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FUNDAMENTAL STUDY OF ASH FORMATION AND DEPOSITION: EFFECT OF REDUCING STOICHIOMETRY

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SECTION 1

EXECUTIVE SUMMARY

1. EXECUTIVE SUMMARY

The technical objectives of this project are:

a. To identify the partitioning of inorganic coal constituents among vapor, submicron fume, and fly ash products generated during the combustion of pulverized coal under a variety of combustion conditions. Fuel lean and fuel rich combustion conditions will be considered.

b. To identify and quantify the fundamental processes by which the transformations of minerals and organically-associated inorganic species occurs. Emphasis will be placed on identifying any changes that occur as a result of combustion under sub-stoichiometric combustion conditions.

c. To incorporate the effects of combustion stoichiometry into an Engineering Model for Ash Formation based upon the understanding developed in (a) and (b). When completed, this model will predict the particle size and chemical composition distributions of ash formed during the combustion of pulverized coal under a broad range of conditions.

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

During the ninth quarter of this project, groups focused on concluding their programmatic activities and beginning to draft the final report. In this report, an outline of the draft final report is presented.

SECTION 2

OVERVIEW OF PROGRAM TASKS
(PSI Technologies)

2. OVERVIEW OF PROGRAM TASKS

This project is designed to examine the effects of combustion stoichiometry on the fundamental aspects of ash formation and ash deposit initiation. Emphasis will be placed on reducing stoichiometries associated with low-NOx combustion, although a range of oxidant/fuel ratios will be considered. Previous work has demonstrated that ash formation depends strongly upon coal mineralogy, including mineral type, size, amount, and the presence of organically associated inorganic species. Combustion temperature and the oxidation state of iron will also play a significant role. As these latter items will vary with changes in stoichiometry, research to determine the net effect on deposition is required.

To achieve these goals, a research program with the following technical objectives will be pursued:

1. identify the partitioning of inorganic coal constituents among vapor, submicron fume, and fly ash products generated from the combustion of pulverized coal under a variety of combustion stoichiometries. Fuel-lean and fuel-rich combustion conditions will be considered.

2. identify and quantify the fundamental processes by which the transformation of minerals and organically-associated inorganic species occur. Identify any differences from standard pulverized coal combustion conditions.

3. modify, to incorporate the effects of combustion stoichiometry and based on the understanding developed in (1) and (2) above, an Engineering Model for Ash Formation. The previously developed model is capable of predicting the size and chemical composition distributions of the final ash products under standard pulverized coal combustion conditions of 20% excess air. These modifications will extend the model to include phenomena that may be dominant under a broad range of stoichiometries.

Experiments, sample analyses, and modeling will be conducted at several facilities as part of this program. Detailed coal and ash sample analysis using Mössbauer spectroscopy, x-ray absorption fine structure spectroscopy (XAFS), and computer controlled scanning electron microscopy will be carried out at the University of Kentucky (UKy). Small-scale drop tube combustion tests using size and density classified coal samples and possibly synthetic char samples will be carried out at the MIT to determine the extent of mineral coalescence and inorganic vaporization as a function of combustion stoichiometry. Combustion experiments utilizing utility grind coals will be conducted at PSI to examine the effects of stoichiometry on mineral interactions. Deposition experiments using ash generated from combustion experiments and using pure minerals will also be conducted to investigate deposit initiation as a function of combustion conditions. The engineering model for ash formation (EMAF) will be modified to include effects of combustion stoichiometry as part of this effort. Self-sustained pilot scale combustion experiments will be conducted in the University of Arizona (UA) 100,000 Btu/h facility to address issues of scaling in combustion processes. The interaction of iron with aluminosilicates as a function of changing combustion conditions will be the focus of this effort. Modeling of the iron-aluminosilicate interaction process will be conducted as part of the UA study. Finally, interaction with an integrated program led by the utility PowerGen will be used to address issues of deposit formation at full scale for comparison with the bench and laboratory scale results of this program. A work breakdown structure containing a brief description of each task follows. The relationship among the participants is illustrated schematically in Figure 2-1.

Task 1 - Program Planning, Management, Reporting, and Peer Review

This task, to be performed by PSI Technologies, consists of: (1) preparing and annually updating a program plan; (2) coordinating, managing, and integrating the subcontracts and project results; (3) preparing project monthly reports; (4) integrating and preparing project quarterly reports; (5) integrating and preparing the program final report; (6) conducting annual peer review and project coordination meetings with the project principal investigators, either as a separate meeting or in conjunction with a technical conference, and including when appropriate the principal investigators of other DoE-supported ash formation research programs identified by the DoE project manager; and (8) acquiring and distributing coals to all of the project principal investigators.

Task 2 - Fundamental Study of Ash Formation and Deposit Initiation Under Reducing Conditions (PSI Technologies)

PSI will study the effect of combustion stoichiometry on mineral matter and inorganic species transformations with an emphasis on sub-stoichiometric combustion. This will occur through a series of experiments to be conducted in a well-characterized laboratory flow reactor on a minimum of two coals. Coal blends may also be examined if of benefit to the program and of mutual interest to PSI and DoE/PETC. One or more of the coals studied in this task may be coals previously studied at PSI under DoE contract number DE-AC22-86PC90751 to permit a direct comparison with results obtained under oxidizing conditions. Model mineral compounds will also be examined as necessary to identify the importance of the oxidation state of iron in determining mineral coalescence and ash deposition. Selection of any coal samples will be coordinated with the DoE/PETC program manager.

PSI will also conduct limited experiments to determine the effect of pyrite weathering on the evolution of an iron oxide fume. These experiments will be coordinated with a similar study at Sandia National Laboratories.

PSI will also conduct in-situ combustion experiments in conjunction with the University of Kentucky and Brookhaven National Laboratories using an in-situ combustion reactor at beamline X19-A of the National Synchrotron Light Source.

Activities under this task will include collection and examination of ash samples at varying combustion temperatures and/or oxidant concentrations. Ash samples will be collected using extractive sampling. In-situ deposit collection techniques will be used to measure ash

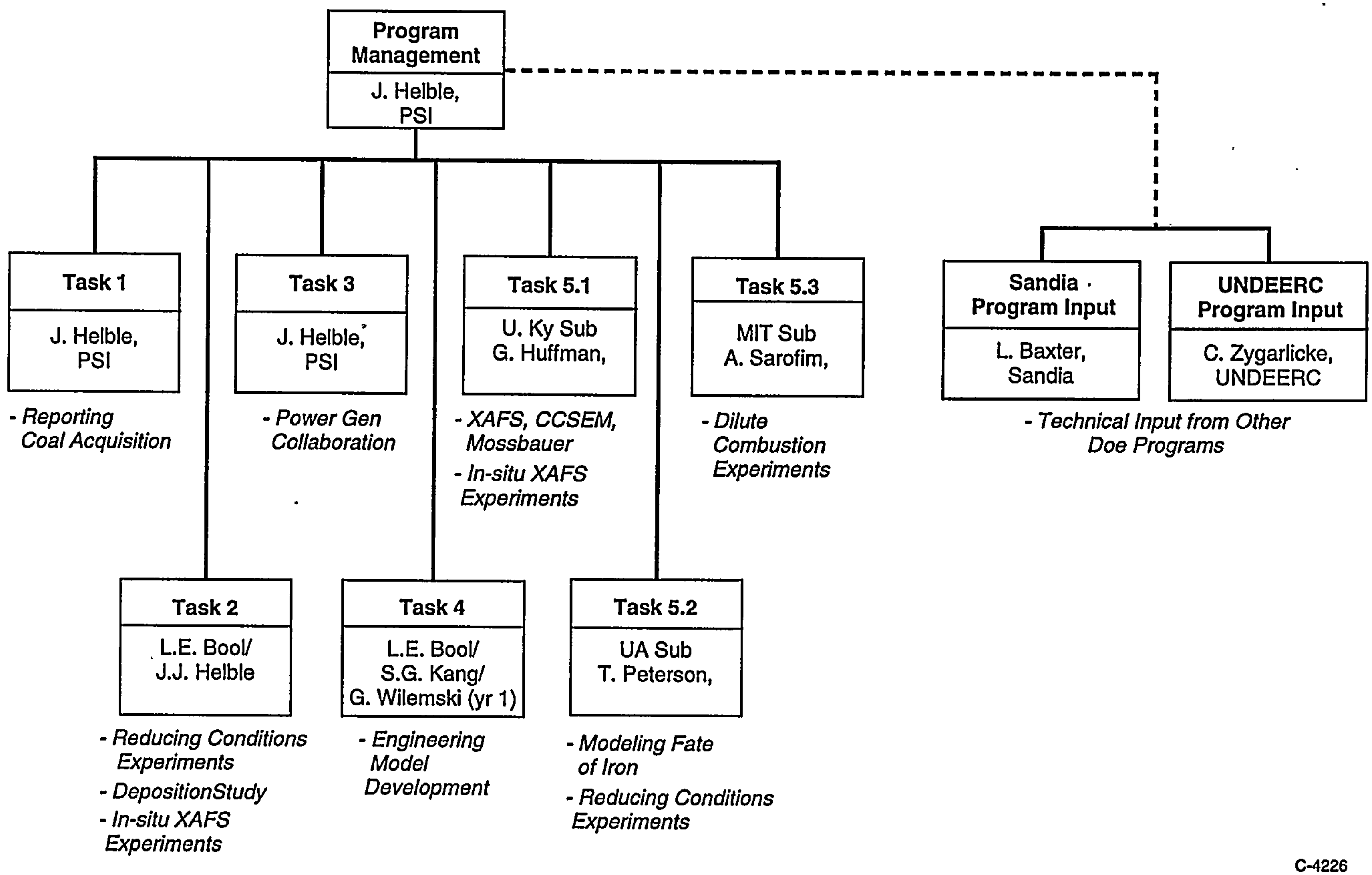

Figure 2-1. Program structure.

particle collection efficiencies as a function of temperature and stoichiometric ratio. Extracted ash and deposit samples will be characterized as necessary to determine particle size and chemical composition distributions as well as the chemical state of key components such as iron and calcium.

Task 3 - PowerGen Collaboration (PSI)

In order to understand the effects of combustion scale on ash formation and deposition under reducing conditions, PSI will interact with a government and industrial program currently underway in Great Britain. Led by the utility PowerGen, this program includes experiments at scales ranging from fundamental bench reactors to operating power plants. As part of a collaborative effort, PSI hopes to conduct laboratory experiments either at PSI, at BNL on the in-situ XAFS combustor, or in both reactors under a range of combustion conditions using a coal provided by PowerGen. If deemed appropriate by PSI, UA, and the DoE/PETC Program Manager, UA may also conduct combustion experiments with one of these coals. These experiments will permit direct comparison of results obtained in this project with those obtained at full scale in the PowerGen program. This interchange will also add to the database used in the modifications of the engineering model for ash formation described under Task 4.

Task 4 - Engineering Model for Ash Formation (PSI)

The results obtained by the organizations participating in this project will be applied by PSI to revise, test, and validate the EMAF developed previously. The work on this subtask includes analyzing the experimental results and identifying data and technical information related to extending EMAF. Specific areas of interest include the formation of ash under reducing stoichiometries, the formation (particularly the chemical composition) of the submicron ash fume, and the influence of char fragmentation on ash formation. As part of this task, PSI will also coordinate modeling activities to be conducted by the MIT and UA subcontractors.

Task 5.1 - Advanced Techniques for Coal and Ash Characterization Including In-situ XAFS Measurements (UKy)

The University of Kentucky will apply advanced analytical techniques such as computer-controlled scanning electron microscopy (CCSEM), Mössbauer spectroscopy, and x-ray absorption fine structure spectroscopy (XAFS) to characterize coal and ash samples from this program as needed by the individual principal investigators. If agreed upon by PSI, UKy, and the DoE program manager, UKy will also analyze selected coal and/or ash samples obtained from the PowerGen program in Great Britain.

As part of this task, UKy will conduct dynamic in-situ XAFS experiments at the Brookhaven National Laboratories (BNL) National Synchrotron Light Source (NSLS) with PSI and BNL using an in-situ drop tube furnace previously constructed by PSI. Static in-situ measurements at elevated temperatures will also be conducted using a cell previously built by UKy. The in-situ measurements will be used to investigate phenomena such as the transformation of pyrite under various conditions, the formation of iron aluminosilicate compositions as a function of combustion conditions, the formation of calcium aluminosilicate ash compositions as a function of combustion conditions, and the composition and oxidation state of key components in sticky, depositing ash particles as a function of combustion conditions.

Task 5.2 - Pulverized Coal Combustion Studies Under Reducing Conditions in a Continuous, Self-sustained Laboratory Scale Reactor (UA)

UA will conduct experiments to assess the interaction of iron and aluminosilicate minerals under reducing combustion conditions. UA will also examine the amount and chemical composition of the submicron fume generated under reducing conditions. This study will be conducted in the UA self-sustained 100,000 Btu/h combustion facility. UA will conduct this study using at least one of the coals studied by PSI and MIT under this program and including at least one coal studied previously under oxidizing conditions. As part of the experimental effort, UA will conduct Auger analyses for samples provided by other principal investigators on an as-needed basis. UA will also conduct Mössbauer analysis on selected ash samples generated at UA.

Based upon the results generated in this program, UA will modify the previously developed model for iron aluminosilicate formation to incorporate additional coals and/or combustion conditions.

Task 5.3 - Fundamental Study of Mineral Interactions and Ash Vaporization Under Reducing Conditions (MIT)

MIT will conduct drop tube experiments to study the fundamental aspects of ash formation under sub-stoichiometric conditions using narrowly sized and density classified coal samples and/or synthetic char samples. Size segregated chemical composition measurements will be conducted to assess the release of inorganic species to the vapor phase under sub-stoichiometric conditions. MIT will also conduct fundamental coalescence experiments under reducing conditions to elucidate the mechanism and rate of interaction of key mineral pairs. MIT will assist in the EMAF model testing and validation as described under Task 4.

SECTION 3

OVERVIEW OF FINAL REPORT
(PSI Technologies)

3. OVERVIEW OF FINAL REPORT

During the ninth quarter of this project, preparation of the Draft Final Report for this project was initiated. A summary and brief description follows.

3.1 Executive Summary

Five major conclusions were reached during the course of this project:

- Under sub-stoichiometric combustion conditions, elevated levels of carbon present in the ash can prevent ash particles from adhering to impaction tube surfaces and may therefore reduce deposition. Particle stickiness under these conditions is simply related to the amount of carbon remaining in the ash.

- The interaction of iron with aluminosilicate minerals is greatly affected by combustion conditions. Under sub-stoichiometric conditions, iron is present as Fe, FeS, and Fe(+2) in glass, with the amount of each phase dependent upon the oxygen partial pressure existing during combustion. Under oxygen rich conditions, iron is primarily present as Fe(+3) glass and hematite, with smaller amounts of Fe(+2) glass also detected.

- The oxidation state of iron contained in glassy aluminosilicate-derived ash particles significantly affects particle stickiness upon impaction. Conversion of nominally 10 to 20% of the iron in a glassy particle from the (+2) oxidation state to the (+3) oxidation state can reduce the fraction of particles sticking to a tube surface by a factor of 2 to 4.

- The oxidation of iron in glassy ash particles from the (+2) oxidation state to the (+3) oxidation state appears to be controlled by the diffusion of oxygen through the iron-glass melt.

- Under sub-stoichiometric conditions, the amount of partially reacted mineral phases detected in the ash is significantly greater than observed under fuel-lean conditions. Simulations of the ash formation process using the Engineering Model for Ash Formation (EMAF) indicate that different phases are observed because of limited coalescence occurring at partial burnout under sub-stoichiometric combustion conditions. This suggests that burning the char to completion (i.e., by addition of secondary air) would produce identical particle size distributions. Combustion stoichiometry therefore does not appear to affect the fly ash particle size distribution.

3.2 Coal Characterization (Standard and advanced techniques)

Five coals were studied in this program. These coals are as follows:

Pittsburgh #8 bituminous	run-of-mine
Pittsburgh #8 bituminous	washed
Pittsburgh #8 bituminous	physically beneficiated
Silverdale bituminous	coal from U.K.
Black Thunder sub-bituminous	Powder River Basin coal

Ultimate, proximate, and ash chemical analyses of all of the coals were obtained. The mineralogy of all five coals was determined by computer-controlled scanning electron microscopy at the University of Kentucky. Mössbauer analysis of the forms of iron in the coals was also conducted at the University of Kentucky. In addition, the run-of-mine Pittsburgh #8 was analyzed by CCSEM at MTI, a commercial laboratory, and the Silverdale and washed Pittsburgh #8 coals were analyzed by CCSEM at Imperial College as part of a government and industrially-supported program in the U.K. The washed Pittsburgh #8 and Black Thunder coals were also characterized independently at Brigham Young University as part of a separate DOE-supported program.

3.3 Combustion Experimentation

Combustion experiments under a range of stoichiometric ratios were conducted at MIT, the University of Arizona, and PSI to characterize mineral interactions occurring during char burnout. During the early stages of the program, it became clear that combustion stoichiometric ratio was primarily affecting the rate and extent of pyritic iron reaction. Studying the transformations of iron therefore became the primary focus of the experimental work. CCSEM, Mössbauer, and AA analyses were used to identify ash composition and phases in ash samples generated under a broad range of combustion conditions (including sub-stoichiometric).

3.4 Engineering Model for Ash Formation (EMAF)

EMAF was modified to allow for the incomplete char burnout associated with sub-stoichiometric combustion in our experiments. EMAF was used to both interpret experimental data and examine, parametrically, the effects of changes in combustion conditions on ash particle size and chemical composition distributions.