing of coal/epoxy pellets prepared for microprobe/SEM studies was found to be a significant problem, requiring pump-down times of at least 24 hr for each sample change. In future work, polished thin sections of coal will be used for ion probe studies, in order to alleviate the sample degassing problem.

New Procedures for Phase II. Procedures are being revised to correct two recurring problems encountered in Phase I. In the first problem, results for Hg were found to be difficult to interpret due to the relatively poor detection limit (0.02 ppm) obtainable by the cold vapor atomic absorption (CVAA) method. In Phase II, Hg sensitivity will be greatly increased by using the cold vapor atomic fluorescence (CVAF) method. Development work for these analyses is underway in the USGS labs in Denver.

Another problem encountered in Phase I involved low totals for some leaching results. For example, this problem was encountered for the Elkhorn/Hazard sample, in the nitric acid leaching step. The low totals were probably due to incomplete sample digestion, but may also be due to re-adsorption of metals in solution onto residual organics. Procedural changes in Phase II include routine SEM examination of residues after leaching, and where necessary, low temperature ashing of solid residues. Preliminary tests (for Cr only) comparing our standard procedure of washing solid residues with distilled water vs. washing with ammonium acetate indicate that re-adsorption of metals onto residual organics is not significant.

For Phase I, we reported on the mode of occurrence of iron and five important HAP elements: arsenic, selenium, chromium, nickel, and mercury. While these data were sufficient for the requirements of Phase I, we routinely determine a much wider range of elements, and plan to do so in Phase II. For example, in a recent report to the International Energy Agency,⁵ we report on the mode of occurrence of 35 elements and the rare earth elements as a group. Expanding the number of elements determined will be useful in interpreting Phase II vaporization studies. For example, Phase I combustion experiments showed that in addition to As and Se, Zn and Sb were highly volatile during combustion (as discussed in Subsection 3.3). Information on the mode of occurrence of these elements would have been useful in interpreting Phase I results. Analysis of a larger group of elements might also help show the behavior of refractory elements in the combustion process.

3.3 Combustion Zone Transformations (PSI)

3.3.1 *Introduction*

During the quarter, a substantial effort was undertaken to review the Phase I experimental data taken at PSI's Entrained Flow Reactor. The results add to the material presented in the Phase I Final Report and are presented here.

The use of a small scale combustion furnace arises out of the desire to collect well-controlled data at a modest cost. By realistic combustion conditions, we mean the use of utility grind coal and air-to-fuel ratios which are similar to those in full scale combustion systems. These experiments serve as a bridge between small scale single particle combustion studies and much larger scale self-sustained combustion studies.

Many of the inorganic elements in coal are volatile at flame temperatures.⁶⁻⁸ In the flame zone, the inorganic vapors homogeneously nucleate to form an ultrafine aerosol with a primary particle size of 0.01 to 0.03 microns.⁹ Post-flame, the combustion gases cool rapidly to near room temperature in a time period of 2 to 5 s. The mean particle size of this condensation aerosol grows by coagulation. Calculations for a typical vapor loading show that the peak of the mass distribution grows to 0.03 to 0.07 microns in the range of 1 to 10 s.⁶

The primary particle size for condensation aerosols generated during combustion of single coal particles in a laminar flow furnace has been measured previously.⁹ Aerosol was collected using an Anderson Mark II cascade impactor followed by a filter. The cutoff diameter for the lowest stage was 0.36 microns. Transmission electron micrographs of the filter and the lowest impactor stage were examined to determine the particle size distribution on individual substrates. For combustion of several different coals in 20% O₂ and at a gas temperature of 1750 K, the mean size of the primary particles on the filter was in the range of 0.02 to 0.03 microns. Surprisingly, these primary particles were also observed on the lowest impactor stage. As some agglomeration was observed, it was hypothesized that large agglomerates of primary particles formed in the wake of the burning coal particles and deposited in the lower stages of the impactor. Furthermore, material collected on the lowest two stages (with cutoff diameters of 0.36 and 0.54 microns) showed concentrations of certain refractory elements which were similar to the concentrations on the filter, but different from the bulk ash. In these experiments, changes in coal particle temperature resulted in changes in mass collected on the filter as well as on the lower two stages. Changing the coal particle temperature during combustion will change the amount of material which vaporizes. Therefore, it was concluded that, in this laboratory scale combustor, ash collected with diameters less than approximately 0.5 microns could be attributed to vaporization.

Measurements of submicron aerosol from full-scale coal-fired power plants show a distinct peak in the mass distribution falling in the range of 0.07 to 0.15 microns.^{10,11} These measurements are made at the ESP inlet, not in the flame zone. In one study,¹¹ two submicron modes were observed with peak diameters at 0.07 microns and 0.4 microns. Scanning electron micrographs of the two submicron modes showed that the 0.4 micron particles were solid

spheres, while the particles below 0.1 microns were agglomerates of ultrafine primary particles. In full-scale combustion systems, therefore, ash collected with diameters less than 0.1 to 0.2 microns could be attributed to vaporization.

The furnace used by PSI in this program lies in between the small-scale, single particle combustor and a full scale combustor. In our experimental apparatus, small amounts of coal are burned in a laminar flow tube furnace. However, the coal particles are burned at realistic stoichiometric ratios. That is, the coal particles do not burn in isolation as in the single particle combustor. In our experiments we sample directly from the combustion zone, rapidly quenching the combustion gases with dilution. Because of this, we expect that any elements which have vaporized during the combustion process will condense to form extremely fine particles. To determine the size range of the vaporization aerosol in our system, we will first look at total ash mass size distributions, followed by size dependence of the concentration of certain elements. We then measure the amount of this vaporization mode for several different coals having varied mineralogy and forms of occurrence of trace elements. The results of these experiments will be used to determine the impact of forms of occurrence on vaporization and, ultimately, to provide validation data for the model being developed.

3.3.2 *Experimental Methods*

Four coals were studied in the Phase I program. The Phase I Final Report gives the coal coal analyses. Three coals are bituminous coals from the eastern United States. The fourth is a sub-bituminous coal from the Powder River Basin (PRB) region of the western United States. Utility grind samples of each coal were obtained.

Combustion experiments were conducted in the entrained flow reactor (EFR) shown schematically in Figure 3-8. Coal was fed into the top of the reactor using an AccuRate auger-type dry materials feeder. Feed rates of 2.5 to 3.5 g/min were used. The coal was blown off the tip of the auger and carried into the swirl-stabilized section with transport air at a flow rate of 4.2 slpm. At the top of the swirl-stabilized section, the coal and transport air were mixed with the remaining combustion air. The coal-gas mixture was then concentrated in the venturi and rapidly expanded to disperse coal across the entire cross section. From the swirl-stabilized section, the coal-gas mixture entered the laminar flow reactor. The reactor consists of an externally heated 8.57 cm inner diameter mullite tube approximately 1.57 m long with three independently controlled temperature zones. For these experiments the wall temperature in the center zone was set at 1773 K. Maximum gas temperature was approximately 50 K lower than the furnace set point. The furnace residence time was approximately 1.6 s.

At the exit of the laminar flow reactor a nitrogen-quenched probe was used to isokinetically collect the ash aerosol. The gas temperature at the collection point was approximately 1423 K (1150°C). Calculated quench rates were 10^4 K/s. The quenched sample passed into the aerosol collection system. Three different configurations were used to collect ash samples. First, a total filter was used in some experiments to check mass balances and calculate the degree of

Figure 3-8. Entrained flow reactor.

burnout. Second, a cascade impactor (as shown in Figure 3-8) was used to obtain size segregated aerosol samples. Third, a cyclone pre-cutter was used in conjunction with a cascade impactor to remove greater than 50% of the mass of particles greater than 4 microns. Without a cyclone to remove the largest particles, we expect to get particle bounce off, as the upper stages of the impactor get overloaded, which will skew the size distribution. Use of a cyclone pre-cutter will produce a more representative submicron size distribution.

Two different cascade impactors were used for this study. Initial experiments were conducted with a Berner low-pressure impactor (BLPI). The BLPI is unique in that it provides a high level of resolution in the submicrometer size range. The impactor, discussed in detail elsewhere,¹² consists of 11 stages, seven of which collect samples 1 micron and smaller. The cutoff diameter of the lowest stage on the impactor is 0.034 micron. BLPI stages were covered with impaction substrates for these experiments, consisting of Nucleopore filters. The impaction substrates were coated with Apiezon type L vacuum grease. The vacuum grease was dissolved in toluene and sprayed across the substrate in a uniform layer as described elsewhere.¹² The filters were baked in a 398 K (125°C) oven for 24 hr to ensure that the toluene completely evaporated before use.

The second impactor used was an Anderson Mark III cascade impactor. This instrument has seven stages; the cutoff diameter for the lowest stage is 0.2 microns. Because we expect the ash vaporization mode to be less than 0.2 microns, the Anderson impactor was followed by a filter. As with the BLPI, the Anderson impactor was used with and without a cyclone pre-cutter. Nucleopore filters were used as impaction substrates. The impaction substrates were coated with Apiezon type L vacuum grease as for the BLPI substrates.

With either impactor, the impactor substrates were weighed before and after each run. Impactor stages, cyclone catch material, and after filters were all analyzed by NAA at the MIT Nuclear Reactor Laboratory. Blank filters were also analyzed for trace metals. Background concentrations, determined from blanks, were subtracted from the samples.

3.3.4 *Results*

An ultrafine aerosol forms from the combustion of pulverized coal as a result of vaporization and condensation. The size and morphology of this aerosol depends on the scale of the combustion system. Our goal in the present work is to measure the amount of material, trace elements in particular, that vaporizes during combustion. The method employed will be to measure the mass (and composition) of the aerosol as a function of size. How will we know which portion of the aerosol corresponds to the vaporized material? The answer to this question is not straightforward, but we can obtain guidance from other combustion systems as discussed in Subsection 3.3.1. First, we examine the mass balance closures for the experiments and then determine criteria for calculation of the vaporization mode.

The Pittsburgh bituminous coal was burned at a stoichiometric ratio of one. Two other bituminous coals and the Wyodak PRB coal were burned at a stoichiometric ratio of 1.2. One bituminous coal, Illinois 6, was burned at sub-stoichiometric conditions ($SR = 0.9$). By measuring the total mass of ash collected, including cyclone, impactor stages, and after-filter, we calculate the ash mass balance closure. The coal feed rate, degree of burnout, and gas flow rates are also needed to close the mass balance. Similarly, mass balance closure for individual elements can be calculated from the measured concentrations in the ash samples and in the parent coal.

Table 3-9 summarizes the mass balance closure for the ash and selected elements. Loss on ignition (LOI) was estimated from separate total filter samples. For the bituminous coals, the LOI values are higher than typically seen in full scale plants, although the degree of burnout calculated from the amount of unburned material is in excess of 90%. The ash mass balance closures range from 93% to 147%. Mass balance closures for the more refractory elements (Ca, Co, Fe, Sc) mirror the total ash balance closure. Chromium has consistently high mass balance closures which may indicate some contamination. Mass balance closures for more volatile elements (As, Sb, Se, Zn) are low. Selenium has a consistently low mass balance closure of 28% on average. Arsenic and zinc show mass balance closures in the range of 20% to 75%. Antimony has a somewhat low mass balance closure, although there seems to be at least one set of data in error.

Table 3-9. Mass Balance Closure for Ash and Selected Elements

Coal	Pittsburgh	Illinois 6	Illinois 6	Elkhorn-Hazard	Wyodak
Stoichiometric ratio	1	1.2	0.9	1.2	1.2
LOI, %	39	40	40	44	ND
Ash mass closure, %	109	140	93	119	147
Element mass closure, %					
As	67	75	34	29	72
Ca	ND	87	76	ND	80
Co	128	126	97	83	104
Cr	-24	169	225	134	158
Fe	196	146	118	102	122
Sb	72	85	9255	32	96
Sc	92	146	103	79	127
Se	190	27	29	20	37
Zn	199	67	44	21	35

ND = Not determined

Theoretical studies of equilibrium chemistry of trace elements in combustion environments⁶⁻⁸ indicate the volatility of the elements in this study. At the sample inlet temperature in the combustion furnace for our experiments (1423 K) and under oxidizing conditions, Sb, Se, and Zn are all predicted to be in the gas phase in the combustion zone. In the presence of calcium, arsenic is predicted to form condensed calcium arsenate at 1400 K.^{8,13} Chromium is also predicted to form a calcium compound at temperatures above 700 to 800 K.⁸ At room temperature, the only element in this group that is still predicted to exist in the vapor phase is selenium. Under reducing conditions,^{6,7} As, Co, Sb, Se, and Zn, but not Cr, are predicted to exist in the gas phase at 1423 K.

Extensive vaporization of some trace elements is predicted in the combustion zone. In our combustion furnace, all of these volatile elements should be driven into the condensed phase in the dilution-quench probe, with the exception of selenium. The volatile elements that are in the gas phase at the sampling temperature should condense homogeneously to form a fine aerosol (<0.1 microns). The rapid quench time prevents significant coagulation of this aerosol. There may be some loss of vapor-phase metals in the combustion furnace due to interaction with surfaces which might account for the low mass balance closures for As, Sb, and Zn. A substantial fraction of the selenium may remain in the vapor phase even at the sampling temperature given the consistently low mass balance closure in our experiments. Previous experiments in

our furnace¹³ in which the BLPI was followed by a final filter and a carbon-impregnated filter to capture vapor phase metals revealed a substantial amount of selenium in the vapor phase.

Initial experiments in the current study were conducted using the BLPI to obtain size segregated ash samples. The BLPI was capable of separating flyash down to an aerodynamic diameter of 0.034 microns. In order to construct a complete aerosol size distribution, BLPI data were obtained with and without a cyclone pre-cutter. The Pittsburgh bituminous coal was burned in the EFR at a stoichiometric ratio of one. The average loss on ignition (LOI) for these runs was 40 wt%. Data from several BLPI samples were averaged to produce a composite mass distribution. Data from experiments using a cyclone were used to calculate the size distribution for particles less than 1 micron, while data from experiments without a cyclone were used to calculate the distribution for particles greater than 1 micron. The average composite size distribution is shown in Figure 3-9. The submicron aerosol shows a peak at approximately 0.1 microns.

In order to determine what constitutes the vaporization mode, we will look at the size dependence of the concentration of iron, an element which does not vaporize extensively for many bituminous coals. Figure 3-10 gives the concentrations of iron on each impactor stage. For reference, the bulk ash concentration is indicated on the figure. The concentration of iron is much greater than the bulk value for diameters greater than 7 microns. From 1 to 7 microns, the iron concentration is near the bulk value. Particles less than approximately 0.5 microns have concentrations of 10 to 20% of the bulk value. Particles less than 0.2 microns, in particular, would appear to be the result of vaporization.

Evidence for a vaporization aerosol can be derived from the data for another bituminous coal, Illinois 6. These data were taken with the Mark III impactor followed by a final filter. Iron and scandium appear relatively non-volatile for this coal. Figure 3-11 shows the concentrations of iron and scandium as a function of particle diameter. Again, the bulk ash concentrations are indicated on the figure. There is a clear drop in the concentration of these elements below 0.4 microns. Based on the comparison of concentrations of refractory elements in ash with their bulk concentrations, we conclude that the aerosol less than approximately 0.4 microns represents the material which vaporizes during combustion.

(a)

(b)

Figure 3-9. Particle size distribution for combustion of Pittsburgh coal at a stoichiometric ratio of one. a) Supermicron particle distribution; b) submicron particle distribution.

Figure 3-10. Concentration of iron as a function of particle diameter in ash collected from combustion of Pittsburgh coal at a stoichiometric ratio of one.

Figure 3-11. Concentration of iron and scandium as a function of particle diameter in ash collected from combustion of Illinois 6 coal at a stoichiometric ratio of 1.2.

The amount of material vaporized during combustion can be calculated from the mass less than 0.4 microns in diameter, that is, the sum of the material on the lowest impactor stage and the final filter. Because some of the ash samples had incomplete burnout, the relative amount of material less than 0.4 microns will be calculated based on the ash coming into the sampling system (as calculated from the coal feed rate and gas flows). As long as the mass balance closure is reasonable, this should provide a good estimate of the mass in the vaporization mode. The percentage of selected elements vaporized (i.e., found in ash less than 0.4 microns diameter) can be calculated in a similar fashion.

Table 3-10 displays the amount of vaporization for three coals at a stoichiometric ratio of 1.2. The total amount of ash in the vaporization mode ranges from 0.3% to 0.7%. These results are in the range of field observations.¹⁰ Figure 3-12 shows the results graphically. The volatile elements, As, Sb, Se, and Zn, generally show 10 to 30% mass less than 0.4 microns (Figure 3-12a). On the order of 1% of the non-volatile elements, Ca, Co, Fe, and Sc, appears in the vaporization mode (Figure 3-12b). Cobalt, iron, and scandium all show higher volatility in the Elkhorn-Hazard coal than in the other coals. The uniformly low volatility of chromium, irrespective of form, suggests that chromium may react with oxides in the bulk ash. Formation of a calcium compound has also been suggested based on equilibrium calculations.⁸

Table 3-10. Fraction of Material less than 0.4 microns for Ash and Selected Elements

Coal	Illinois 6	Wyodak	Elk./Haz.
Stoichiometric ratio	1.2	1.2	1.2
Wt% ash	0.27%	0.56%	0.71%
Wt% element			
As	16.67%	25.78%	11.19%
Ca	0.15%	0.92%	ND
Co	0.34%	1.23%	3.12%
Cr	4.21%	2.85%	2.78%
Fe	0.07%	0.99%	1.72%
Sb	26.48%	44.54%	15.40%
Sc	0.12%	0.95%	1.60%
Se	16.73%	20.17%	3.57%
Zn	24.31%	24.91%	7.76%

(a)

(b)

Figure 3-12. Percent of mass less than 0.4 microns for combustion of coals at SR = 1.2.
a) Volatile elements; b) Non-volatile elements.

As discussed above, the volatile elements show mass balance closures that are consistently less than 100%. Since these elements are predicted to exist predominantly in the gas phase at the sampling temperature, the low mass balance closure may be due to loss of vapors in the high temperature furnace or to lack of condensation in the sampling system. In either case, the amount of material appearing in the finest ash fraction represents a lower bound on vaporization. An upper bound on vaporization can be calculated by taking into account the mass of element not accounted for in the mass balance closure when calculating the fraction vaporized.

Figure 3-13 illustrates the upper and lower bounds on vaporization for arsenic at a stoichiometric ratio of 1.2. A maximum of 40 to 80% of the arsenic is vaporized in the combustion zone. Elkhorn-Hazard ash shows the highest arsenic vaporization. Antimony shows similar maximum vaporization (Figure 3-14). Significantly higher vaporization of arsenic and antimony is indicated for the Elkhorn-Hazard coal as compared to the other coals. Since both arsenic and antimony are soluble in silicate glass and Illinois 6 has a higher ash content than the other coals, perhaps this indicates that arsenic is retained in the glassy ash particles which form by coalescence of minerals at combustion temperatures. Arsenic is thought to form calcium arsenate at temperatures below 1400 K.^{8,13} The Wyodak ash is high in calcium which may

Figure 3-13. Range of vaporization for Arsenic at SR = 1.2.

Figure 3-14. Range of vaporization for Antimony at SR = 1.2.

account for the apparent low vaporization of arsenic. Results of Phase I work in the EFR and at pilot scale have demonstrated a correlation between arsenic concentration and calcium concentration in the fly ash, pointing to the formation of calcium arsenate. There may be significant interaction of arsenic and the bulk fly ash, even at high temperatures.

Selenium (Figure 3-15) shows a maximum vaporization of 80 to 90% commensurate with its high volatility. Zinc (Figure 3-16) also shows maximum vaporization in excess of 80%. Therefore, there is little evidence for interaction of these elements with the bulk ash at combustion temperatures.

3.3.5 Summary of EFR Studies

Small-scale combustion experiments were conducted on the vaporization of trace elements during the combustion of pulverized coal. The combustion process was sampled at high temperatures (1423 K). Rapid quenching and dilution of the combustion products were followed by a cascade impactor to collect a size-segregated ash sample. A cyclone was used before the impactor in order to produce a representative submicron particle size distribution.

Figure 3-15. Range of vaporization of Selenium at SR = 1.2

Figure 3-16. Range of vaporization of Zinc at SR = 1.2

The cascade impactor was followed by a filter to collect ash less than 0.2 microns aerodynamic diameter. Based on the comparison of concentrations of refractory elements in ash with their bulk concentrations, we conclude that the aerosol less than approximately 0.4 microns represents the material which vaporizes during combustion.

Initial experiments with a low pressure impactor yielded detailed information on the submicron aerosol size distribution down to 0.03 microns. Good mass balance closure (90 to 140%) was obtained overall for ash in the sampling system. More refractory elements had good mass balance closure with the exception of chromium. High chromium mass balance closure may have been due to contamination. The volatile elements As, Sb, Se, and Zn showed mass balance closures significantly less than 100%.

Thermochemical equilibrium predictions reported in the literature indicate that the elements As, Sb, Se, and Zn should be completely volatile in the flame, although As is predicted to form condensed calcium arsenate at the sampling temperature in our system. Only 3 to 4% of the chromium was found in the vaporization mode in our experiments. The uniformly low volatility of chromium suggests that chromium may react with oxides in the bulk ash. An upper bound on the amount of the more volatile elements which vaporized was computed. This upper bound accounted for the amount of the element in the finest ash and the material "losses" indicated by the mass balance closure. A maximum of 40 to 80% of the arsenic and antimony are vaporized in the combustion zone. For two of the three coals tested, the upper bound on vaporization of As and Sb indicated only half of the element vaporized. We speculate that these elements may be interacting with the bulk ash at combustion temperatures, either by dissolving in silicate glasses or by forming calcium compounds. Selenium and zinc showed maximum vaporization in excess of 80%. Therefore, there was little evidence for interaction of these elements with the bulk ash at combustion temperatures.

The results of these experiments for the first time suggest almost complete vaporization of certain trace elements (Se, Zn) from coal combustion in the flame zone, in accordance with theoretical equilibrium predictions. Other elements (As, Sb, Cr) appeared considerably less volatile and may react with constituents in the bulk ash at combustion temperatures. Confirmation of these experiment results will require gas-phase sampling in addition to aerosol sampling in order to close the mass balance for the volatile elements.

Full-scale or pilot scale data indicate much lower vaporization for volatile trace elements because samples are obtained after the flue gas has cooled over several seconds. This period allows coagulation of vaporization nuclei and condensation of vapors on larger ash particles. We can compare the percentage of ash and selected elements in the vaporization mode for the EFR experiments on Wyodak coal and the pilot-scale combustion experiments conducted at ABB. Results from the latter experiments are reported in the Phase I Final Report.

Figure 3-17 shows the comparison for the laboratory and pilot-scale data of the total amount of ash in the vaporization mode and the amount vaporized for several refractory elements. Generally good agreement is seen for the refractory elements as well as for the total

Figure 3-17. Comparison of amount of total ash and refractory elements in the vaporization mode for combustion of Wyodak coal at pilot-scale (ABB) and laboratory-scale (PSI).

amount of ash. This is to be expected since vaporization and condensation of these elements takes place in the flame zone. The post-combustion time-temperature history of the flue gas should not affect the amount in the vaporization mode.

Turning to certain volatile trace elements (Figure 3-18), we see very large differences between laboratory and pilot scale data. The volatile elements (As, Sb, Se, Zn) are more concentrated in the vaporization mode in the laboratory experiments because the gas is sampled at a high enough temperature to have these elements predominantly in the vapor phase. The rapid quench in the laboratory experiments drives the vapors toward homogeneous nucleation. In the pilot scale experiments, as in full scale systems, the vapors can interact with the residual ash as well as the submicron ash when the flue gases cool. This figure illustrates the importance of the pilot scale experiments in determining the partitioning of volatile elements in the post-combustion zone.

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

3.4.1 *Large Scale Integrated Combustion Studies*

The combustion section of the University of Arizona's Downflow Combustor was completely rebuilt. The rebuilt section is composed of four feet of a new slag-resistant refractory from Thermal Ceramics and six feet of low-Si alumina oxide (from Zircar products) coated with silica carbide (from Zyp coatings). Concurrently, an air preheater was constructed and commissioned.

Figure 3-18. Comparison of amount of volatile elements in the vaporization mode for combustion of Wyodak coal at pilot-scale (ABB) and laboratory-scale (PSI).

3.4.2 Experimental Studies of Chlorine Transformations in Flue Gas

The University of Utah worked on setting up EPA Method 26A to give the capability to measure chlorine in flue gas. The impinger train has been assembled and vacuum checked for leaks. A calibration gas, based on material balance and the assumption that approximately 1% of the total chlorine (HCl and Cl_2) would be in the form of Cl_2 , has been ordered to enable calibration of the system. We have located an ion chromatograph for use in the analysis of the impinger solutions and have found it to give accurate results using an NaCl standard. The concentration of the standard was in the range expected. All necessary reagents for the impinger train and IC analysis have been assembled and tested. In the next few months we intend to finish calibration of the impinger train and hook up the train on the 100,000 Btu/hr furnace running with coal.

3.4.3 Kinetics of Chlorine Transformations in Flue Gas

Understanding the speciation of mercury in full scale combustion systems must take into consideration the kinetics of mercury and chlorine species in flue gas. As a first step, we look at the rate of formation of Cl_2 in flue gas. These calculations were performed as part of the Phase I program, but there was an error in the initial conditions used for the calculations. The results reported in the Phase I Final Report had 1/10 the amount of hydrogen typically found in coal. Therefore, the calculations were re-done this quarter with the correct starting conditions.

The formation of Cl_2 in the gas phase is thermodynamically favored at low temperatures. For example, the equilibrium calculations carried out in this program on four different coal predict that 30 to 60% of the chlorine to be Cl_2 at 423 K. The recent DOE sponsored field study reported molecular chlorine levels of 4, 5, and 45% of total chlorine for the three plants reporting such data.¹⁴ The formation of Cl_2 may be kinetically limited in the rapidly cooling flue gas which might reduce the gas-phase oxidation of elemental mercury relative to the equilibrium value.

Kinetic calculations were carried out using the SENKIN code developed at the Sandia National Laboratories. This code models the time evolution of a homogeneous reacting gas mixture in an open system with a constant flow rate.

The governing equations for the system are the mass balance, energy balance, and reaction rates (Eqs. (1) through (3)).

$$dY_i/dt = v \tilde{n}_i M_i \quad (1)$$

$$C_p dT/dt + v \sum h_i \tilde{n}_i M_i = 0 \quad (2)$$

$$k_f = AT^\beta \exp(-E/RT) \quad (3)$$

In these equations, Y_i is the mass fraction of the i th species, v is the specific volume, $\tilde{n}_i$ is the molar production rate of the i th species by elementary reaction, M_i is the molecular weight of species i , C_p is the mean specific heat of the mixture, h_i is the specific enthalpy of the i th species, A is the pre-exponential constant, β is the temperature exponent, and E is the activation energy.

Calculations were made for chlorine transformations under conditions similar to those in a coal-fired boiler by using the CH_3Cl mechanism in the standard CHEMKIN-II code. The CH_3Cl mechanism includes 264 elementary reactions (documented in the Phase I Final Report). The initial composition was calculated according to the overall combustion reaction:

where ζ is the amount of excess air relative to stoichiometric and ξ is the chlorine content of the coal. The code used in this study assumes constant pressure, but allows the temperature to vary as a function of time. We use a typical time-temperature history from furnace exit to APCD inlet in a power plant as shown in the Phase I Final Report corresponding to a cooling rate of approximately 300 K/s. The amount of excess air and the coal chlorine content were varied in the calculations in order to investigate their effects on chlorine speciation in the flue gas.

Figure 3-19 shows the percentage of total chlorine calculated to be Cl_2 as a function of time. The initial chlorine content of the coal was assumed to be 2000 ppm and 25% excess air was assumed for the combustion stoichiometry. Cl_2 is produced only when the temperature falls below 1200 K. At the end condition, 0.7% of the total initial chlorine has been transformed into Cl_2 .

Figure 3-20 shows that as the concentration of chlorine in the coal increases, more is transformed into Cl_2 at the end condition. However, a ten-fold increase on coal chlorine content only increases the amount converted to Cl_2 by approximately 50%. This shows that the conversion has a weak dependence on concentration. The effect of changes in excess air is shown in Figure 3-21. As the excess air increases, more chlorine will be transformed into Cl_2 , but the increase is very small. At stoichiometric conditions, calculations showed no production of Cl_2 , perhaps because formation of HCl is favored in the absence of O_2 .

These calculations show that the conversion of HCl to Cl_2 in the flue gas of a coal-fired power plant is kinetically limited. At flame temperatures, chlorine is predicted to be HCl . At APCD inlet temperature, equilibrium predicts as much as half of the chlorine to be in the form of Cl_2 , but kinetic calculations show that less than 1% of the chlorine is converted to Cl_2 . Kinetic limitations on the conversion of HCl to Cl_2 support the hypothesis that oxidation of elemental mercury in the gas phase is kinetically limited in coal-fired power plants.

Figure 3-19. Percentage of total chlorine in flue gas found as Cl_2 as a function of time assuming 2000 ppm Cl in coal and 25% excess air.

Figure 3-20. Final percentage of total chlorine in flue gas found as Cl_2 as a function of chlorine content of coal, assuming 25% excess air.

Figure 3-21. Final percentage of total chlorine in flue gas found as Cl_2 as a function of excess air, assuming 500 ppm Cl in coal.

3.5 Field Studies (UC)

A general model for trace element emissions must be based upon fundamental partitioning behavior within the combustion environment. It must address coal-specific trace element concentrations, element specific volatility, element specific partitioning among the different size classes of ash particles, and element and particle size-specific penetration through air pollution control devices such as the electrostatic precipitator. Our ultimate goal is to develop a model based on physical and chemical transformations of trace elements in combustion systems. The Toxics Partitioning Engineering Model (ToPEM) will predict the partitioning of trace elements from combustion zone to air heater exit in a coal-fired power plant. In order to predict stack emissions, a model of behavior of trace metals in the air pollution control devices is needed. Therefore, a quasi-empirical emission model using published data to estimate the needed parameters was developed in Phase I and reported in the Phase I Final Report. This model considers element-specific partitioning by utilizing simple assumptions for heterogeneous condensation, surface reaction, or retention within the mineral phase that are element-specific and derived from fundamental combustion studies of trace element partitioning. This quarter, further development work was completed on the emission model.

3.5.1 *Emission Model Development*

Extensive field data on trace element emissions recently obtained in DOE and EPRI-sponsored projects provides a large database which can be used to assess model predictions of trace element emissions. This database provides information on coal rank, ash content, sulfur content, trace element concentrations, coal higher heating value, trace element emissions rate, and particulate matter emissions rate for the ten trace elements listed in Table 3-11 at over 40 U.S. sites. From this tabulated data, the capture efficiency of air pollution control devices for total particulate matter as well as individual trace metals can be derived. Comparison of these efficiencies provides a means for determining whether selected trace elements are preferentially emitted from coal-fired utility power plants, and whether there is any rank, control device, or facility-type dependence in such emissions.

The particulate collection efficiency of an air pollution control device is defined as

$$\eta = 1 - \text{PM}_{\text{out}}/\text{PM}_{\text{in}} \quad (5)$$

where PM_{out} is the particulate matter concentration (mass per unit heat input, e.g., lb per million Btu) at the outlet of the air pollution control device, and PM_{in} is the corresponding value at the inlet of the air pollution control device. PM_{out} can be expressed in terms of coal parameters as

$$\text{PM}_{\text{out}} = \text{PM}_{\text{in}} (1 - \eta) = f_a (1 - \eta) / H \quad (6)$$

where f_a is the mass fraction of ash in coal on an as-received basis, and H is the higher heating value of the coal on an energy content per unit mass basis. For any trace element i present in the

Table 3-11. Trace Metal Enrichment in Submicron Fly Ash Particulate
(elements identified in Title III of 1990 Clean Air Act Amendments, excluding Hg)

Coal Type/Source	Boiler Size	Enriched	No Trend or Depleted	Method	Reference ^{Citation No.}
<i>Field Studies</i>					
B Ill./Ky.	290 MWe cyclone	Sb, As, Cd, Cr, Pb, Ni, Se	Co, Mn	[c] FA BA	Klein et al. ¹⁵
B U	350 MWe	Sb, As, Pb, Hg, Se		[c] f(dp), ESP-O	Gladney et al. ¹⁶
B Poland	17.2 kg/s	As	Mn, Ni	[c] FA BA	Kauppinen and Pakkan ¹⁷
B Colombia	350 MWe	As, Cd, Pb, Se	Cr, Ni	[c] FA BA	Sander ¹⁸
B Russia/Can	250 MWe	As, Cd, Pb, Se	Cr, Ni	[c] FA BA	Sander ¹⁸
B US	295 MWe	As, Cd, Pb, Se	Cr, Ni	[c] FA BA	Sander ¹⁸
B US, Austral.	115-645 MWe	Sb, As, Se		RE FA BA	Meij ¹⁹
B UK	2000 MWe station	As, Pb	Cr, Mn, Ni	[c] FA BA	Martinez-Tarazona, Spears ²⁰
B Illinois	U	As, Sb, Se	Cr, Ni, Mn	RE FA BA	Demir et al. ²¹
B Poland	160, 113 MWe	As, Cd, Co, Pb, Se	Be, Cr, Mn, Ni	RE FA BA	Aunela-Tapola et al. ²²
S US	750 MWe	Sb, As, Se		[c] f(dp), APCD-O	Ondov et al. ²³
S US	160, 203, 654 kg/s			[c] f(dp), APCD-O	Ondov et al. ²⁴
S US	520 MWe	Sb, As, Cd, Cr, Ni, Se	Mn	[c] f(dp), ESP-I	Markowski et al. ²⁵
S Wyoming	37.5 MWe	Sb, As, Hg, Ni, Se		[c] f(dp), FF-I	Shendrikar et al. ²⁶
S US	113 MWe	Sb, As, Se	Mn	[c] f(dp), APCD-I	Markowski and Filby ²⁷
S Spain	1050MWe station		Be, Cr, Mn, Ni	[c] f(dp), ESP-I	Querol et al. ²⁸
S Spain	1050MWe station			[c] f(dp), ESP ash	Querol et al. ²⁸
L Texas	U	As, Sb, Se	Mn	[c] FA BA	James and Acevedo ²⁹
Br, L Bulgaria	U	As	Cr, Pb, Ni	[c] FA BA	Vassilev ³⁰
L Greece	U	As		[c] f(dp), ESP ash	Bogdanovic et al. ³¹
U	U	Sb, As, Cd, Cr, Pb, Ni, Se	Mn	[c] f(dp), FA	Davison et al. ³²
U	180 MWe	Sb, As, Pb, Se		[c] FA BA	Kaakinen et al. ³³
U	U	Sb, As, Cd, Pb, Se,	Mn	[c] f(dp) ESP-O	Coles et al. ³⁴
U	500 – 700 MWe	As, Pb (Sb, Cr, Ni, Se also but data not shown)		[c] f(dp), ESP ash	Smith et al. ³⁵
U	U	As, Cr, Pb, Se	Mn	[c] f(dp), ESP ash	Smith et al. ³⁶
U	430, 750, 180 MWe	As, Se		[c] f(dp) ESP-O	Bierman and Ondov ³⁷
U	25 MWe	As, Ni	Se	RE f(dp) ESP-I	McElroy et al. ¹⁰

Table 3-11. Trace Metal Enrichment in Submicron Fly Ash Particulate (continued)
(elements identified in Title III of 1990 Clean Air Act Amendments, excluding Hg)

Coal Type/Source	Boiler Size	Enriched	No Trend or Depleted	Method	Reference ^{Citation No.}
<i>Laboratory and Pilot Scale Studies</i>					
B Pittsburgh	Pilot 1.5 MM Btu h ⁻¹	Sb, As, Cd, Pb	Se	c f(dp), ESP-I	Tumati and Devito ³⁸
L No. Dakota	Lab 17 kW	As, Pb	Mn	RE f(dp)	Linak and Peterson ³⁹
<i>Bench Scale (Drop Tube) Studies</i>					
B, S, L	US	20% O ₂	Sb, As, Co, Cr, Mn	RE f(dp)	Quann et al. ⁴⁰
B Illinois (b)	10.5% O ₂	As Sb	Cr, Co	[c] f(dp)	Helble ⁴¹
B, S Pitt., Wyo.	SR 1.2	Sb, As, Cr, Se		[c] f(dp)	Bool and Helble ¹³
S Wyoming	30% O ₂	Mn, Cr		[c] f(dp)	Helble ⁴¹
L Montana	20% O ₂	Sb, As		[c] f(dp)	Neville and Sarofim ⁴²
L Montana	20% O ₂	Sb, As, Cr, Co		[c] f(dp)	Quann et al. ⁴³
L Montana	20% O ₂	Sb, As, Mn, Hg		[c] f(dp)	Haynes et al. ⁴⁵
L Montana	20% O ₂	Sb, As, Cr		[c] f(dp)	Neville et al. ⁴⁶

Key: Coal: B Bituminous S Subbituminous L Lignite Br Brown coal
U Unspecified
ESP Electrostatic precipitator
FF Fabric filter (baghouse)
APCD Air pollution control device (various)
RE Relative enrichment factor as defined by Meij (1994) in ref. (19). $RE = \{(TE \text{ conc. in ash})(\% \text{ ash in coal})\}/(TE \text{ conc. in coal})$
RE > 3 considered enriched, a more restrictive definition than that adopted by Meij.
TE Trace element
BA Bottom ash
FA Fly ash, either extractively sampled at the inlet to an air pollution control device, or removed from ESP hoppers
[c] f(dp) Concentration measured as function of particle size, I at ESP or APCD inlet, O at ESP or APCD outlet
(b) Beneficiated coal
SR Stoichiometric ratio

Coal source information listed as nation, state (US), or region of origin as specified in cited reference.

Elements not listed were either not measured, or presented RE: $1.5 < RE < 3$.

Table represents expansion and reclassification of studies summarized by Linak and Wendt.⁴⁷

coal, the emissions E_i on a mass per fuel energy content basis (e.g., lb trace element i per 10^{12} Btu) can be determined by analogy to Eq. (6),

$$E_i = A_{i,\text{in}} (1 - \eta_i) = C_i (1 - \eta_i) / H \quad (7)$$

where $A_{i,\text{in}}$ is the concentration of trace element i at the inlet to the air pollution control device (mass per unit fuel energy content), C_i is the concentration (mass fraction) of trace element i in the coal on an as received basis, and η_i is the capture efficiency of trace element i in the air pollution control device, defined as in Eq. (5). Combination of Eqs. (6) and (7) yields an expression for trace element emissions as a function of measurable parameters:

$$E_i = \frac{C_i \text{PM}_{\text{out}} (1 - \eta_i)}{f_a (1 - \eta)} \quad (8)$$

Thus, if trace element capture efficiency were correlated with particulate capture efficiency, a linear plot of E_i as a function of $(C_i \text{PM}_{\text{out}} / f_a)$ would pass through the origin with slope equal to $(1 - \eta_i) / (1 - \eta)$. Typically, however, a broad range is observed in emissions measurements made at different facilities. Modification of Eq. (8) to the empirical

$$E_i = a_i \left[\frac{(C_i \text{PM}_{\text{out}})}{f_a} \right]^{b_i} \quad (9)$$

can also be considered, and is the form recommended by EPRI for interpretation of the DOE and PISCES data.⁴⁷ Although the large size of the underlying database makes it probable that the development of Eq. (9) for each trace metal will be more accurate than emissions factors proposed elsewhere (cf. Tables 3-12 and 3-13), this approach remains a correlational one that does not account for the enrichment of many trace metals in the smallest particle sizes.

A more accurate model useful for predicting the emissions of trace metals from pulverized coal combustion sources equipped with electrostatic precipitators can be derived if trace element concentrations are predicted as a function of ash particle size, and if size-dependent particulate capture efficiencies are considered. Previous efforts have addressed these issues, but have used thermodynamic models for trace element vaporization⁵¹ and have restricted consideration to homogeneous and heterogeneous condensation.^{51,52} Fundamental bench scale studies have demonstrated, however, that minerals and trace elements transform through condensation as well as by surface reaction of vapor phase species with ash particles and by coalescence of ash particles within the burning coal char.^{41,44,46,53,54} Trace element concentrations can therefore exhibit size dependence expressed as

$$\text{CE}_{i,j \text{ ash}} = k_{i,j} \text{dp}_j^n \quad (10)$$

Table 3-12. Median of Emissions Factors for Selected Trace Metals Emitted by Utility Pulverized Coal Combustion (lb/10¹² Btu); Range Shown in Parentheses

	Brooks (1989)*	Chow et al. (1994) [†]
As	42 (0.17 – 242)	32 (6-120)
Cd	3.8 (0.22-52.8)	2 (0.06-8)
Cr	2300 (1.6-7970)	22 (9-45)
Mn	440 (1-9240)	-
Pb	44 (1.1-184)	12 (4-40)
Ni	2100 (70-5760)	15 (5-30)

*From Ref. 48. Average of all coal types for utility boilers firing pulverized coal and utilizing electrostatic precipitators. Both wet and dry bottom units included in average. Individual boilers treated as single data points in deriving Table 3-12.

[†] From Ref. 49. ESPs and fabric filters combined.

Table 3-13. Average Capture Efficiency for Selected Trace Metals

	Brooks ESPs (1989)*	Szupnar (1993) [†]
As	87.5	97.2
Cd	74.6	97.3
Cr	71.5	99.0
Mn	78.1	98.0
Pb	-	98.2
Ni	79.1	99.6

*data from Reference 48

[†]data from Reference 50

where $CE_{i,j,ash}$ represents the concentration of trace element i in ash particles of size dp_j , $k_{i,j}$ is a proportionality constant, and n is the exponent representing the size dependence of concentration. The exponent n will equal -1 for heterogeneous condensation in the free molecular regime, -2 for heterogeneous condensation in the continuum regime, -1 for heterogeneous surface reaction control, and 0 for complete mass apportionment resulting from mineral coalescence (size independence).^{44,46,53} Recall that in a previous model, Rizeq et al. treated only

condensation, but allowed for size-regime dependent condensation flux.^{51,55} Messerole and Chow incorporated a $1/d_p$ dependence in trace element concentration, which, although labeled as condensation, represents assumptions of condensation on the smallest submicrometer-scale ash particles (free molecular regime) and external surface reaction control on the larger fly ash particles (continuum regime).⁵² In the work described herein, the size dependence was selected from mechanistic assessments derived from bench-scale experimental studies and is element-specific.

In order to predict trace element emissions, ash particle size distributions at the inlet to the electrostatic precipitator are needed. Models that predict the size distribution of fly ash particles formed during pulverized coal combustion are available, but require coal mineralogical data as input.⁵⁶ Because such data were not provided as part of any published field studies, site-specific calculation of fly ash particle size and composition distributions, a long-term goal of this program, is not presently possible. Fly ash particle size distributions were therefore derived from field measurements of ash particle size distributions conducted at the inlet to a power station cold-side electrostatic precipitator. Measurements were conducted on two separate occasions, permitting sampling of ash during combustion of two bituminous coals.⁵⁷ Data (Figure 3-22) were obtained by extractive sampling and subsequent size segregation using cyclones and a low pressure impactor (BLPI). An average particle size distribution at the ESP inlet was then obtained by averaging the two distributions and renormalizing. In the 4 to 8 μm region where data collected by the cyclone and impactor overlapped, particle concentrations

Figure 3-22. Fly ash particle size distributions obtained from field measurements (Lind, 1996) and used to assign baseline size distribution at ESP inlet. CO represents Colombian coal, SA South African.

were considered additive. The fraction of ash in the submicron particle size range calculated from these combined data was 1.9%, comparable to the 0.5 to 2% observed in prior field studies.^{10,58,59} Fly ash particle size distributions were subsequently calculated for individual facilities by adjusting the mass in each size bin by the relative ash content of the fuel. The normalized fly ash particle size distribution (i.e., percentage of total fly ash mass within a given size range) remained fixed at the value derived from Figure 3-22.

Particulate penetration through the electrostatic precipitator was determined through additional low pressure impactor and cyclone measurements at the electrostatic precipitator outlet at the same facility represented by the data in Figure 3-22. Aluminum penetration data⁵⁷ were used rather than total mass penetration data to avoid complications introduced by condensation and particle formation within cold-side ESPs.⁶⁰ The penetration curve derived from these measurements is presented in Figure 3-23 along with other ESP penetration measurements from the published literature. Data reported by McElroy et al.¹⁰ demonstrate higher penetration, whereas 1998 data reported by Ylatalo and Hautanen⁶¹ for combustion of a Polish coal are similar to the aluminum penetration data of Lind.⁵⁷ Mohr et al.⁶⁰ data are overall

Figure 3-23. Particle penetration through cold-side electrostatic precipitators as a function of particle size. Lind (1996) data used in the model are reported for aluminum, all others are for total mass. Ylatalo and Hautanen data are for the 234 MWe baseline case with all fields operative. Ensor et al. (1983) data for hot-side ESP. Penetration peak at particle sizes less than 0.1 μm reported by Mohr et al. (1996) excluded from figure.

mass penetration data in the submicron regime for the two coals used to derive the aluminum data of Lind.⁵⁷ Although these data demonstrate higher penetration in the 0.1 to 0.6 μm range for the same two coals, evidence of particulate formation within the precipitator was observed. The aluminum data of Lind were therefore taken as being representative of particulate penetration through a well-operated current-generation ESP neglecting particle formation within the precipitator.

With the establishment of a fly ash particle size distribution at the electrostatic precipitator inlet, the distribution of trace elements as a function of ash particle size can be established. This was accomplished by defining the fraction of a trace element associated with the submicron fly ash, and then distributing it among all fly ash particles as a function of particle size. Selenium, arsenic, and chromium were selected for detailed modeling because of differences in partitioning behavior observed at the bench scale. Selenium is a volatile element that may remain partially in the vapor phase at stack conditions. Arsenic is representative of a second type of volatile element that will vaporize significantly during combustion, but will condense completely before exiting the power plant. Based upon the field and bench studies summarized in Table 3-11, antimony, cadmium, cobalt, and lead are expected to follow similar partitioning patterns. Chromium is representative of elements that are only partially volatile, with enrichment sensitive to coal type or combustion conditions. Nickel has demonstrated behavior similar to that of chromium in field and laboratory studies (Table 3-11). Based upon these observations and data from bench scale studies, the trace elements were distributed as indicated in Table 3-14. Particle size-dependent electrostatic precipitator penetration efficiencies were then used to determine the fraction of particulate and thus the fraction of trace element emitted.

Table 3-14. Partitioning Functions Used in Development of Emissions Model

	Submicron	Supermicron
Chromium	Heterogenous condensation	Coalescence (mass apportionment)
Arsenic	Surface reaction	Surface reaction
Selenium	Vapor + surface reaction	Surface reaction

Using these partition functions, trace element emissions from a given facility can be expressed as

$$E_{ijk} = P_{t_j} [P_{t_k}/P_{t_{\text{baseline}}}] CE_{ijk} \quad (11)$$

here i represents a specific trace element, j represents a specific size (bin) of fly ash, k represents a specific utility boiler or site, E represents trace element emissions (mass per unit heat input of the fuel), P_t represents overall particulate mass penetration through the electrostatic precipitator, $P_{t_{\text{baseline}}}$ represents the overall particulate mass penetration through the baseline electrostatic precipitator (Figure 3-23), and CE represents the concentration of the trace element in a specific size class of fly ash particles at the inlet to the electrostatic precipitator. Overall

emissions of trace element i from site k can then be determined from the mass weighted sum over all size bins,

$$E_{i\ k} = \sum_j m_{j\ k} E_{i\ j\ k} \quad (12)$$

where $m_{j\ k}$ represents the mass of fly ash in size bin j at site k . CE is a discontinuous function of particle size,

$$CE = k_{1ik} dp^n f_{v,i} \quad dp < 1\ \mu m \quad (13a)$$

$$CE = k_{2ik} dp^n (1-f_{v,i}) \quad dp > 1\ \mu m \quad (13b)$$

where k_1 and k_2 are normalization constants and f_v represents the fraction of trace element i associated with the submicron fly ash. Although size dependencies reported for heterogeneous condensation are strictly valid only for particle sizes much greater than or less than the mean free path of the gas (approximately $0.1\ \mu m$ at typical cold side ESP inlet temperatures of $140^\circ C$, and $0.4\ \mu m$ at $1500^\circ C$), they are taken as being valid throughout the transition regime, with sharp transitions in mechanism occurring at a particle size of $1\ \mu m$. A cutoff size of $1\ \mu m$ is convenient because experimental studies have assigned trace element volatility from the fraction of an element appearing in the submicron size range.⁴¹

3.5.2 Model Results

An initial characterization of trace metal emissions can be obtained by applying Eq. (5) through (9) to field data generated in the EPRI PISCES and DOE sampling programs. Taking arsenic as a typical element, a plot of the data shows a lack of correlation between stack emissions E and the parameter C_i PM/fa specified by Eq. (8) (Figure 3-24). The linear least squares correlation coefficient R^2 was determined to be 0.20 for thirty-six sites in the Phase I work, with emissions ranging from less than one pound arsenic per 10^{12} Btu up to several hundred pounds per 10^{12} Btu. Using the empirical approach described by Eq. (9), an improved fit is obtained (Figure 3-25, $R^2 = 0.72$), a trend that holds true for all ten of the trace elements considered. Further improvement in agreement between predicted and measured arsenic emissions was observed when the subset of facilities using fabric filtration for particulate control was considered ($R^2 = 0.92$), suggesting that much of the variability observed in Figure 3-24 stems from the emission of small particulate enriched in arsenic.

The dependence of arsenic emissions on air pollution control device type further suggests that the approach outlined by Eqs. (10) through (13) should be useful in improving emissions estimates for arsenic and other compounds with comparable combustion partitioning behavior. It is not clear, however, whether improved prediction would be obtained for less volatile elements such as chromium. The partitioning / penetration emissions model outlined by Eqs. (10) through (13) was thus applied to chromium by generating emissions estimates and comparing them to data measured in the DOE and EPRI PISCES studies. The amount of chromium present in the submicron ash particle size range was used as an adjustable parameter to obtain the best fit

(a)

(b)

Figure 3-24. Arsenic emissions data obtained from field measurements as a function of Cl PM/fa as per Eq. (8). Different symbols represent different types of particulate control device. $R^2 = 0.20$ for these data. (a) entire dataset, (b) $\text{Cl PM/fa} < 5$ only.

Figure 3-25. Arsenic emissions data obtained from field measurements as a function of $C_i \text{PM/fa}$, plotted according to Eq. (9). Different symbols represent different types of particulate control device. $R^2 = 0.72$ for these data.

to measured data. Goodness of fit was determined by minimizing the sum of squared residuals R , defined as

$$R_i = \sum_k (E_{ik, \text{predicted}} - E_{ik, \text{measured}})^2 \quad (14)$$

A comparison of the model-predicted values of chromium emissions with those derived from Eq. (9), using an a_i value of 6.10 and b_i of 0.284 (both derived from EPRI PISCES data for coal-fired facilities utilizing ESPs, with or without flue gas desulfurization) is shown in Figure 3-26. The partitioning / penetration model demonstrates no difference when compared to the empirical approach. This is attributed to the relatively low volatility of chromium and the small percentage of sub-bituminous coal-fired boilers in the dataset. In the discussion of Table 3-11 it was noted that chromium enrichment was only observed at field sites burning sub-bituminous coal. Analysis of the EPRI/DOE database suggests similar results for facilities burning sub-bituminous coal (Figure 3-27), but given the dominance of bituminous coal-fired systems in the database, the influence of selective partitioning in sub-bituminous systems on the overall correlation is minimal. Bench scale experiments in which the amount of chromium in the submicron ash particulate correlated with the fraction of silicon in the submicron particulate, rather than the amount of chromium in the coal, provide further evidence in support of coal-specific chromium volatility.⁴⁰

Figure 3-26. Comparison of field measurements of chromium emissions with empirical model derived from database fit and partitioning / penetration model described by Eq. (10) through (13). COND represents condensation, MA mass apportionment.

Figure 3-27. Chromium emissions data obtained from field measurements as a function of $C_i PM / fa$ as per Eq. (8). Different symbols represent different coal rank as indicated. Data shown for facilities using ESP or ESP in conjunction with flue gas desulfurization only. $R^2 = 0.57$ for these data ($R^2 = 0.26$ using Eq. (8)).

Application of the model described in Eqs. (10) through (13) to arsenic yields different results. Comparison of model-predicted arsenic emissions with those derived from Eq. (9), using an a_i value of 3.14 and b_i of 0.887 is shown in Figure 3-28. Using the fraction of arsenic in the submicron ash as an adjustable parameter, improved agreement with measured field emissions data is found for fractions of arsenic in the submicron ash between 0.01 and 0.28. When the fractional partitioning of arsenic is set equal to 0.14, the minimum in the curve shown in Figure 3-28, agreement with measurements is greater than 20% improved over that derived from empirical correlation of the field data. Predicted emissions based on particulate capture alone are also shown in Figure 3-28; greater than 50% improvement in agreement with the data is observed for the partitioning model.

Figure 3-28. Comparison of field measurements of arsenic emissions with (a) empirical model derived from database fit and (b) partitioning / penetration model described by Eqs. (10) through (13).

The arsenic fractional partitioning of 0.14 found by minimizing the difference between predicted and measured emissions in the available field data is consistent with reported experimental values. In Table 3-15, experimental partitioning data are provided for several trace elements. For arsenic, most data cluster between fractions of 0.10 and 0.42 in the submicron ash. Values determined in field measurements were generally lower than those observed in the laboratory, with an average value of 0.15 obtained from the four field measurements. Although the single bituminous coal field measurement yielded a value greater than those derived from the sub-bituminous coals, the extensive laboratory dataset reported by Quann et al.⁴⁰ did not identify any rank-specific differences for arsenic. The model fit value of 0.14 is thus within the range of reported partitioning values for arsenic, and is in good agreement with the small amount of data available from field measurements.

Table 3-15. Fraction of Trace Element Associated with Submicron Ash

Scale	Coal Type	As	Sb	Cr	Mn	Cd	Se	Reference ^{Citation no.}	Comment
Bench	B	33	36				67	Bool and Helble ¹³	1 coal, all size fractions < 0.97 µm included
Bench	B	42*		2-24				Quann et al. ⁴⁰	4 coals, size segregated
Bench	B	20	23				16	Phase I Final Report	3 coals
Bench	B+L	42*		12				Zeng ⁶²	Size segregated coals
Lab	B (I6)	10-12						Wendt et al. ⁶³	Illinois 6; all size fractions LE 0.535 µm
Lab	B (P8)	70						Wendt et al. ⁶³	Pittsburgh 8; all size fractions LE 0.535 µm
Pilot	B	20	32	1	12	61	42	Tumati and Devito ³⁸	Fraction present 'fine' mode $d_{\text{mean}} = 0.7 \mu\text{m}$
Field	B	10		6	3			Martinez-T. and Spears ²⁰	Total < 2.5 µm
Bench	S	18	22				19	Phase I Final Report	1 coal
Bench	S	8	11				35	Bool and Helble ¹³	1 coal, all size fractions < 0.97 µm included
Bench	S	42*		13-20				Quann et al. ⁴⁰	2 coals, size segregated
Bench	S	42*		35				Zeng ⁶²	3 coals, size segregated
Field	S	22	19	21	13			Shendrikar et al. ²⁶	Derived from dm/dlog(dp) data at FF inlet
Field	S	15	10	21	10			Ensor et al. ⁶⁴	Derived from dm/dlog(dp) at ESP inlet
Field	S	14	24		1		9	Markoswki and Filby ²⁷	Tabulated data
Bench	L	42*		7-15				Quann et al. ⁴⁰	3 coals, size segregated.

* value derived from entire combined Quann et al.⁴⁰ and Zeng⁶² database and therefore taken to be independent of coal type.

Using the quasi-empirical penetration / partitioning model, arsenic emissions were predicted for three Canadian power plants comprising twelve boilers in total and representing units not contained within the PISCES field testing database.⁶⁵ Emissions predictions were also made using the PISCES database-derived empirical parameters and by assuming that arsenic emissions were proportional to total particulate emissions. As shown in Figure 3-29, the partitioning model provided the best agreement with measured emissions, with the sum of the residuals being at least 80% less than that derived from the other two models. A partitioning value of 0.14 derived from the study of the PISCES database was used in this calculation. The partitioning value of 0.14 does not represent the minimum in the residuals curve for this dataset (the minimum occurred at 0.20); nevertheless, a significant improvement over other approaches was identified.

Figure 3-29. Comparison of field measurements of arsenic emissions from twelve Canadian boilers with (a) empirical model derived from database fit, using U.S. database, ($\square$), and (b) partitioning / penetration model described by Eqs. (10) through (13), ($\blacklozenge$), and (c) empirical model with As collection equal to particulate collection efficiency ($\blacktriangle$).

Similar calculations were performed to assess selenium emissions for the facilities contained within the PISCES database. Meij,¹⁹ in a study of trace element emissions from a power station in the Netherlands burning a coal from the eastern U.S., reported that 25% of the selenium remained in the vapor phase at stack conditions. The partitioning model for selenium was thus modified to incorporate the fraction of vapor phase selenium as an adjustable parameter. Four values of the fraction of selenium in the vapor phase were considered: 0, 0.05, 0.10, and 0.20. As shown in Figure 3-30, best agreement with experimental measurements was obtained for vapor fractions of 0.05 to 0.10, with 80% of the remaining selenium associated with the submicron ash particulate. At these optimum conditions, a 50% improvement in agreement (versus the empirical database-derived model) was obtained. Using a value of 20% vapor and 30% of the remainder in the submicron size range, consistent with the limited selenium partitioning data reported in Table 3-15, provided 40% improvement over the database-derived

Figure 3-30. Comparison of field measurements of selenium emissions with empirical model derived from database fit (solid line) and partitioning / penetration model described by Eqs. (10) through (13), with ! 0% selenium vapor, # 5% vapor, x 10% vapor, ▲ 20% vapor.

model. In either case, calculations indicate that improved emissions estimates could be obtained by considering size-dependent partitioning for this element.

3.5.3 Summary and Conclusions

A quasi-empirical model for the emission of trace elements from electric utility coal-fired power plants has been developed. The model partitions trace elements among fly ash particles as a function of ash particle size, and incorporates size-dependent particulate penetration through electrostatic precipitators to obtain emissions estimates. Comparison with recent field measurements and a database-derived model demonstrated that improved agreement could be obtained for relatively volatile elements such as arsenic and selenium. In contrast, agreement for chromium was comparable to that obtained with the database-derived model, and was attributed to the relatively low volatility of this element. A review of the literature in this area suggests that this conclusion may be restricted to facilities combusting bituminous coals, as facilities firing sub-bituminous coals generally produced greater fractions of chromium in the submicron ash particulate. The partitioning model might thus be a more appropriate mechanism for predicting chromium emissions for such facilities.

The first principles prediction of elemental partitioning to be developed in this program, when coupled to the emission model presented herein, will provide the most accurate model of trace element emissions for all coals over a broad range of combustion conditions.

3.6 ToPEM Model Development (PSI)

3.6.1 *Overview*

The objective of the modeling task is to develop a fundamentally-based predictive model to predict the partitioning of trace elements in coal-fired power plants. Development of ToPEM will be based on PSI's existing EMAF.

The existing program (EMAF) consists of the following blocks, see also Figure 3-31

1. Data reading
2.
 - A Generation of coal particles at various sizes with a particle size distribution similar to the input
 - B Generation of mineral particles and formation of included and excluded
3.
 - A Distribution of mineral particles to coal particles
 - B Combustion of coal particles
 - C Formation of ash particles assuming a certain degree of coalescence.

Figure 3-31. Flow chart for Engineering Model for Ash Formation.

As a first step in developing the ToPEM, we developed a sub- model that calculates the evaporation of major elements (Na, K, Fe, Si, Al, Ca and Mg) from both inherent and extraneous minerals of coal. Subsequently, this sub-model was included into EMAF, which formed the ToPEM. Experimental data were used to test and modify the sub-model and the ToPEM.

3.6.2 Vaporization of Major Elements During Combustion

Theoretical analysis. Previous work on vaporization of inorganic elements during single particle combustion in the DTF was done by Quann⁶⁶ and Quann and Sarofim.⁶⁷ This work was both experimental and theoretical. The effects of coal rank, particle size, particle temperature and oxygen concentration were examined experimentally. Also, a theoretical analysis on vaporization from included, excluded and atomically dispersed minerals was accomplished. This theoretical analysis indicates that the element vaporization depends on one or more of the following parameters: bulk oxygen concentration, particle size and composition of inherent ash. Results of this effort for Si, Ca and Mg were in very good agreement with the experiments.

For the case where we have vaporization from both internal inclusions and exposed inclusion on the char surface (See Figure 3-32), Quann gives:

Figure 3-32. Schematic of trace element vaporization mechanisms.

$$N_{t_b} = N_I^0 4 \pi c r_i t_b \left[\frac{2}{5} D_e x_m^e + \frac{3}{5} D_m x_m^e \right] \quad (15)$$

and:

$$N_I^0 = \theta \frac{r_0^3}{r_i^3} \quad (16)$$

where:

- N_{tb} = moles of metal vaporized per gram coal burned
- N_I^0 = number of inclusions in the char particle
- c = molar concentration
- r_i = inclusion radius
- r_0 = char radius
- t_b = burnout time
- D_e = effective diffusivity
- D_m = metal diffusivity
- x_m^3 = equilibrium mole fraction metal at internal inclusion surface
- x_m^{es} = equilibrium mole fraction metal at surface of exposed inclusion
- θ = volume ratio of inclusions.

Based on these equations, Mims et al.⁶⁸ derived an expression for the fractional vaporization, f_v , divided by the burnout time, t_b :

$$\frac{f_v}{t_b} = \frac{9 \pi \theta c}{r_i^2 C_o \rho_p} \left[\frac{r_i D_e x_m^e}{2 r_o (3\theta)^{1/2}} + \frac{D_m x_m^e}{5} \right] \quad (17)$$

where C_o is the concentration of the metal in the coal and ρ_p is the density of the char particle. For vaporization from the external particles we assume $D_e \ll D_m$ then:

$$\frac{f_v}{t_b} \sim \frac{1}{C_o r_i^2} \quad (18)$$

This indicates that the parameter is independent of char radius.

For the case where internal diffusion is limiting, the effective diffusivity term in Eq. (17) is much higher than the metal diffusion term. Thus:

$$\frac{f_v}{t_b} \sim \frac{1}{C_o r_o} \quad (19)$$

For external diffusion control, as would occur with very fine inclusions or organically associated elements, we have:⁶⁹

$$\frac{f_v}{t_b} = \frac{4 D_m c x_m^e}{C_o r_o^2} \quad (20)$$

Thus, when external diffusion is controlling we would expect to see a $1/r_o^2$ dependence.

Development of Semi-Empirical Vaporization Formulas. Based on the analysis presented in the previous section, we derived easy to use formulas that can be applied to any type of coal, burning under any conditions. The idea behind this development is to use existing vaporization data related to a particular coal and certain combustion conditions, and predict vaporization from another type of coal burning at different conditions.

The experimental data consisted of fractional vaporization rates of metals from combustion of well characterized coal particles, 50 to 60 μ m in diameter. The reference combustion conditions were a gas temperature of 1750 K and a bulk oxygen partial pressure of 0.2. The particle temperature under such combustion conditions was measured to be 2100K.^{66,67} Two sets of reference data were used: one for bituminous coals and another for low rank coals.

The following equations that use reference data (denoted by subscript r) were derived from Eqs. (17) through (20):

For external (excluded) mineral particles:

$$f_v/t_b = (f_v/t_b)_r (r_o/r_o)^2 (C_o/C_o) \quad (21)$$

For included mineral particles:

$$f_v/t_b = (f_v/t_b)_r (x_i/x_i) (r_o/r_o) (C_o/C_o) \quad (22)$$

And finally, for organically-bound elements:

$$f_v/t_b = (f_v/t_b)_r (x_i/x_{ir}) (r_{or}/r_o)^2 (C_{or}/C_o) \quad (23)$$

Note that for Eqs. (21) through (23) we assumed that the volume metal inclusions, θ , was independent of the coal type.

$$t_b \propto d_o^2 / \ln(1+x_{O_2}) \quad (24)$$

The fraction of a certain element that vaporizes can be calculated if an expression for the burnout time, t_b , is known. This expression was obtained experimentally by Quann⁶⁶: where x_{O_2} is the molar fraction of oxygen in the combustion gases. This expression is essentially the D²-Law, which describes the diffusion controlled combustion of particles and droplets.

Using Eq. (24), Eqs. (22) and (23) become:

$$f_v = f_{vr} (x_i/x_{ir}) (r_o/r_{or}) (1+x_{O_2}) / (1+x_{O_2r}) (C_{or}/C_o) \quad (25)$$

for included mineral particles, and

$$f_v = f_{vr} (x_i/x_{ir}) (1+x_{O_2}) / (1+x_{O_2r}) (C_{or}/C_o) \quad (26)$$

for organically-bound elements.

Equation (25) suggests that for discrete inclusions the fraction of the metal that vaporizes, f_v , is proportional to the particle radius (or diameter), r_o (or d_o). Equation (26) suggests that for atomically dispersed metals f_v is independent of the particle size.

Reference (69) indicates that there is the following correlation between the vaporization of Na and K:

$$f_k = 0.007706 + 0.615746 f_{Na} \quad (27)$$

This correlation was used to calculate vaporization of potassium.

The metal gaseous mole fractions, x_i and x_{ir} , are calculated by assuming that the metal oxides undergo reduction during evaporation, for example:

And the partial pressure of SiO is equal to:

$$P_{\text{SiO}} = (a_{\text{SiO}_2} K_{\text{eq}} P_{\text{CO}})^{1/2}$$

where a_{SiO_2} is the activity coefficient and K_{eq} is the equilibrium constant. The activity coefficient is assumed to be independent of coal type and combustion conditions, so it cancels out in Eqs. (22) and (23) (or (25) and (26)). The equilibrium constants used were curvefits from JANAF data over a temperature range of 1500 to 2500 K as shown in Table 3-16.⁶⁸

Table 3-16. Equilibrium Constants for Vaporization of Metals

$\ln(K) = a + 10^4 b/T$	a	b
$\text{SiO}_{2(l)} + \text{CO} \rightleftharpoons \text{SiO} + \text{CO}_2$	18.6621	-5.9507
$\text{Al}_2\text{O}_{3(l)} + \text{CO} \rightleftharpoons 2\text{AlO} + \text{CO}_2$	38.2805	-16.7937
$\text{FeO}_{(l)} + \text{CO} \rightleftharpoons \text{Fe} + \text{CO}_2$	11.0258	-4.2495
$\text{CaO}_{(l)} + \text{CO} \rightleftharpoons \text{Ca} + \text{CO}_2$	10.1895	-5.1918
$\text{MgO}_{(l)} + \text{CO} \rightleftharpoons \text{Mg} + \text{CO}_2$	11.8032	-4.5773
$\text{Na}_2\text{O}_{(l)} + \text{CO} \rightleftharpoons 2\text{Na} + \text{CO}_2$	17.7349	-2.8271
$\text{K}_2\text{O}_{(l)} + \text{CO} \rightleftharpoons 2\text{K} + \text{CO}_2$	19.1685	-2.1940

The simple equilibria between CO and CO₂ can be used for each metal species of interest, assuming that oxygen diffusing to the char particle surface is completely consumed and that CO is the only product of combustion. In this case, the bulk oxygen concentration, $P_{\text{O}_{2b}}$, will determine the concentration of CO at the surface:

$$P_{\text{COs}} = 2 P_{\text{O}_{2b}} / (1 + P_{\text{O}_{2b}})$$

The bulk oxygen concentration can be calculated by assuming that all the volatiles burn first.

Comparison with Experimental Results. For validation purposes, we used our model to predict metal vaporization from a variety of coals burning at different conditions. Subsequently, we compared our predictions with experimental data. The purpose of this effort was to assess the accuracy of our model with respect to parameters that affect vaporization and then improve the accuracy by making proper corrections. The following parameters that affect the vaporization were examined: (a) the coal type, (b) the coal rank, (c) the coal particle diameter, (d) the oxygen concentration and (e) the element concentration in the coal.

Experimental results were used to improve the accuracy of Eqs. (25) and (26). Data from Quann indicate that the vaporization rate of Mg and, to a lesser extent of Fe, are rather independent of the element concentration in the coal. To explore the effect of Mg and Fe concentration on the vaporization rates we performed several sets of calculations based on different assumptions: (1) we assumed that vaporization of Mg only was independent of concentration, (2) we assumed that vaporization of both Mg and Fe was independent of concentration, and (3) we assumed that vaporization was independent of element concentration.

Once again Quann provided us with a complete set of vaporization data that involved a variety of coals, particle sizes and combustion conditions. In those experiments, vaporization from excluded minerals was negligible. Therefore, in our calculations we only accounted for vaporization from included and organically bound minerals.

Initially we calculated the fraction of Si, Na, K, Ca, Fe, Al and Mg that vaporized as oxides, namely: SiO_2 , Na_2O , K_2O , CaO , FeO , Al_2O_3 and MgO . Subsequently, the amounts of the individual amounts of vaporized oxides were estimated. Finally, the amounts of oxides vaporized were summed to get a calculated value of the total ash vaporized. Results of this effort are given in the Appendix (Tables A-1 to A-7) and in Figures 3-33 to 3-45.

As reference values for Eqs. (25) and (26), the following experimental data we used: (a) for vaporization of Na, Si, Fe and Al from bituminous coals, we used data for Illinois 6 from Quann,^{67,68} and (b) for vaporization of Na, Si, Fe, Al, Ca and Mg from sub-bituminous coals and lignites, we used data for Montana Savage lignite from Quann.^{67,68}

Bituminous Coals. Vaporization of major elements from Illinois 6 was calculated at four different cases (Figures 3-33 and 3-34): (a) 50 μm particles burning at 1750 K and 20% O_2 , (b) 120 μm particles burning at 1750 K and 20% O_2 , (c) 50 μm particles burning at 1750 K and 40% O_2 , and (d) 120 μm particles burning at 1750 K and 40% O_2 .

The calculations predict within 12% the total amount of ash that vaporizes from combustion of 50 μm particles at 20% and 40% oxygen. The predicted submicron ash composition for these cases is generally good. However, the evaporation of K is substantially overpredicted and the evaporation of Si underpredicted. The calculations overpredict the amount of ash that evaporates from 120 μm particles by two or three times.

Note that Illinois 6 is the reference coal for the vaporization calculations from bituminous coals. As such, the reference concentration C_{or} is equal to the concentration C_o for each element in Eqs. (22), (23), (25) and (26). Therefore, the results presented in Figures 3-33 and 3-34 are not affected by the assumption on the effect of concentration on element vaporization.

Figure 3-33. Effect of oxygen concentration on ash vaporization from Illinois 6. Particles burning at 1750 K, 20% and 40% oxygen. Particle diameter is 50 μ m.

Figure 3-34. Effect of oxygen concentration on ash vaporization from Illinois 6. Particles burning at 1750 K, 20% and 40% oxygen. Particle diameter is 120 μ m.

Figure 3-35 and Table A-2 display predicted and actual values for ash vaporization from three bituminous coals, Illinois 6, Alabama Rosa and Pittsburgh. The three calculated values for each coal correspond to the three assumptions regarding the dependence of vaporization on the

Figure 3-35. Effect of coal type on ash vaporization from bituminous coals. Particles burning at 1750 K and 20% oxygen. Particle diameter is 50 μm .

metal concentration in coals. The combustion conditions were 1750 K and 20% oxygen. The coal particle size was 50 μm .

These are three very different coals with respect to their ash and extraneous mineral content. The ash content varied in the range of 6.6 to 13.7% and the extraneous mineral content varied in the range of 16 to 56%. The inherent ash composition is similar in all these coals, with the exception of CaO in Pittsburgh, which has 2.5 to 3.5 times as much CaO as the other coals.

In most cases the amount of submicron ash is predicted within 1.5% to 25% for all sets of calculation. A notable exception is the estimation of submicron ash from Alabama Rosa assuming vaporization does not depend on element concentration (Calculation 3). In this case the amount of submicron ash is underestimated by 55%.

The actual and the predicted submicron ash composition are shown in Figures 3-36 to 3-38. Overall, the predictions of all three sets of calculations are similar. However, Fe is predicted more accurately assuming that vaporization does not depend on the concentration of Fe in coal. The percentage of Na is predicted very well (within 3%) by all sets of calculations. The percentages of K from Illinois 6 and Alabama Rosa are overpredicted by 40% by all sets of calculations. The percentage of K is accurately predicted for Pittsburgh 8 by all sets of calculations. The percentage of Fe is generally overpredicted, while the percentage of SiO_2 is under-predicted.

Figure 3-36. Submicron ash composition from Illinois 6. Particles burning at 1750 K and 20% oxygen. Particle diameter is 50 μm .

Figure 3-37. Submicron ash composition from Alabama Rosa. Particles burning at 1750 K and 20% oxygen. Particle diameter is 50 μm .

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Figure 3-38. Submicron ash composition from Pittsburgh coal. Particles burning at 1750 K and 20% oxygen. Particle diameter is 50 μm .

Low Rank Coals. Figures 3-39 and 3-40 as well as Table A-4 contain calculated and actual values for Montana Savage Lignite at four different cases: (a) 60 μm particles burned at 1750 K and 20% O₂, (b) 120 μm particles burned at 1750 K and 20% O₂, (c) 60 μm particles burned at 1750 K and 40% O₂, and (d) 120 μm particles burned at 1750 K and 40% O₂.

These calculations predict within 26% and 5% the total amount of ash that vaporizes from combustion of 60 and 120 μm particles, respectively, at 20% oxygen. The calculated submicron ash composition agrees well with the experimental data. The calculations at 40% oxygen concentrations over-predict the amount of ash that evaporates by 46 to 53%.

Figure 3-41 and Tables A-5 through A-7 contain predicted and actual values of submicron ash from four low rank coals, Montana Savage lignite, Montana Rosebud sub-bituminous, Montana Powder River Basin (PRB) sub-bituminous and N. Dakota lignite. The figure shows three calculated values for each coal corresponding to the three assumptions regarding the dependence of the vaporization on metal concentration in coals. The combustion conditions were 1750 K and 20% oxygen. The coal particle size was 60 μm .

The ash content of these coals is in the range of 7.5 to 13.6 % and extraneous mineral content is in the range of 14 to 64% of the total ash content. The inherent ash composition varied substantially between these coals. As an example Na₂O in the inherent ash varied in the range of 0.41 for Montana PRB to 16.44% for N. Dakota lignite.

Figure 3-39. Effect of oxygen concentration on ash vaporization from Montana Savage lignite. Particles burning at 1750 K, 20% and 40% oxygen. Particle diameter is 60 μm .

Figure 3-40. Effect of oxygen concentration on ash vaporization from Montana Savage lignite. Particles burning at 1750 K, 20% and 40% oxygen. Particle diameter is 120 μm .

Figure 3-41. Effect of coal type on ash vaporization from low rank coals. Particles burning at 1750 K and 20% oxygen. Particle diameter is 60 μm .

The amount of submicron ash is predicted within 50% for all types of coal and all three sets of calculation. The accuracy of these calculations is not affected greatly by the assumption regarding the dependence of evaporation on metal concentration. A notable exception is North Dakota lignite. The assumption (3) that vaporization is independent of concentration results in more accurate results than the other two assumption result in.

Figures 3-42 through 3-45 show the actual and predicted composition of sub-micron ash for the four types of coal. For the reference coal, the Montana Savage lignite, the three sets of predicted values agreed amongst themselves and with the measured values within 25%. For the Montana PRB and the Montana Rosebud sub-bituminous the predictions generally agreed within 50% with the measurements. Finally, for North Dakota lignite, which has a very high Na concentration, the assumption that the metal vaporization is independent of concentration results in accurate predictions. The predictions agree with the measurements within 22%. In contrast, the assumption that vaporization of some or all metals depends on the concentration results in less accurate predictions.

Figure 3-42. Submicron ash composition from Montana Savage lignite. Particles burning at 1750 K and 20% oxygen. Particle diameter is 60 μm .

Figure 3-43. Submicron ash composition from Montana Rosebud coal. Particles burning at 1750 K and 20% oxygen. Particle diameter is 60 μm .

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Figure 3-44. Submicron ash composition from North Dakota lignite. Particles burning at 1750 K and 20% oxygen. Particle diameter is 60 μm .

E-0427z

Figure 3-45. Submicron ash composition from Montana PRB coal. Particles burning at 1750 K and 20% oxygen. Particle diameter is 60 μm .

3.6.3 *Development of ToPEM*

Incorporation of Vaporization Sub-Model into EMAF The existing program, EMAF, was substantially modified to accommodate the vaporization sub-model. The flow diagram of the ToPEM, which is the EMAF with the vaporization sub-model, is shown in Figure 3-46.

The program reads the data file and generates mineral and coal particles of various sizes as before. Subsequently it starts a loop and goes through each coal particle size starting from the largest size. The last loop corresponds to excluded mineral particles. During this loop, the minerals, both discrete and organically bound, are distributed to the coal particles as before. In addition, now the mineral mass and composition of discrete minerals are calculated. The combustion of coal particles follows. For the excluded mineral particles, the mineral distribution and char combustion steps are omitted.

Subsequently, the program calculates the vaporization fraction of each element based on the combustion conditions and the coal characteristics. For the excluded minerals, the particle temperature is assumed to be equal to the gas temperature and the residence time is assumed to be 500 ms. Based on the vaporization fraction, the mass and the composition of the submicron ash are estimated. After vaporization, the mass and the composition of the remaining mineral matter is calculated. Finally, the remaining mineral matter is transformed into flyash particles, following the original program.

The main inputs of the vaporization subroutine are: the coal rank, the ash composition, the coal particle distribution, the gas temperature and the oxygen concentration. The main outputs are: the amount and composition of submicron ash produced from each coal particle size and from the total coal sample.

Testing and Optimization of ToPEM. The program was tested with experimental data from three bituminous coals used in Phase I: Illinois 6, Wyodak and Elkhorn-Hazard. CCSEM, coal particle size distribution and ASTM ash data exist for all these coals. These coals were burned at controlled conditions: stoichiometric ratios of 1.2 and a gas temperature of about 1770 K in the combustion zone. The mass of submicron ash and vaporization fraction of Fe (and selected trace elements) were measured. The measured values were, then, compared with results from ToPEM.

To improve the agreement between the measured and predicted results we explored the effects of several assumptions, as discussed earlier: (1) we assumed that the metal vaporization depended on the particle diameter, or (2) it was independent, and (3) we assumed that the vaporization of iron depended on iron concentration in coal or it was independent.

E-0428

Figure 3-46. Organization of ToPEM, including bulk ash vaporization.

Results from the previous section indicate that our model may not account accurately for the effect of the coal particle size on the vaporization of metals. A comparison between the results obtained under Assumption #2 and those obtained under assumption #3 will indicate the magnitude of the error related to the diameter of the coal particles.

Results. Figures 3-47 and 3-48 show vaporization results from ToPEM for various types of bituminous coals. The combustion conditions were 1750 K and 0.04% oxygen. The particle size varied between 10 and 170 μm .

Figure 3-47 shows the calculated and the actual amounts of ash that vaporize. It is apparent that these calculations are not affected substantially by any of the three assumptions. The predicted values overestimate the percentage of ash that vaporizes by 26 to 35% for the Wyodak and Elkhorn-Hazard coals and by more than 3.5 times for the Illinois 6 coal.

Figure 3-48 shows the calculated and the actual amounts of iron that vaporize. These results suggest that the calculations are affected substantially by our assumptions. The assumption that the vaporization rate of iron is inversely proportional to the iron concentration (Assumption #1) results in overestimation of iron that vaporizes by up to 10 times. Assumptions #2 and #3 give good results for both Wyodak and Elkhorn-Hazard coals.

Figure 3-47. Comparison of data for ash vaporization from EFR with model predictions.

Figure 3-48. Comparison of data for iron vaporization from EFR with model predictions.

3.6.4 Summary

This work aimed to develop a model that predicts the vaporization of metals during coal combustion and to incorporate this model into the existing program EMAF. The model is based on theoretical analysis for metal vaporization, experimental data and data correlations.

The main factors that affect the metal vaporization are: the coal rank, the coal type, the coal particle size, the oxygen content (and therefore the particle temperature) and the metal concentration in the coal. However, the vaporization of each metal may be affected by these factors in different ways.

Bituminous Coals. The vaporization of the following metals was considered: Na, K, Fe, Si and Al. Our model predicts fairly accurately the amount of ash that vaporizes and the sub-micron ash composition of bituminous coals based on a fixed reference condition. The effects of oxygen concentration and coal type on metal vaporization are predicted well, most often within 25%.

Our model predicts a linear relationship between the metal vaporization and the coal particle diameter, while experimental results suggest that metal vaporization for bituminous coals is independent of coal particle diameter. However, the overall effect of the particle size on our calculations is negligible when polydisperse coal samples are modeled.

The effect of metal concentration on vaporization was found to be rather challenging to predict. Results up to now indicate that vaporization of Fe is rather independent of concentration, while the vaporization of the other metals is inversely proportional to concentration.

Low Rank Coals. The vaporization of the following metals was considered: Na, K, Fe, Si, Al, Ca and Mg. Our model predicts fairly accurately the amounts of ash that vaporizes and the submicron ash composition from a variety of low rank coals based on a fixed reference condition.

The model predicts the effect of coal particle size on the ash vaporization better than it does the effect of oxygen concentration, unlike the case of the bituminous coals.

The effect of metal concentration on vaporization was, again, found to be rather challenging to predict. Results up to now indicate that vaporization of Fe and Mg is rather independent of concentration, while the vaporization of the other metals is inversely proportional to concentration.

SECTION 4

SUMMARY AND FUTURE PLANS

4. SUMMARY AND FUTURE PLANS

4.1 Summary

4.1.1 *Coal Characterization*

During the last quarter, distribution of all three Phase II coals was completed. Standard analyses for the whole coal samples were also completed. Mössbauer analysis of all project coals and fractions received to date has been completed in order to obtain details of the iron mineralogy.

The analysis of arsenic XAFS data for two of the project coals and for some high arsenic coals has been completed. The reason for studying the high-As coals is to try to get a better understanding of the oxidation behavior of arsenic, which is so prevalent in virtually all coals that we have examined with the XAFS technique. In addition, complementary Mössbauer analyses of the high-As coals have also been completed. As in Phase I bituminous coals, both As/pyrite and arsenate forms are readily apparent in the spectra of the Ohio bituminous coal and fractions. Half of the arsenic in the North Dakota lignite is found as arsenate; the rest is either in pyrite or as arsenite. Some exploratory mercury L_{III} XAFS work was carried out during August at the Advanced Photon Source (APS), the new synchrotron facility at Argonne National Laboratory, Chicago, IL. Comparable quality data were obtained for mercury in carbonaceous systems using a Lytle detector at APS to that obtained at SSRL using a more sensitive 13-element germanium detector. However, for mercury in an aluminosilicate matrix (zeolite), the quality of the data from SSRL was superior because of the effectiveness of the 13-element germanium detector in reducing the background signal.

During the reporting period, duplicate splits of the Ohio 5,6,7 and North Dakota lignite samples were taken through all four steps of the selective leaching procedure. Results for whole-coal splits are not available. Leaching analysis of the Wyodak coal has recently commenced. Preparation of polished coal/epoxy pellets for probe/SEM studies is underway.

4.1.2 *Combustion Zone Transformations*

Further analysis of small-scale combustion experiments conducted at PSI in Phase I was completed this quarter. Good mass balance closure (90 to 140%) was obtained overall for ash in the sampling system. Refractory elements had good mass balance closure with the exception of chromium. High chromium mass balance closure may have been due to contamination. The volatile elements As, Sb, Se, and Zn showed mass balance closures significantly less than 100%. The results of these experiments for the first time suggest almost complete vaporization of certain trace elements (Se, Zn) from coal combustion in the flame zone, in accordance with theoretical equilibrium predictions. Other elements (As, Sb, Cr) appeared considerably less volatile and may react with constituents in the bulk ash at combustion temperatures. Confirmation of these experiment results will require gas-phase sampling in addition to aerosol sampling in order to close the mass balance for the volatile elements.

4.1.3 *Post-Combustion Transformations*

The combustion section of the University of Arizona's Downflow Combustor was completely rebuilt. Concurrently, an air preheater was constructed and commissioned. The University of Utah worked on setting up EPA Method 26A to give the capability to measure chlorine in flue gas. In the next few months calibration of the impinger train will be finished and it will be connected to the 100,000 Btu/hr furnace running with coal.

The chlorine kinetic calculations performed as part of the Phase I program were found to have an error in the initial conditions. The results reported in the Phase I Final Report had 1/10 the amount of hydrogen typically found in coal. Therefore, the calculations were re-done this quarter with the correct starting conditions.

4.1.4 *Field Studies*

Development of a quasi-empirical emission model based on reported emissions of particulate matter from field measurements was continued this quarter. Comparison with recent field measurements demonstrated that improved prediction of emission of relatively volatile elements (As, Se) could be achieved using the quasi-empirical model.

4.1.5 *Model Development*

As a first step in developing the ToPEM, we developed a sub-model that calculates the evaporation of major elements (Na, K, Fe, Si, Al, Ca and Mg) from both inherent and extraneous minerals of coal. During this quarter, this sub-model was included into EMAF, which formed the ToPEM. Experimental data from the Phase I program were used to test and modify the sub-model and the ToPEM.

4.2 Future Plans

A new XAFS experimental session has been scheduled for 20-24 November at NSLS, Brookhaven National Laboratory. Both a high-Z (Fe - ??) beam-line and a low-Z (S- Fe) beam-line will be available to us during this time. We hope to complete the arsenic and possibly also the chromium XANES of the project coals during this session. In addition, work should be completed on the CCSEM mineralogy of the project coals; but it may be dependent on whether some minor hardware modifications are completed to the CCSEM hardware. At present leaching studies at USGS are well underway. In the first half of FY99, priority will be given to completing the first round of leaching studies and obtaining supporting probe, SEM, and XRD analyses.

Experimental work will continue at the University of Arizona and the University of Utah on setting up the large scale combustion system and the drop tube furnace, respectively, for coal combustion experiments. Work will also continue at the University of Arizona on graphite furnace atomic absorption spectroscopy (GFAAS) analysis of Phase I ash samples. Experi-

mental work at the University of Utah and the University of Connecticut will continue on post-combustion transformations of chlorine and mercury.

Modeling work in the next quarter will focus on modification of EMAF to account for trace metals.

SECTION 5
REFERENCES

5. REFERENCES

1. G. P. Huffman, and F. E. Huggins, "Mössbauer Studies of Coal and Coke: Quantitative Phase Identification and Direct Determination of Pyritic and Iron Sulphide Sulphur Content," *Fuel* **57**, pp. 592-604, 1978.
2. F. E. Huggins, J. Zhao, N. Shah, F. Lu, G. P. Huffman, L. E. Bool, III, and C. L. Senior, "Investigation of the Oxidation of Arsenical Pyrite in Coal and its Effect on the Behavior of Arsenic During Combustion," *Proceedings, ICCS '97, 9th International Conference on Coal Science, (Essen, Germany)*, ed. A. Ziegler, K. H. van Heek, J. Klein, and W. Wanzl, **1**, pp. 381-384, P&W Druck und Verlag GMBH, Essen 1997.
3. F. E. Huggins, N. Shah, J. Zhao, F. Lu, and G. P. Huffman, "Nondestructive Determination of Trace Element Speciation in Coal and Ash by XAFS Spectroscopy," *Energy & Fuels*, **7**, pp. 482-489, 1993.
4. F. E. Huggins, S. Srikantapura, B. K. Parekh, L. Blanchard, and J. D. Robertson, "XANES Spectroscopic Characterization of Selected Elements in Deep-Cleaned Fractions of Kentucky #9 Coal," *Energy & Fuels*, **11**, pp. 691-701, 1997.
5. C.A. Palmer, A. Kolker, J.C. Willett, S.J. Mroczkowski, R.B. Finkelman, K.C. Taylor, F.T. Dulong, J.J. Bullock, Jr., "Draft Final Report on the ICA Mode of Occurrence Round Robin, Phase I," International Energy Agency, 1998.
6. W.P. Linak and J.O.L. Wendt, "Trace Metal Transformation Mechanisms During Coal Combustion," *Fuel Process. Tech.*, **39**, pp. 173-198, 1994.
7. F. Fransden, K. Dam-Johansen, and P.R. Rasmussen, "Trace Elements from Combustion and Gasification of Coal – An Equilibrium Approach," *Prog. Energy. Comb. Sci.*, **20**, pp. 115-138, 1994.
8. F.J. Fransden, J.J. Helble, T.A. Erickson, and V. Kühnel, "Prediction of Trace Element Partitioning in Utility Boilers," *EPRI-DOE-EPA Combined Utility Air Pollutant Control Symposium*, EPRI TR-108683-V3, Palo Alto: Electric Power Research Institute, 1997.
9. J.J. Helble, and A.F. Sarofim, "Factors Determining the Primary Particle Size of Flame Generated Inorganic Aerosols," *J. Colloid Interface Sci.*, **128**, pp. 348-362, 1989.
10. M.W. McElroy, R.C. Carr, D.S. Ensor, and G.R. Markowski, G.R. "Size Distribution of Fine Particles from Coal Combustion," *Science*, **215**, pp. 13-19, 1982.
11. J. Joutsenaari, E.I. Kauppinen, J.K. Jokiniemi, and J.J. Helble, "Studies on Ash Vaporization in Power Plant Scale Coal Combustion," in *The Impact of Ash Deposition*

- on Coal Fired Plant*, ed. J. Williamson and F. Wigley, Washington, D.C.: Taylor & Francis, pp. 613-624, 1994.
12. R. Hillamo and E.I. Kauppinen, *Aerosol Sci. Tech.*, **14**, p. 33, 1991.
 13. L.E. Bool, III and J.J. Helble, "A Laboratory Study of the Partitioning of Trace Elements During Pulverized Coal Combustion," *Energy & Fuels*, **9**, pp. 880-887, 1995.
 14. S.M. Miller, S.R. Ness, G.F. Weber, T.A. Erickson, D.J. Hassett, S.B. Hawthorne, K.A. Katrinak, and P.K.K. Louie, "A Comprehensive Assessment of Toxic Emissions from Coal-Fired Power Plants: Phase I Results from the U.S. Department of Energy Study," Energy & Environmental Research Center, University of North Dakota, Final Report on Contract DE-FC21-93MC30097, September, 1996.
 15. D.H. Klein, A.W. Andren, J.A. Carter, J.F. Enery, C. Feldman, W. Fulkerson, W.S. Lyon, J.C. Ogle, Y. Talmi, R.I. Van Hook, and N. Bolton, "Pathways of Thirty-Seven Trace Elements Through Coal-fired Power Plant," *Environ. Sci. Tech.* **9**(10): pp. 973-979, 1975.
 16. E.S. Gladney, J.A. Small, G.E. Gordon, and W.H. Zoller, "Composition and Size Distribution of In-Stack Particulate Material at a Coal-Fired Power Plant," *Atmospheric Environment* **10**, pp. 1071-1077, 1976.
 17. E.I. Kauppinen and T.A. Pakkanen, "Coal Combustion Aerosols: a Field Study," *Environ. Sci. Tech.* **24**(12), pp. 1811-1818, 1990.
 18. B. Sander, "Measurements of Trace Element Mass Balances in Coal-Fired Power Plants Equipped with Different Types of FGD Systems," *Proceedings of the 2nd EPRI International Conference on Managing Hazardous Air Pollutants*, Washington DC, July 1993.
 19. R. Meij, "Trace Element Behavior in Coal-Fired Power Plants," *Fuel Processing Technology* **39**, pp. 199-217, 1994.
 20. M.R. Martinez-Tarazona and D.A. Spears, "The Fate of Trace Elements and Bulk Minerals in Pulverized Coal Combustion in a Power Station," *Fuel Processing Technology* **47**, pp. 79-92, 1996.
 21. I. Demir, R.E. Hughes, J.M. Lytle, and K.K. Ho, "Atmospheric Emissions of Trace Elements at Three Types of Coal-fired Power Plants," American Chemical Society Division of Fuel Chemistry Preprints, **42**(1), pp. 1101-1106, 1997.
 22. A. Aunela-Tapola, E. Hatanpaa, H. Hoffren, T. Laitinen, K. Larjava, P. Rasila, and M. Tolvanen, "A Study of Trace Element Behaviour in Two Modern Coal-Fired Power

- Plants II: Trace Element Balances in Two Plants Equipped with Semi-Dry Flue Gas Desulphurization Facilities,” *Fuel Process. Tech.* **55**, pp. 13-34, 1998.
23. J.M. Ondov, R.C. Ragaini, and A.H. Biermann, “Elemental Particle Size Emissions from Coal-Fired Power Plants: Use of an Inertial Cascade Impactor,” *Atmospheric Environment* **12**, pp. 1175-1185, 1978.
 24. J.M. Ondov, R.C. Ragaini, and A.H. Biermann, “Elemental Emissions from Coal-Fired Power Plant. Comparison of a Venturi Wet Scrubber System with a Cold-Side Electrostatic Precipitator,” *Environ. Sci. Tech.* **13**(5), pp. 598-607, 1979.
 25. G.R. Markowski, D.S. Ensor, R.C. Hooper, and R.C. Carr, “A Submicron Aerosol Mode in Flue Gas from a Pulverized Coal Utility Boiler,” *Environ. Sci. Tech.* **14**(11), pp. 1400-1402, 1980.
 26. A.D. Shendrikar, D.S. Ensor, S.J. Cowen, G.J. Woffinden, and M.W. McElroy, “Size-Dependent Penetration of Trace Elements Through a Utility Baghouse,” *Atmospheric Environment* **17**(8), pp. 1411-1421, 1983.
 27. G.R. Markowski, and R. Filby, “Trace Element Concentration as a Function of Particle Size in Fly Ash from a Pulverized Coal Utility Boiler,” *Environ. Sci. Tech.* **19**(9), pp. 796-804, 1985.
 28. X. Querol, J.L. Fernandez-Turiel, and A. Lopez-Soler, “Trace Elements in Coal and their Behaviour During Combustion in a Large Power Station,” *Fuel* **74**(3), pp. 331-343, 1995.
 29. W.D. James and L.E. Acevedo, “Trace Element Partitioning in Texas Lignite Combustion,” *J. Radioanalytical and Nuc. Chem.* **171**(2), pp. 287-302, 1993.
 30. S.V. Vassilev, “Trace Elements in Solid Waste Products from Coal Burning at Some Bulgarian Thermoelectric Power Stations,” *Fuel* **73**(3), pp. 367-374, 1994.
 31. I. Bogdanovic, S. Fazinic, S. Itskos, M. Jaksic, E. Karydas, V. Katselis, T. Paradellis, T. Tadic, O. Valkovic, and V. Valkovic, “Trace Element Characterization of Coal Fly Ash Particles,” *Nuc. Instrum. and Methods in Phys. Res. B* **99**, pp. 402-405, 1995.
 32. R.L. Davison, D.F.S. Natusch, J.R. Wallace, and C.A. Evans, Jr., “Trace Elements in Fly Ash: Dependence of Concentration on Particle Size,” *Environ. Sci. Tech.* **8**(13), pp. 1107-1113, 1974.
 33. J.W. Kaakinen, R.M. Jorden, M.H. Lawasani, and R.E. West, “Trace Element Behavior in Coal-fired Power Plant,” *Environ. Sci. Tech.* **9**(9), pp. 862-869, 1975.

34. D.G. Coles, R.C. Ragaini, J.M. Ondov, G.L. Fisher, D. Silberman, and B.A. Prentice, "Chemical Studies of Stack Fly Ash from a Coal-Fired Power Plant," *Environ. Sci. Tech.* **13**(4), pp. 455-459, 1979.
35. R.D. Smith, J.A. Campbell, and K.K. Nielson, "Characterization and Formation of Submicron Particles in Coal-Fired Plants," *Atmospheric Environment* **13**, pp. 607-617, 1979.
36. R.D. Smith, J.A. Campbell, and K.K. Nielson, "Volatility of Fly Ash and Coal," *Fuel* **59**, pp. 661-665, 1980.
37. A.H. Biermann and J.M. Ondov, "Application of Surface Deposition Models to Size-Fractionated Fly Ash," *Atmospheric Environment* **14**, pp. 289-295, 1980.
38. P.S. Tumati and M.S. Devito, "Retention of Condensed/Solid Phase Trace Elements in an Electrostatic Precipitator," *Proceedings of the 1st EPRI International Conference on Managing Hazardous Air Pollutants: State of the Art*, Washington DC, November 1991.
39. W.P. Linak and T.W. Peterson, "Mechanisms Governing the Composition and Size Distribution of Ash Aerosol in a Laboratory Pulverized Coal Combustor," *Proc. of the 21st Symposium (Int'l) on Combustion*, The Combustion Institute, Pittsburgh, pp. 399-410, 1986.
40. R.J. Quann, M. Neville, and A.F. Sarofim, "A Laboratory Study of the Effect of Coal Selection on the Amount and Composition of Combustion Generated Submicron Particles," *Combust. Sci. Tech.* **74**, pp. 245-265, 1990.
41. J.J. Helble, "Trace Element Behavior During Coal Combustion: Results of a Laboratory Study," *Fuel Processing Technology* **39**, pp. 159-172, 1994.
42. M. Neville and A.F. Sarofim, "The Stratified Composition of Inorganic Submicron Particles Produced During Coal Combustion," *Proc. of the 19th Symposium (Int'l) on Combustion*, The Combustion Institute, Pittsburgh, pp. 1441-1449, 1982.
43. R.J. Quann, M. Neville, M. Janghorbani, C.A. Mims, and A.F. Sarofim, "Mineral Matter and Trace Element Vaporization in a Laboratory Pulverized Coal Combustion System," *Environ. Sci. Tech.* **16**(11), pp. 776-781, 1982.
44. B.S. Haynes, M. Neville, R.J. Quann, and A.F. Sarofim, "Factors Governing the Surface Enrichment of Fly Ash in Volatile Trace Species," *J. Colloid Interface Science* **87**(1), pp. 266-278, 1982.
45. M. Neville, J.F. McCarthy, and A.F. Sarofim, "Size Fractionation of Submicrometer Coal Combustion Aerosol for Chemical Analysis," *Atmospheric Environment* **17**(12), pp. 2599-2604, 1983.

46. W.P. Linak and J.O.L. Wendt, "Toxic Metal Emissions from Incineration: Mechanisms and Control," *Prog., Energy Combust. Sci.* **19**, pp. 145-185, 1993.
47. Electric Power Research Institute, "Electric Utility Trace Substances Synthesis Report," Report No. EPRI TR-104614, Project 3081, 1994.
48. G. Brooks, "Estimating Air Toxic Emissions from Coal and Oil Combustion Sources," Radian Corporation Report to the U.S. Environmental Protection Agency, EPA Report No. EPA-450/2-89-001, 1989.
49. W. Chow, M.J. Miller, and I.M. Torrens, "Pathways of Trace Elements in Power Plants: Interim Research Results and Implications," *Fuel Process. Technol.* **39**, pp. 5-20, 1994.
50. C.B. Szpunar, "Projections of Air Toxic Emissions from Coal-fired Utility Combustion: Input for Hazardous Air Pollutant Regulators," *Proceedings of the 2nd EPRI International Conference on Managing Hazardous Air Pollutants*, Washington DC, July 1993.
51. R.G. Rizeq, D.W. Hansell, and W.R. Seeker, "Predictions of Metals Emissions and Partitioning in Coal-fired Combustion Systems," *Fuel Processing Tech.* **39**, pp. 219-236, 1994.
52. F.B. Meserole, and W. Chow, "Controlling Trace Species in the Utility Industry," *Proceedings of the 1st EPRI International Conference on Managing Hazardous Air Pollutants: State of the Art*, Washington DC, November, 1991.
53. J.J. Helble, S. Srinivasachar, and A.A. Boni, "Factors Influencing the Transformation of Minerals During Pulverized Coal Combustion," *Progr. in Energy and Combust. Sci.* **16**(4), pp. 267-280, 1990.
54. M. Neville and A.F. Sarofim, "The Fate of Sodium During Pulverized Coal Combustion," *Fuel* **64**, pp. 384-390, 1985.
55. R.G. Barton, W.D. Clark, and W.R. Seeker, "Fate of Metals in Waste Combustion Systems," *Combust. Sci. Technol.* **74**(6), pp. 327-342, 1990.
56. G. Wilemski and S. Srinivasachar, "Prediction of Ash Formation in Pulverized Coal Combustion with Mineral Distribution and Char Fragmentation Models," in The Impact of Ash Deposition on Coal Fired Plants, ed. J. Williamson and F. Wigley, Taylor and Francis Publishers, London, pp. 151-164, 1994.
57. T. Lind, Ash particle size distributions and electrostatic precipitator penetration data obtained in field measurements were generously provided by Ms. Terttaliisa Lind of the Aerosol Technology Group, VTT, Espoo Finland. Samples were obtained during 1994 measurements at the facility described by Mohr et al., 1996.

58. E.J. Schulz, R.B. Engdahl, and T.T. Frankenberg, "Submicron Particles from a Pulverized Coal Fired Boiler," *Atmospheric Environment* **9**, pp. 111-119, 1975.
59. E.W. Schmidt, J.A. Gieseke, and J.M. Allen, "Size Distribution of Fine Particulate Emissions from a Coal-Fired Power Plant," *Atmospheric Environment* **10**, pp. 1065-1069, 1976.
60. M. Mohr, S. Ylatalo, N. Klippel, E.I. Kauppinen, O. Riccius, and H. Burtscher, "Submicron Fly Ash Penetration Through Electrostatic Precipitators at Two Coal Power Plants," *Aerosol Sci. Tech.* **24**, pp. 191-204, 1996.
61. S.I. Ylatalo and J. Hautanen, "Electrostatic Precipitator Penetration Function for Pulverized Coal Combustion," *Aerosol Sci. Tech.* **29**, pp. 17-30, 1998.
62. T. Zeng, "Transformation of Iron and Trace Elements During Coal Combustion," Sc.D. Thesis, Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge MA, March 1998.
63. J.O.L. Wendt, S.D. Davis, T.K. Gale, and W.S. Seames, "Formation and Control of Semi-volatile Toxic Metals in Combustion Processes," Proc. 12th Members Conference, International Flame Research Foundation, Noordwijkerhout, The Netherlands, May 1998.
64. D.S. Ensor, G. Markowski, G. Woffinden, R. Legg, S. Cowen, M. Murphy, A.D. Shendrikar, R. Pearson, and R. Scheck, "Evaluation of Electrostatic Precipitator Performance at San Juan Unit Number 1," Final Report submitted to the Electric Power Research Institute, report number EPRI CS-3252, Project 780-1, 1983.
65. D. Orr, Radian Corporation compiled database, 1996. Original data taken from J.C. Evans, K.H. Abel, K.B. Olsen, E.A. Lepel, R.W. Sanders, C.L. Wilkerson, and D.J. Hayes, "Characterization of Trace Constituents at Canadian Coal-Fired Plants. Phase I – Final Report, Appendices H to K (Data)," Battelle Pacific Northwest Laboratories report to the Canadian Electrical Association, 1985.
66. R.J. Quann, Sc.D. Thesis, Department of Chemical Engineering, MIT, Cambridge, MA, 1982.
67. R.J. Quann, and A.F. Sarofim, "Vaporization of Refractory Oxides During Pulverized Coal Combustion." *Nineteenth (International) Symposium on Combustion*, The Combustion Institute, pp. 1429-1440, 1982.
68. C.A. Mims, M. Neville, R.J. Quann, and A.F. Sarofim, "Laboratory Studies of Trace Element Transformations During Coal Combustion," presented at 87th AIChE Meeting, Boston, MA, 1979.

69. L.E. Bool, II, J.J. Heble, N. Shah, A. Shah, G.P. Huffman, F.E. Huggins, K.R.P.M. Rao, A.F. Sarofim, T. Zeng, R. Reschke, D. Gallien, and T.W. Peterson, “ Fundamental Study of Ash Formation and Deposition: Effect of Reducing Stoichiometry,” Final Report prepared for Department of Energy, PETC, under Contract No. DE-AC22-93PC92190, PSIT-1178/TR-1407, September 1995.

APPENDIX

Predicted and Measured Vaporization of Major Elements During Coal Combustion

Table A-1. Illinois 6 Effect of Particle Size and Oxygen Concentration on Metal Vaporization

TR-1178 fv/tb=(fv/tb)r* xi/sr*Dr/D	x=0.2, 50 μ m 1750 K - calc. (Measured)	x=0.4, 50 μ m 1750 K - calc. (Measured)	x=0.2, 120 μ m 1750 K - calc. (Measured)	x=0.4, 120 μ m 1750 K - calc. (Measured)
mg ash ev/g coal	1.19 (1.24)	6.18 (5.5)	2.84 (1.24)	14.77 (5.5)
% ash coal vap.	0.87 (0.90)	4.54 (5)	2.09 (0.90)	10.86 (5)
% Na ₂ O, subash μ g Na v/gr coal	14.70 (14.5) 130 (155)	4.093 186 (160)	14.88 310 (230)	4.10 452 (280)
% K ₂ O, subash μ g K v/gr coal	28.30 (15.6) 280 (116)	6.865 350	27.77 274	6.433 783
% FeO, subash μ g Fe v/gr coal	30.64 (26.0) 280 (180)	27.02	30.90 690 (180)	27.11
% SiO ₂ subash μ g Si v/gr coal	24.73 (34.6) 137 (202)	41.40	24.94	41.55 2860 (202)
% Al ₂ O ₃ , subash	1.50 (1.6)	2.06	14.98	2.06

Table A-2. Bituminous Coals - Effect of Coal Type on Metal Vaporization

(Metal Concentration of Coal is Accounted for
Combustion Conditions: 1750 K and x=0.2, Coal Particle Size 50 μ m)

TR-1178 fv/tb=(fv/tb)r* xi/xr*Dr/D	Illinois 6 Calculated (Measured)	Alabama Rosa Calculated (Measured)	Pittsburgh Calculated (Measured)
mg ash ev/g coal	1.19 (1.24)	0.46 (1.03)	0.97 (1.19)
% ash coal vap.	0.87 (0.90)	0.70 (1.56)	1.32 (1.63)
% Na ₂ O, subash	14.70 (14.5)	16.96 (14.71)	26.19 (16.64)
% K ₂ O, subash	28.30 (15.6)	26.39 (4.60)	16.48 (11.20)
% FeO, subash	30.64 (26.0)	31.35 (47.40)	33.92 (18.40)
% SiO ₂ , subash	24.73 (34.6)	23.45 (19.60)	21.63 (41.20)
% Al ₂ O ₃ , subash	1.50 (1.6)	1.84 (1.60)	1.76 (1.31)
Note: Alabama Rosa has the highest amount of extraneous minerals of all bituminous coals			

Table A-3. Bituminous Coals - Effect of Coal Type on Metal Vaporization

(Metal Concentration of Coal is Not Accounted for
Combustion Conditions: 1750 K and $x=0.2$, Coal Particle Size 50 μm)

TR-1178 $f_v/t_b=(f_v/t_b)r^*$ $x_i/x_r*Dr/D*Cor/Co$	Illinois 6 Calculated (Measured)	Alabama Rosa Calculated (Measured)	Pittsburgh Calculated (Measured)
mg ash ev/g coal	1.19 (1.24)	1.12 (1.03)	0.97 (1.19)
% ash coal vap.	0.87 (0.90)	1.71 (1.56)	1.32 (1.63)
% Na_2O , subash	14.7 (14.5)	15.69 (14.71)	18.20 (16.64)
% K_2O , subash	28.3 (15.6)	23.85 (4.60)	11.67 (11.20)
% FeO , subash	30.64 (26.0)	32.57 (47.40)	37.78 (18.40)
% SiO_2 , subash	24.73 (34.6)	26.29 (19.60)	30.50 (41.20)
% Al_2O_3 , subash	1.50 (1.6)	1.58 (1.60)	1.83 (1.31)

Table A-4. Montana Lignite - Effect of Particle Size and Oxygen Concentration on Metal Vaporization

TR-1178 $f_v/t_b=(f_v/t_b)r^*$ $x_i/x_r*Dr/D$	$x=0.2$, 60 μm 1750 K - calc. (Measured)	$x=0.4$, 60 μm 1750 K - calc. (Measured)	$x=0.2$, 120 μm 1750 K - calc. (Measured)	$x=0.4$, 120 μm 1750 K - calc. (Measured)
mg ash ev/g coal	3.19 (2.51)	17.66 (13)	3.98 (3.8)	21.70 (15)
% ash coal vap.	3.63 (2.86)	20.07 (11.0)	4.52 (3.0)	24.66 (15.0)
% Na_2O , subash	3.20 (3.7)	0.83	5.14	1.35
% K_2O , subash	1.67 (1.4)	0.37	2.64	0.58
% FeO , subash $\mu\text{g Fe ug/gr coal}$	12.68 (11.5) 315 (185)	8.03	20.34	6.54
% SiO_2 subash $\mu\text{g Si v/gr coal}$	6.20 (3.67) (93) (40)	9.75	10.00	15.87
% Al_2O_3 , subash $\mu\text{g Al v/gr coal}$	0.92 (0.56)	11.90	1.47	19.41
% CaO , subash $\mu\text{g Ca v/gr coal}$	11.66 (7.8) 534 (135)	13.24	9.35	10.78
% MgO , subash $\mu\text{g Mg v/gr coal}$	63.62 (64.40) (1733)	55.84	51.05	45.45

Table A-5. Sub-Bituminous Coals and Lignites - Effect of Coal Type on Metal Vaporization

(Metal Concentration of Coal is Not Accounted for
Combustion Conditions: 1750 K and $x=0.2$, Coal Particle Size 60 μm)

TR-1178 $f_v/t_b=(f_v/t_b)r^*$ $x_i/x_r*Dr/D*C/Cr$	Montana Savage Lignite Calculated (Measured)	Montana Rosebud Sub. Calculated (Measured)	N. Dakota Lignite Calculated (Measured)	Montana PRB sub. Calculated (Measured)
mg ash ev/g coal	3.4 (2.51)	2.62 (2.38)	8.10 (6.60)	2.87 (1.41)
% ash coal vap.	3.85 (2.86)	1.93 (1.74)	10.80 (8.85)	2.31 (1.13)
% Na_2O , subash	3.03 (3.70)	3.95 (6.5)	42.76 (54.00)	3.85 (5.70)
% K_2O , subash	1.58 (1.40)	2.84 (3.6)	10.47 (0.82)	3.48 (3.80)
% FeO , subash	11.93 (11.50)	47.15 (35.4)	19.20 (20.00)	24.33 (7.10)
% SiO_2 , subash	5.90 (3.67)	9.45 (17.5)	2.16 (1.62)	18.81 (9.90)
% Al_2O_3 , subash	0.87 (0.56)	0.85 (0.80)	0.24 (0.27)	1.52 (0.78)
% CaO , subash	16.67 (7.80)	11.64 (6.60)	5.3 (2.65)	12.06 (10.40)
MgO , subash	59.90 (64.40)	23.97 (27.20)	19.85 (19.00)	35.99 (61.00)

Table A-6. Sub-Bituminous Coals and Lignites - Effect of Coal Type on Metal Vaporization

(Metal Concentration of Coal is Accounted for
Combustion Conditions: 1750 K and $x=0.2$, Coal Particle Size 60 μm)

TR-1178 $f_v/t_b=(f_v/t_b)r^*$ $x_i/x_r*Dr/D*C/Cr$	Montana Savage Lignite Calculated (Measured)	Montana Rosebud Sub. Calculated (Measured)	N. Dakota Lignite Calculated (Measured)	Montana PRB sub. Calculated (Measured)
mg ash ev/g coal	3.4 (2.51)	3.43 (2.38)	3.40 (6.6)	3.32 (1.41)
% ash coal vap.	3.85 (2.86)	2.74 (1.74)	4.52 (8.85)	2.58 (1.13)
% Na_2O , subash	3.03 (3.70)	3.00 (6.5)	3.03 (54.00)	3.16 (5.70)
% K_2O , subash	1.58 (1.40)	2.76 (3.6)	1.63 (0.82)	2.92 (3.80)
% FeO , subash	11.93 (11.50)	11.79 (35.4)	11.93 (20.00)	12.5 (7.10)
% SiO_2 , subash	5.90 (3.67)	5.84 (17.5)	5.90 (1.62)	6.51 (9.90)
% Al_2O_3 , subash	0.87 (0.56)	0.86 (0.80)	0.87 (0.27)	0.90 (0.78)
% CaO , subash	16.67 (7.80)	16.56 (6.60)	16.75 (2.65)	11.51 (10.40)
MgO , subash	59.90 (64.40)	59.18 (27.20)	59.87 (19.00)	62.81 (61.00)

Table A-7. Sub-Bituminous Coals and Lignites - Effect of Coal Type on Metal Vaporization

(Metal Concentration of Coal is Accounted for, except for Magnesium
Combustion Conditions: 1750 K and $x=0.2$, Coal Particle Size 60 μm)

TR-1178 $\text{fv/tb}=(\text{fv/tb})r^*$ $x_i/x_r^*Dr/D^*C/Cr$	Montana Savage Lignite Calculated (Measured)	Montana Rosebud Sub. Calculated (Measured)	N. Dakota Lignite Calculated (Measured)	Montana PRB sub. Calculated (Measured)
mg ash ev/g coal	3.20 (2.51)	1.81 (2.38)	2.77 (6.60)	2.23 (1.41)
% ash coal vap.	3.63 (2.86)	1.33 (1.74)	3.69 (8.85)	1.79 (1.13)
% Na_2O , subash	3.20 (3.70)	5.64 (6.5)	3.69 (54.00)	4.57 (5.70)
% K_2O , subash	1.67 (1.40)	4.05 (3.6)	2.00 (0.82)	4.21 (3.80)
% FeO , subash	12.68 (11.50)	22.35 (35.4)	14.60 (20.00)	18.09 (7.10)
% SiO_2 , subash	6.23 (3.67)	11.00 (17.5)	7.18 (1.62)	8.90 (9.90)
% Al_2O_3 , subash	0.92 (0.56)	1.62 (0.80)	1.06 (0.27)	1.31 (0.78)
% CaO , subash	11.66 (7.80)	20.55 (6.60)	13.43 (2.65)	16.63 (10.40)
MgO , subash	63.62 (64.40)	34.76 (27.20)	58.02 (19.00)	46.26 (61.00)