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

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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 a frame work for incorporating the results of the program into the Engineering Model for Ash Formation (EMAF).

A description of the work plan for accomplishing these objectives is presented in Section 2 of this report.

The work discussed in this report highlights the accomplishments of the third quarter of this program. These accomplishments include the acquisition and dispersion to team members of the third program coal, the Illinois No. 6. Standard coal analysis, CCSEM, and Mössbauer analysis were completed for the three coals obtained to date. Trace element concentrations in the Pittsburgh and Elkhorn/Hazard coals were measured with NAA. Coal samples were size and density-segregated by MIT, analyzed by NAA, and sent for XAFS analysis. Forms of occurrence of arsenic in the high density fraction were measured for two coals using XAFS analysis. Finally, preliminary combustion experiments were begun at both MIT and PSI.

Specifically, in Section 3 of this report we present the ultimate, proximate, and ash chemistry analysis for the three bituminous coals. Ash contents were similar between the Elkhorn/Hazard and Pittsburgh coals, approximately 7%. The ash content in the Illinois No. 6 is slightly higher at approximately 10%. The ash chemistry of the Pittsburgh and Illinois No. 6 coals were typical of American bituminous coals, while the iron content of the Elkhorn/Hazard ash was substantially lower than a 'typical' bituminous coal ash. The mineralogy and forms of occurrence for these coals are also presented and are consistent with these observations.

In Section 4 Mössbauer and preliminary XAFS analyses by UKy personnel are discussed. Mössbauer analyses of the Illinois No. 6 and the Pittsburgh coals indicate that the iron is almost completely in the form of pyrite. Iron in the Elkhorn/Hazard coal was split between pyrite, iron in clays, and jarosite. Size and density segregated samples and the raw coals were analyzed with

XAFS to determine the forms of arsenic in the coal. Arsenic in the Pittsburgh coal was primarily associated with pyrite. Arsenic in the Elkhorn/Hazard was primarily arsenate. These results are consistent with the iron distributions from the Mössbauer analysis.

Section 5 consists of a discussion of trace element analysis (NAA) of size and density-segregated fractions of the Elkhorn-Hazard coal. Operation of an aerodynamic classifier (to avoid contamination by solvents) at MIT for density segregation is also reported. Preliminary combustion experiments were performed and the form of arsenic in the ash is reported.

In Section 6 modifications to the entrained flow reactor at PSI are described. These modifications include the addition of an ash trap with a filter to condense water and to remove ash from the flue gas before it enters the exhaust duct. Further modifications were completed on the sample system to yield reproducible and well characterized particulate samples. Combustion experiments were begun and are also discussed in this section.

SECTION 2

OVERVIEW OF PROGRAM TASKS

2. OVERVIEW OF PROGRAM TASKS

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 (specifically in Phase I, As, Se, Cr, and possibly Hg). PSI Technologies (PSIT) 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 I program is to develop an experimental and conceptual framework for the behavior of selected trace elements (arsenic, selenium, chromium, and mercury) in combustion systems. This Phase I objective will be achieved by a team of researchers from MIT, the University of Arizona, the University of Kentucky, Princeton University, the University of Connecticut, and PSIT. Model development and commercialization will be carried out by PSIT. Our approach will include the following:

- (1) Direct identification of the modes of occurrence of trace inorganic species in coal and ash using unique techniques such as XAFS analysis and selective leaching;
- (2) Combustion testing to evaluate the formation and partitioning of inorganic toxic compounds as a function of mode of occurrence and combustion conditions at a range of combustion scales;
- (3) An analysis of steady state and transient organic emissions from field data to determine whether organic toxic emissions pose a concern and should therefore be included in ToPEM;
- (4) Model development to assess complex silicate equilibria and gas-phase kinetics, used to predict behavior such as mercury speciation and partitioning of chlorine;
- (5) Development of the framework for ToPEM based on the existing Engineering Model for Ash Formation (EMAF) including review of potential data for model validation from power plants available from DOE, EPRI, and VTT (Finland).

Experiments, sample analysis, and modeling will be conducted at several facilities as part of this program. Combustion experiments will be performed on a number of facilities of differing scale, including a small-scale drop tube, an intermediate scale entrained flow reactor, and a self-sustained combustor experiments. The small scale drop tube experiments will be used to

focus on specific important mechanisms. The larger scale entrained flow reactor will be used to explore the interactions between the various mechanisms to determine the dominant partitioning behavior of trace elements. The self-sustained reactor will be used to test the hypothesis developed from the results obtained in the smaller scale experiments under time-temperature profiles similar to coal fired boilers. Additional experiments will be performed to assess metal capture by minerals (thermogravimetric analysis). Coal and ash samples will be analyzed by various techniques, including Mössbauer spectroscopy, computer controlled scanning electron microscopy, X-Ray absorption fine structure (XAFS) spectroscopy, instrumental neutron activation analysis (INAA), and the USGS leaching protocol. The goal of this sample analysis effort will be to elucidate the modes of occurrence of trace elements in coal, the major mineral species present in coal, and the forms of trace elements in combustion generated coal ash. Fundamental modeling efforts include kinetic modeling to determine the partitioning of chlorine between HCL and Cl_2 under combustion conditions, equilibrium modeling of the chemical speciation of vapor phase trace elements, and equilibrium modeling of vaporization and condensation from complex aluminosilicate melts. A work breakdown structure containing a brief description of each task follows. The relationship among program participants is illustrated schematically in Figure 2-1.

Task 1 - Program Management (PSIT)

Program management and reporting activities at PSIT will be conducted under Task 1. Specifically, this task will include (1) preparing and submitting all reports and forms required for the performance of this contract; (2) coordinating, managing, and integrating the subcontractor efforts and results; (3) integrating and delivering to DoE the final work output of all tasks; this includes delivery of models, data, and the Final Report; and (4) planning and conducting program review meetings at a frequency of approximately once per 9 months, including task Principal Investigators, DoE personnel, members of the Technical Advisory Board, and a representative from VTT/ATG, provider of field samples and data, and EPRI.

Task 2 - Coal Acquisition and Characterization (PSIT)

Because of the importance of elemental form (e.g., sulfate v. silicate mineral) on partitioning, it is critical that coals representing a broad range of elemental forms be examined in this program. In this task we will select and acquire a total of four coals for study in this program. The coals chosen will (1) represent a broad range of elemental forms of occurrence; (2) represent the major coal ranks and commercial coal seams used for pulverized coal (pc) power generation in the U.S; and (3) include "future fuels" such as blends and beneficiated coals. 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. Analysis of the coals by advanced techniques, such as CCSEM, will be accomplished under Task 3.

Task 3 - Analysis of Coal and Ash for Forms-of-Occurrence of Inorganic Elements (UK)

In this task advanced analytical techniques such as Mössbauer spectroscopy and CCSEM will be used to determine the major mineral species present in the program coals and the

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Figure 2-1. Project organization chart showing major tasks and lines of managerial responsibility

combustion generated ash. 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.

Another important issue is the form-of-occurrence of the trace elements both in the coal and in the combustion generated ash. In this task the mode of occurrence of As, Cr, and Se in coals and combustion products will be determined by combining XAFS and the Mössbauer/CCSEM derived data discussed above. Hg will also be evaluated. 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 other halogens) in coals, chars, and ash samples (if present) will be investigated.

Task 4 - Forms of Occurrence Analysis Using USGS Protocol

As a complement to the time-intensive XAFS analysis mentioned above, a unique protocol developed by USGS will be used to analyze selected raw coal, and size and density segregated coal, samples for trace element forms of occurrence. This protocol combines low temperature ($< 200^{\circ}\text{C}$) 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. In addition, a relatively new technique, synchrotron radiation x-ray fluorescence microscopy (SRXFM), available at the National Synchrotron Light Source, will be tested for application in this area by UK. This technique uses x-ray fluorescence excited by a focussed synchrotron x-ray beam for imaging and compositional analysis. The x-ray yield obtained from a given element is orders of magnitude greater than that possible in an electron microscope or microprobe; hence, its sensitivity to trace element modes is much better, particularly for modes of occurrence involving highly dispersed elements.

Task 5.1 - Bench Study Focusing on Partitioning: Trace Elements and Chlorine (MIT)

In this task calculations will be performed on the gas-phase reactions of chlorine to determine the partitioning of chlorine between HCL and Cl_2 using full kinetic codes available at MIT for the gas-phase chemistry of hydrocarbon oxidation including the chlorine reactions. Temperature histories representative of boilers and advanced combustion cycles will be selected. The effect of air staging will be evaluated. In addition heterogeneous reactions will be included for the rate of chlorine capture by alkali and alkaline earth metals.

The effect of coal type and combustion conditions on the emission of the toxic trace elements will be will also be investigated using the MIT laminar-flow drop tube reactor. 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. Individual size-segregated ash samples (collected with a cascade impactor) will then be analyzed by INAA for total composition, 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 under Task 3 of this program.

Measurements will be made of the partitioning of the trace elements in the four coals as a function of temperature and equivalence ratio. These measurements will provide the baseline data on the fraction vaporized for the different elements to be studied in greater detail in Phase II of the program.

Task 5.2 - Mercury Sampling and Elemental Analysis (MIT)

Under Task 5.2, two subtasks will be conducted. In the first, MIT will analyze, using INAA, commercially available charcoal and carbon sorbents to determine which contains the lowest background levels of mercury. In prior work at MIT, steam-activated coconut charcoal was found to have extremely low background Hg levels (in the range $10 \pm 2 \mu\text{g/kg}$); these charcoals will be examined first. Once the best Hg capture carbon has been identified, acid washed Teflon collection tubes will be filled with charcoal according to procedures developed at MIT. The design is similar to commercially available sorbent tubes for Hg collection (which will not be used here because of unacceptably high background Hg concentrations). These tubes will then be used by program experimentalists (Tasks 5.1, 6.1, 6.2, and 8) to capture Hg for analysis. Mercury will be analyzed at MIT by neutron activation using the Hg-197 isotope for detection. Prior work has shown the Hg-197 isotope to be more sensitive than the more common Hg-203 isotope because of its higher production cross section and shorter half life.¹⁵

In the second subtask of Task 5.2, coal and ash samples will be analyzed for trace element concentrations by INAA and techniques such as ICP-AES. All measurements will take place at the MIT Nuclear Reactor Laboratory.

Task 6.1 - Mechanistic Study (UA)

This task will involve both experimental and modeling efforts to explore the fundamental kinetics and mechanisms for metals vaporization and metal vapor-mineral interactions. Also in this task a series of numerical calculations using thermodynamic equilibrium approximations will be performed to determine likely metal compounds evolving from coal combustion. The data from our vapor evolution studies and a typical flue gas composition for different combustion conditions and thermodynamics to predict the formation of various forms of a specific metal in the gas phase. These calculations also show which compounds are likely to saturate and condense at a given set of conditions.

Metal vapor-mineral interactions will be studied in this task using thermogravimetric analysis (TGA). The primary experimental parameters to be studied are temperature, gas composition (particularly the concentration of the metal species in the gas phase), the composition of the sorbent (silica, alumino-silicate, etc.), sorbent particle size and porosity, and exposure time (residence time). The primary properties that will be analyzed are the concentration of toxic trace metals in the particles as functions of time, the final chemical form of the

trace metal, the leachability of the trace metal in the final particles, and if possible, the distribution of metal in the particles.

Task 6.2 - Large Scale Integrated Combustion Study (UA)

In this task, we 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. Other tasks focus, one at a time, on individual aspects of toxic metal partitioning. In this task, experiments are performed with time-temperature profiles similar to those in pc combustors. Therefore, the hypothesis derived from the smaller scale facilities can be tested under 'real world' conditions to determine the dominant mechanisms for trace element partitioning. Results from this portion of the project, together with the other portions, will lead to a quantitative model that will predict the fate of all toxic species as functions of coal quality and combustion configuration (Task 9).

In this task select coals will be burned in the UA self-sustained combustor under premixed conditions where all the coal is mixed with all the air prior to combustion. 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 the exhaust port. 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. This data will then be examined to determine particle size dependence in order to infer possible mechanisms governing the fate of each metal.

Task 7 - Field and Literature Emissions Data (Univ. of Connecticut/Princeton)

Some organic emissions associated with coal combustors can have deleterious effects on the environment and/or human health. It is therefore very important (1) to know the identities, quantities, and toxicities of the organic species released from coal combustion systems and (2) to understand the chemical and physical processes that govern these species' formation, destruction, and release. Organic emissions data from the DoE Air Toxics and EPRI PISCES programs, soon to be released, have the potential of benefitting the evaluation of the problem of organic emissions from coal combustion.

Consistent with objectives (1) and (2) above, we propose to (a) to critically evaluate the emissions data obtained in the DoE and EPRI studies -- with particular attention organic compounds, focusing on (1) the appropriateness, thoroughness, and reliability of the experimental techniques employed; (2) comparison with previously published emissions data; and (3) the implications of the results; (b) to similarly evaluate comparable data available from other countries, particularly Europe and Australia; (c) review emerging technical literature on coal pyrolysis and combustion processes that affect organic emissions; (d) to stay abreast of new results in the toxicity literature, relating to organic emissions from coal; and (e) to communicate

regularly with the other principal investigators of the air toxics team so that all will be cognizant of the ties between the organic and inorganic air toxics issues.

It is expected that the above efforts of analysis and literature review will lead to (1) comprehensive understanding of what is currently known about organic emissions from coal and (2) identification of the important questions that may still need to be addressed in future research.

Task 8 - Integrated Combustion Study (PSIT)

In this task a detailed experimental study will be performed to determine the fundamental behavior of toxic species during combustion, especially under low NO_x conditions. The work will use the PSIT Entrained Flow Reactor (EFR) that has been used in many previous combustion studies on mineral matter transformations during pc combustion. This reactor is on a scale intermediate between the bench top apparatus to be used by other team members (UA, MIT) and the UA laboratory-scale combustor. Therefore the combustor will yield a better understanding of the overall behavior of toxic species while avoiding some of the confounding influences related to self-sustained combustion in the larger furnace. Utility-grind samples of the program coals will be combusted under three different stoichiometric ratios, and two temperatures. Size segregated ash samples, and carbon filter samples will be collected. Ash samples collected during the combustion experiments will be analyzed by INAA and other techniques at MIT (Task 5.2). Selected samples will also be analyzed by ICPES and AA. By performing an elemental analysis on the size classified ash samples, we will identify the major mechanisms (e.g., vaporization and condensation) that govern the behavior of specific toxic species during the combustion process -- especially under reducing conditions.

Task 9 - Modeling, Including Development of Fundamental Engineering Model (PSIT)

In this task PSIT will use its silicate equilibrium model accounts for the *non-ideal* behavior of multicomponent silicate solutions in combination with its trace element database to calculate Cr and As partitioning. These results will be compared with laboratory data generated under Tasks 5.1, 6.1, 6.2, and 8, and inorganic species field data reviewed as part of Task 7. These calculations may be repeated for Se and/or other elements if experimental data warrant interpretation of vaporization under conditions where silicate chemistry is dominant.

The existing Engineering Model for Ash Formation (EMAF) algorithm will be modified to incorporate several general mechanisms that have been shown to play a major role in the partitioning for trace species.

SECTION 3

TASK 2. COAL SELECTION AND ACQUISITION (PSIT)

3. COAL SELECTION AND ACQUISITION

In the past quarter the third of four coals to be used in this program, the Illinois No. 6 coal, was obtained from CONSOL. As with the previous two coals, the Pittsburgh and the Elkhorn/Hazard coals, samples were sent to each of the team members and the drums were purged with argon to prevent weathering. All samples of this coal were stored under argon by the various team members. In addition, a small sample of this coal was sent to a commercial laboratory for analysis. These data are presented below.

Preparations to acquire the final program coal, the Wyodak-Anderson, were completed in the last quarter. As discussed in the previous Quarterly Report (Bool et. al., 1996) we have teamed with ABB to investigate a common coal in the two DOE funded programs. This collaboration will allow us to evaluate trace element partitioning at the pilot scale for this coal -- data that will be critical in extrapolating results obtained on the smaller scale facilities to full scale boilers. The coal to be used in both programs, the Wyodak-Anderson, is expected to be received at ABB and a subsample sent to PSI and program participants in late August.

In the last quarter standard coal analysis of the three program coals obtained to date was completed. Coal mineralogy data for these three coals was also obtained from UKy. NAA of two program coals, the Pittsburgh and the Elkhorn-Hazard, was completed in the last quarter. These analyses are discussed in the following sections.

3.1 Ultimate, Proximate, and Ash Chemistry

Table 3-1 shows the ultimate, proximate, and ash composition for the three program coals acquired to date. As can be seen from this table, the ash contents of the Pittsburgh and the Elkhorn/Hazard coal are very similar. The Pittsburgh coal contains 7.01% ash, and the Elkhorn/Hazard coal contains 7.41%. The Illinois No. 6 has a higher ash content, 10.26%. This coal also has a much higher sulfur content than the other two coals. The ash composition of the Pittsburgh and Illinois No. 6 coals are very similar. The ash from these two coals is fairly typical of American bituminous coals, containing primarily silica, alumina, and iron oxide. The Elkhorn/Hazard coal, however, is somewhat atypical as it contains a relatively low iron concentration in the ash. This, and the lower sulfur content of this coal, suggest that the pyrite content of the coal is low.

The forms of sulfur analysis for the three bituminous coals was also completed by the USGS in the last quarter. However the total sulfur data for the Pittsburgh coal was much higher for the USGS analysis than was reported by Galbraith Laboratories (Table 3-1). The USGS analysis is being repeated and will be included in the next report. The data for the other two coals are presented in Table 3-2. As can be seen from this table, the USGS analysis for total sulfur agreed with that from Galbraith Laboratories (Table 3-1) for these two coals. The data in Table 3-2 indicate that the Illinois No. 6 coal contains significant amounts of both pyritic and organic sulfur. The Elkhorn/Hazard contains primarily organic sulfur.

Table 3-1. Coal Properties for Three Program Coals

	Elkhorn/Hazard		Pittsburgh		Illinois No. 6	
	Dry Basis	As Received	Dry Basis	As Received	Dry Basis	As Received
<u>Proximate (wt %):</u>						
Fixed Carbon	57.80	56.46	62.23	61.99	54.98	53.16
Volatile Matter	34.61	33.80	30.66	30.22	34.41	33.27
Moisture	0.00	2.33	0.00	1.44	0.00	3.31
Ash	7.59	7.41	7.11	7.01	10.61	10.26
<u>Ultimate (wt %):</u>						
Carbon	76.66	74.87	77.74	76.62	70.02	67.70
Hydrogen	4.70	4.59	4.87	4.80	4.89	4.73
Nitrogen	1.46	1.43	1.50	1.48	1.22	1.18
Sulfur	0.84	0.82	1.66	1.64	3.72	3.60
Oxygen	8.58	8.38	7.01	6.91	9.50	9.20
Chlorine	0.17	0.17	0.099	0.098	0.035	0.034
Moisture	0.00	2.33	0.00	1.44	0.00	3.31
Ash	7.59	7.41	7.11	7.01	10.61	10.26
<u>Ash Composition (wt%):</u>						
SiO ₂	55.83		42.92		44.38	
Al ₂ O ₃	34.27		22.87		17.35	
Fe ₂ O ₃	5.18		19.18		19.80	
TiO ₂	1.71		1.08		0.91	
CaO	1.84		4.51		4.00	
MgO	0.60		0.97		0.85	
Na ₂ O	0.32		1.28		0.63	
K ₂ O	1.53		1.21		1.80	
SO ₃	1.45		5.40		4.62	
P ₂ O ₅	0.23		0.57		0.12	

Table 3-2. Forms of Sulfur in the Elkhorn/Hazard and Illinois No. 6 Coals

	Elkhorn/Hazard		Illinois No. 6	
Sulfur (wt%, dry basis)	0.87		3.82	
Forms of sulfur:	Wt Percent in Coal (Dry Basis)	Percent of Total Sulfur	Wt Percent in Coal (Dry Basis)	Percent of Total Sulfur
Sulfate	0.03	3.4	0.04	1.0
Pyritic	0.12	13.8	1.57	41.1
Organic	0.72	82.8	2.21	57.9

3.2 Coal Mineralogy

In the past quarter CCSEM analysis of the three bituminous coals in this program was completed by the University of Kentucky. These results will be discussed in more detail in upcoming quarterly reports, but are summarized below for each coal.

3.2.1 *Mineralogy of the Elkhorn/Hazard coal*

Table 3-3 shows the mineralogy of the Elkhorn/Hazard coal. The mineralogy for this coal is dominated by clays and mixed silicates, with quartz and pyrite making up only 12 and 6.1% of the minerals, respectively. These minerals tend to be relatively fine, with 83% less than 20 μm (Table 3-4). This is particularly true for the pyrite, the miscellaneous silicates, and the minor minerals. The quartz, in contrast, has a coarse distribution with approximately 39% of the mass greater than 20 μm .

Table 3-3. Coal Mineralogy for the Elkhorn/Hazard Coal

#	MINERAL SPECIES	AVERAGE SPECIES COMPOSITION											Weight %
		Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Fe	
122	Quartz	0.	0.	0.	99.	0.	1.	0.	0.	0.	0.	0.	12.0
281	Kaolinite	0.	0.	45.	52.	0.	1.	0.	1.	0.	0.	0.	25.8
195	Illite	0.	0.	31.	52.	0.	2.	0.	11.	0.	1.	2.	14.5
383	Misc. Silicates	0.	0.	34.	55.	0.	4.	0.	4.	1.	1.	1.	29.2
31	Pyrite	0.	0.	1.	1.	0.	64.	0.	0.	0.	0.	35.	6.1
MINOR MINERALS:													
3	K-Feldspar	0.	0.	17.	58.	0.	1.	0.	18.	0.	2.	5.	0.3
1	Montmorillonite	0.	0.	27.	61.	0.	8.	0.	0.	4.	0.	0.	0.0
2	Chalcopyrite	0.	0.	0.	0.	0.	52.	0.	0.	0.	0.	25.	0.5
8	Misc. sulf.	0.	0.	4.	8.	1.	50.	0.	3.	6.	0.	28.	0.4
2	Apatite	0.	0.	2.	0.	27.	0.	1.	0.	70.	0.	0.	0.3
7	Misc. Phosphate	0.	1.	1.	46.	30.	0.	3.	0.	17.	2.	0.	1.5
7	Fe-rich	0.	0.	0.	0.	0.	0.	0.	0.	4.	0.	96.	1.1
4	Calcite	0.	0.	0.	3.	0.	0.	0.	0.	97.	0.	0.	0.8
9	Mixed Carbonate	0.	0.	0.	0.	16.	4.	0.	0.	55.	0.	24.	1.6
1	Ti oxide	0.	0.	0.	0.	0.	0.	0.	0.	0.	100.	0.	0.2
7	Ti-rich	0.	0.	1.	9.	0.	7.	0.	0.	0.	67.	13.	0.9
3	Quartz-Sulfate	0.	0.	0.	39.	0.	31.	19.	11.	0.	0.	0.	0.1
1	Quartz-Pyrite	0.	0.	7.	24.	0.	45.	0.	0.	0.	0.	23.	0.6
29	Sil-sulf	0.	0.	26.	40.	0.	26.	4.	1.	0.	1.	0.	0.5
6	Silicate-Pyrite	0.	0.	16.	23.	0.	28.	1.	4.	1.	0.	26.	0.2
1	Alumina-rich	0.	0.	93.	0.	0.	5.	0.	0.	0.	0.	0.	0.1
81	Misc. Mixed	0.	0.	24.	34.	2.	13.	3.	2.	9.	1.	10.	3.4
1184	GRAND TOTALS	0.	0.	27.	51.	1.	7.	0.	3.	3.	1.	5.	100.0

Table 3-4. Mineral Size Distribution for the Elkhorn/Hazard Coal

WEIGHT DISTRIBUTION								
MINERAL SPECIES	WT. %	Size Ranges (Microns)						
		0.1 2.5	2.5 5.0	5.0 10.0	10. 20.	20. 40.	40. 80.	80. 500.
Quartz	12.0	10.	24.	16.	12.	10.	5.	24.
Kaolinite	25.8	6.	30.	15.	29.	10.	7.	1.
Illite	14.5	16.	24.	28.	14.	8.	10.	0.
Misc. Silicates	29.2	31.	26.	20.	15.	3.	4.	0.
Pyrite	6.1	8.	22.	15.	41.	7.	7.	0.
MINOR MINERALS	12.4	31.	39.	12.	6.	4.	2.	5.
GRAND TOTALS	100.0	19.	28.	18.	19.	7.	6.	4.

3.2.2 Mineralogy of the Pittsburgh coal

The mineralogy of the Pittsburgh coal can be seen in Tables 3-5 and 3-6. Although clays and miscellaneous silicates make up over 60% of the mineral mass, this coal also contains significant amounts of non-silicate species. For example, the data in Table 3-5 indicate 18% by weight of the minerals in this coal is pyrite. Calcium-rich minerals (calcite and mixed carbonates) comprise approximately 8.3% of the minerals. The minerals in this coal, with the exception of the pyrite, are predominantly less than 20 μm (Table 3-6). The pyrite is primarily found in the larger size ranges, with approximately 73% of the pyrite larger than 20 μm .

Table 3-5. Coal Mineralogy for the Pittsburgh Coal

#	MINERAL SPECIES	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Fe	Weight %
142	Quartz	0.	0.	0.	98.	0.	1.	0.	1.	0.	0.	0.	11.1
133	Kaolinite	0.	0.	46.	53.	0.	1.	0.	1.	0.	0.	0.	9.2
122	Illite	0.	0.	30.	53.	0.	4.	0.	11.	0.	1.	1.	12.8
291	Misc. Silicates	0.	0.	30.	58.	0.	5.	0.	4.	1.	0.	0.	28.8
152	Pyrite	0.	0.	0.	0.	0.	64.	0.	0.	0.	0.	36.	18.0
51	Calcite	0.	1.	0.	0.	0.	0.	0.	0.	98.	0.	0.	6.0
127	Misc. Mixed	1.	0.	18.	35.	2.	17.	2.	5.	17.	1.	2.	5.9
MINOR MINERALS:													
7	K-Feldspar	0.	0.	20.	52.	0.	2.	0.	23.	0.	1.	2.	1.4
1	Chlorite	0.	9.	20.	32.	0.	0.	0.	0.	3.	0.	36.	0.0
8	Montmorillonite	10.	0.	19.	67.	0.	0.	1.	0.	2.	0.	0.	0.4
11	Misc. sulf.	0.	0.	1.	4.	0.	50.	0.	0.	22.	0.	23.	0.2
1	Apatite	0.	0.	0.	0.	26.	5.	3.	0.	61.	5.	0.	0.1
1	Misc. Phosphate	0.	0.	44.	0.	37.	5.	0.	0.	14.	0.	0.	0.0
2	Fe-rich	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	100.	0.6
28	Mixed Carbonate	0.	4.	0.	2.	17.	2.	0.	0.	72.	0.	2.	2.3
3	Ti oxide	0.	0.	0.	0.	1.	0.	0.	0.	2.	97.	0.	0.1
1	Ti-rich	0.	0.	0.	11.	0.	0.	0.	3.	0.	86.	0.	0.0
1	Trace-comp	10.	0.	0.	8.	0.	22.	0.	0.	33.	0.	0.	0.1
9	Quartz-Sulfate	0.	0.	4.	56.	0.	32.	2.	5.	0.	0.	0.	0.2
3	Quartz-Pyrite	0.	0.	0.	47.	0.	36.	0.	0.	0.	0.	17.	0.0
62	Sil-sulf	0.	0.	26.	41.	0.	26.	1.	3.	1.	1.	0.	2.2
4	Silicate-Pyrite	0.	0.	16.	28.	0.	32.	0.	5.	1.	0.	16.	0.3
1	Alumina-rich	0.	0.	100.	0.	0.	0.	0.	0.	0.	0.	0.	0.1
1161	GRAND TOTALS	0.	0.	19.	44.	1.	16.	0.	3.	9.	0.	8.	100.0

Table 3-6. Mineral Size Distribution for the Pittsburgh Coal

MINERAL SPECIES	WT. %	Size Ranges (Microns)						
		0.1	2.5	5.0	10.	20.	40.	80.
		2.5	5.0	10.0	20.	40.	80.	500.
Quartz	11.1	10.	38.	21.	19.	3.	3.	7.
Kaolinite	9.2	3.	38.	23.	30.	5.	1.	0.
Illite	12.8	30.	51.	10.	6.	1.	1.	0.
Misc. Silicates	28.8	28.	53.	10.	5.	2.	1.	0.
Pyrite	18.0	3.	0.	14.	10.	16.	34.	23.
Calcite	6.0	2.	65.	13.	8.	5.	8.	0.
Misc. Mixed	5.9	62.	29.	5.	1.	2.	0.	0.
MINOR MINERALS	8.1	47.	34.	9.	6.	2.	1.	0.
GRAND TOTALS	100.0	21.	38.	13.	10.	5.	8.	5.

3.2.3 Mineralogy Illinois No. 6 Coal

The mineralogy of the Illinois No. 6 coal (Table 3-7) is more iron/sulfur rich than the previous two coals. Non-quartz silicate minerals, such as clays and miscellaneous silicates, make up approximately 40% of the mineral matter. 'Pure' pyrite, or pyrite that is not intimately associated with other minerals, accounts for almost 30% of the mineral mass. There is also a significant amount of pyrite associated with silicate minerals in this coal, as evidenced by the large number of silicate-sulfate and silicate-pyrite particles found during the analysis. In addition, the data in Table 3-8 indicate that the minerals in this coal have a very fine size distribution, with approximately 90% of the mass less than 20 μ m in size.

Table 3-7. Coal Mineralogy for the Illinois No. 6 Coal

#	MINERAL SPECIES	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Fe	Weight %
144	Quartz	0.	0.	0.	99.	0.	1.	0.	0.	0.	0.	0.	12.8
68	Kaolinite	0.	0.	46.	53.	0.	1.	0.	0.	0.	0.	0.	5.4
97	Illite	0.	0.	27.	53.	0.	5.	0.	11.	0.	0.	2.	11.1
273	Misc. Silicates	0.	0.	19.	64.	0.	9.	0.	6.	0.	0.	1.	22.9
260	Pyrite	0.	0.	0.	0.	0.	65.	0.	0.	0.	0.	35.	29.8
MINOR MINERALS:													
4	K-Feldspar	0.	0.	16.	51.	0.	12.	2.	17.	2.	0.	0.	0.1
2	Chlorite	0.	0.	19.	30.	0.	5.	0.	1.	0.	0.	45.	0.2
1	Montmorillonite	0.	0.	20.	77.	0.	0.	0.	0.	3.	0.	0.	0.0
3	Elem. Sulfur	0.	0.	0.	0.	0.	73.	10.	8.	0.	0.	0.	0.0
2	Ferrous Sulfate	0.	0.	0.	0.	0.	49.	0.	0.	0.	0.	51.	0.2
1	Gypsum	0.	0.	0.	0.	0.	47.	0.	0.	53.	0.	0.	0.0
24	Misc. sulf.	0.	0.	1.	8.	0.	67.	0.	1.	0.	0.	24.	1.5
3	Fe-rich	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	100.	0.3
53	Calcite	0.	0.	0.	0.	0.	0.	0.	0.	100.	0.	0.	3.2
7	Mixed Carbonate	0.	0.	0.	5.	7.	5.	0.	0.	68.	0.	14.	0.7
1	Ti oxide	0.	0.	0.	0.	0.	0.	0.	0.	0.	100.	0.	0.1
1	Ti-rich	0.	0.	0.	0.	0.	36.	0.	0.	0.	64.	0.	0.1
73	Quartz-Sulfate	0.	0.	4.	58.	0.	33.	0.	3.	1.	1.	0.	3.7
4	Quartz-Pyrite	0.	0.	0.	39.	0.	39.	0.	0.	2.	0.	20.	0.7
109	Sil-sulf	0.	0.	18.	40.	0.	30.	0.	8.	1.	1.	2.	4.1
4	Silicate-Pyrite	0.	0.	16.	44.	0.	21.	0.	9.	0.	0.	9.	0.3
56	Misc. Mixed	0.	0.	18.	38.	2.	23.	1.	8.	4.	0.	5.	2.7
1190	GRAND TOTALS	0.	0.	11.	42.	0.	27.	0.	3.	4.	0.	12.	100.0

Table 3-8. Mineral Size Distribution for the Pittsburgh Coal

MINERAL SPECIES	WT. %	Size Ranges (Microns)						
		0.1	2.5	5.0	10.	20.	40.	80.
		2.5	5.0	10.0	20.	40.	80.	500.
Quartz	12.8	3.	29.	34.	24.	1.	0.	7.
Kaolinite	5.4	2.	15.	31.	43.	6.	3.	0.
Illite	11.1	8.	48.	19.	21.	1.	2.	0.
Misc. Silicates	22.9	18.	41.	26.	13.	2.	0.	0.
Pyrite	29.8	2.	17.	20.	40.	13.	4.	3.
MINOR MINERALS	18.0	38.	23.	14.	14.	5.	4.	1.

GRAND TOTALS	100.0	13.	29.	23.	25.	6.	2.	2.

3.3 Trace Element Concentrations

In the past quarter trace element analysis of two coals by Neutron Activation Analysis (NAA) at MIT was completed. These data are presented in Table 3-9. It is interesting to note that the concentrations of arsenic and mercury were similar between the two coals. The selenium concentration was higher in the Elkhorn/Hazard coal. As these elements are commonly associated with pyrite one might expect their concentrations to be higher in the higher pyrite coal. The fact that the concentrations either stay the same or actually increase with decreasing pyrite content suggest that a significant fraction of these elements may be organically associated in the Elkhorn/Hazard coal. Leaching analysis of this coal at USGS is currently underway and will be completed in the next quarter.

Table 3-9. Trace Element Concentrations for Pittsburgh and Elkhorn/Hazard Coals

Element	Pittsburgh		Elkhorn/Hazard	
	Concentration (ppm)	σ (ppm)	Concentration (ppm)	σ (ppm)
Na	600	60	340	20
Sc	1.8	0.1	3.9	0.4
Cr	13	4	20	5
Fe	8220	790	2970	410
Co	2.5	0.3	6.2	0.5
Zn	17	5	18	5
As	4.1	0.9	4	1.1
Se	0.62	0.51	3.1	0.8
Br	17	2	25	3
Rb	8	0.1	5.1	1.1
Sr	160	60	120	70
Mo	0.85	0.18	4	1
Cd	0.06	0.013	0.31	0.07
Sb	0.26	0.03	1	0.1
Cs	0.55	0.19	0.45	0.09
Ba	110	20	130	10
La	4.5	0.1	14	1
Ce	8.8	0.3	27	4
Sm	0.78	0.05	2.5	0.2
Eu	0.2	0.06	0.37	0.12
Yb	0.38	0.06	1.4	0.2
Lu	0.063	0.005	0.24	0.02
Hf	0.44	0.04	1.1	0.2
Au (in ppb)	0.95	0.22	0.98	0.49
Hg	0.11	0.04	0.13	0.03
Th	1.2	0.1	4.3	0.5
U	0.31	0.15	1.9	0.8

SECTION 4

TASK 3 ANALYSIS OF COAL AND ASH FOR FORMS-OF-OCCURRENCE OF INORGANIC ELEMENTS

4. ANALYSIS OF COAL AND ASH FOR FORMS-OF-OCCURRENCE OF INORGANIC ELEMENTS

During the past quarter CCSEM analyses of the Elkhorn/Hazard, the Pittsburgh, and the Illinois No. 6 coals were completed. Summaries of these results were presented in Section 3 and will be discussed in more detail in future reports.

Previous programs at PSI and elsewhere have suggested that coal weathering, or oxidation of pyrite species, can significantly alter the form of arsenic in the coal. As the form of arsenic affects its partitioning during combustion, it is important to determine the degree of pyrite oxidation (and hence potential arsenate formation) in each coal. In the past quarter efforts were made to measure the forms of iron in the coal (to assess pyrite oxidation) and the forms of arsenic in the pyrite fractions. These results are discussed below. Further, ash samples obtained from MIT were analyzed by XAFS to determine the forms of arsenic, particularly the oxidation state of arsenic. These results are included with a discussion of the combustion experiments in Section 4.

4.1 Mössbauer

In the past quarter Mössbauer spectroscopy was used to measure the forms of iron in the three bituminous coals received to date. Mössbauer analysis of the Illinois No. 6 coal showed that >98% of the iron was in the form of pyrite. As can be seen in Figure 4-1 no silicate lines are visible in the spectrum. The two dominant features on the spectrum are indicative of an FeS_2 phase. The asymmetry of the two features suggests a significant amount of the marcasite phase may be present. Data for the Pittsburgh and Elkhorn/Hazard coals are shown in Table 4-1. Virtually all the iron in the Pittsburgh coal is present as pyrite, whereas almost one-third of the iron in the Elkhorn/Hazard coal is present in other forms (clays, siderite, and jarosite). The presence of jarosite (an iron sulfate) may be an indication of oxidation of pyrite in the coal. The Elkhorn/Hazard coal showed 12% of the iron as jarosite, while for the Pittsburgh coal only 2% jarosite was detected. Mössbauer data are consistent with the forms of sulfur analysis.

4.2 Forms of Arsenic

Based on a previous XAFS study of arsenic occurrence in U.S. bituminous coals, three forms of arsenic have been identified in these coals. Arsenical pyrite, in which arsenic substitutes for Fe in FeS_2 , is the most common. Arsenate compounds (AsO_4^{-3}) are the next most common and arsenopyrite (FeAsS) is the least common. Oxidation of arsenical pyrite has been shown to produce arsenate compounds. In the present work XANES spectroscopy for arsenic was conducted on both coals as well as on high density fractions (which are predominantly pyrite) separated by a float/sink technique using bromoform (Figure 4-2). Note that the raw coal samples of Pittsburgh and Elkhorn/Hazard coals each contain 4 ppm of arsenic.

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

Figure 4-1. Mössbauer spectrum for Illinois #6 coal.

Table 4-1. Mössbauer Data for Pittsburgh and Elkhorn/Hazard Coals

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

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

Figure 4-2. XANES spectra for Arsenic: Pittsburgh and Elkhorn/Hazard coals and high density fractions. Peaks corresponding to arsenate (A) and pyrite-associated (P) species are marked.

SECTION 5

TASK 5.1 BENCH SCALE STUDY OF TRACE ELEMENT AND CHLORINE
PARTITIONING (MIT)

5. BENCH SCALE STUDY OF TRACE ELEMENT AND CHLORINE PARTITIONING

In the past quarter, the Pittsburgh and Elkhorn/Hazard coals were size-segregated and density-segregated. The trace element concentrations in three density fractions and two size cuts of these coals were measured by NAA. Preliminary combustion experiments were also performed and samples sent to the University of Kentucky for XAFS analysis.

5.1 Size and Density Segregation

During the density and size-segregation a significant effort was devoted to repeating runs to ensure that the results were reproducible. In the preparation of the test samples, the coal was first put into seven standard (ASTM) sieves and was vibrated for 45 minutes. Since the fine particles adhere to the larger particles, a small vacuum was applied through the bottom of the sieve to separate and remove the fine particles. The homogeneity of the coal size fractions was examined using microscopy. It was found that the coals were in the well-defined size ranges.

The next step was to obtain density-segregated coals using the size segregated samples. An air separator, a small fluidized bed that was discussed in the previous Quarterly Report, was used to separate the coals into three different densities. Each time, samples of coal up to a height of 27 cm in the separator were utilized. Compressed Ar or He was the working fluid. First, a high gas flow rate was used to fluidize the coal particles well, then the flow rates were decreased gradually to the point when the particles were at the incipient fluidization velocity. The condition of incipient fluidization was maintained for about 5 minutes, and then the gas flow was stopped. A small vacuum pump was used to extract the stratified coals. The coals in the top 9 cm was selected as the low density fraction, and the coal in the bottom 9 cm as the high density fraction.

The trace elements concentrations in the splits from the Elkhorn/Hazard coal were analyzed NAA. The results are tabulated in Table 5-1. Based on these data it is interesting to note that:

- (1) Nearly all the concentrations of elements were higher in the high density fraction than that in the middle and the low density fractions.
- (2) The concentrations of Fe and As showed a major dependence on coal density.
- (3) The concentrations of Zn, Br, Cd and Hg showed a major dependence on coal particle size.

Table 5-1. Concentrations of Elements in Elkhorn/Hazard Coal (ppm)

	High 45<d<63	Medium 45<d<63	Low 45<d<63	High 90<d<106	Medium 90<d<106	Low 90<d<106
Na	283+20	235+16	245+16	300+20	220+15	203+13
Sc	3.9+.1	3.4+.2	3.6+.2	4.0+.3	3.8+.2	3.4+.2
Cr	17+1	14+1	15+1	13+1	14+1	12+1
Fe	4125+175	1428+75	1433+80	4055+210	1190+70	1073+70
Co	6.9+.4	5.7+.4	6.4+.4	6.5+.4	6.3+.4	5.7+.3
Zn	35+5	34+6	33+5	21+3	17+3	16+3
As	5.6+.6	1.8+.2	1.9+.2	2.6+.8	2.2+.3	1.4+.2
Se	3.3+.9	2.6+.8	3+.8	2.8+.7	3.8+.8	2.5+.7
Br	28+8	26+7	28+7	125+35	144+40	135+40
Rb	3.7+1.2	1.4+.6	2.9+1.2	2.5+1.5	2.7+1.4	2.6+1.6
Mo	4.2+1.0	3.4+.9	3.6+.9	2.8+.7	2.6+.7	2.3+.6
Cd	.17+0.12	.18+.11	.11+.07	.20+.19	.26+.2	.31+.12
Sb	1.1+.1	.89+.07	.97+.1	.85+.06	.86+.07	.79+.06
Cs	.23+.1	.22+.09	.30+.1	.25+.11	.34+.1	.29+.1
Ba	110+17	83+13	67+13	70+15	73+14	65+15
La	14+1	12+1	12+1	14+1	13+1	11+1
Ce	25+1	22+1	21+1	27+1	25+1	21+1
Sm	2.5+.2	2.2+.2	2.3+.2	2.6+.2	2.4+.2	2.1+.2
Eu	.37+.07	.41+.08	.34+.07	.57+.09	.45+.07	.37+.07
Yb	1.5+.0	1.3+.2	1.3+.2	1.5+.3	1.4+.2	1.2+.2
Lu	.23+.06	.22+.06	.23+.06	.24+.05	.23+.05	.21+.05
Hf	1.2+.1	.73+.06	.75+.12	1.3+.1	.86+.08	.82+.07
Au*	.88+.24	.73+.17	.71+.22	.58+.28	1.0+.3	.95+.29
Hg	.13+.03	.11+.02	.095+.03	.077+.023	.042+.021	.049+.021
Th	4.2+.2	3.6+.2	3.9+.2	4.4+.3	4.0+.2	3.6+.2

* ppb

5.2 Preliminary Combustion Experiments

Preliminary combustion experiments were performed on the 45-63 μm split of the Pittsburgh coal. This sample was burned in the laminar flow furnace at a gas temperature of 1700 K using a gas composition of either 20% O_2 in N_2 or 100% N_2 . XAFS analysis of the oxidation state of arsenic in the ash/char (Figure 5-1) shows that under 20% oxygen, virtually all the arsenic is present in the As^{+5} oxidation state. For the samples heated under pure nitrogen, the dominant oxidation state appears to be As^{+3} . However, 40% of the arsenic in these samples is in the +5 oxidation state. Whether the As^{+5} reflects oxidized arsenic (arsenate) present in the original coal remains to be demonstrated.

Figure 5-1. XAFS spectra from preliminary combustion experiments.

SECTION 6

TASK 8. INTEGRATED COMBUSTION STUDIES (PSI)

6. INTEGRATED COMBUSTION STUDIES

In the past quarter modifications were made to the PSI entrained flow reactor (EFR) to allow for better control of both the combustion conditions and the particulate sampling. Preliminary experiments were also performed to test the planned procedure for measuring gas phase mercury and to shakedown the furnace.

6.1 Modification of the EFR

In earlier experiments gases exiting the EFR passed directly into the building exhaust duct. This system was problematic, however, as the draw in the building exhaust was often insufficient to operate the EFR at or slightly below atmospheric pressure. To alleviate this problem a blower system was installed to allow the furnace to be operated in a balanced draft mode. The exhaust gases now pass through a lined airtight 55 gallon drum with cooling coils installed. The drum acts as an ash trap/baghouse to cool the gas, condense the moisture in the flue gas, and remove the particulate before the gases pass through a second blower. A filter is installed at the inlet of the blower, inside the barrel, to prevent particulate carryover. The gases then pass through the blower and a valve/rotameter assembly before exhausting to the building exhaust. By carefully monitoring the inlet gas flow, the pressure at the top of the furnace, and the exhaust flow we are able to operate the furnace under well controlled conditions. Leak rates from these measurements, defined as the difference between the inlet gas flowrate and the total gas withdrawal rate, are approximately 5% of the total flow -- within the measurement error for all the combined flowmeters.

The particulate sampling train was also modified to ensure reproducible and well defined gas and particulate sampling. A critical orifice was installed to provide a constant, and reproducible, flow of nitrogen into the water cooled nitrogen quench probe. This flow was also passed through a mass flow meter to provide a direct measurement of the nitrogen flowrate during sampling. A mass flow meter was also connected after the condenser at the exit of the impactor or filter holder to provide a direct measurement of the total sampling rate. These mass flow meters were carefully calibrated before being installed in the nitrogen and total sample lines. By obtaining an accurate measurement of the total flow through the sample probe, and the nitrogen flow into the sample probe, we can calculate the sampling flowrate from the furnace. These measurements are critical as even small variations in either flow can cause the sampling to be severely non-isokinetic.

6.2 Preliminary Combustion Experiments

The primary goal of the preliminary combustion experiments was to shakedown the modified EFR and at the same time test our sampling system for measuring mercury in the flue gas. In the first test the Pittsburgh coal was fed into the furnace at approximately 2.5 g/min. The furnace setpoint was 1500°C, and the total flow through the furnace was 28.3 slpm. This yields a stoichiometric ratio of 1.3. The water-cooled nitrogen quench probe was used to draw a sample from the reactor and quench it. The quenched sample was then passed through a quartz filter to collect the ash. A small slipstream, approximately 40 cc/min, was removed immediately after

the filter and passed through a dosimeter for a JEROME 431-X mercury vapor analyzer. These measurements indicated that the mercury concentration in the furnace was approximately $6 \mu\text{g}/\text{m}^3$ -- suggesting that approximately 50% of the mercury was in the gas phase at the furnace exit. This 50% partitioning was consistent with earlier experiments utilizing this coal (Bool and Helble, 1995).

Once the mercury measurements were complete we were forced to replace the furnace retort (a 62 in. long mullite tube). When this was completed a number of additional experiments were performed to determine the mass closure of the EFR. The conditions for these experiments were identical to the earlier experiments with the exception that the coal feedrate was changed to 2.7 g/min, yielding a stoichiometric ratio of 1.2. Several of these experiments utilized the nitrogen quench probe and a total filter to collect the ash samples. In others the entire flue gas stream was passed through a 1.5 m long tube with the same ID as the furnace, after exiting to allow the gas to cool before passing through a quartz filter. The mass closure in several of these experiments was extremely low. In addition, we found significant variations in the LOI (loss on ignition) in the ash. After performing several experiments we identified and remedied several minor problems, such as plugging of the coal pipe, and leakage from the top of the furnace. At the end of the quarter the system was sufficiently well characterized to begin the low pressure impactor experiments. These experiments are currently underway and are expected to be completed in the next quarter.

References

Bool, L.E., Senior, C.L., Huggins, F., Huffman, G.P., Shah, N., Wendt, J.O.L., Sarofim, A.F., and Zeng, T., Quarterly Report No. 2, DoE Contract No. DE-AC22-95PC95101

Bool, L.E., and Helble, J.J., *Energy and Fuels* (1995), **9**, 880-887 .