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TOXIC SUBSTANCES FROM COAL COMBUSTION -- A COMPREHENSIVE ASSESSMENT

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TABLE OF CONTENTS

Section Page

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LIST OF FIGURES

LIST OF TABLES

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 second quarter of this program. These accomplishments include the development of a summary of the deliverables required from each team member to successfully complete this Phase I effort. In addition, coal selection and acquisition of two coals was completed in the last quarter. These coals were sent for analysis and distributed to team members. Preliminary analysis of size-segregated Elkhorn-Hazard coal was completed by the MIT team. XAFS analysis was begun by the University of Kentucky team. Modification and refurbishing of the UA self-sustained combustor was completed. Finally, a detailed quality assurance/quality control list protocol and an experimental plan for the Physical Sciencs Inc. (PSI) integrated combustion studies was developed.

Specifically, in Section 3 of this report we define a detailed list of 'deliverables' expected from each group. During the kickoff meeting it was decided that a detailed list of data to be collected by each team member, and how that data will be used to develop ToPEM was critical to the success of this Phase I program. Therefore, Section 3 consists of a group by group breakdown of the critical experiments to be performed by each group, and a discussion of how that data fits into the overall program.

In Section 4 the four coals selected for this program are reported. These coals include a coal from the Pittsburgh seam (P8), a coal that consists of a mixture of the Elkhorn No.'s 1 and 3 and Hazard No. 4 seams (EH), an Illinois No. 6 coal (I6), and a coal from the

Wyodak-Anderson seam (WA) in the Powder River Basin. In the last quarter the Pittsburgh and Elkhorn-Hazard coals were procured from CONSOL. Data for the Elkhorn Hazard is presented.

In Section 5 preliminary XAFS analysis by UKy personnel is discussed. To date, these efforts have focussed on collecting XAFS data for standards in preparation for interpreting coal or ash data later in the program.

Section 6 consists of a discussion of trace element analysis (INAA) of two size fractions of the Elkhorn-Hazard coal. Several elements showed markedly different concentrations in these two size fractions. These data suggest that the iron bearing minerals, and the elements commonly associated with pyrite, are relatively fine (<38μm) particles. Construction of a non-solvent based apparatus at MIT for density segregation is also reported.

A discussion of the modifications to the U.Arizona self-sustained combustor is presented in Section 7. Modifications included addition of a baghouse and improvements in the on-line safety and analytical systems.

In Section 8 a detailed QA/QC protocol is presented. This protocol discusses important procedures for inspection and maintenance of sampling equipment, sample collection and handling, and data analysis. These procedures are designed to minimize the introduction of errors in these areas. A detailed experimental matrix for the Integrated Combustion Studies (Task 8) is also included. This matrix includes the critical questions to addressed in each test and the link between these tests and experiments to be performed by other team members.

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.

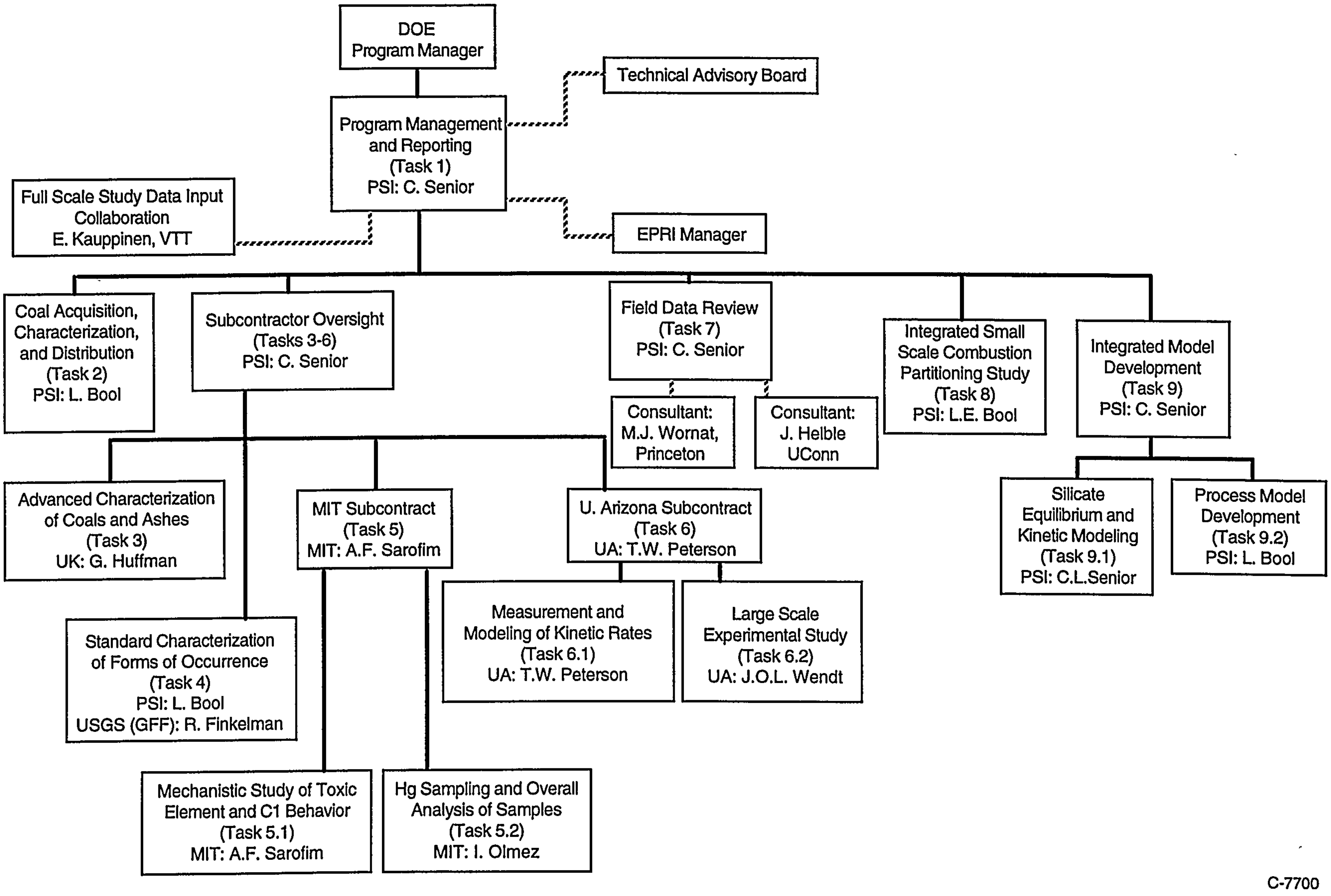

Figure 2-1. Project organization chart showing major tasks and lines of managerial responsibility.

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 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°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 ±2 μg/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.

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 pre-mixed 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 form 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 1. PROGRAM MANAGEMENT (PSIT)

3. PROGRAM MANAGEMENT

One of the comments that we received at the kick-off meeting was a request for a better definition of "deliverables," that is, the way in which individual program tasks are interconnected and contribute to the program goal of delivering a new model for toxic emissions from coal combustion. This quarter, more detail was added to the Management Plan on the relationship between individual contributors and the overall program deliverable.

The overall goal of the 5-year program is to develop a new tool called the Toxics Partitioning Engineering Model (ToPEM) which can be used to predict toxic emissions from coal combustion. The 2-year Phase I program will create the framework for ToPEM, while the 3-year Phase II program will create a final engineering model based on the integration with PSIT's existing Engineering Model for Ash Formation (EMAF) with wholly new submodels. Figure 3-1 illustrates the way in which each team member's work will contribute to the final (Phase II) engineering model.

Critical Hypotheses

In Phase I, our team will undertake experimental and theoretical investigations which will be needed to test hypotheses that underlie the structure of the model. These critical experiments are related to hypotheses about the emission of hazardous air pollutants (HAPs) from coal combustion.

- Emissions of organic HAPs from coal combustion for power generation are not significant compared to emissions of inorganic HAPs.
- The forms of occurrence of As, Cr, Hg, and Se in coal affect the partitioning between condensed and gaseous phases in the combustion zone.
- High temperature interactions between mineral species and vapor phase toxic species affects the partitioning between condensed and gaseous phases in the combustion zone for As, Cr, Hg, and Se.
- Certain constituents in the ash and/or unburned carbon can act as sorbents for the trace metals of interest in the post-combustion flue gas thereby removing vapor-phase species before condensation occurs.
- Speciation of chlorine in the post-combustion gas influences the emissions of inorganic HAPs.

Phase I Critical Experiments

Certain key results (from either experimental or theoretical efforts) will be needed to meet the program objectives in Phase I. These critical results are summarized below, followed by a list of key program milestones.

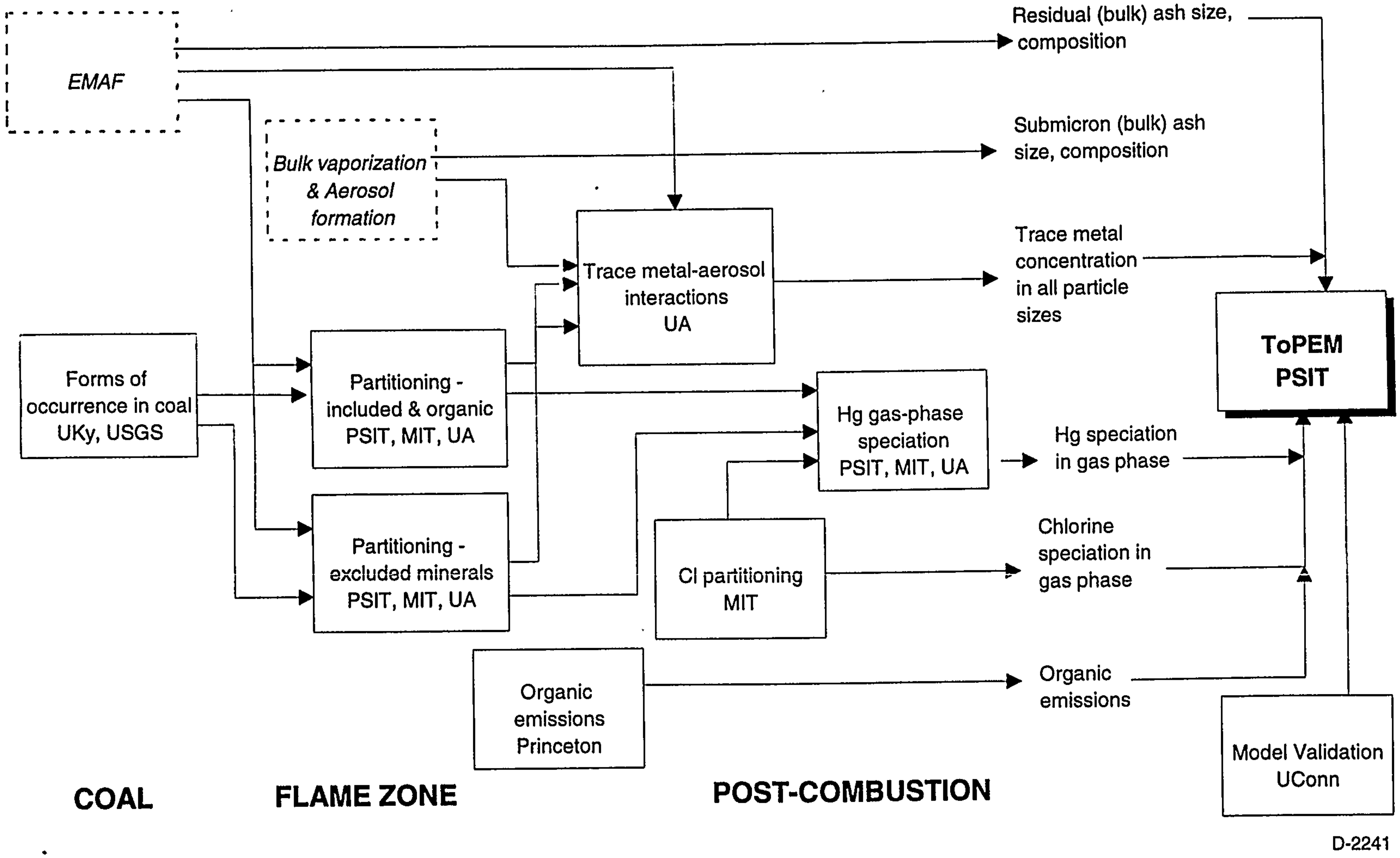

Figure 3-1. Elements of toxic partitioning engineering model: Phase I and Phase II.

1. USGS: Forms of occurrence of the trace metals of interest in the coal using the USGS protocol.
   - Forms of As, Se, Cr, and Hg in four program coals.

2. *UKy:* Characterization of coal mineralogy of the coal, XAFS determination of speciation of trace elements in coal, excluded minerals, and ash.
   - CCSEM analysis of mineral phases in four program coals
   - Forms of As, Se, Cr in program coals which have sufficiently high levels of the element of interest
   - Forms of As in density-separated coal provided by MIT
   - Forms of As Se, or Cr in ash (total filter or cyclone-separated) for up to four coals burned at baseline conditions by PSIT, UA, and/or MIT, plus CCSEM analysis of major phases in ash
   - Cl XAFS analysis of selected samples from combustion studies at PSIT and MIT.

3. *MIT (Olmez):* Neutron Activation Analysis (NAA) and mercury trap development.
   - NAA analysis of selected coal and ash samples
   - Specification of special low-background mercury traps
   - NAA analysis of carbon filters for mercury generated at PSIT.

4. *MIT (Sarofim):* Fundamental data on Cl and trace element partitioning using size- and density-segregated coals.
   - Vaporization data on As, Se, and Cr at various conditions which support a mechanistic interpretation of the phenomena for both included and excluded minerals
   - Provide density-classified coal samples for XAFS analysis on forms of As in excluded minerals
   - Concentration of chlorine compounds as a function of time and temperature in post-combustion gases calculated from full kinetic codes using representative time-temperature histories.

5. *PSIT:* Fundamental data on trace element partitioning in the flame zone at a higher level of complexity (i.e., using utility grind coals and controlled combustion conditions).
   - Concentration of As, Se, Cr, and Hg in ash as a function of particle size at various combustion conditions and at two gas temperatures for up to four program coals (utility grind) with a corresponding determination of vapor phase Hg
   - Gas phase equilibrium calculations for As and Cr partitioning between gas and silicate liquids in char particle
   - Mercury speciation in the gas phase for one coal and one combustion conditions at two different chlorine levels to assess $HgCl_2(g)$ formation using the ANET instrument prototype.

6. *UA (Wendt):* Fundamental data on trace element partitioning in the flame zone at a highest level of complexity (i.e.,using utility grind coals, self-sustained combustion, and more realistic post-combustion cooling).
    - Concentration of As, Se, Cr, and Hg in ash as a function of particle size and of Hg in vapor phase for combustion at staged and premixed conditions for one program coal (utility grind). If possible, Hg speciation measurements may be made in the self-sustained combustor using Method 29.

7. UA (Peterson): Determination of trace vapor-ash particle reactions rates in post-combustion gases.
    - Adsorption of gaseous As, Se, and Cr on selected substrates including flyash components as a function of time for different substrate temperatures under conditions representative of the post-combustion environment.

8. UConn: Field data review for program guidance and for model validation.
    - One or more sets of model validation data from DoE or EPRI field studies consisting of coal composition, combustion conditions, and concentrations of trace metals in solid and gaseous streams, including the effects of back end conditions on trace metal partitioning
    - Effect of coal type and combustion conditions on submicron ash morphology using VTT data.

9. *Princeton:* Review of organic air toxic formation and emissions.
    - Critical review of existing data on organic emissions from pc combustion.

Phase I Program Milestones

- Identify forms of occurrence of trace metals (As, Hg, Se, Cr) and mineralogy of four program coals.
- Identify forms of trace metals (As, Hg, Se, Cr) in ash generated from combustion of program coals.
- Identify "reactive" and "non-reactive" forms of trace metals in combustion zone (i.e., vaporization versus reaction with ash during combustion).
- Identify major minerals which have sorbent properties for trace metals of interest in the combustion and post-combustion zones.
- Quantify vaporization process for trace metals in flame zone: effects of temperature, O_2, particle size, etc.
- Identify conditions for post-combustion interaction of unburned carbon and trace metals, particularly Hg.
- Determine importance of chlorine on speciation of trace metals, especially Hg.
- Establish conceptual framework for Toxics Partitioning Engineering Model (ToPEM) based on PSIT's EMAF code.

SECTION 4

TASK 2. COAL SELECTION AND ACQUISITION (PSIT)

4. COAL SELECTION AND ACQUISITION

Four coals will be studied during this program. During the past quarter coal selection was finalized. The study coals will include: an Illinois No. 6 bituminous coal, a washed Pittsburgh seam bituminous coal, a bituminous coal from the Elkhorn and Hazard seams, and subbituminous coal from the Wyodak-Anderson seam in the Powder River Basin.

The Illinois No. 6 coal will be obtained from CONSOL. The coal is expected to be delivered to the Principal Investigators in late April. The coal will then be sent to a commercial laboratory for analysis. The coal data (ultimate, proximate, ash chemistry) will be dispersed to the team members when the analysis is complete.

The Black Thunder coal will be obtained directly from the mine through efforts by ABB, who will also use this coal on their DOE-funded ESP performance program. The coal and coal data will be delivered to team members when they become available.

The washed Pittsburgh coal was obtained from CONSOL late in the last quarter. Coal analysis (ultimate, proximate, ash chemistry) is currently underway and is expected to be completed in the next quarter. Samples of this coal have been delivered to the University of Arizona and the University of Kentucky. These samples have been stored under argon by these two team members. The remaining barrels were purged with argon at PSI. Three of these barrels will be returned to CONSOL for storage. Coal samples will be sent to the remaining team members in early April.

The Elkhorn-Hazard coal was also obtained from CONSOL in the last quarter. Samples of this coal have been delivered to MIT, U.Az., and U.Ky. These samples have also been stored under argon. A sample will be sent to USGS in early April. Four barrels of coal were purged with argon at PSI. Three of these will be returned to CONSOL for storage.

The coal data for the Elkhorn-Hazard coal can be seen in Table 4-1. This coal is a low sulfur "compliance" coal from eastern Kentucky, with only 0.84% sulfur. The coal contains 7.6% ash, with silica and alumina dominating the ash chemistry. Iron, on the other hand, makes up only 5.2% of the ash. This low iron content is probably due to a low pyrite content, and therefore low sulfur content. The concentration of two trace elements commonly associated with pyrite are also fairly low, with 1.00 and 0.05 ppm measured for arsenic and mercury, respectively. Trace element analysis (by neutron activation) and coal mineral analysis (by CCSEM) of this coal are expected to be complete in the next quarter.

Table 4-1. Coal Analysis of Elkhorn/Hazard Coal

	Dry Basis	As Received
Proximate (wt %):		
Fixed Carbon	57.80	56.46
Volatile Matter	34.61	33.80
Moisture	0.00	2.33
Ash	7.59	7.41
Ultimate (wt %):		
Carbon	76.66	74.87
Hydrogen	4.70	4.59
Nitrogen	1.46	1.43
Sulfur	0.84	0.82
Oxygen	8.58	8.38
Chlorine	0.17	0.17
Moisture	0.00	2.33
Ash	7.59	7.41
Trace Elements (ppm):		
Arsenic		1.00
Mercury		0.05
Ash Composition (wt%):		
SiO_2	55.83	
Al_2O_3	34.27	
Fe_2O_3	5.18	
TiO_2	1.71	
CaO	1.84	
MgO	0.60	
Na_2O	0.32	
K_2O	1.53	
SO_3	1.45	
P_2O_5	0.23	

SECTION 5

TASK 3. ANALYSIS OF COAL AND ASH FOR FORMS-OF-OCCURRENCE OF INORGANIC ELEMENTS (U Ky)

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

In this portion of the project, to be carried out by University of Kentucky personnel, the modes of occurrence of various trace elements that have been designated as potential hazardous air pollutants (HAPs) in the 1990 Amendments to the Clean Air Act are to be determined in coal and ash samples generated by other groups in the project. This information will be complemented by determination of the mineralogy of the coals so that an overall understanding of both elemental modes of occurrence and the association of trace elements with major minerals can be obtained for the coals to be investigated.

The principal technique that is being utilized by University of Kentucky personnel for characterization of trace elements is X-ray absorption fine structure (XAFS) spectroscopy. Our initial studies[1,2] demonstrated that this technique has an unparalleled ability to probe a complex material such as coal or ash and obtain information about the local structure and bonding of a specific element at concentrations as little as 5 ppm. From this information, the mode of occurrence of the element in the coal or ash can often be deduced. Such information is basically a description of how an element occurs in coal or ash and is complementary to information on the concentration of the element or how much of an element is present in the coal or ash. Information on both the concentration and the mode of occurrence is necessary to understand fully the behavior of an element during combustion and for assessing the potential threat to human health posed by the "air-toxic" group of trace elements.

The approach we are taking to determine elemental modes of occurrence in this project is to examine not just the coal itself but also ash-rich and ash-poor fractions generated from the coal by float/sink or other physical separative method. We have found[3] that such an approach is much more definitive in establishing the mode of occurrence, particularly when the mode of occurrence consists of more than one significant elemental form. Furthermore, this approach clearly ties in well with investigation of removal of HAPs using physical coal cleaning methods.

XAFS spectroscopy of trace elements will be carried out at a synchrotron X-ray source, either the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory, New York, or the Stanford Synchrotron Radiation Laboratory (SSRL) at Stanford University, California. As we have done in earlier work[1-3], a 13-channel germanium solid-state detector will be used to maximize the signal/noise ratio of the XAFS spectrum. Other signal-enhancing devices, such as filters and multiple scans, will also be used whenever necessary.

In addition to XAFS spectroscopy, we will also be characterizing the mineralogy of the coals and coal fractions by using a combination of iron Mössbauer spectroscopy and computer-controlled scanning electron microscopy (CCSEM). Such techniques proved valuable in earlier work[4] for providing a mineralogical description of the coal for interpretation of the behavior of major minerals in coal combustion. In the present investigation, such studies should provide information on the association of individual trace elements with specific minerals. Both Mössbauer spectroscopy and CCSEM analysis will be carried out at the University of Kentucky.

As the experimental portion of this program is in the inital stages, efforts in the last quarter have focussed on improving the XAFS database for various HAP elements, notably Cr and As. As a result, we have re-examined many of the data we have obtained on standards and coals in previous investigations and are now better aware of correlations between standard spectra and the gaps that need to be filled in the database. Much of this work was presented in two invited review papers on XAFS spectroscopy of elements in coal that have been accepted for publication. [5]

References:

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5. F. E. Huggins, and G. P. Huffman, Modes of occurrence of trace elements in coal from XAFS spectroscopy. to be published in Int. J. Coal Geol. F. E. Huggins, and G.P. Huffman, Application of XAFS spectroscopy to coal geochemistry. to be published in Geochim. Cosmochim. Acta (R. G. Burns, Mem. Vol.).

SECTION 6

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

6. BENCH SCALE STUDY OF TRACE ELEMENT AND CHLORINE PARTITIONING

In the experimental effort at MIT size and density classified coal samples will be combusted under a wide range of combustion conditions in the MIT droptube reactor. In the past quarter, the first coal, the Elkhorn-Hazard coal, was size classified into three size cuts using standard sieves. The two size cuts containing the bulk of the mass, less than 38 μm and greater than 75 μm, were analyzed by Instrumented Neutron Activation Analysis (INAA) to explore differences in the trace element concentrations between the two size cuts. These data, shown in Table 6-1, suggest that the concentrations of some elements differ substantially between these two size cuts. For example, the iron concentration is significantly higher in the <38 μm size cut. This suggests that the dominant iron form, possibly pyrite, either is included (inside the carbon matrix), or is found in small excluded particles. The difference in the iron concentration may also explain the noted differences in the concentrations of the other elements. Most of the elements showing significant changes in concentration between the two size classes are commonly associated with pyrite. For example, the arsenic and selenium concentrations show the same trend of concentration versus size seen in the iron. Therefore it is likely that the concentration differences between the two size cuts is due largely to differences in the iron-compound (i.e., pyrite) concentration. Further analysis by CCSEM, Mössbauer, and the USGS protocol will be required to fully resolve this issue.

Another task begun in the last quarter was the design and fabrication of a density segregation device. As the trace elements of interest may react with the solvents commonly used in liquid based density separation techniques, a device is being built that uses air to avoid contamination of the samples. This apparatus is similar to that used by Hurt et. al[1] for separation of char from fly ash. A size classified sample is placed into a chamber and air is introduced until the bed is almost fluidized (incipient fluidization). In this bed, higher density particles settle to the bottom of the bed while low density particles float on the top. By carefully removing the segregated layers it is possible to collect uncontaminated density segregated samples. Fabrication and testing of this apparatus is expected to be complete in April, and will lead to size and density segregation of a program coal for testing in the next quarter.

References:

1. Hurt, R., Davis, K., Yang, N., and Hardesty, D., The Organic and Properties of Unburned Carbon From Pulverized-Coal Combustion, Final Report to EPRI (Report No. TR-105743), Sandia National Laboratories, November, 1995

Table 6-1. Trace Element Concentration in Two Size Cuts of the Elkhorn-Hazard Coal

Element	$d_p < 38$ µm (ppm)	$d_p \geq 75$ µm (ppm)
Na	255.10	175.84
Sc	39.89	35.82
Cr	18.45	13.79
Fe	3881.11	1246.81
Co	6.36	6.54
Zn	17.43	3.08
As	5.86	2.72
Se	3.18	2.17
Br	25.32	63.97
Rb	8.17	3.54
Sr	142.31	107.96
Zr	31.57	115.81
Mo	4.09	3.42
Ag*	189.50	43.70
Cd*	120.24	275.95
Sb	1.14	0.85
Te*	39.39	36.88
Ba	179.83	81.54
Ce*	508.69	221.97
Nd	12.99	11.47
Gd	3.34	2.68
Yb	1.60	1.37
Hf*	1228.71	937.94
Ta*	192.23	90.68
W*	384.95	274.96
Ir*	13.09	8.61
Au*	179.35	69.78
Th	4.14	3.91
U	2.03	3.84
Hg*	126.24	148.04

* concentration in ppb

SECTION 7

TASK 6.2 LARGE SCALE COMBUSTOR STUDIES (UA)

7. LARGE SCALE COMBUSTOR STUDIES

Work this quarter focused on improving the pilot-scale downflow laboratory combustor ("furnace") system which will be utilized for Task 6.2 work activities. A new baghouse was constructed and installed to reduce toxic emissions from the furnace. The bottom section of the furnace was completely rebuilt to improve the ability to safely remove and dispose of accumulated solid debris.

Concurrent to these physical modifications, the instrumentation and controls associated with the combustor were improved. Safety interlocks were installed to reduce the hazard potential during furnace operation. Additionally, a new instrument control system was designed and installed for controlling the pressure (vacuum) throughout the furnace. Improved pressure and temperature monitoring equipment were also installed. The CO analyzer was completely rebuilt. Modifications began to the labtech control system to accommodate improved data collection. This modifications will be completed next quarter.

In addition, 850 pounds of ground East Kentucky coal were received. The barrels were blanketed with Argon to avoid specie transformation due to oxygen and nitrogen contamination.

Parametric testing of the furnace using natural gas is scheduled for next quarter. These tests will be used to determine the baseline leakage rate of air into the furnace through the furnace walls (the furnace operates at a vacuum). The labtech control configuration will be finalized and loop tuning will be accomplished during these tests. In addition, a new sample probe will be designed and constructed for use in the upcoming test runs.

SECTION 8

TASK 8. INTEGRATED COMBUSTION STUDIES (PSIT)

8. INTEGRATED COMBUSTION STUDIES

One of the goals of this Task, and of the program as a whole, is to collect quality data on trace element partitioning in an efficient, timely fashion. To ensure that the data collected by all the investigators in this program is of the highest quality, a quality assurance/quality control (QA/QC) document was drafted during the last quarter. This protocol is outlined in detail below. In addition, to maximize the efficiency of the integrated combustion studies a detailed experimental matrix was compiled during the last quarter. This matrix is discussed in detail in Section 8.2.

8.1 QA/QC Protocol

In order to maximize the quality of the data collected in this program, and enhance our abilities to draw meaningfully conclusions from these data, it is important to follow some basic QA/QC procedures. These fall into four major areas; experimental and sampling equipment, sample collection and handling, analytical procedures (i.e. AA procedures), and data analysis. Although a wide range of experimental facilities and analytical techniques will be used in this program, there are several general QA/QC protocols that **must** be followed in each of these areas.

General protocols are discussed below. This list is considered a *minimum* effort for QA/QC, individual facilities may require additional procedures. (Note: in the discussion below a "run" denotes a sample collection run in an experiment.)

8.1.1 Experimental and Sampling Equipment

The goal of the QA/QC efforts in this area are to minimize errors associated with faulty experimental equipment or sampling equipment. This can be accomplished by the following steps outlined below.

- All flow meters must be calibrated. Temperature and pressure corrections should be included as part of this calibration procedure.

- Coal hoppers, etc., should be cleaned as well as possible between coals to prevent cross-contamination. Specifically, the hoppers should be completely vacuumed clean of coal and wiped down to remove all the coal.

- Sources for possible metal contamination in the coal feeder, gas lines, high temperature furnace, etc, such as screws rubbing against transport tubes, should be identified and removed.

- The reactor should be 'cleaned out,' run at temperature with gas flows, but with no coal (or vapor) feed, between experiments with different coals (or vapors) to prevent cross contamination. This will serve to clean out any loose ash or vaporizable material from the reactor before the next experiment. This must be done with **all** reactors, from the TGA to the self-sustained combustor, in this program.

- The experimental apparatus must be inspected for leaks before each experiment. Areas to examine include faulty seals, furnace retort cracks, leaking cooling jackets, leaking air and coal feed lines.

- The sampling apparatus must be visually inspected before each experiment. During long experiments (over 5 hours) the sampling apparatus should be re-inspected. Areas to examine include faulty seals (such as impactor o-rings), leaking sample lines, leaking air/nitrogen lines, cleanliness of sampling equipment. Leakage of the sampling equipment will be addressed under the next topic.

8.1.2 Sample Collection and Handling

The information presented in this section deals with protocols for sample collection during combustion experiments and with the handling of the filters, etc, before and after sampling for **all** experiments. Given the trace concentrations of the elements of interest, it is extremely important to avoid contamination of the samples. In addition, it is critical to record **all** important sampling information on data sheets and to accurately label the samples. These points are discussed in more detail below.

Sample collection:

- A 'blank' sample must be collected as part of each experiment to track the cleanliness of the reactor. For example, the filter blank could consist of a total filter sample collected from the furnace with all experimental conditions, such as gas flows and temperature, set at the appropriate values but with no coal (or vapor) input. This sample will provide a check against material shedding or vaporizing from the walls and contaminating the samples.

- Sample lines, probes, etc. should be blown out with compressed air between runs to prevent ash 'carry over' from one run to the next.

- Before each experiment, and after at least every third sample run, the sampling system must be checked for leaks. In some systems this can be accomplished by sampling a pure nitrogen stream from the reactor and measuring the oxygen concentration in the sample gas. Other systems can be sealed under vacuum to check for air-tightness. If a leak is found it must be quantified. If the leak is greater than 4% of the desired sample rate the sample system must be repaired before further runs are attempted.

- Sample collection from flue gas streams (i.e. at the PSIT EFR and the UAz self-sustained combustor) should be as isokinetic as possible. Samples varying from isokinetic by more than 20% must be corrected as discussed in the data analysis section.

- Before each experiment on any of the facilities in this program, all of the goals of the experiment and the planned experimental parameters must be clearly defined in a experiment log sheet contains, at minimum:
  - — fuel or vapor identification,
  - — temperature and pressure,
  - — coal and furnace gas rates,
  - — gas composition.

- For *each run* a data sheet must be filled out. This applies to **all** experiments under this program. The sample rates, including the quench rate, etc, must be calculated and reported on this sheet. These sheets should be completed in ink and stored with the resulting data for these runs (i.e.; ash mass distributions) and the experiment sheet outlined above. These data sheets must be written such that a qualified analyst from DoE or any of the team members can independently evaluate the sampling *without* additional data. Critical information includes:
  - — the date and time of the sample period,
  - — the operator's signature,
  - — the *actual* values for the experimental parameters outlined above during the sampling period,
  - — type of sample collected (impactor, total filter, etc),
  - — sample rates (including total flue gas sampled) and quench rates,
  - — total sampling time,
  - — sample run identification string (see sample handling section),
  - — any abnormal occurrences and the steps taken to compensate during the sample period (this includes the sample system *and* the experimental system) -- this is critical for data analysis as discussed later.

- Impactor plates, filter holders, and substrate supports (ie; for the TGA) must be cleaned well with reagent grade solvents between each sample run. Impactor stages should also be cleaned in an ultrasonic bath to clean material from the jets.

- Clean disposable gloves must be worn when handling samples or sampling equipment.

Sample handling:

- Filters, impaction substrates, and ash (or sorbent) samples should be stored in air-tight petri dishes. Air-tight dishes can be purchased from Fisher (cat No. 08-757-105).

- Petri dishes for sample storage should be soaked in a 1:3 solution of reagent grade nitric acid and DI water for 4 hours and air dried.

- Filters and impaction substrates should be made of 'clean' material, such as teflon or polycarbonate, that doesn't contain the species of interest -- no paper or glass filters.

- Impactors and filter assemblies **must** be assembled and disassembled in a clean, dust-free environment. Replacing filters or impaction substrates in the furnace region is **not** acceptable. Sampling equipment (impactors, cyclones, and filter assemblies) must be sealed with a cap or teflon tape when not connected to the sampling system and in use.

- Samples must be removed from the impactor/filter assembly and immediately placed into the cleaned petri dishes.

- Petri dishes ***must*** be labeled with the run and sample identification *as soon as the samples are placed in the petri dish.* An example of an appropriate run ID is:

  wP8-2-imp-im1

  indicating the coal- run number with that coal - type of sample - sample ID (im1 indicates impactor stage 1).

- At the end of each experiment all data sheets should be checked for completeness.

- All foreign material, such as old samples, powders, and food, must be removed from both the sampling area and the sample handling area.

- As the integrity of some samples may degrade over time, samples should be analyzed as quickly as possible (less than 2 weeks recommended). Liquid samples, from EPA method 29 for example, must be stabilized per EPA recommendations.

- Duplicate samples not immediately analyzed should be stored in cool, clean, dry environments, preferably in a desiccator. These samples must be clearly labeled for the following:
  - time and date samples were collected (in addition to normal ID code discussed above),
  - time and date samples were placed in storage, and by whom.

- Coal samples **must always** be stored under Argon to prevent oxidation. After a sample is removed for use in an experiment the remainder must be purged with argon.

- Clean disposable gloves must be worn during coal handling. Containers used to transport coal (eg; scoops) should be as clean as possible (e.g. wiped clean with a solvent). Plastic scoops, etc, are preferable and should be leached with an HNO_3-DI water solution before their first use.

- Care should be taken to minimize contamination of samples from all the metal parts of sampling equipment. For example, metal parts showing signs of corrosion should be replaced to prevent metal contamination of the sample. Another example is impactors with metal hold-down rings on each stage (i.e.; the PSIT BLPI). The impaction substrates must be greased such that the grease does not contact the metal ring.

8.1.3 Analytical Instrumentation and Laboratory Analysis

The previous two sections outline several important QA/QC procedures to minimize errors associated with the collection and handling of trace element samples. This section discusses issues related to the analytical tools and laboratory techniques used to analyze these samples. Although various certified laboratories and expert analysts will be used in this program for sample analysis, some team members will also perform in-house analysis of their ash samples. Therefore, the QA/QC procedures outlined below include both procedures applicable to certified or expert laboratories and in-house analysis, and procedures for groups performing in-house analysis. The second set of procedures are normally performed as part of sample analysis by certified laboratories or expert analysts. However, it is important to request copies of the laboratory's QA/QC procedures.

The sample analysis QA/QC issues are discussed in detail below. As previously mentioned, this list represents the *minimum* QA/QC effort for sample analysis -- individual techniques may require additional steps.

Procedures For All Samples Analyzed:

- An NIST Standard Reference Materials (SRM) coal fly ash (available from PSI) will be used to determine the accuracy and precision of both the pre-analysis sample preparation and the analysis. For example, some problems occur when digestion methods used to liberate the metals, etc, from the ash are changed -- leading to incomplete digestion. The fly ash standard should be sent in as a 'blind' sample to test the digestion technique and the analytical technique.

- The recovery of elements in the SRM material must be 100 ± 15%. The recovery is calculated as:

$$\text{Recovery (\%)} = \frac{C_{\text{analysis}}}{C_{\text{standard}}} \times 100\%$$

- Replicate samples must be analyzed to check precision. For example, multiple samples of the certified SRM ash can be analyzed "blind" to determine the variability of the analysis. Ash samples with sufficient mass can also be divided into two samples for analysis to provide replicates.

- The precision of the data, expressed as the relative percent difference (RPD), must be <20%. The RPD will be calculated as:

$$\text{RPD (\%)} = \frac{C_1 - C_2}{\left(\dfrac{C_1 + C_2}{2}\right)} \times 100\%$$

where C_1 is the concentration of a given element in the first sample and C_2 is the concentration in the duplicate sample.

- Sample "blanks" (eg; greased or ungreased filters) must be analyzed frequently to determine background concentrations. Background concentrations **must** be determined by every analytical tool used. For example, background concentrations determined from AA or ICP-MS can **not** be used to correct INAA results.
- Detection limits must be determined for each sample and analytical technique. For example, if a given analytical tool and procedure has a detection limit of 1 ng, then the overall detection limit (ppm) will be different for a 10 mg sample than for a 0.1 mg sample. The detection limit for the first sample would be 0.1 ppm, while the detection limit for the second sample would be 100 ppm. The detection limit can be calculated from:

$$\text{Limit (ppm)} = \frac{\text{Instrument limit (ng)}}{\text{sample mass (mg)}}$$

- If any sample fails the QA/QC analysis, it must be reanalyzed. For example, if the recovery of elements from the SRM ash fall outside the range given above, the samples must be reanalyzed to explain the discrepancy.

For In-House Analysis (e.g. AA or ICP-MS):

- Blanks must be used to monitor contamination of reagent solutions and instrument drift.
- The instrument must be calibrated with certified standards at least every 10 to 20 samples.
- A solution of known concentration (made from the certified standards) should be analyzed frequently to monitor drift. Greater than 10% variation from the known value indicates that the instrument must be recalibrated.

8.1.4 Data Reduction and Validation

A critical aspect of our program is the final data reduction and validation. The data obtained from analysis of the ash samples (e.g., masses of individual elements in a given sample) must be reduced to a form that can be cross-compared among the various team members. For example, elemental masses in impactor samples must be converted to mass concentrations to determine the particle size dependence of the concentration suggestive of condensation. It is critical that the data reduction be performed carefully and that outliers be identified. This step will provide the final determination of the confidence with which our data can be used to define important mechanisms.

Critical points are as follows:

- All of the calculations involved in the data reduction must be carefully checked. These calculations must be periodically checked by people who did not take the data. For example, Connie Senior will periodically check the PSIT data reduction calculations. Hard copies of all spreadsheets or program output files for the data reduction calculations should be stored with the raw data sheets.

- All data, including outliers, will be considered valid and reported. If unusual results are obtained, efforts will be made to identify the causes, such as errors in sample handling. For this reason it is extremely important that *each sample* is very well documented. If errors leading to the unusual data can be identified, they should be reported with the data to qualify the results.

- When target compounds are below the detection limit, as defined by both the volume of gas sampled and the detection limit of the analytical tool, a "less than" value should be reported.

- Mass closure should be reported for each element of interest for each sample (or cumulative samples in impactors). Mass closure will be defined as:

$$\text{Closure (\%)} = \frac{C_{\text{gas sampled}}}{C_{\text{flue gas}}} \times 100\%$$

  where $C_{\text{gas sampled}}$ is the concentration of the element in the gas sampled by the impactor as calculated from the total mass of the element collected in the sample run and the total volume of gas ($\mu g/Nm^3$). $C_{\text{flue gas}}$ is the concentration of the element in the furnace as calculated by the fuel and gas feedrates. Mass closure should be 100 ± 25% (100 ± 15% is desired).

- Duplicate samples in a given experiment must be used to ensure reproducibility. For example, mass distributions in impactor samples taken under identical conditions should satisfy the RPD criterion discussed in Section 8.1.3.

- "Non-reactive" tracer elements could be used to verify impactor performance. Further, major species whose behavior is better defined, such as Na and K, can be used as a tracer element for vaporization.

- Error analysis must be performed and errors reported when data are reported. The reported errors should be cumulative and include errors associated with sampling and sample analysis. For example, the error in a reported elemental concentration must include the errors associated with:

- — weighing the sample,
- — collecting the sample, including the sample to sample variation in the mass collected at a given condition,
- — analyzing the sample.

The equations used to estimate the errors can be obtained from standard statistics references.

- All calculations, such as conversion of mass data to concentrations, will use the measured values for that particular sample, not averages for a number of samples (replicates) or values from other runs. Similarly, mass closure calculations will utilize the isokinetic sampling rate from that particular sample run. Averages will also be calculated from the replicate samples to determine the standard deviations (90% confidence intervals) of the data.

- If the isokinetic sampling ratio for a given sample is outside the 100 ± 10% range, but within 100 ± 50%, the concentration of the largest concentration range will be corrected according to Shigehara.[1] Both the corrected and the uncorrected data will be reported. If the isokinetic ratio is outside the 100 ± 50% range the data will be discarded.

$$C_{\text{corrected}} = C_{\text{measured}} \frac{\text{Isokinetic percent}}{100}$$

$$C = \frac{C_{\text{measured}} + C_{\text{corrected}}}{2}$$

8.2 Experimental Plan for Integrated Combustion Studies

One of the unique aspects of this program is that investigators from several institutions are working in concert to use their specific tools and expertise to develop a model to predict toxic element partitioning during combustion. To maximize the usefulness of this team approach, it is important that each institution understand where their individual efforts fit into the overall program. Further, it is important that team members from each institution devise experimental plans that answer specific questions and enhance or build upon the efforts of other team members. With this goal in mind a detailed experimental plan was developed during the last quarter for the integrated combustion studies at PSI. This plan is outlined in Table 8-1. The experiments are divided into four major groups. In Table 8-1 the conditions for each set of experiments, the data to be collected, the objectives of the experiment, and the relationship of the results to the efforts of other team members are outlined.

The first set of experiments, designated as the baseline, are designed to determine whether the mineralogy of the coals and the trace element associations affect trace element partitioning. If this is the case it will be important to explore the effect of the reactive minerals (e.g. pyrite). In addition, if there is evidence for post-flame capture of specific elements

Table 8-1. PSIT Phase I Experiments

SR = 1.2 T=1500 °C	SR=0.6 T=1500 °C	SR=0.9 T=1500 °C	SR=1.2 T=1300 °C	High Cl vs low Cl SR=1.2,T=1500°C
Total filter, total Hg, and Hg speciation, BLPI	Mark III Impactor, total Hg	Mark III Impactor	BLPI Mark III Impactor, total Hg	Total filter, total Hg, Hg speciation
Does mineralogy affect vaporization? Does mineralogy affect post-flame capture?	Do combustion conditions affect vaporization or capture?	Is there a significant change in partitioning as LOI changes?	Does temperature during combustion affect partitioning?	Does chlorine content affect partitioning and Hg speciation at furnace exit?
YES: Define reactive vs non-reactive forms. FURTHER WORK BY MIT. Identify major minerals with sorbent properties. FURTHER WORK BY UA.	YES: Effects of LOI and/or char conditions during combustion. FURTHER WORK BY MIT.	YES: Properties of high carbon ash as sorbent? FURTHER WORK BY UA.	YES: Define parameters for vaporization rate. FURTHER WORK BY MIT.	YES: Define Phase II experiments.
	NO: Vaporization occurs during devolatilization/ pyrite oxidation only.	NO: What else affects Hg partitioning? Define Phase II experiments.	NO: Vaporization occurs during devolatilization/ pyrite oxidation only.	NO: Post-combustion conditions are more important. FURTHER WORK BY UA.

(e.g. capture of arsenic and selenium by calcium) we will try to determine the minerals that act as effective sorbents. In the next two sets of experiments, stoichiometric ratios of 0.6 and 0.9, we try to determine when vaporization occurs from the organic matrix, and whether there is an effect of unburned carbon on the trace element partitioning. These results will tie into the work to be performed by MIT and the University of Arizona. In the last set of experiments we will explore the effect of chlorine (as HCL) on the partitioning of mercury. Specifically, we will determine if the addition of chlorine changes the partitioning of mercury between the vapor and condensed phases and between elemental and oxidized mercury. These experiments will play an important role in determining the partitioning of mercury in combustion environments, and will lead directly to the experiments planned in Phase II of this program.

<u>References:</u>

1. Shigehara, R.T., "A Guideline for Evaluating Compliance Test Results (Isokinetic Sampling Rate Criterion) ," Emissions Measurement Branch, EPED, Office of Air Quality and Standards, U.S. Environmental Protection Agency