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

Quarterly Report No. 2
for the Period
1 July 1993 - 30 September 1993

Dr. J.J. Helble, Dr. S. Srinivasachar, Dr. G. Wilemski, and Dr. S.G. Kang
PSI PowerServe

Prof. A.F. Sarofim
Massachusetts Institute of Technology

Prof. T.W. Peterson and Dr. L.E. Bool
University of Arizona

Prof. G.P. Huffman, F.E. Huggins, and N. Shah
University of Kentucky

DATE PUBLISHED - November 1993
Prepared Under
DOE Contract No. DE-AC22-93PC92190

U.S. DEPARTMENT OF ENERGY
Pittsburgh Energy Technology Center
P.O. Box 10940
Pittsburgh, PA 15236

MASTER

1996L 4 2 NOV

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

PowerServe

A DIVISION OF PHYSICAL SCIENCES INC.

20 New England Business Center, Andover, MA 01810

TABLE OF CONTENTS

<u>Section</u>		<u>Page</u>
1.	EXECUTIVE SUMMARY	1-1
2.	OVERVIEW OF PROGRAM TASKS	2-1
3.	COAL SELECTION AND ACQUISITION	3-1
4.	ADVANCED TECHNIQUES FOR COAL, MINERAL, AND ASH CHARACTERIZATION	4-1
4.1	In-situ Furnace	4-3
4.2.1	Repairs	4-3
4.2.2	Modifications to the In-Situ XAFS Furnace	4-5
4.3	Results	4-6
4.3.1	Experimental Matrix	4-6
4.3.2	Pyrite Experiments	4-6
4.3.3	Kentucky #9 Coal Feed	4-8
4.4	Future Work	4-9
5.	FUNDAMENTAL COMBUSTION STUDIES UNDER REDUCING CONDITIONS	5-1
5.1	Background	5-3
5.2	Mineral Characterization	5-4
5.2.1	CCSEM	5-5
5.2.2	Other Analyses	5-5
5.3	Mineral Transformations	5-6
5.3.1	Ash Particle Size	5-6
5.3.2	Bulk Composition	5-11
5.3.3	Vaporization	5-11
5.3.4	Ash Particle Surface Composition	5-12
5.4	Deposition Mechanisms	5-13
5.4.1	Condensation	5-13
5.4.2	Thermophoresis	5-13
5.4.3	Impaction	5-14
5.4.4	Sticking Coefficient	5-14
5.4.5	Deposit Strength	5-15
5.5	Model Applications	5-16
5.6	Concluding Comments	5-16

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

TABLE OF CONTENTS (Continued)

<u>Section</u>		<u>Page</u>
6.	SELF-SUSTAINED COMBUSTION UNDER REDUCING CONDITIONS	6-1
6.1	Effect of Combustion Conditions and Ash Composition on Iron Partitioning	6-3
6.2	Practical Applications of Model	6-7
7.	ASH FORMATION UNDER REDUCING CONDITIONS: LABORATORY-SCALE STUDY	7-1
7.1	Experimental Procedure	7-3
7.2	Results	7-4
8.	ENGINEERING MODEL FOR ASH FORMATION	8-1
8.1	Background	8-3
8.2	Description of Model	8-4
8.2.1	Mineral Redistribution Model	8-4
8.2.2	Ash Formation Modes	8-5
8.2.3	Ash Release from Cenospheric Char Particles	8-6
8.2.4	Description of Ash Release Algorithm	8-9
8.3	Results	8-9
8.3.1	Behavior of Shell Thickness Based Upon Coal Properties	8-9
8.3.2	Comparison with Experimental Results	8-12
8.4	Conclusions	8-15
8.5	Plans for Coming Quarter	8-16
9.	REFERENCES	9-1

LIST OF FIGURES

<u>Figure No.</u>		<u>Page</u>
2-1	Program Structure	2-5
4-1	Schematic of in-situ XAFS furnace system	4-4
4-2	Cut-away view of six-way cross used for in-situ XAFS observation of ash stream and ash deposit	4-5
4-3	Fe K edge XANES of in-situ pyrite deposit at 1300°C after varying exposure under combustion conditions	4-7
4-4	Fe K edge XANES of in-situ deposits of pyrite at 1300°C	4-8
4-5	Fe K edge XANES of in-situ deposit of Kentucky #9 coal at various furnace temperature settings	4-9
4-6	Fe K edge XANES of in-situ deposition of Kentucky #9 coal at 1500°C under reducing conditions	4-10
5-1	Schematic diagram of processes governing the formation and deposition of ash during coal combustion	5-4
5-2	Probability of finding j ash particles in a coal particle for $k = 1000$, $m = 100$	5-7
5-3	Distribution of compositions in size classified ash (impactor stages 2, 3, and 4) from the combustion of an Illinois #6 bituminous coal at the University of Arizona (Shah et al., 1992)	5-8
5-4	Ash size composition for a San Miguel coal burned at two oxygen partial pressures compared with the full (1 ash/coal) and no coalescence (1 ash/mineral) models	5-9
5-5	Mineral and ash particle composition distributions obtained from the combustion of a chemically beneficiated 0.6% ash coal	5-10
5-6	Ash vaporization fraction ϕ per unit burnout time t_b for a Montana lignite	5-12
5-7	Size distributions of fly ash from a Polish coal burned in a 200 MW boiler using a low pressure impactor (Joutsensaari et al., 1993) for the smaller particles and sieve analysis for the larger	5-15

LIST OF FIGURES (Continued)

<u>Figure No.</u>		<u>Page</u>
6-1	Effect of peak char temperature on iron partitioning	6-4
6-2	Effect of silicon/pyrite ratio in coal	6-5
6-3	Effect of stoichiometric ratio on (1-fraction iron oxide)	6-6
6-4	Effect of stoichiometric ratio on fraction iron as glass	6-7
6-5	Collection efficiency (adhesion) from Boni et al. (1989)	6-11
6-6	Fraction of iron as glass for study coals	6-11
6-7	Partitioning of iron as a function of time, run 22 - Beulah Lignite	6-12
6-8	Iron partitioning as a function of time, run 61 - Eagle Butte	6-12
6-9	Iron partitioning as a function of time, run 67 - Kentucky No. 9	6-13
6-10	Iron partitioning as a function of time, run 73B - Kentucky No. 11	6-13
7-1	SEM image of Eagle Butte char particles. Cyclone sample, magnification = 250x	7-6
7-2	SEM image of Eagle Butte char particles. Cyclone sample, magnification = 1,000x	7-6
7-3	SEM image of Eagle Butte char particles. Cyclone sample, magnification = 2,500x	7-7
7-4	SEM image of Eagle Butte char particles. Impactor sample, magnification = 250x	7-7
7-5	SEM image of Eagle Butte char particles. Impactor sample, magnification = 1,010x	7-7
7-6	SEM image of Kentucky #9 char particles. Cyclone sample, magnification = 252x	7-8
7-7	SEM image of Kentucky #9 char particles. Cyclone sample, magnification = 1,000x	7-9

LIST OF FIGURES (Continued)

<u>Figure No.</u>		<u>Page</u>
7-8	SEM image of Kentucky #9 char particles. Cyclone sample, magnification = 5,000x	7-9
7-9	SEM image of Kentucky #9 char particles. Cyclone sample, magnification = 2,520x	7-10
7-10	SEM image of Kentucky #9 char particles. Cyclone sample, magnification = 2,480x	7-10
7-11	SEM image of Kentucky #9 char particles. Impactor sample, magnification = 250x	7-11
7-12	Backscattered SEM image of Kentucky #9 char particles. Cyclone sample, magnification = 252x	7-11
7-13	Backscattered SEM image of Kentucky #9 char particles. Cyclone sample, magnification = 152x	7-12
7-14	Backscattered SEM image of Kentucky #9 char particles. Cyclone sample, magnification = 505x	7-12
7-15	Backscattered SEM image of Kentucky #9 char particles. Cyclone sample, magnification = 750x	7-13
8-1	Two-dimensional schematic of interaction region swept out by mineral inclusions of diameter D_i and D_j during burnout	8-7
8-2	Two-dimensional illustration of conical volume swept out by two mineral inclusions due to spherical shape of char particle	8-8
8-3	Schematic representation of ash particle formation and release from a cenospheric char particle	8-10
8-4	Shell thickness versus shell porosity	8-11
8-5	Char shell thickness versus volatile wt%	8-11
8-6	Shell thickness versus swelling index	8-11
8-7	Shell thickness versus particle size	8-11

LIST OF FIGURES (Continued)

<u>Figure No.</u>		<u>Page</u>
8-8	Mineral and ash size distributions	8-13
8-9	Number of minerals per ash particle	8-13
8-10	Number of ash versus coal particle size	8-13
8-11	Ash size distributions for Illinois #6 cleaned coal	8-13
8-12	Ash composition for Illinois #6 cleaned coal	8-14
8-13	Mineral and ash size distributions for Pocahontas coal	8-14

LIST OF TABLES

<u>Table No.</u>		<u>Page</u>
3.1	ABB/CE Analysis of Beneficiated Pittsburgh #8	3-3
4.1	Experimental Conditions	4-7
6.1	Slagging Classifications (Raask, 1985)	6-8
6.2	Slagging Classifications Based on F_s (Raask, 1985)	6-8
6-3	Slag Indices and Model Predictions for Bituminous Study Coals	6-10

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 occur. 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.

The work discussed in this report highlights the accomplishments of the second quarter of this two year project. This includes the final selection of coals by PSI PowerServe, the results of initial in-situ XAFS combustion measurements by the University of Kentucky, a review of the status of ash formation and deposition models by MIT, modeling of iron behavior during coal combustion by the University of Arizona, preliminary work on the redistribution of minerals within char during the early stages of combustion by PSI PowerServe, and the incorporation of a char fragmentation mechanism into the ash formation model by PSI PowerServe.

Specifically, in Section 3 of this report we briefly discuss the three coals selected for this project: Black Thunder sub-bituminous coal from the Powder River Basin, Pittsburgh #8 bituminous coal, and a beneficiated Pittsburgh #8 coal.

In Section 4, the results of initial XAFS measurements using an in-situ combustion test facility are reported by the University of Kentucky. Data are reported for samples collected via inertial impaction on tubes in cross-flow, held at temperatures of approximately 500°C. Samples of pyrite and Kentucky #9 coal were studied at gas temperatures of 1100 - 1500°C and oxygen concentrations of 5 to 20%. By varying the pyrite and coal particle feed rates, both oxidizing and reducing conditions were examined.

The initial layer of deposits derived from pyrite combustion was studied by XANES and was found to be slightly less oxidized than succeeding deposition layers. This suggests

that the initial deposit is formed by a less oxidized molten pyrite product. More oxidized (and presumably less molten) pyrite oxidation products may not stick initially, but are able to adhere to the stickier initial layers of a deposit. Experiments with Kentucky #9 coal revealed similar trends. At low oxygen partial pressures, the depositing layer appeared to be an iron oxy-sulfide melt for both pyrite and the coal. Again, this suggests that the presence of a partially oxidized molten pyrite combustion product can create a sticky initial depositing layer on tube surfaces.

In Section 5, an overview of the processes of ash and deposit formation is presented by MIT. This analysis, developed for the Engineering Foundation Conference on The Impact of Ash on Coal Fired Power Plants held earlier this year, summarizes our knowledge to date and will serve as the starting point for much of the work to be conducted by MIT under this program.

In Section 6, the results of modeling using an iron partitioning model developed at the University of Arizona are discussed. The model predicts the fraction of iron present in sulfur bearing, oxide, and glassy phases at the end of combustion as a function of coal mineralogy and combustion conditions. Trends derived from experimental data collected previously at UA were generally consistent with model results. No significant changes in iron partitioning were observed nor predicted with changes in peak char temperature. Although a few coals showed a slight increase in the amount of iron present in the glassy phase as char temperature exceeded 1600 K, no major trends emerged. The ratio of inherent silicates to iron was the parameter having the greatest effect on the amount of iron in the oxide phase. As the Si/Fe ratio increased, the amount of iron as oxide decreased, suggesting increased iron-glass formation. For the one bituminous coal examined in detail, the amount of iron as iron oxide did not change as combustion stoichiometry was varied from sub-stoichiometric to excess oxygen conditions.

In Section 7, results of a preliminary study to provide data on the distribution of minerals within devolatilized cenospheric chars are presented by PSI PowerServe. Scanning electron microscope images provided evidence of fine minerals distributed within the walls of thin-shelled cenospheric char particles, suggesting that fine minerals may be retained by devolatilizing, swelling coal particles.

In Section 8, the development of a fragmentation submodel and its subsequent incorporation into the Engineering Model for Ash Formation are described by PSI PowerServe. The char fragmentation model allows for cenosphere formation, and predicts subsequent mineral coalescence by encounter probabilities derived by analogy to gas kinetic theory. In this manner, coalescence of different sized mineral inclusions is allowed. Depending upon char type and its associated fragmentation behavior, one to thousands of ash particles can be generated per char particle. These findings and plans for future work in this area are described in Section 8 of this report.

SECTION 2
OVERVIEW OF PROGRAM TASKS

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-NO_x 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 occurs. 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 Massachusetts Institute of Technology (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 PowerServe, 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 PowerServe)

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.

C-4226

Figure 2-1. Program Structure

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 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 Engineering Model for Ash Formation (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 (UKy) 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/hr 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
COAL SELECTION AND ACQUISITION

3. COAL SELECTION AND ACQUISITION

Three coals will be studied during this program. During the second quarter, final selection of these coals was made. The coals are 1) Black Thunder sub-bituminous from the Powder River Basin, 2) Pittsburgh #8 bituminous from the Appalachian Basin, and 3) a beneficiated product produced from Pittsburgh #8 coal.

The Black Thunder coal is being obtained from the University of North Dakota Energy and Environmental Research Center (UNDEERC). This coal and the associated analytical data (ultimate, proximate, ash chemistry) are expected to be delivered to the program Principal Investigators sometime during November.

The Pittsburgh #8 parent coal is being obtained through the Pittsburgh Energy Technology Center of DOE. This coal should also be delivered sometime in November.

The beneficiated Pittsburgh #8 coal is a Southern Company agglomerate product being studied as part of the DOE-funded ABB/Combustion Engineering program "Combustion Characterization of Beneficiated Coal-based Fuels." This coal will be obtained from ABB/CE after their tests are completed in early November. Typical analytical data for this coal as reported by ABB/CE are presented in Table 3-1.

Table 3-1. ABB/CE Analysis of Beneficiated Pittsburgh #8

Proximate (wt %)	
Moisture	32.5
Volatile Matter	24.1
Fixed Carbon	39.9
Ash	3.5
Ultimate (wt %, dry)	
C	80.6
H	5.0
N	1.4
O	6.1
S	1.8
Ash	5.1
HHV, Btu/lb	14,540
Sulfur (wt % of coal)	
Pyritic	0.66
Sulfatic	0.05
Organic	1.09

Table 3-1. ABB/CE Analysis of Beneficiated Pittsburgh #8 (Continued)

Ash Chemistry (wt % of ash)	
SiO ₂	42.7
Al ₂ O ₃	25.2
Fe ₂ O ₃	20.8
CaO	2.8
MgO	1.0
Na ₂ O	0.1
K ₂ O	1.3
TiO ₂	1.4
P ₂ O ₅	0.4
SO ₃	2.6

SECTION 4

ADVANCED TECHNIQUES FOR COAL, MINERAL, AND ASH CHARACTERIZATION

University of Kentucky

4. ADVANCED TECHNIQUES FOR COAL, MINERAL, AND ASH CHARACTERIZATION

4.1 In-situ Furnace

Figure 4-1 is a schematic diagram of the furnace system built by PSI for these experiments. It is designed to be separable into top and bottom sections so that it can be wheeled into the experimental hutch at the Brookhaven National Synchrotron Light Source and reassembled. The drop tube furnace is designed for one standard cubic foot per minute (scfm) total gas flow and one to 10 g/min of reactant feed rate. The input gas can be a mixture of two gases (nitrogen and oxygen) to produce varying oxidizing/reducing combustion conditions. About 80% of the total gas flow (primary air) is preheated to about 900 K before being injected to the diffuser, while the remaining 20% of gas flow is used to entrain the utility grind reactant (coal or mineral) from the auger feeder. The diffuser, at the top of the furnace, is designed to thoroughly mix the primary and feeder air and to distribute the solid particles uniformly across the entire flow cross sections in the alumina retort of the furnace. The 30-in. long, 3-in. i.d. alumina retort is electrically heated to achieve up to 1750 K wall temperature with a constant temperature zone of 20 in. At 1 scfm gas flow rate and 1500 K gas temperature the residence time of coal particles is about 2.5 s which is sufficient to achieve complete combustion of most coal particles. A conical ceramic venturi at the exit of the furnace reduces the outlet gas stream diameter from 3 to 1 in. diameter before it enters the X-ray section of the facility.

Figure 4-2 is a cut-away view of the analysis section which consists of a six-way cross designed to allow the X-ray beam and the detectors full access to the combustion product stream. During the assembly, the six-way cross is aligned with respect to the X-ray beam so that a thin X-ray beam passes through the center of the cross without contacting any of the walls. On a water cooled port, a solid state X-ray detector with 0.003-in. thick beryllium window is mounted, orthogonal to both the X-ray beam and the ash stream. Helium gas is purged through the X-ray inlet and exit ports as well as the detector port toward the center of the cross to reduce x-ray attenuation and to prevent fly ash particles from flowing outward toward the windows. A port across from the detector port is used for insertion of an ash deposition probe. A boron nitride (BN) disk is placed at 45 deg to all major axes (X-ray beam, ash stream and detector) to optimize both the collection efficiency and the X-ray signal. Downstream of the six-way cross the ash and exit gas stream is cleaned and the gas flow rate is monitored (to check for any leaks) before venting it to the exhaust. Since the experiment is carried out inside the experimental hutch, where personnel are not allowed when the X-ray beam is on, the entire operation of the furnace is remotely controlled and several safety features were installed for emergency shutdown.

4.2.1 Repairs

Several critical components were stolen from the furnace assembly while in storage at the National Synchrotron Light Source. A list of the principal components that were missing includes: (1) detector mounting and aligning bracket system; (2) auger feeder tip fittings and

Figure 4-1. Schematic of in-situ XAFS furnace system.

C-5375

C-5376

Figure 4-2. Cut-away view of six-way cross used for in-situ XAFS observation of ash stream and ash deposits.

coal injector line; (3) feeder plexiglass top to prevent reverse blowout and 20 C-clamps to hold it down; (4) preheater transfer line, heating elements and insulation; (5) furnace pressure sensor and over-pressure safety shutdown system; (6) exhaust pump gas line fittings; and (7) several swagelock and thermocouple fittings. Four days of beam time were spent acquiring the replacement parts, machining custom made components, and assembling the furnace system. The system is now stored in a more secure location to reduce the chance of additional theft.

4.2.2 Modifications to the In-Situ XAFS Furnace

Aligning the furnace with respect to the X-ray beam is a difficult and time consuming procedure. As a result, a laser alignment system was bought and used to first align the laser with the X-ray beam and then to align the furnace system with the laser beam. Such an arrangement allowed us to align the system in a short time and to keep track of the alignment during the experiment.

In our previous experiments, the fly ash filter was clogging shortly after the start of furnace operation. A larger 'Balston' filter was placed in the exhaust stream to capture more of the fly ash and unburnt char. This filter can hold up to a pound of material without clogging and allows us to run the furnace for the entire beam time without replacing it. Such

a filter is crucial for reducing condition furnace operations that will generate significant amounts of unburnt char as well as fly ash.

The deposition probe was also modified. Since the deposition probe is at least a foot away from the end of the hot alumina retort and is at the center of water cooled six-way cross, the temperature at the probe is several hundred kelvin lower than the furnace temperature. A coaxial thermocouple was installed to record the deposit temperature. This thermocouple measured backside temperature of the boron nitride thin disk used to collect deposits.

4.3 Results

When the solid state detector was cooled down with liquid nitrogen, we noticed a significant vacuum loss in the detector. On further testing, we found a major leak in the water line used for cooling the beryllium window of the detector. Without water cooling and good vacuum, if operated at high voltage, the solid-state detector can suffer major permanent damage. As a result it was not possible to use the solid state detector. Since it is under warranty, the manufacturer has agreed to repair the detector free of charge. As a backup measure, we used a 'Lytle' fluorescence detector for this set of experiments. A Mn filter was used to attenuate the elastically scattered X-ray radiation. Since the six-way cross was not designed to use such a detector, we could not achieve a gas-tight seal between the detector and the six-way cross. We were also unable to flow a sufficient quantity of He from the detector port in toward the center of the cross. Because of this, even under high negative furnace pressure, a substantial amount of fly ash and unburnt char bounced off the deposition probe and was collected in the detector port of the six-way cross. This unburnt char was highly reactive and at a high enough temperature to spontaneously burn at higher oxygen partial pressure near the detector port. A constant flame was observed over the deposition probe. This problem was more severe under reducing operating conditions. Despite these problems, we obtained several good Fe K-edge XANES spectra during this run.

4.3.1 Experimental Matrix

Table 4-1 indicates the experimental conditions for in-situ experiments in our August 1993 run.

4.3.2 Pyrite Experiments

Figure 4-3 shows Fe K-edge XANES of a deposit formed while pyrite was fed at a 1 g./min feed rate to the 1300°C furnace. The deposition probe temperature was about 460°C. Air was used for the primary air supply and for the pyrite feed stream. The initial deposit (bottom spectrum in the figure) showed less oxidation as compared to the outer deposit (middle spectrum). Pyrite feed was then stopped and hot air was allowed to pass over the deposit to monitor further transformations in the deposit. After 2 h of 'aging', the XANES spectra of the deposit did not indicate any further changes in the deposit.

Table 4.1 Experimental Conditions

Sample	Feed Rate (g./min)	Furnace Temperature (°C)	Percent O ₂	Measured Substrate Temperature (°C)	Approximate Stoichiometric Ratio*
Pyrite	1	1300	20	460	8
Pyrite	1	1300	14	520	5
Pyrite	1	1300	5	560	2
KY #9	2	1100	20	400	2
KY #9	4	1300	20	480	1
KY #9	4	1400	20	500	1
KY #9	6	1500	20	650	0.6
KY #9	6	1500	5	700	0.2

*Precise value unavailable because of feeder fluctuations.

C-5377

Figure 4-3. Fe K edge XANES of in-situ pyrite deposit at 1300°C after varying exposure under combustion conditions.

Oxygen partial pressure was reduced to 5% by substituting nitrogen for feeder air and by mixing nitrogen with the primary air. The bottom spectra in Figure 4-4 shows Fe XANES of the deposit collected at 1300°C furnace temperature and 5% oxygen concentration. Under these conditions, corresponding to an approximate stoichiometric ratio of 2, pyrite did not oxidize completely but formed what may be an Fe-oxy-sulfide phase. The pre-edge peak in the spectra indicates the onset of iron oxide phase formation. When the partial pressure of oxygen was increased to 14%, the pre-edge peak was better defined. In fact, the spectrum for 14% oxygen was similar to that collected at 20% oxygen (see Figure 4-3).

Figure 4-4. Fe K edge XANES of in-situ deposits of pyrite at 1300°C.

4.3.3 Kentucky #9 Coal Feed

The feeder and feed line were emptied and cleaned to remove oxy remaining pyrite and the feeder was replenished with utility grind Kentucky #9 coal. Since the coal has lower iron content than pyrite, the feed rate was increased and detector gains were optimized to improve the signal to noise ratio.

Figure 4-5 shows a series of XANES spectra collected at an oxygen concentration of 20% and at varying furnace temperature settings. The spectra are quite similar to each other, but show subtle differences in the pre-edge feature. The spectrum is also similar to that of the deposit obtained when pure pyrite was fed to the furnace.

Figure 4-5. Fe K edge XANES of in-situ deposit of Kentucky #9 coal at various furnace temperature settings.

Figure 4-6 is a comparison between XANES spectra obtained for Kentucky #9 coal under reducing (20% O₂, approximate S.R. of 0.6-0.9) and severely reducing (5% O₂, approximate S.R. of 0.2-0.4) operating conditions at 1500°C furnace set point. Just like pure pyrite feed (Figure 4-4), at lower oxygen partial pressures, iron does not completely oxidize but appears to be incorporated in an oxide-sulfide mixture. This phase is quite sticky and easily forms an initial deposit. During this experiment, a substantial amount of this highly viscous slag phase was deposited in the alumina retort and plugged up the ash stream concentrator at the bottom of the furnace. At longer residence times, even under reducing conditions, this slag transformed into a very tenacious deposit and was impossible to remove.

4.4 Future Work

In the present run, several experimental difficulties were encountered. The following prerequisites must be met for the success of future experiments:

1. The Ge-detector has to be repaired for the vacuum leak.
2. Feeder fluctuations should be reduced by incorporating a damping chamber.

Figure 4-6. Fe K edge XANES of in-situ deposition of Kentucky #9 coal at 1500°C under reducing conditions.

3. The furnace should be better characterized. It should be operated for a longer time period under actual experimental conditions (coal feed, higher feed rates, lower oxygen partial pressure, higher temperatures, etc.) so that all the deposit/clogging problems are resolved. The feed rate and temperature profile should be recalibrated for actual operating conditions.
4. A detailed analysis of the XANES spectra already obtained will be carried out.

In the future, we plan to carry out Fe XANES measurements using coals fed at varying temperature and oxygen partial pressure conditions. Also, other elements (e.g., Ca, K) will be examined.

SECTION 5

FUNDAMENTAL COMBUSTION STUDIES UNDER REDUCING CONDITIONS

Massachusetts Institute of Technology

Task 5.2

5. FUNDAMENTAL COMBUSTION STUDIES UNDER REDUCING CONDITIONS

During the first quarter of this program, a review of the major mechanisms affecting the size distribution, chemical composition distribution, and deposition potential of combustion derived ash was undertaken. This review provides the framework for subsequent studies of the effect of reducing stoichiometry on ash formation and deposition. In this section of the report, a summary of the review is presented. An oral presentation of this review was given at the 1993 Engineering Foundation Conference on the Impact of Ash Deposition on Coal Fired Plants.

5.1 Background

Pulverized coal combustion in utility boilers was introduced over 70 years ago. Since that time, extensive experience has been gained in managing problems such as slagging, fouling, and corrosion associated with the inorganic constituents or ash in coal. Despite this experience, there continues to be major uncertainty on how to cope with fouling and slagging problems resulting from changes in design, operation, and, most importantly, fuel composition. Many of these changes, such as the introduction of low-NO_x burners and the use of fuel blending to reduce the emission of the oxides of sulfur, are driven by environmental legislation such as the 1990 Amendments to the Clean Air Act.

Excellent descriptions of the problems associated with the mineral constituents in coal and empirical methods for anticipating and overcoming them are given in the texts by Reid (1971) and Raask (1985). More recent information, particularly that presented at major symposia and conferences, was summarized by Bryers (1992) in the proceedings of the Engineering Foundation Conference held at Palm Coast in 1991. In his concluding statements, he highlights the divergence between the parallel mechanistic and empirical approaches to the problems of fouling and slagging. He notes that researchers have tackled individual aspects of the problems associated with ash, but have not taken these findings and directly applied them to full-scale units. In this review, some of the progress that has been made in understanding the mechanisms of the processes governing fouling and slagging is described, noting the gaps that require additional well-defined studies. In addition, progress that has been made since the Palm Coast meeting in integrating the fundamental knowledge into the total process and bridging the gap between research and applications is discussed in this review. Some appreciation of the complexity of the processes governing fouling and slagging can be gained from the schematic diagram shown in Figure 5-1, focusing mainly on the transformation of the minerals in coal during combustion.

Inorganic elements may be present in micron or larger sized mineral inclusions, or in extraneous mineral particles. Inorganic elements may also be intimately dispersed within the organic matrix of the coal. This latter inorganic component is generally referred to as "atomically dispersed" or "organically bound." During combustion, the majority of the inorganic species remain within the char, coalescing to form one to many ash particles, with the number governed by the fragmentation pattern of the char and the minerals themselves. The extraneous minerals - those liberated from the coal during grinding - will also undergo

C-5083

Figure 5-1. Schematic diagram of processes governing the formation and deposition of ash during coal combustion. Open arrows represent vapor phase routes.

physical and chemical transformations as they pass through the hot zones in the boiler. A small portion of the inorganic constituents contained within coal are released during devolatilization (Baxter et al., 1993) and others vaporized during char burnout (Quann and Sarofim, 1982). The vaporized constituents can homogeneously nucleate to form a submicron aerosol or condense on or react with the surfaces provided by boiler heat transfer tubes and the fly ash. The particles, vapor, and aerosol will be carried to the boiler walls by a series of mechanisms, predictions of which require knowledge of complex, dynamic flow and temperature fields, changing with time because of ash deposition. In view of the multiplicity of processes which govern deposition, it is not surprising that the development of mechanistic models has been slow and that empirical models are imperfect. In this section of the quarterly report, the status of these efforts is reviewed.

5.2 Mineral Characterization

The underpinning of mechanistically based models of fouling and deposition is the prediction of ash particle size and composition distributions. Major progress has been made in the allowance of particle size and particle-to-particle variation in the composition of fly ash as a result of developments in instrumental analysis, most notably automated computer controlled electron microscopy, referred to hereafter as CCSEM although there are closely related analogs described by other names.

5.2.1 CCSEM

Detailed knowledge of the mineral distribution within pulverized coal is critical to the understanding of the ash composition and particle size distributions. Significant progress in characterizing the mineral distribution has been made in recent years. In one approach, the mineral distribution in the pulverized coal is measured as a function of coal particle size (Zygarlicke et al., 1992). In a second approach, the size and abundance of the different minerals in the coal are first determined without regard to particle size. The minerals are subsequently redistributed throughout the coal using Monte Carlo techniques and Poisson statistics (Wilemski et al., 1992; Barta et al., 1990). In both approaches, cross-sections of the pulverized coal are analyzed under the scanning electron microscope (i.e., CCSEM). For differentiation between included and excluded mineral matter, an imbedding material such as carnauba wax that can be distinguished from coal under the electron microscope must be used (Zygarlicke et al., 1992).

Because the CCSEM measures the cross sections of the mineral particles, results are artificially biased toward smaller particle sizes. This is because sections of, for example, a spherical particle of a given size will have a projected area that will vary from zero to that at the meridian section. Methods for inverting the data for particles of known shape are available and have been applied to the mineral inclusions in coal (Monroe, 1989). Such inversions have been applied to minerals in the whole coal particles but would be difficult to apply, because of counting statistics, to a pulverized coal where the distribution of minerals in different size fractions is desired. The CCSEM has to be applied with care to eliminate biases; e.g., changes in the resolution of the instrument can result in treating aggregates as single particles. Care must be taken to obtain a statistically valid representation of each important size and composition class (Barta et al., 1990; Yang and Baxter, 1992). In addition, the current limitations on electron beam size restrict the lower limit of resolution to a mineral inclusion of about 1 μm . Although inclusions down to sizes of tens of nanometers have been observed using other techniques (Field et al., 1967; Allen and VanderSande, 1984), the mineral inclusions below 1 μm usually account for a small fraction of the mass of the total mineral content. Nevertheless, the failure of CCSEM to measure smaller particles should be remembered in applying the method. It is also essential to consider the inorganic content that is organically bound in the coal as discussed below.

5.2.2 Other Analyses

The atomically dispersed elements which have either precipitated with or been ion-exchanged into coal can be determined by water washes or ion-exchange with ammonium acetate. For low rank coals, these organically associated inorganic species can constitute a major fraction of the total inorganic content of the coal. For example, for many U.S. Western coals the ion-exchangeable calcium may account for more than 20% of the mass of the ash. Sequential dissolution in water, ammonium acetate, and hydrochloric acid can be used to separate the soluble species such as chlorides, hydroxides, oxides, carbonates, and organically coordinated species from insolubles such as clay, quartz, and pyrites (Zygarlicke et al., 1992; Benson and Holm, 1985). Other tools that are useful in characterizing the

minerals in coal include X-ray diffraction for crystalline mineral phases, Mössbauer spectroscopy for iron forms, scanning transmission electron microscopy (STEM) for characterizing submicron minerals, and X-ray absorption fine structure spectroscopy (XAFS) analysis for the valence state and chemical forms of many elements.

From a combination of the elemental analysis of coal, CCSEM, and other characterization techniques, a fairly complete description of the mineral inclusions and organically associated inorganic species can be obtained.

5.3 Mineral Transformations

The deposition of the ash on boiler heat transfer surfaces must depend upon the ash particle size and density which will determine the aerodynamic behavior of the particles. In addition, the retention of the particles will be determined by their sticking coefficient, which is dependent upon the viscosity of the surface layers of the particles. The first step in any modeling effort is therefore the calculation of ash properties from the distribution of mineral matter and from the combustion conditions.

5.3.1 Ash Particle Size

Two extreme models can be considered for the behavior of the mineral inclusions during coal combustion. In the first, each mineral inclusion yields a single ash particle. The atomically dispersed ash is deposited on adjacent individual mineral inclusions as the elements are released by the reacting char. In the second model, the mineral inclusions in a coal particle coalesce into one single ash particle, or into n equally sized ash particles. For this model, the ash particle diameter d_a can be related to the coal particle diameter d_c , the fraction f_a of the mass of coal that is ash, the ratio ρ_a/ρ_c of the densities of the ash and coal by a simple mass balance:

$$d_a = d_c \left[(f_a \rho_c) / (n \rho_a) \right]^{1/3} \quad . \quad (5-1)$$

Note that this simple expression is less accurate for coals with high *included* ash contents (e.g., >20%); for such coals, the volume occupied by the minerals within coal particles must be considered (Wall et al., 1990). Typically the mass mean diameter of pulverized coal is approximately 50 μm . For a coal with 10% ash by weight, a specific gravity of ash twice that of coal, and n of one, the ash mean particle diameter is then 18.4 μm . A size *distribution* is obtained in practice because of the spread in the sizes of the coal, the variations in the density ratio of ash and coal, and the fragmentation of both mineral particles and char particles which will yield values for n greater than one and variable from particle to particle (Helble and Sarofim, 1989).

The coal size distribution can be well approximated by the Rosin-Rammler equation (Field et al., 1967). The coal particle-to-particle variations in ash content, f_a can be obtained

by density fractionation since f_a and f_c are correlated, but it may also be estimated from the Monte Carlo simulation of ash distribution between coal particles of different size. For a number of mineral inclusions k distributed among m coal particles where the particle volume is much larger than the mineral volume, the distribution can be described by a Poisson distribution (Barta et al., 1990). The probability P_j of finding j mineral particles in a given coal particle is given by:

$$P_j = \lambda^j e^{-\lambda} / j! \quad (5-2)$$

where λ is equal to k/m , the mean number of mineral particles per coal particle. An example of the distribution of 1000 mineral particles in 100 coal particles is given in Figure 5-2. It can be seen that the distribution is approximately Gaussian about the mean particle number of 10. This approach can be extended to mixtures of minerals to yield information on both the amount and composition of the mineral matter in different coal particles.

C-5084

Figure 5-2. Probability of finding j ash particles in a coal particle for $k = 1000$, $m = 100$.

Further variations in the ash particle size result from variations in the density of the ash particles. This is in part due to variations in the ash composition. In Figure 5-3 the variation in the content of the oxides of iron, aluminum and silicon in size segregated ash particles collected on an impactor stage at the University of Arizona burning an Illinois #6 bituminous coal are presented. In the figure, each composition represents at least one ash particle containing at least 80 mole% Fe + Al + Si. The height of each peak represents the number of particles of given composition in the sample. The specific gravity ranges from that of quartz (2.5) to that of iron oxides (> 5) for solid ash particles (Shah et al., 1992). The density will vary to a much greater extent because of bubbles in the ash with the extreme cases being cenospheres (Wall et al., 1990). For an ash particle originally 20 μm in diameter and growing, as is not unusual, to 100 μm the specific gravity will decrease from about 2.5 to 0.02 and the wall thickness will be 0.13 μm . Cenosphere formation is a result of chemical reactions leading to gas evolution while the ash is in a molten state and is

Figure 5-3. Distribution of compositions in size classified ash (Impactor stages 2, 3, and 4) from the combustion of an Illinois #6 bituminous coal at the University of Arizona (Shah et al., 1992).

therefore dependent upon particle composition and reaction conditions. Cenospheres with a specific gravity of less than 1.0 can be harvested from ash ponds for use as low density fill and typically account for less than 5% of the ash mass (Raask, 1985).

The number of ash particles that can be produced per coal particle (n) is an additional variable that influences particle size and size distribution. The number of ash particles produced is increased by both fragmentation of the mineral inclusions, by the shedding of ash particles from the burning char surface during char reaction, and by the fragmentation of char with each char segment carrying its aliquot of the inorganic content of a coal particle. These different mechanisms have been studied in some detail (e.g., Monroe, 1989; Helble and Sarofim, 1989; Kang et al., 1990). Some generalizations may be derived from the mechanistic studies. The most important is that the factors that have the greatest impact on the ash particle size are the coal particle size distribution and the variability in the ash content of different coal particles, from practically mineral free particles to extraneous minerals. The char particle fragmentation is governed by char macroporosity (i.e., macroporosity after devolatilization) and is therefore most important for coals that form cenospheric char particles (Monroe, 1989). Char fragmentation is generally of secondary importance for moderate to high ash content (>5%, included) coals (Kang, 1991). Estimation of the fragmentation behavior of chars therefore requires knowledge of the ash content and swelling behavior of the coals during devolatilization. Mineral fragmentation is

only important for reactive minerals such as pyrite and calcite (Helble et al., 1993); fragmentation of clays has not been observed under laboratory conditions (Srinivasachar et al., 1990). While fragmentation of excluded minerals may be an important process, fragmentation of included minerals does not appear to be.

A good starting point in calculating the size distribution of ash for use in ash deposition models is the single ash particle per coal particle model. This model is indicative of full coalescence of all inorganic species within any given coal particle. Results of a comparison of ash particle size distributions measured in a drop tube furnace with those obtained from the single ash particle per coal particle model are shown in Figure 5-4. The extensive mineral coalescence that occurred during combustion can be seen from a comparison of the experimental results with the size distribution of the mineral inclusions.

Figure 5-4. Ash size composition for a San Miguel coal burned at two oxygen partial pressures compared with the full (1 ash/coal) and no coalescence (1 ash/mineral) models. From Wilemski et al. (1992).

In contrast, little mineral interaction is observed for coals with very low ash contents. In Figure 5-5, mineral and ash composition distributions for the Fe-Al-Si system are shown for ash generated during laboratory experiments with a chemically beneficiated 0.6% ash bituminous coal. Very little interaction between iron and aluminosilicate minerals was observed.

Figure 5-5. Mineral (a) and ash (b) particle composition distributions obtained from the combustion of a chemically beneficiated 0.6% ash coal. Analysis by CCSEM.

5.3.2 Bulk Composition

The ash particle composition is determined by the formation mechanisms described above. The ash particle-to-particle variations in Figure 5-3 are consistent with the expected variations in mineral content of different coal particles. These values are in fair agreement with the predictions of the random mineral matter redistribution among coal particles followed by complete coalescence of the mineral inclusions in each coal particle (Wilemski et al., 1992; Barta et al., 1990). In other words, the distribution of minerals among coal particles accounts for much of the observed particle to particle variation in ash composition. The ash particle compositions in Figure 5-3 lie on the tie lines between the apex for Fe corresponding to pyrite inclusions and the band on the Al/Si axis corresponding to the aluminosilicates in the raw coal, with different compositions reflecting the different ratios of pyrite to aluminosilicates in each coal particle.

The importance of the variation of the composition of the individual ash particles arises from the impact of the variation on the viscosity of the molten ash particles. Estimates of the viscosities can be obtained from ash particle compositions using correlations available in the literature. One such application, by Barta et al. (1990), to obtain the viscosity (μ in poise) distribution of a Texas lignite yielded:

$$\begin{array}{lll} \text{at 1273 K} & \log \mu = 7.7, & \sigma(\log \mu) = 1.98 \\ \text{at 1773 K} & \log \mu = 2.8, & \sigma(\log \mu) = 1.02 \end{array}$$

The absolute value of the estimate of the viscosity can be questioned, being based on the Watt and Fereday correlation (Quann et al., 1990). Other correlations, developed using higher viscosity slag and glass data, have been suggested (Kalmanovitch et al., 1990; Srinivasachar et al., 1992). However, the importance of the method is in the finding of the wide spread in ash viscosities. An ash can therefore have a high viscosity based on its mean composition and be of no apparent concern, yet have low melting components that can be the source of fouling and slagging. The determination of the individual particle composition can therefore serve as a more potent index of potential deposition problems than the traditional mean compositions.

5.3.3 Vaporization

At flame temperatures, some of the inorganic constituents in coal will vaporize, in amounts that are governed by the vapor pressures of the constituents in the char. The vapor pressure is enhanced for some compounds by their reduction within the char to more volatile species; for example, silicon dioxide can be reduced to the more volatile silicon monoxide (Quann and Sarofim, 1982). The fractional vaporization ϕ divided by the time t_b for combustion is shown in Figure 5-6 as a function of temperature. The results for a Montana lignite illustrate that at 2000 K, the value of ϕ/t_b for sodium is about 5. In other words, approximately 10% of the sodium will be vaporized in a residence time of 2 s. The fractional vaporization of the major elements will be less. Typically, of the order of 1% of the coal inorganics will vaporize during pulverized coal combustion (Quann et al., 1990;

Figure 5-6. Ash vaporization fraction ϕ per unit burnout time t_b for a Montana lignite. From Mims et al. (1980).

Kauppinen and Pakkanen, 1990). Recent work has shown that inorganic material may also be convectively removed from coal particles during devolatilization (Baxter et al., 1993).

5.3.4 Ash Particle Surface Composition

The vaporized ash can homogeneously nucleate and grow by agglomeration to form a submicron aerosol about $0.1 \mu\text{m}$ in size, or condense on the surfaces of the tubes and fly ash. The alkali and alkaline earth elements are of particular importance because they have relatively high vapor pressures and can condense or chemically react to form low melting temperature salts and eutectics. The surface composition of fly ash has been shown to be enriched in the composition of the alkaline and other volatile elements. Studies by Wall and coworkers (Wibberley and Wall, 1982; Lindner and Wall, 1991). have shown that sodium forms low melting salts by surface reaction with ash particles that can lead to enhanced deposition of the fly ash.

5.4 Deposition Mechanisms

The characterization of the mineral matter transformation process is intended to provide inputs to models, mathematical or interpretive, of the mechanisms for ash deposition. In this section estimates will be provided of deposition by condensation from the vapor, by turbulent transport augmented by thermophoresis of the submicron condensation aerosol, and by the inertial impaction of the residual ash. An excellent survey of the principles governing the deposition of fly ash has been given by Rosner (1986) and the presentation below will closely follow his treatment. In order to provide an estimate of magnitudes, deposition rates will be calculated for the case selected by Rosner of a coal with 10% ash, 2% of which is a condensation aerosol with a diameter of $0.1\ \mu\text{m}$, and the remainder residual ash particles with a diameter of $20\ \mu\text{m}$. The products of combustion of a mixture of 10% coal by weight in air are assumed to approach the heat transfer tubes (5 cm in diameter and 800 K) at a velocity of 10 m/s and a particle temperature of 1200 K. In addition, it is postulated that the ash contains 1% by weight sodium, 10% of which vaporizes and eventually forms a sodium sulfate deposit. In order to put the deposition rates in perspective, times will be estimated for the buildup of deposit layers $10\ \mu\text{m}$ and 2 mm thick. The ten micron thick layer is selected as representative of a surface 'glue' thick enough to half submerge a $20\ \mu\text{m}$ ash particle impinging on a surface. The 2 mm layer is selected to provide enough of a thermal resistance to yield a temperature differential across the deposit of more than 100°C and thus emulate layers that might become "sticky".

5.4.1 Condensation

The deposition rate for a vapor at a concentration of C_∞ can be expressed in terms of the Sherwood number Sh , the diffusivity D_p , and the tube diameter d_t by

$$m'' = (D_p/d_t)(Sh)C_\infty$$

where the saturation vapor pressure at the surface is small enough to be neglected. The mass transfer coefficient can be obtained from the correlation for Sherwood number as a function of Reynolds and Schmidt numbers for cylinders in cross flow. For the above conditions, the Sherwood number is 36, or for a gas diffusivity of $1.6\ \text{m}^2/\text{s}$, the mass transfer coefficient to the tube is 11.5 cm/s. For a coal with 1% sodium in the ash, and 10% of the sodium vaporized, the concentration of condensing sodium vapor is $3 \times 10^{-9}\ \text{g}/\text{cm}^3$, yielding a condensation rate of $10^{-7}\ \text{g}/(\text{cm}^2)(\text{s})$. At this rate, a 10-micron layer would build up in 20,000 s, and a 2-mm layer in 46 days. The effect of changes in parameters can be estimated by noting that the Sherwood number is approximately proportional to $(\text{Re})^{1/2}$ and $(\text{Sc})^{1/3}$.

5.4.2 Thermophoresis

The particle turbulent deposition rate can be estimated from the same turbulent mass transfer coefficient as for the vapor, with two corrections. The first is for the reduced diffusivity of the particles. The mass transfer coefficient is proportional to $(\text{diffusivity})^{2/3}$.

For the 0.1 μm aerosol the diffusivity is $4 \times 10^{-5} \text{ cm}^2/\text{s}$ resulting in a reduction in the mass transfer coefficient by a factor of 1000. Partial compensation for this is provided by the thermophoretic force. The thermophoretic velocity u_t of particles with sizes below the mean free path of the gas can be approximated by

$$u_t = (3/4)\nu_g [-(\nabla T)/T]$$

where ν_g is the kinematic gas viscosity. The thermophoretic velocity will augment the transfer of the particles to the wall by a factor F given by

$$F = \text{Pe}/[1 - \exp(-\text{Pe})]$$

where Pe is the Peclet number given by $u_t d_p / (D_p \text{Sh})$. For the conditions selected F is equal to about 200. Thus the mass transfer coefficient for submicron particles is only a factor of five lower than that for condensation, or 2.3 cm/s . The deposition rate of the submicron aerosol is therefore $4 \times 10^{-7} \text{ g}/(\text{cm}^2)(\text{s})$. The times to build up 10 μm and 2 mm layers are 5000 s and 12 days, respectively.

5.4.3 Impaction

The rate of particle impaction is determined by the inertial separation of the particles. The efficiency of collection η_I of the particles flowing in the streamlines intercepted by a tube has been correlated by Rosner and coworkers (see, e.g., Rosner, 1986) as a function of the particle Stokes and Reynolds numbers. The value of the Stokes parameter needs to exceed 1/8 for particle deposition by inertial impaction. For the 20 μm particles the value of the parameter is 0.46 which corresponds to an impaction efficiency of about 0.2. The rate of deposition assuming a sticking coefficient of unity is 0.00018 $\text{g}/(\text{cm}^2)(\text{s})$. The times required to build up 10 μm and 2 mm deposits are then 11 and 2200 s. This value of the deposition rate is artificially high. First, Rosner for purposes of simplification assumed that all of the residual ash was 20 μm in size. A representative measurement of an ash particle size distribution from careful field measurements (Joutsensaari et al., 1993) is shown in Figure 5-7 from which it can be seen that about 20% of the ash is in sizes that would be captured. Second the sticking coefficient is less than one and can be effectively negative as impaction can lead to erosion as well as deposit build up.

5.4.4 Sticking Coefficient

The factors that govern the sticking efficiency are incompletely quantified. One criterion (Wibberley and Wall, 1982) for sticking is that the kinetic energy of the impinging particles be less than the interfacial energy between the tube surface and the particle. The complication not currently included in the analysis is that of viscous dissipation, a factor that will depend upon the viscosity of the wetted layer on the particle or the tube. Viscosity has indeed been found to be a useful means of correlating the viscosity of different ashes, with a critical value reported in the range of 10^5 to $10^7 \text{ Pa}\cdot\text{s}$ (Helble et al., 1992). The uncertainty in the methods for predicting sticking coefficient is one of the reasons why mechanistic

Figure 5.7. Size distributions of fly ash from a Polish coal burned in a 200 MW boiler using a low pressure impactor (Joutsensaari et al., 1993) for the smaller particles and sieve analysis for the larger. Impaction efficiency curves and particles impacting are shown for larger particles.

models are better considered to be tools for ranking deposition from various coals rather than predicting absolute deposition rates. Uncertainty in the sticking coefficient is reduced for the limiting case in which the tube surface is covered with a slag layer for which the sticking coefficient approaches one.

5.4.5 Deposit Strength

The deposit strength is often more important to boiler operation than the rate of deposition. This is a second area in which the predictive capability is low. Two mechanisms affecting deposit strengths have been identified. The first is the sintering of particles by solid state diffusion or viscous necking of contiguous particles, at a rate identified by Frenkel to be determined by the viscosity and to be inversely proportional to particle radius. The second is the bonding of particles by chemical deposition or reaction. Well defined laboratory experiments (Skrifvars et al., 1991) have shown great increases in sintering strength when lime containing deposits undergo either carbonation or sulfation. These results were corroborated by probe tests in a 500 MW boiler where severe deposit formation coincided with the region of carbonation and sulfation. Sintering and chemical deposition models are not as well developed at this stage as mineral transformation and deposition models, but the understanding of the mechanisms can be useful to the identification of problems and defining improved indices for fouling.

5.5 Model Applications

In view of the multiplicity and complexity of the processes governing fouling and slagging it is unlikely that validated models that can predict the amount and strength of deposits will be developed in the short term. Significant progress has been made in the application of the mechanistic approach by several groups who have made the judicious use of empiricism to fill in some of the gaps in our knowledge. These groups include PSI Technology Co. (Helble et al., 1993; Wilemski et al., 1992), Energy and Environmental Research Center (Benson et al., 1993), M.I.T. (Barta et al., 1993; Walsh et al., 1992), Sandia Combustion Research Facility (Baxter and Dora, 1992; Baxter and De Sollar, 1993), and the University of Newcastle (Gupta et al., 1992). Similarities between the programs are the characterization of the minerals by a variety of techniques, an ash particle formation model, aerodynamic models, a sticking coefficient guided by experimental tests, validation or application of the models using pilot or full scale tests. Also common to the programs are interactions or active involvement by industry in the development or use of the models.

The success of the models to date include the calculation of particle size and composition on a full scale boiler, the ranking of the rates of deposition of coals (Barta et al., 1993), the prediction of the differential deposition of selected elements (Benson et al., 1993), the assessment of the effects of blends on deposit tenacity (Baxter and Dora, 1992), the evaluation of the effect of burner aerodynamics on slagging potential (Gupta et al., 1992), and the development of slagging and fouling advisors which translate the results from the mechanistic studies together with their empirical extensions in user friendly software (Helble et al., 1992; Benson et al., 1993). An encouraging start has been made in response to Bryers' challenge.

5.6 Concluding Comments

Major progress has been made in characterizing the mineral matter in coal and its transformation but there is still room for improvement in the models for predicting ash particle size and composition. One example, shown in Figure 5-7, of a gap in our understanding is the recent observation of an unexplained peak between 0.1 and 1.0 μm in the size distribution of fly ash upstream of the air pollution control device of a full scale utility boiler. This peak lies between those for the submicron condensation aerosol and the residual fly ash. The available models on mineral transformation can, however, be combined with transport models to determine deposition by different mechanisms. Collection efficiencies calculated by Rosner show that thermophoretic augmented turbulent mass transfer dominates the deposition of the submicron particles and that inertial separation dominates the deposition of the residual fly ash on tubes in crossflow for ash particle diameters greater than about 10 μm . Models for the sticking efficiency of particles reaching the surface and the strengthening of deposits once formed are less robust. Despite these uncertainties, there is increasing use of mechanistic models for assessing the fouling and slagging of coals. It is anticipated that the mechanistic models will displace current empirical indices. The complexity of the problem, however, necessitates considerable interaction between the more fundamental and field studies to bring these tools to fruition.

SECTION 6

SELF-SUSTAINED COMBUSTION UNDER REDUCING CONDITIONS

University of Arizona

6. SELF-SUSTAINED COMBUSTION UNDER REDUCING CONDITIONS

As presented in earlier DOE work, a quantitative model has been developed to predict the fate of iron during combustion. With this model, it was shown that agglomeration of iron oxide and silicate ash particles during burnout is the dominant mechanism for iron-silicate interaction during combustion. This mechanism, in conjunction with the mechanism for extraneous pyrite oxidation, has now been used in a comprehensive model to predict the partitioning of the original iron between slag enhancing, sticky phases and crystalline phases. This report presents recent results from the exercising of that model for various conditions of peak char temperature, iron and silicate distribution and stoichiometric ratio.

6.1 Effect of Combustion Conditions and Ash Composition on Iron Partitioning

Although the model developed adequately describes the partitioning of iron during combustion, it requires knowledge of several characteristic parameters. Unfortunately, due to the detailed ash and coal analysis needed to determine these parameters, they are not always readily available for coals of interest. Therefore the model, in conjunction with experimental results, was used to qualitatively describe the partitioning of iron in fly ash as a function of several important variables. These variables include the peak char temperature, the iron and silicate distribution, and the stoichiometric ratio.

The effect of the peak char temperature, seen in Figure 6-1, is fairly small, suggesting that pyrrhotite is the major iron species captured into the glassy phase. The primary temperature effect occurs around 1600 K. Those coals that have data around this temperature exhibit a slight increase in iron capture when char temperatures exceed 1600 K. This effect can be attributed to the solidification of iron oxide melts at temperatures less than 1600 K. Therefore, at temperatures greater than 1600 K there are more molten iron species (i.e., both oxide and sulfide) available for capture into the glass phase. Data for some coals, specifically the Eagle Butte and Kentucky No. 11, suggest an additional increase in iron capture with temperature. However, in general the additional increase in capture is minimal.

Another important parameter for iron partitioning is the ash composition and its distribution through the coal. The fraction of pyrite as extraneous pyrite, for example, has a large effect on the overall iron captured in the glassy phase. This effect is due to the fact that the extraneous pyrite does not interact with extraneous silicates or with silicates within the char. Therefore, the larger the fraction of extraneous pyrite, the lower the pyrite fraction available for glass capture. This does not say, however, that the extraneous pyrites are not a problem. Rather, it says that the ash obtained at the end of the combustion process will be lower in iron as glass. Therefore, for superstoichiometric conditions, the final ash will be less sticky (Abbot and Austin, 1985). The effect of extraneous pyrites on potential slagging, as predicted from this work, will be discussed in the next section.

The next major coal composition effect is the mass of inherent silicates relative to the mass of inherent pyrite. As the relative amount of silicates increases, the possibility that inherent pyrites can oxidize and solidify (under the appropriate conditions) coming in contact

Figure 6-1. Effect of peak char temperature on iron partitioning.

with the molten silicates decreases. Therefore, the amount of iron in the glass phase should increase. This is described by the following parameter, the silicate to pyrite ratio adjusted for the amount of extraneous pyrite:

$$P_{Si/Fe} = \left(\frac{\frac{g \text{ silicate}}{g \text{ coal}}}{\frac{g \text{ pyrite}}{g \text{ coal}}} \right)_{inh} \left(\frac{\frac{g \text{ pyrite}_{inh}}{g \text{ coal}}}{\frac{g \text{ pyrite}}{g \text{ coal}}} \right)$$

Note that the mass fraction (pyrite as extraneous pyrite) was included to take into account the previously mentioned effect of extraneous pyrite. Figure 6-2 shows that the iron capture does, in fact, increase with this parameter. The only coal that varies slightly from this trend, the Upper Freeport, contains a significant fraction of iron as silicate in the original mineral matter.

Figure 6-2. Effect of silicon/pyrite ratio in coal.

The final parameter under consideration is the effect of stoichiometric ratio on iron partitioning. For superstoichiometric conditions the primary iron containing slag contributor in the fly ash is iron glass. This assumes that all available pyrite is either oxidized or captured. As the stoichiometric ratio is decreased, however, significant pyrrhotite can remain in the fly ash. In general the iron fraction in the glass and/or pyrrhotite phases increases dramatically with decreasing stoichiometric ratio (Figure 6-3). This increase is due primarily to the increase in unoxidized pyrites (as pyrrhotite). The iron fraction as glass, Figure 6-4, is relatively constant with stoichiometric ratio for the one coal (Kentucky #11 bituminous) examined in detail.

In general, the iron fraction in slag contributing phases, glass and/or pyrrhotite, increases if char temperatures exceed 1600 K. This fraction also increases (under superstoichiometric conditions) with the ratio $(\text{mass silicates}/\text{mass pyrite})_{\text{inh}}$ multiplied by the fraction of pyrite as extraneous pyrite. Finally, decreasing the stoichiometric ratio causes more pyrrhotite to remain in the fly ash, creating a net increase in the iron fraction in slag contributing phases.

Figure 6-3. Effect of stoichiometric ratio on (1-fraction iron oxide).

Figure 6-4. Effect of stoichiometric ratio on fraction iron as glass.

6.2 Practical Applications of Model

The first part of exploring the practical applications of a model is a comparison of model derived predictions with predictive techniques currently used in practice. Although many empirical indices have been proposed to predict slagging and fouling propensities, only a few "typical" indices will be discussed here (primarily those discussed by Raask, 1985).

Before looking at the various predictions, it is important to note that many other factors not investigated as part of this subcontract work (alkali and calcium content, for example) have been implicated as major factors in enhancing slagging and fouling. For this reason, only results for the high iron (bituminous) ashes will be compared to empirical slagging and fouling indices.

The first set of empirical indices are those developed by Raask (1985) for high iron British coals. The fraction of iron, as Fe_2O_3 , in the ash is the first such parameter. In general, the higher the iron content, the higher the slagging propensity (Table 6-1). The silica ratio, developed by Reid and Cohen (1944), is another index used by Raask to evaluate high iron content coals. This index is defined by Eq. (6-1),

$$\text{Silica Ratio} = \frac{\text{SiO}_2 \times 100}{\text{SiO}_2 + \text{Fe}_2\text{O}_3 + \text{CaO} + \text{MgO}} \quad (1)$$

Table 6.1 Slagging Classifications (Raask, 1985)

Slagging Index	No Slagging	Some Slagging	High Slagging
Weight % Iron Oxide in Ash	3-8	8-15	15-23
Silica Ratio	72-80	65-72	50-65

where SiO_2 , etc., is the mass fraction of that species in the ash. The higher the silica ratio, the lower the slagging propensity (probably due to an increase in melting temperatures and melt viscosities). The various slagging classifications can be seen in Table 6-1.

Another major slagging index was developed by Gray and Moore (1974) based on the deformation temperatures determined in ash fusion tests. The index, F_s , is given by Eq. (6-2). It is the initial deformation temperature, and HT is the hemisphere temperature. Slagging classifications for this parameter are given in Table 6-2.

$$F_s = \frac{4 \text{ IT} + \text{HT}}{5} \quad (6-2)$$

Table 6.2 Slagging Classifications Based on F_s (Raask, 1985)

Slagging Index (F_s , K)	Slagging Classification
1505-1615	Medium
1325-1505	High
< 1325	Severe

The final slagging index considered here is the ratio of basic to acidic oxides in the ash. This index is given by Eq. (6-3), where the species are given as weight percent of the ash. The critical value for this parameter has been determined as 0.55 by Duzy (1965) and by Duzy and Walker (1965). At this value the ash fusion temperature is at it's minimum (thus fouling and slagging is at a maximum). Raask (1985) mentions a maximum value of 0.50 for pulverized coal fired boilers.

$$R_{b/a} = \frac{\text{Fe}_2\text{O}_3 + \text{CaO} + \text{MgO} + \text{K}_2\text{O} + \text{Na}_2\text{O}}{\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{TiO}_2} \quad (6-3)$$

In order to compare model predictions for the bituminous coals in this study with the empirical slag indices, it is necessary to define a new parameter to take into account both slagging and fouling. It is well known that the extraneous pyrite is a major slagging contributor, therefore a good measure of the slagging and fouling propensity of the ash is given by the fraction of iron in the glassy phase (assumed to be sticky) and the fraction of iron originally present as extraneous pyrite. Thus the model results, in conjunction with coal mineral matter information, can be used to predict the slagging and fouling propensities for high iron coals. The empirical predictions for the study coals, and the newly defined parameter can be seen in Table 6-3.

From these results we can see that three of the study coals, Illinois No. 6, Kentucky No. 11, and Kentucky No. 9, are predicted to be medium to high slaggers. This corresponds well with the model prediction that approximately half of the iron is in slagging and fouling enhancing phases. The only coal where model predictions do not correspond to the empirical indices is the Upper Freeport. This coal, according to the model predictions, should be a high slagging coal. However, the empirical indices predict a fairly low slagging propensity for this coal. Unfortunately, quantitative data are not available to determine which of the predictions are in error. However, the discrepancy for the Upper Freeport may be due to the fact that this coal has the lowest iron content of the bituminous coals.

Much of the driving force for developing this partitioning model has been the assumption that the amount of iron captured in the glassy phase has a large effect on the stickiness of the resulting ash. Although other factors may influence ash stickiness, it is important to compare the fraction of iron captured and the stickiness of the ash. Early in this project researchers at PSI evaluated the stickiness of fly ash from the coals in this study under various conditions. The results of this study can be seen in Figure 6-5. In Figure 6-6 the coals used in this part of the overall project were ranked according to the fraction of iron in the glassy phase. The PSI researchers speculated that the high sticking tendency of the western coal ashes resulted from high calcium concentrations in the ash. For the bituminous coals, however, a comparison of the two figures shows (with the exception of the Upper Freeport) a fairly good qualitative correlation between the fraction iron as glass and the ash stickiness. Interestingly, the western coals were also consistent with the predicted trend. This is especially true if the Eagle Butte is ranked higher for stickiness than the Beulah Lignite. (Figure 6-5 suggests may be the case).

This partitioning model has one unique practical application. This model allows a design engineer to predict where the critical slagging and fouling points are for a given coal under certain conditions. For example, if an engineer knows (or can estimate) the coal time-temperature history, he can determine how the iron is partitioned as a function of residence time. This information can then be used to predict areas in the furnace where slagging and fouling may occur. In order to clarify this process, simulations for different study coals under varied conditions were performed (Figures 6-7 through 6-10). In the super-stoichiometric simulations (Figures 6-7 through 6-9) the first critical slagging point occurs at 0.40, 0.20, and 0.23 s, respectively. This represents the time when the extraneous pyrrhotite has reached its melting point (creating a sticky molten phase). The second critical point for

Table 6-3. Slag Indices and Model Predictions for Bituminous Study Coals

Coal	Slag Index				
	Wt% Fe ₂ O ₃ in Ash	Silica Ratio	R _{b/a} (base/acid ratio)	F _s (Temperature, K)	Model Prediction
Illinois No. 6	20.5: High Slag	64: High Slag	0.46	1500: High Slag	0.63
Kentucky No. 11	20.2: High Slag	65: High Slag	0.45	1540: High Slag	0.57
Kentucky No. 9	22.4: High Slag	63: High Slag	0.46	1517: High Slag	0.60
Upper Freeport	13.5: Some Slag	75: No Slag	0.27	1606: Low Slag	0.54

Figure 6-5. Collection efficiency (adhesion) from Boni et al. (1989)

Figure 6-6. Fraction of iron as glass for study coals.

Figure 6-7. Partitioning of iron as a function of time, run 22 - Beulah Lignite

Figure 6-8. Iron partitioning as a function of time, run 61 - Eagle Butte.

Figure 6-9. Iron partitioning as a function of time, run 67 - Kentucky No. 9

Figure 6-10. Iron partitioning as a function of time, run 73B - Kentucky No. 11.

these three experiments occurs when char burnout is complete. In most cases (Figures 6-8 and 6-9), all of the pyrrhotite has either oxidized or been captured into glass by this point. Therefore the slagging propensity remains reasonably constant until the particle temperature drops below the melting point of the glassy phase. However, in the case of the Beulah Lignite, Figure 6-7, the char burnout kinetics are very fast. The char burns away and exposes the inherent mineral matter faster than the pyrrhotite can oxidize or be captured. In this case the slagging propensity decreases slightly as some of the remaining pyrrhotite oxidizes.

For substoichiometric conditions, Figure 6-10, the iron partitioning becomes more interesting. In this case, although the first critical point occurs at approximately 0.25 s, appreciable molten pyrrhotite remains through out the process. This pyrrhotite is molten until the mixture drops below the crystallization temperature of the melt (taken as 1356 K in this case). The same process is true for the inherent mineral matter. The exposed mineral matter contains a large fraction of unoxidized pyrrhotite and glass. Therefore the second critical area begins at approximately 0.6 s and continues until both the glass and the molten pyrrhotite solidify at approximately 1.0 and 1.2 s, respectively.

In conclusion, the model developed as part of this work is consistent, for high iron content coals, with the slagging and fouling indices currently used in practice. This model can also be used to qualitatively predict the adhesiveness of fly ash from various coals. Finally, and probably most importantly, this model provides a unique method for predicting problem areas during combustion.

SECTION 7

**ASH FORMATION UNDER REDUCING CONDITIONS:
LABORATORY-SCALE STUDY**

PSI PowerServe

7. ASH FORMATION UNDER REDUCING CONDITIONS: LABORATORY-SCALE STUDY

To model the formation of ash during combustion (Task 4 of this program), it is important to understand the process of mineral coalescence. Prior experimental and modeling work has demonstrated that mineral coalescence is affected by mineral size, the mineral content of a coal particle, mineral type, particle combustion temperature, and the proximity of minerals to one another within a char particle. This is particularly true for the combustion of swelling bituminous coals, where the formation of cenospheres may drastically change the distance between minerals.

Many of the parameters affecting ash formation have been studied in detail. Little work assessing the distribution of minerals in devolatilized coal particles has been published, however. Hurley and Schobert (1992, 1993) have recently examined the evolution of inorganic species during the combustion of a pulverized sub-bituminous coal, and found that most mineral coalescence occurs during the latter stages of burnout. Kang (1991) and Kang et al. (1988) reported similar findings in their experimental and modeling studies of ash formation and char fragmentation. To help expand our understanding in this area, a preliminary study of devolatilized coal particles was conducted during the second quarter of this project with the goal of comparing mineral distributions within bituminous and sub-bituminous coals. This study, utilizing coals already available at PSI, was meant to provide a framework for additional efforts that will utilize the coals selected specifically for this program.

7.1 Experimental Procedure

Samples of Kentucky #9 bituminous coal and Eagle Butte sub-bituminous coal were devolatilized under a flowing nitrogen atmosphere in the PSI laboratory furnace described elsewhere (Helble et al., 1992). In these experiments, utility grind samples of Kentucky #9 and Eagle Butte were mechanically injected into the top of the furnace at feed rates of 0.6 g/min. Furnace wall temperatures were held at 1773 K. At the exit of the furnace, corresponding to 1.6 s residence time for this study, particles were extracted isokinetically using a water cooled, nitrogen quenched sampling probe. Large particles were collected with a cyclone at the exit of the furnace, whereas smaller char particles (those nominally $< 10 \mu\text{m}$, with the size being highly dependent upon particle density) passed through the cyclone and were collected on the stages of a Pollution Control Systems Corporation cascade impactor. Impactor stages were greased with Apiezon Type T grease to prevent particle bounce and re-entrainment. A polycarbonate filter with $0.4 \mu\text{m}$ pores was placed downstream of the impactor to collect particles too small to deposit on the impactor stages. Oxygen concentrations were continuously monitored at the filter exit using a Teledyne portable oxygen analyzer. Values of 0.5% oxygen were typically recorded. Subsequent addition of a small stream of nitrogen gas at the filter exit reduced in leakage, producing typical O_2 levels of 0.1%.

Char samples collected with the cyclone and cascade impactor were then analyzed via scanning electron microscopy (SEM) to assess particle morphology and, where possible, mineral distributions within the chars. Selected samples were embedded in epoxy and cross-sectioned to permit examination of char particle interiors.

7.2 Results

SEM micrographs of char samples collected during devolatilization experiments with Eagle Butte sub-bituminous coal are presented in Figures 7-1 through 7-5. In Figures 7-1 through 7-3, char samples collected from the cyclone preseparator are shown. There is some variation in char morphology apparent, although, as expected, there is no evidence of cenosphere formation. Consistent with the observations of Hurley and Schobert (1992, 1993), there is little evidence for mineral coalescence in the surface views shown here. Higher magnification images of chars that appear to have reacted more extensively (Figures 7-4 and 7-5) also show little evidence of mineral coalescence.

Experiments conducted with the Kentucky #9 coal demonstrated clear evidence of cenospheric char formation. As shown in Figures 7-6 through 7-10, many cenospheric particles were seen, with multiple "blow holes" observed in many of the cenospheric particles. Although a few 1 μm ash particles were observed in highly reacted particles (e.g., Figure 7-10), little evidence of significant mineral coalescence was found. Lighter spots on the surfaces of the char particles, best seen in Figures 7-8 through 7-10, may be minerals coalescing on the particle surface. X-ray spectral analysis to determine the composition of these areas was, however, inconclusive.

In addition to the cenospheric particles collected in the cyclone, char particles with a more "open" structure, similar to those seen in the Eagle Butte sample, were also collected on the stages of the cascade impactor. Examples of a few such particles are shown in Figure 7-11. The inorganic composition of the particles was typical of Kentucky #9, confirming that these particles were not the result of contamination from prior experiments with Eagle Butte. A few large (of order 10 μm) ash particles were observed on the surfaces of these open-structured particles as shown in Figure 7-11.

Samples of Kentucky #9 char collected with the cyclone were cast in epoxy, cross-sectioned, and analyzed by SEM in backscattered electron mode (BSE). By operating the SEM in BSE mode, large Z-number minerals (principally pyrite) appear as highly reflective regions, thus providing an approximate indication of the presence or absence of mineral matter in Kentucky #9 char cenospheres.

Low magnification backscattered electron SEM images of Kentucky #9 char are shown in Figures 7-12 and 7-13. Nearly all of the particles visible are cenospheric, with wall thicknesses ranging from 0.05 to 0.25 times the particle diameter. Qualitatively, wall thickness appears to decrease with increasing char particle diameter. Higher magnification BSE images are shown in Figures 7-14 and 7-15. Fine mineral grains are evident within many of the thin walled sections. The presence of the fine minerals suggests either the

retention of fine minerals (i.e., a lack of ejection during devolatilization), or the fragmentation of larger minerals (e.g., pyrite) during devolatilization, with subsequent retention of the fine mineral fragments within the char walls.

In conclusion, these initial experiments have demonstrated a broad variety of char structures resulting from devolatilization. Cenospheric structures produced during devolatilization of a bituminous coal showed clear evidence of retention of fine minerals within the thin cenosphere walls. A more detailed study, utilizing the Pittsburgh #8 coals being acquired for this program, will examine quantitatively the mineral content and composition of coals and chars to further our understanding of mineral interactions during combustion.

V-808

Figure 7-1. SEM image of Eagle Butte char particles. Cyclone sample, magnification = 250x.

V-809

Figure 7-2. SEM image of Eagle Butte char particles. Cyclone sample, magnification = 1,000x.

V-810

Figure 7-3. SEM image of Eagle Butte char particles. Cyclone sample, magnification = 2,500x.

V-811

Figure 7-4. SEM image of Eagle Butte char particles. Impactor sample, magnification = 250x.

V-812

Figure 7-5. SEM image of Eagle Butte char particles. Impactor sample, magnification = 1,010x.

V-813

Figure 7-6. SEM image of Kentucky #9 char particles. Cyclone sample, magnification = 252x.

V-814

Figure 7-7. SEM image of Kentucky #9 char particles. Cyclone sample, magnification = 1,000x.

V-815

Figure 7-8. SEM image of Kentucky #9 char particles. Cyclone sample, magnification = 5,000x.

V-816

Figure 7-9. SEM image of Kentucky #9 char particles. Cyclone sample, magnification = 2,520x.

V-817

Figure 7-10. SEM image of Kentucky #9 char particles. Cyclone sample, magnification = 2,480x.

V-818

Figure 7-11. SEM image of Kentucky #9 char particles. Impactor sample, magnification = 250x.

V-819

Figure 7-12. Backscattered SEM image of Kentucky #9 char particles. Cyclone sample, magnification = 252x.

V-820

Figure 7-13. Backscattered SEM image of Kentucky #9 char particles. Cyclone sample, magnification = 152x.

V-821

Figure 7-14. Backscattered SEM image of Kentucky #9 char particles. Cyclone sample, magnification = 505x.

Figure 7-15. Backscattered SEM image of Kentucky #9 char particles. Cyclone sample, magnification = 750x.

SECTION 8
ENGINEERING MODEL FOR ASH FORMATION

Task 4

PSI PowerServe

8. ENGINEERING MODEL FOR ASH FORMATION

During the first quarter, a fragmentation submodel was incorporated in to the Engineering Model for Ash Formation (EMAF). This model was then used to examine the ash formation process. Comparisons with laboratory experimental data indicate that the addition of the fragmentation model improves agreement between model and experiment in some cases.

The development and incorporation of the fragmentation submodel and the development of a scaled Monte Carlo technique for reducing computation time with EMAF are described below.

8.1 Background

Mineral matter in pulverized coal undergoes a number of transformations and interactions to form ash particles during combustion. Processes such as mineral coalescence, mineral fragmentation, char fragmentation, and coalescence with organically-bound inorganic elements will affect ash production from included minerals (those imbedded in the carbonaceous coal particles), whereas mineral melting and fragmentation will affect ash production from excluded minerals (those liberated during grinding of the coal). All of these processes influence the final distributions of ash particle size and chemical composition and, consequently, ash deposition.

If predictive techniques for deposition are to supplant labor intensive and time consuming laboratory and pilot scale measurements, it is essential that ash particle size and composition distributions be accurately predicted. Models to predict ash size and composition from coal mineralogy have been developed by several researchers (Barta et al., 1992; Kang, 1991; Monroe, 1989; Wilemski et al., 1992). In this report, we describe progress on a fundamental approach for simulating the formation of fly ash during pulverized coal combustion. The model uses coal particle size distributions, coal mineral composition and size distributions derived from computer controlled scanning electron microscopy (CCSEM), bulk ash content, volatile fraction, and swelling indices as inputs to generate ash particle size and composition distributions. By accounting for particle-to-particle variations in mineral content, size, and composition, and by including phenomena such as char fragmentation and limited mineral coalescence, the model provides a physically realistic analog of the processes involved in fly ash formation. From a predictive standpoint, one limitation of the present approach is its reliance on measured distributions of excluded minerals. As explained below, all current mineral redistribution models incorrectly predict that no small mineral particles are excluded, and no realistic model for the effect of grinding on producing small mineral exclusions is yet available. Use of the measured distribution of excluded minerals thus improves the accuracy of the predictions while compromising the model's status as fully predictive.

8.2 Description of Model

As noted, our model predicts ash particle size and composition distributions based upon coal properties. The key features of the model are a mineral redistribution routine to simulate the variability of the mineral content of individual coal particles and a mineral interaction routine to simulate the transformation of the distributed minerals into ash particles during combustion.

During combustion, ash particles are produced from extraneous mineral particles and from mineral inclusions contained in mainly carbonaceous particles. Thus the first step in our approach to modeling ash formation is the computer generation of a set of coal particles whose individual mineral inventories fluctuate in amount and composition in a fairly realistic way. In principle, CCSEM analysis could provide this information exactly, but until CCSEM data are routinely available for the compositions and sizes of the mineral inclusions found in a large number of individual coal particles, an alternative means for generating this information must be used. The mineral redistribution procedure fills this need in our model.

8.2.1 Mineral Redistribution Model

Mineral redistribution models have been developed by several researchers and used in attempts to predict ash size and composition. Charon et al. (1990) applied Monte Carlo methods to simulate the random distribution of minerals among a set of coal particles. Barta et al. (1992) developed an analytical "Urn Model" based on Poisson statistics for determining the (joint) size and chemical composition distribution for the mineral inclusions based on CCSEM data. They then used a random coalescence model to calculate the ash distributions. Wilemski et al. (1992) used a composite method that combines Poisson statistics for distributing the smallest minerals among the smallest coal particles with a Monte Carlo method for handling all of the larger minerals and coal particles. Ash distributions were predicted in the full and no coalescence limits. Zygarlicke et al. (1992) are developing an expert system using a large data base of measured ash properties to derive "mixing rules" for coal mineral properties to predict the ash size and composition distributions.

In our model, the mineral redistribution procedure is performed using a composite method that combines straightforward Monte Carlo techniques with Poisson statistics. First, a discrete representation of the coal particle size distribution is generated by subdividing the distribution into a sequence of (generally) 10 μm wide size ranges. The number of coal particles assigned to each size range is directly proportional to the volume fraction of coal found experimentally in that range. These baseline numbers are chosen to ensure that at least one mineral particle of each size and type is present in each coal size range, except where size restrictions apply. Next, a discrete representation of the mineral population is generated. The mineral matter is imagined to be subdivided into idealized particles of different sizes and types. These "particles" are then randomly distributed among the computer coal "particles" just as if one were randomly tossing balls of different sizes and colors into a set of boxes of different sizes. In our procedure, the mineral particles are assumed to be of six different diameters (2, 4, 8, 16, 30, and 60 μm) and seven different

types (quartz, kaolinite, illite or montmorillonite, miscellaneous silicates, pyrite, calcite and/or gypsum, and others).

As an example of results generated using this procedure, consider an Illinois 6 bituminous coal. There are roughly 10^8 coal particles in the representation with 7×10^7 in the $10 \mu\text{m}$ range and about one thousand particles in the largest size ($160 \mu\text{m}$) range. For the mineral particle representation, the simulation produces 4.9×10^8 particles of $2\text{-}\mu\text{m}$ diameter and another 6×10^7 particles of all of the larger sizes combined.

In practice it is impractical to use these large numbers. Instead, a small number of coal particles ranging from several tens to thousands is used in each size range with an appropriately reduced mineral population. Some care is needed in selecting these sizes in order to preserve the statistical significance of the results. Generally smaller numbers are used for the largest coal size ranges and the value is gradually increased as the coal size decreases. Thus the mineral redistribution is actually performed on a scaled set of coal particles for each size range whose number is usually much smaller than the baseline value in order to make the simulation feasible on computers with modest memory and speed capabilities. After the mineral redistribution is performed over the reduced sample for each size range, the ash is produced and analyzed, and the results are rescaled to values representative of the original sample size. The results are judged adequate when they are insensitive to the scaling factors.

When the average number of mineral inclusions of a particular size and type is expected to be large per coal particle the redistribution of mineral particles is handled using Poisson distributions. When the average is small, the mineral redistribution is performed with standard Monte Carlo methods. The rationale for these differences is to reduce the computer memory and time requirements to a reasonable level.

Since the volume fraction of the minerals in coal is small (around 0.1) and since the coal particles are typically much larger than the minerals, the random placement of all of the mineral particles results in a smaller fraction of excluded minerals compared to what is experimentally observed. To remedy this, measured excluded and included mineral size distributions are used when available, and only included minerals are randomly distributed among the coal particles.

8.2.2 Ash Formation Modes

With a complete inventory available for the mineral content of each coal particle in the simulated coal particle size distribution, the composition and size distributions of ash produced during combustion are then predicted in accordance with the char fragmentation and mineral coalescence behavior expected during combustion. Ash particles are produced during combustion by the transformations and interactions of the mineral inclusions within a coal particle. Organically bound elements are assumed to coalesce with the included ash, with the amount adding to any particular ash particle proportional to the surface area of that particle. Each extraneous mineral particle is assumed to form one ash particle.

There are three principal modes for generating ash distributions: (1) In the "no coalescence" mode, each mineral inclusion is assumed to produce one ash particle. (2) In the "full coalescence" mode, the minerals in each coal particle are assumed to coalesce fully, producing one ash particle per coal particle. (3) In the "char fragmentation" mode, which applies to cenospheric chars, ash particles are formed by the coalescence of inclusions that have high probabilities of encountering each other as the cenospheric char shell burns away.

The generation of ash under the "full coalescence" and "no coalescence" modes was addressed in a previous article (Wilemski et al., 1992). The algorithm discussed here was developed primarily to treat ash formation from cenospheric char particles. However, it is also applicable to non-cenospheric char particles for which it predicts nearly full coalescence. The approach that we have taken is a direct outgrowth of many of the ideas developed by Kang (1991) in his Ph.D thesis. In the following sections we describe the basic ideas underlying the computation of the number and sizes of ash particles released from the char particle. Then we indicate in general terms how the ash release algorithm operates in the present mineral redistribution code. Finally, results are presented for several coals.

8.2.3 Ash Release from Cenospheric Char Particles

During the pyrolysis and devolatilization of pulverized bituminous coal, many coal particles become plastic and deform into thin-walled cenospheres due to high internal gas pressure. We assume that most of the initial mineral content of each coal particle is retained in or on the cenosphere shell. During the subsequent burnout of the cenospheric char particle, the shell becomes thinner and weaker. Any large pores (blowholes) in the shell will lead to lateral burning of the shell and further weaken it. As the char matrix shrinks, mineral inclusions trapped within are brought into contact. If the inclusions are molten, they may then coalesce. Eventually, the shell either burns out fully or breaks into a number of fragments. Either way, the coalesced mineral inclusions are released, producing ash particles whose size and composition are determined by the mineral inclusions found within localized sections of the shell or in the shell fragments. In our model, we assume complete coalescence for each pair of contacting mineral inclusions. We also account for chemical transformations affecting different minerals when computing the chemical composition of the resulting ash particle.

The mineral redistribution code provides us with a discrete set of coal particles of known mineral content giving us the capability of generating ash particles from each coal particle. In order to determine the number and size of the mineral inclusions that coalesce during burnout we adapt the ideas of Kang (1991) whose approach was analogous to that used to treat molecular collisions in the kinetic theory of gases. The basic idea is that as the cenosphere shell burns and becomes thinner, mineral inclusions at the edges of the shell are brought into contact with other inclusions that become exposed as the char burns away. If we assume that all such contacts result in coalescence, we need only estimate the number of such "collisions" for each mineral inclusion in order to calculate the final size of the ash particle released.

The number of mineral inclusions of diameter D_j contacted by a larger mineral inclusion of diameter D_i can be estimated by computing the volume encompassed by these two inclusions as the shell burns out and multiplying this volume by the number density of minerals of size j in the shell. As sketched in Figure 8-1, this volume is proportional to the effective "collision cross-section" of the two inclusions times an effective thickness δ_e of the cenosphere. The volume of inclusion i should also be subtracted from the volume swept out because the "collision partners" (the size j inclusions) are excluded from char occupied by the size i inclusion. Similarly, in computing the number density of mineral inclusions of a given size in the cenosphere, the shell volume should be corrected for the volume of all larger mineral inclusions. Smaller mineral inclusions are obviously excluded from shell volume occupied by the larger minerals, effectively increasing their number density in the remaining carbon matrix.

Figure 8-1. Two-dimensional schematic of interaction region swept out by mineral inclusions of diameter D_i and D_j during burnout. Only inclusions whose centers lie within the circular cross section of diameter $D_i + D_j$ will be intercepted by the larger mineral inclusion.

We next consider how to determine the cenosphere shell thickness δ , an important parameter strongly influencing ash formation. We imagine the char particles to be spherical shells with uniform thickness δ as shown in Figure 8-2. The value of δ is found using a volume conservation argument involving the following coal particle properties: initial unswollen volume V , swelling index S , swollen particle diameter D_O , diameter of inner spherical cavity D_I , porosity of the shell ϕ , and the volatile fraction of mineral-free coal matrix f_v . This last parameter is related to the more familiar volatile weight fraction of the coal, f , through the relation $f = f_v(1 - \phi_M)$, where ϕ_M is the volume fraction of mineral in the coal. To obtain δ , we first equate the volume of the swollen char particle ($S^3V = \pi D_O^3/6$) to the sum of the mineral volume V_M , the residual "carbon" volume $(V - V_M)(1 - f_v)$, the volume of the inner cavity $\pi D_I^3/6$, and the shell pore volume formed during devolatilization $\phi \pi (D_O^3 - D_I^3)/6$. The resulting equation is then solved for the ratio $\gamma = D_I/D_O$ which, in turn, yields δ through the definition, $\delta = D_O(1 - \gamma)/2$. The expression for γ is

$$\gamma^3 = 1 - S^{-3}(1 - f_v + f_v V_M/V)/(1 - \phi), \quad (8-1)$$

Figure 8-2. Two-dimensional illustration of conical volume swept out by two mineral inclusions due to spherical shape of char particle.

which shows that δ depends most strongly on S , f_v , and ϕ . The behavior of δ predicted by this simple model is discussed later.

The effective length, δ_e is related to δ , the thickness of the cenosphere shell, but its specific value depends on two principal considerations. First, δ_e should reflect the radial dimension of the shell volume containing all of the mineral inclusions destined to end up as a single ash particle. Clearly, δ is an upper bound for this value. A smaller value is possible if the shell contained a sizeable fraction of pores large enough to disengage any ash particle encountering such a pore. Kang (1991) has shown that the separation length can be estimated from the formula

$$L_s = (2/3)D_p(1-\phi_p)/\phi_p, \quad (8-2)$$

where D_p is the diameter of the pore encountered by the ash particle and ϕ_p is the porosity associated with those pores. Obviously, in most situations, D_p must exceed the ash particle diameter in order for the ash particle to be released. As discussed later, δ is typically 10 to 30% of D_o , that is, between 1 and 3 μm for the smallest coal particles and between 20 and 60 μm for the largest. Mineral inclusions larger than δ will not undergo coalescence for geometric reasons unless they are captured within the cenosphere interior - a special case. Purely geometric considerations imply that for mineral inclusions occupying a substantial fraction of the shell thickness, for example those with $D_i > \delta/3$, it is unlikely that large pores with $D_p > D_i$ will be found between the mineral inclusion and the shell boundaries often enough to effect significant ash release. Thus, for this case we must have $L_s \approx \delta$. In larger coal particles, smaller mineral inclusions will be captured efficiently by larger mineral inclusions precluding their release by intercepting a smaller pore. Again, we have $L_s \approx \delta$. Finally, if we consider small mineral inclusions ($D = 2.5 \mu\text{m}$) in small coal particles ($D_o = 10$ to $20 \mu\text{m}$), we find from Eq. (8-2) (with $D_p = 2.5 \mu\text{m}$ and $\phi_p = 0.2$) that $L_s = 6.7 \mu\text{m}$, a value larger or, at best, comparable to δ . Thus we conclude that δ is a suitable initial estimate for the separation length. A second consideration addressed by Kang (1991) concerns the effect of the geometry of the spherical shell on the coalescence process. As burning proceeds, inclusions initially too far apart to coalesce in a linear burning geometry can approach each other as the spherical particle shrinks. Thus additional volume is consumed bringing more mineral inclusions together. The situation is illustrated in Figure 8-2. Kang (1991) estimated a conical correction factor for this effect by taking the shell volume times the ratio of the mineral inclusion cross-sectional area to the total area of the spherical surface at the inner ash separation distance. In this case, that corresponds to the inner surface of the cenosphere.

A more general result can be found by computing the fraction of the total shell volume occupied by the cross-hatched "interaction" region in Figure 8-2. This fraction

equals $(1-\cos\theta)/2$ where $\sin\theta = (D_i + D_j)/(D_i + D_j + D_I)$. This result reduces to that obtained by Kang (1991) when $D_I \gg (D_i + D_j)$, but in the opposite limit, for very small values of D_I , it yields the volume of the hemisphere for the interaction volume. This implies that two ash particles per coal particle will form in this limit. Thus, in this limit the shell fragmentation model yields results that are very close to the full coalescence limit.

8.2.4 Description of Ash Release Algorithm

To implement the above description of ash release in the engineering model computer code, the following procedure is used. The initial stages of the calculation are carried out using the mineral redistribution code described above. After the mineral inventory of each coal particle is established, the ash release procedure is begun. In the present version of the code, to simplify the bookkeeping involved, coal particles are analyzed in order of largest to smallest, followed by the analysis of all excluded mineral particles. To compute the ash released from a given coal particle, the code first calculates δ and the number densities of the different sized mineral inclusions. The final preliminary step involves calculating the average numbers of various sized mineral inclusions that coalesce into a single ash particle.

The next step determines the fate of all mineral inclusions whose diameter exceeds δ . These are placed into the excluded mineral category on the grounds that they would be released from the char during burnout with little or no coalescence with smaller inclusions. After this step only minerals smaller than δ are left in the shell. These minerals are then combined to form ash particles in a sequential process beginning with the largest mineral inclusions, since these occupy the largest volume of char.

The mineral inclusions of each size to be combined with a given inclusion are selected randomly (averages are used if the numbers are large), and the inventory of mineral sizes and types is adjusted at each step. After the smallest mineral inclusions have been added, organically bound inorganics are added in proportion to the char volume "consumed" in forming this ash particle. The ash particle is then analyzed to determine its size and composition, and the results are stored to await statistical analysis after all ash particles have been treated. When inclusions of a given size are exhausted in the shell, mineral inclusions of the next smaller size are then considered as the seed particles for the accumulation of the remaining smaller mineral inclusions. In this way, a sequence of ash particles of descending size is generated from each coal particle. Figure 8-3 schematically illustrates the ash generation procedure from a cenospheric char particle.

8.3 Results

8.3.1 Behavior of Shell Thickness Based Upon Coal Properties

To investigate the dependence of δ predicted by Eq. (8-1) and its influence on the calculated ash size distribution, a number of calculations were performed using the characteristics of a nominal Illinois #6 bituminous coal. For baseline properties, we assumed a mineral content of 10 wt%, a shell porosity, ϕ , of 15%, and a volatile weight percent of

Figure 8-3. Schematic representation of ash particle formation and release from a cenospheric char particle. Minerals within the dashed sectors come into contact and coalesce during burnout. Only four ash particles are shown, although many hundreds may be produced from the larger coal particles.

60, which yields $f_v \approx 0.63$ after renormalizing for the mineral volume. Figure 8-4 shows how δ varies with ϕ for four values of the shell porosity. Only for $S=1$ and as ϕ approaches f_v is the variation significant. In this case, the increasing shell porosity consumes so much of the total particle volume that the inner cavity is forced to shrink substantially to conserve volume. For other values of S , the increased size of the particle permits δ to remain a small fraction of the particle diameter despite the increase in ϕ . Figure 8-5 shows how δ depends on f . The behavior is similar to that in Figure 8-4. For $S > 1$, not much variation is evident. The results for $f < 0.15$ may be unphysical since it is not clear how the excess porosity would be created in such a low volatile coal. For $S=1$ the sharp transition to a noncenospheric char is seen as f drops just below the value of ϕ . The explanation is the same as that provided for Figure 8-4. A limitation of the model is the independence of the parameters f and ϕ . It is thus possible to specify values $\phi > f$ such that the physically impossible results $\gamma < 0$ and $\delta > D_0/2$ occur. In such a case, the noncenospheric limit is always assumed to hold. Figure 8-6 shows how δ depends on S for four different values of f with ϕ held at 0.15. The most significant influence is seen to occur as S approaches one for the smaller values of f . The approach to the noncenospheric limit is also seen when $f=0.15$.

Finally in Figure 8-7, the dependence of δ on the unswollen coal particle diameter D is shown. For this plot, the average value of δ was obtained for each 10 μm wide size cut of an ensemble of coal particles whose sizes ranged from 10 to 160 μm and whose fluctuating mineral contents were determined using the mineral distribution model described earlier. For this exercise, no excluded mineral particles were allowed. All of the curves were calculated with the volatile weight fraction f equal to 0.6. The shell porosity was varied from 15 to 65%. Three of the curves were computed with $S=1$; $S=1.1$ was used for the remaining curve. From the figure, we see that the two lower porosity, nonswelling cases show little dependence of δ on D . The highest porosity nonswelling case shows the strongest dependence, the thickest shells, and the transition to noncenospheric chars for the larger coal particles. The thicker shells are the result of the large value of the porosity as discussed for Figure 8-4. Since the shells are so thick, the value of δ is more sensitive to the mineral

Figure 8-4. Shell thickness versus shell porosity. 60 wt% volatiles, 10 wt% mineral.

Figure 8-5. Char shell thickness versus volatile wt%. 15% char porosity, 10 wt% mineral.

Figure 8-6. Shell thickness versus swelling index. 15% shell porosity, 10 wt% mineral.

Figure 8-7. Shell thickness versus particle size. 60 wt% volatiles, 10 wt% mineral, ϕ and S are porosity and swelling factor respectively.

content of the coal particles than is true in the thin shell regime. In this case, with mineral inclusions randomly distributed, the smaller coal particles receive less than the average amount of mineral matter because minerals larger than the coal particle cannot be placed in that size range. Thus as the average mineral content increases with increasing coal particle size, the shell thickens to accommodate the additional volume until it equals the particle radius. The other highest porosity curve shows what happens when the particle is allowed to swell somewhat ($S=1.1$). In this case, the additional particle volume readily accommodates the added mineral content, and the shell thickness is considerably smaller and shows much less variation with D .

The influence of the shell thickness on ash formation can be inferred from the ash size distributions predicted by the char fragmentation/mineral coalescence model described above. The results are shown in Figure 8-8 on a cumulative volume percent basis. The upper curve corresponds to the mineral distribution and the no coalescence limit. The lowest curve depicts the full coalescence results. All but one of the remaining curves are for nonswelling ($S=1$) conditions. Only the highest porosity nonswelling case, for which the thickest shells occurred, is seen to approach the full coalescence results. The remaining cases, including the only swelling high porosity case, all cluster near the no coalescence limit. Some deviation from this limit is seen for the smaller sizes.

This indicates that some of the smallest mineral particles have coalesced with the largest. The results are very sensitive to small changes in porosity or swelling index for the given value of f . An indication of the degree of coalescence is given in Figure 8-9 which shows the average number of mineral particles used per ash particle as a function of D . For the thin shell cases the number never exceeds five, whereas for the thick shell case the number rapidly grows into the thousands. An indicator of the degree of char fragmentation, inversely related to the Figure 8-9 results, is given in Figure 8-10 where the number of ash particles per coal particle is plotted versus D . Here the thick shell and full coalescence results are indistinguishable along the x-axis. The thin shell chars first start producing substantial numbers of ash particles at about $50\text{ }\mu\text{m}$. The thin shell results lie closer to the no coalescence results as δ diminishes, but for the cases studied there was always some coalescence evident in the larger coal particles.

8.3.2 Comparison with Experimental Results

We turn now to some limited comparisons of measured and predicted ash distributions. Two coals were studied: a cleaned Illinois #6 and a Pocahontas bituminous coal. Ash size distributions were measured in PSIT's drop tube furnace discussed elsewhere (Helble et al., 1993). Figure 8-11 shows the results for the cleaned Illinois #6 compared with the model predictions for the full coalescence limit and for extensive char fragmentation. The full coalescence results fail to describe the experimental behavior, whereas the fragmentation results are highly acceptable. The lack of coalescence in the experimental ash is not surprising when we consider that the cleaning process removes about half of the included mineral from the parent coal. Relative abundances of the major ash

Figure 8-8. Mineral and ash size distributions. 60 wt% volatiles, 10 wt% mineral.

Figure 8-9. Number of minerals per ash particle. 60 volatile wt% 10 wt% mineral.

Figure 8-10. Number of ash versus coal particle size. 60 volatile wt% 10 wt% mineral.

Figure 8-11. Ash size distributions for Illinois #6 cleaned coal.

categories are shown in Figure 8-12. Again, the fragmentation results are in substantially better agreement with the experimental results with the exception of the iron-rich ash particles.

Results for the Pocahontas coal are compared in Figure 8-13. The experimental ash distribution shows that a high degree of coalescence has occurred. Therefore the model was first run in the full coalescence limit. Surprisingly, the full coalescence limit (Model-1 in Figure 8-13) overpredicts the ash in the two finest size ranges and underpredicts the ash in the largest size range. Since the full coalescence limit predicts the coarsest possible ash distribution for a given mineral distribution, these discrepancies strongly suggest that the assumption of a random mineral distribution may be at fault. In a random distribution, the number of minerals placed in each coal size range is directly proportional to the volume fraction of the coal in that size range. In the Pocahontas coal, 40% of the volume is found in the 10 μm coal particles. Thus, 40% of the 2, 4, and 8 μm mineral particles would be allocated to this coal size. If just 2- μm minerals are considered, and these are uniformly distributed in the bulk coal on a simple cubic lattice, the average interparticle distance would be about 11 μm . This agrees with the result of the random distribution which places about one such small mineral inclusion per 10 μm coal particle. On the other hand, knowing that mineral-rich veins occur in unground coal, we might anticipate on statistical grounds that the small coal particles would be largely mineral free, that significant amounts of extraneous minerals would be produced, and that only the larger coal particles would contain significant numbers of mineral inclusions.

Figure 8-12. Ash composition for Illinois #6 cleaned coal.

Figure 8-13. Mineral and ash size distributions for Pocahontas coal.

To test the effect of such a nonrandom mineral distribution on the fly ash distribution, we modified the mineral distribution scheme to allocate to the smallest coal size range only a specified fraction of the minerals that would otherwise be randomly placed in it. The nonallocated minerals were proportionately redistributed over the larger coal sizes thus enhancing their share of the mineral loading. Since we had no CCSEM data available regarding the distribution of extraneous minerals, we were forced to rely on simple volume exclusion tests to generate excluded minerals. This procedure results in no excluded 2, 4, or 8 μm minerals which is likely to be incorrect. However, the experimental ash distribution provides an upper bound for the amount of extraneous mineral in these sizes if we assume that all ash of these sizes was formed from extraneous mineral matter. The small amount of ash observed below 5 μm indicates that at least the 2 and 4 μm minerals were mainly included within carbonaceous coal particles. When the modified mineral distribution procedure was used with the 10 μm coal particles receiving only 5% of the random mineral allotment, the full coalescence results (not shown) now underpredicted the ash in the three smallest size ranges as well as in the largest size. This seemed to indicate that a small degree of char fragmentation could be responsible for the finer ash. We thus ran the model in the fragmentation mode (Model-2 in Figure 8-13) with parameters chosen to produce very thick shells: δ/D ranged from 0.4 to 0.49 as D varied from 10 to 130 μm . With these parameters the model generated 3 to 4 ash particles per coal particle from the larger (90 to 130 μm) coal particles and 5 or 6 ash particles for each smaller coal particle (20 to 80 μm). Only one out of ten of the mineral-deficient 10 μm coal particles produced an ash particle. The resulting ash size distribution is seen in the figure to be quite accurate for the largest and two smallest size ranges; the intermediate size ranges are either under- or overpredicted significantly.

8.4 Conclusions

What do these results mean? What can we learn from the failure of the model to accurately predict the ash particle size distribution in the case of the Pocahontas coal? First, with random mineral distributions, the inability of full coalescence to correctly predict the finest and largest ash particle indicates that at least for this coal the assumption of random mineral distribution is inadequate. The failure of either full coalescence or fragmentation to adequately represent the particle size distribution even with a simple, crude nonrandom mineral distribution should probably be taken as evidence for the importance of knowing what distribution of char structures occurs for a given coal. Clearly, it will often be inadequate to assume that every coal particle in the sample has the same char structure. Depending on the maceral distribution for the coal, some particles may swell and become cenospheric, others will not, and the ash particle size distribution will depend on the frequency and types of char structures occurring. We have not even addressed the importance of an additional type of nonrandomness, that due to associations of specific types of minerals. Work by Harb and Wigley reported at this conference will enable us to account for these effects in modeling ash formation.

8.5 Plans for Coming Quarter

Although the model has been tested for several cases, a detailed parameter variation study has not been conducted. Prior to incorporating the effects of reducing stoichiometry in the model, it is necessary to explore the capabilities and limitations of the current model in some detail. At PSI, an existing coal and ash database will be used to provide comparison with model-generated results. The model will be tested against experimental data generated during the combustion of approximately fifteen coals by carrying out parametric studies; a set of parameters that gives the best fit will be identified. Based upon these test run results and additional sensitivity analyses on the adjustable parameters, rules for selecting appropriate values for these parameters will be developed. Comparison between the modeling and the experimental results will be mainly a comparison of ash particle size and composition distributions. A more systematic comparison might be possible by introducing an index that can quantify the extent of coalescence between ash particles in terms of chemical composition changes. The development of such an index will also be explored during the coming quarter.

SECTION 9
REFERENCES

9. REFERENCES

- Abbot, M.F. and Austin L.G. (1985) Studies on Slag Deposit Formation in Pulverized-Coal Combustors, *Fuel* 64.
- Allen, R.M. and VanderSande, J.B., 1984, *Fuel*, Vol. 63, p. 24.
- Barta, L. E., Beér, J. M., Sarofim, A. F., Teare, J. D., and Toqan, M. A., 1993, Coal Fouling Tendency Model, *Proceedings Engineering Foundation Conference on the Impact of Ash Deposition on Coal-Fired Plants*, Solihull, UK, June.
- Barta, L.E., Toqan, M.A., Beér, J.M., and Sarofim, A.F., 1992, *Twenty-fourth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, PA, pp. 1135-1144.
- Barta, L. E., Vámos, G., Toqan, M. A., Teare, J. D., Beér, J. M., and Sarofim, A. F., 1990, *Mat. Res. Soc. Symp. Proc.*, Vol. 178, pp. 67-82.
- Barta, L. E., Horváth, Beér, J. M., and Sarofim, A. F., 1990, *Twenty-third Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, PA, pp. 1289-1296.
- Baxter, L.L., Mitchell, R.E., and Fletcher, T.H., 1993, Release of Inorganic Material During Coal Devolatilization. *Combustion and Flame* (to appear).
- Baxter, L. L., and De Sollar, 1993, A Mechanistic Description of Ash Deposition during Coal Combustion: Predictions Compared to Observations, *Fuel* (to appear).
- Baxter, L.L. and Dora, L., 1992, The Combustion Behavior of Eastern and Western Coals: Comparison between a Blend and Its Individual Components, *ASME Paper 92-JPGC-FACT-14*.
- Benson, S. A., Hurley, J. P., Zygarlicke, C. J., Steadman, E. N., Erickson, T. A., 1993, Predicting Ash Behavior in Utility Boilers, *7th Annual Advanced Combustion Engineering Research Conference on Clean and Efficient Combustion of Fossil Fuel and Toxic Waste*, Park City.
- Benson, S.A. and Holm, P.L., 1985, *Ind. Eng. Chem. Prod. Res. Dev.*, Vol. 24, p. 145.
- Boni A., et. al (1989) Transformations of Inorganic Coal Constituents in Combustion Systems. Quarterly Report No. 4, US DOE Contract No. DE-AC22-86PC90751, Pittsburgh Energy Technology Center, Pittsburgh PA.
- Bryers, R. W., 1992, Fireside Behavior of Mineral Impurities in Fuels: From Marchwood 1963 to Palm Coast 1992, *Proceedings of the Engineering Foundation Conference on Inorganic Transformations and Ash Deposition during Combustion*, Ed., S. A. Benson, A.S.M.E. Press, New York, pp. 3-68.

Charon, O., Sarofim, A.F., and Beér, J.M., 1990, *Prog. Energy Combust. Sci.* vol. 16, pp. 319.

Duzy A.F. (1965) Fusibility of Lignite Type Ash. ASME Paper 65-WA/FU-7.

Duzy A.F. and Walker J.B. (1965) Utilization of Solid Fuels Having Lignite Type Ash. US Bureau Mines Inf. Circ. 8304.

Field, M. A., Gill, D. W., Morgan, B. B., and Hawksley, P. G. W., 1967, *Combustion of Pulverized Coal*, BCURA, Leatherhead, U.K.

Gray R.J. and Moore G.F. (1974) Burning the Sub-Bituminous Coals of Montana and Wyoming in Large Utility Boilers. ASME paper 74-WA/FU-1.

Gupta, R. P., Truelove, J. S., Wall, T. F., Miyama, S. K., and Hattori, C., 1992, Ash Deposition on the Burner Walls of Coal Fired Furnaces, *Proceedings of the Engineering Foundation Conference on Inorganic Transformations and Ash Deposition during Combustion*, Ed., S. A. Benson, A.S.M.E. Press, New York, p. 639-658.

Helble, J.J., Srinivasachar, S., Wilemski, G., Boni, A.A., Kang, S.-G., Sarofim, A.F., Graham, K.A., Beér, J.M., Peterson, T.W., Wendt, J.O.L., Gallagher, N.B., Bool, L., Huggins, F.E., Huffman, G.P., Shah, N., and Shah, A., 1992, Transformations of Inorganic Coal Constituents in Combustion Systems, Final Report submitted to the U.S. DOE/PETC, November, Available from NTIS, Document DE/PC/90751-T15 (BE93013076). 3 volumes.

Helble, J. J. and Sarofim, A. F., 1989, *Combustion and Flame*, Vol. 76, pp. 183-196.

Helble, J. J., Srinivasachar, S., Senior, C. L., Wilemski, G., Baker, J. E., Simons, G. A., and Johnson, S. A., 1992, A Fundamentally Based Model of Slag Formation in Utility Boilers, *The Second Australian Workshop on Ash Deposition*, Brisbane, Queensland, Australia.

Huggins, F.E., Huffman, G.P., Shah, N., and Shah, A., 1992, Transformations of Inorganic Coal Constituents in Combustion Systems, Final Report submitted to the U.S. DOE Pittsburgh Energy Technology Center under contract DE-AC22-86PC90751.

Hurley, J.P., and Schobert, H.H., "Ash Formation During Pulverized Subbituminous Coal Combustion. 1. Characterization of Coals, and Inorganic Transformations during Early Stages of Burnout," *Energy & Fuels* 6, 47-58 (1992).

Hurley, J.P., and Schobert, H.H., "Ash Formation During Pulverized Subbituminous Coal Combustion. 2. Inorganic Transformations during Middle and Late Stages of Burnout," *Energy & Fuels* (in press) (1993).

Joutensaari, J., Kauppinen, E.J., and Jokiniemi, J., 1993, Studies on Ash Vaporization in Real Scale Pulverized Coal Combustion, *Proceedings Engineering Foundation Conference on the Impact of Ash Deposition on Coal-Fired Plants*, Solihull UK, June.

Kang, S.G., "Fundamental Studies of Mineral Matter Transformation during Pulverized Coal Combustion: Residual Ash Formation," Ph.D. Thesis, M.I.T. Department of Chemical Engineering, Cambridge MA (1991).

Kang, S. G., Kerstein, A. R., Helble, J. J., and Sarofim, A. F., 1990, *Aerosol Science and Technology*, Vol. 13, pp. 401-412.

Kang, S.G., Helble, J.J., Sarofim, A.F., and Béer, J.M., "Time Resolved Evolution of Fly Ash During Pulverized Coal Combustion," *Twenty-Second Symposium (Int'l) on Combustion*, The Combustion Institute, 231-238 (1988).

Kauppinen, E. I. and Pakkanen, T. A., 1990, *Environ. Sci. Technol.*, Vol. 2, pp. 1881-1818.

Lindner, E. R., and Wall, T. F., 1991, *The Twenty-third Symposium (International) on Combustion*, pp. 1313, The Combustion Institute, PA.

Mims, C.A., Neville, M., Quann, R.J., House, K., and Sarofim, A.F., 1980, *AIChE Sympos. Series*, No. 201, Vol. 76, pp. 188-194.

Monroe, L. S., 1989, An Experimental and Modeling Study of Residual Fly Ash Formation in Combustion of a Bituminous Coal, Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, MA.

Monroe, L.S., 1989, An Experimental and Modeling Study of Residual Fly Ash Formation During Combustion of Bituminous Coal, Ph.D. thesis, Massachusetts Institute of Technology, Cambridge, Mass.

Quann, R.J., Neville, M., and Sarofim, A. F., 1990, *Combust. Sci. Tech.*, Vol. 74, pp. 245-265.

Quann, R.J. and Sarofim, A.F., 1982, *The Nineteenth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, p. 1429.

Raask, E., 1985, *Mineral Impurities in Coal Combustion*, Springer Verlag, New York.

Raask E. (1985) Mineral Impurities in Coal Combustion. Hemisphere Publ. Co., NY, NY.

Reid, W. T., 1971, *External Corrosions and Deposits*, Elsevier, New York.

Reid W.T. and Cohen P. (1944) Factors Affecting the Thickness of Coal-Ash Slag on Furnace Wall Tubes. Trans. ASME 66.

Rosner, D. E., 1986, *Transport Processes in Chemically Reacting Flow*, Butterworth.

Shah, N., Huffman, G. P., Huggins, F. E., and Shah, A., 1992, Graphical Representation of CCSEM Data for Coal Minerals and Ash Particles, *Proceedings of the Engineering Foundation Conference on Inorganic Transformations and Ash Deposition during Combustion*, Ed., S. A. Benson, A.S.M.E. Press, New York, pp. 179-190.

Skrifvars, B. J., Hupa, M., and Hyulty, P. H., 1991, *Journal of Institute of Energy*, Vol. 64, pp. 196-201.

Srinivasachar, S., Helble, J.J., Boni, A.A., Shah, N., Huffman, G.P., and Huggins, F.E., 1990, *Prog. Energy Combust. Sci.*, Vol. 16, 293.

Srinivasachar, S., Senior, C.L., Helble, J.J., and Moore, J.W., 1992, *Twenty-Fourth Symposia (International) on Combustion*, The Combustion Institute, Pittsburgh, p. 1179.

Wall, T.F., Bailey, J.G., and Wibberley, L.J., 1990, *Proceedings of the Engineering Foundation Conference on Mineral Matter and Ash Deposition from Coal*, R.W. Bryers and K.S. Vorres, Eds., p. 249.

Walsh, P. M., Sarofim, A. F., and Beér, J. M., 1992, *Energy and Fuels*, Vol. 6, pp. 709-715.

Wibberley, L. J. and Wall, T. F., 1982, *Fuel*, Vol. 61, pp. 87-93.

Wilemski, G., Srinivasachar, S., and Sarofim, A. F., 1992, Modeling of Mineral Matter Redistribution and Ash Formation in Pulverized Coal Combustion, *Proceedings of the Engineering Foundation Conference on Inorganic Transformations and Ash Deposition during Combustion*, Ed., S. A. Benson, A.S.M.E. Press, New York, pp. 545-564.

Yang, N. Y., and Baxter, L. L., 1992, Instrument and Sample Preparation Considerations for Computer-Controlled Scanning Electron Microscopy (CCSEM) Analyses, *Proceedings of the Engineering Foundation Conference on Inorganic Transformations and Ash Deposition during Combustion*, Ed., S. A. Benson, A.S.M.E. Press, New York, pp. 191-206.

Zygarlicke, C.J., Ramanathan, M. and Erickson, T.A., 1992, Fly Ash Particle-Size Distribution and Composition: Experimental and Phenomenological Approach, in *Inorganic Transformations and Ash Deposition During Combustion*, ed by S.A. Benson, p. 525, ASME, New York.

END

**DATE
FILMED**

2/24/94