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

Quarterly Report No. 4
for the Period 1 January to 31 March 1994

Drs. J.J. Helble, L.E. Bool, and C.L. Senior
PSI PowerServe

Prof. A.F. Sarofim and Mr. Taofang Zeng
Massachusetts Institute of Technology

and

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

DATE PUBLISHED - May 1994
Prepared under
DoE Contract No. DE-AC22-93PC92190

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

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SECTION 1
EXECUTIVE SUMMARY

1. EXECUTIVE SUMMARY

The technical objectives of this project are:

- a. To identify the partitioning of inorganic coal constituents among vapor, submicron fume, and fly ash products generated during the combustion of pulverized coal under a variety of combustion conditions. Fuel lean and fuel rich combustion conditions will be considered.
- b. To identify and quantify the fundamental processes by which the transformations of minerals and organically-associated inorganic species occurs. Emphasis will be placed on identifying any changes that occur as a result of combustion under sub-stoichiometric combustion conditions.
- c. To incorporate the effects of combustion stoichiometry into an engineering model for ash formation based upon the understanding developed in (a) and (b). When completed, this model will predict the particle size and chemical composition distributions of ash formed during the combustion of pulverized coal under a broad range of conditions.

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

The work discussed in this report highlights the accomplishments of the fourth quarter of this 2-year project. This includes a summary of analytical data for Silverdale coal, a bituminous coal provided by National Power; a discussion of additional coal analytical data by PSI PowerServe; the results of preliminary University of Kentucky Mössbauer analysis of combustion ash samples generated previously by PSI PowerServe; the results of preliminary combustion experiments conducted at the Massachusetts Institute of Technology (MIT); a discussion of stickiness experiments that were conducted by PSI PowerServe using the program coals; the results of model calculations using PSI PowerServe's engineering model for ash formation (EMAF) of ash particle size and composition distributions for two different coals, and the results of subsequent comparison with field data. Finally, a brief discussion of a submicron ash formation model that will be added to EMAF is presented by PSI PowerServe.

Specifically, in Section 3 of this report we report data for Silverdale bituminous coal that were obtained from researchers at Imperial College. Also in Section 3, the results of additional CCSEM analysis of the run-of-mine Pittsburgh #8 coal are reported. Ternary diagrams derived from CCSEM data for all four of the U.S. coals are also shown in this

diagrams derived from CCSEM data for all four of the U.S. coals are also shown in this section; data suggest that the composition range of certain classes of mineral matter may narrow with increasing extent of coal cleaning.

In Section 4, the results of University of Kentucky Mössbauer characterization of ash samples generated by PSI PowerServe are presented. Results for all coals and conditions considered demonstrate increasing oxidation of iron from the (+2) to the (+3) state in glass. For the washed Pittsburgh #8 bituminous coal, the total amount of iron contained in glassy phases decreased slightly as residence time prior to sampling was increased. This suggests little chemical interaction between iron minerals and aluminosilicate minerals during the late stages of burnout. For the Black Thunder sub-bituminous coal, Mössbauer data suggest incorporation of small amounts of crystalline iron oxide into the glassy phases occurs as the stoichiometric ratio is increased to more oxidizing conditions; a weak signal, however, prevents absolute determination of this interaction.

In Section 5, the results of additional furnace characterization tests and data generated during screening experiments using beneficiated Pittsburgh #8 are reported by MIT.

In Section 6, experimental results obtained during stickiness testing with the four U.S. coals are described by PSI PowerServe. Combustion experiments were conducted under stoichiometric ratios ranging from 0.6 to 1.2, and samples were extracted at residence times ranging from 0.25 to approximately 3 s. In each experiment, the ash was collected and analyzed for forms of iron by Mössbauer spectroscopy, and particle stickiness was measured in laboratory deposition tests. As discussed in detail in Section 6, the amount of carbon in the ash and the amount of iron present in glassy phases are both believed to influence the deposition and sticking behavior of these particles.

In Section 7, ash particle size and chemical composition distributions calculated for two non-U.S. coals are discussed by PSI PowerServe. These results compared favorably with field data obtained from the first hopper of an electrostatic precipitator from two utility boilers burning these coals. Field data were provided by the Aerosol Technology Group of VTT Technical Research Center of Finland (VTT). Also in Section 7, a model for the formation of submicron ash is described.

SECTION 2

OVERVIEW OF PROGRAM TASKS (PSI PowerServe)

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 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.

Figure 2-1. Program structure.

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

Activities under this task will include collection and examination of ash samples at varying combustion temperatures and/or oxidant concentrations. Ash samples will be collected using extractive sampling. In-situ deposit collection techniques will be used to measure ash particle collection efficiencies as a function of temperature and stoichiometric ratio. Extracted ash and deposit samples will be characterized as necessary to determine particle size and chemical composition distributions as well as the chemical state of key components such as iron and calcium.

Task 3 - PowerGen Collaboration (PSI)

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

Task 4 - Engineering Model for Ash Formation (PSI)

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

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

The University of Kentucky will apply advanced analytical techniques such as computer-controlled scanning electron microscopy (CCSEM), Mössbauer spectroscopy, and x-ray absorption fine structure spectroscopy (XAFS) to characterize coal and ash samples from this program as needed by the individual principal investigators. If agreed upon by PSI,

UKy, and the DoE program manager, UKy will also analyze selected coal and/or ash samples obtained from the PowerGen program in Great Britain.

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

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

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

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

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

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

SECTION 3

COAL SELECTION AND ACQUISITION (PSI PowerServe)

3. COAL SELECTION AND ACQUISITION

Four U.S. coals are being studied in this program. These coals are (1) Black Thunder sub-bituminous coal from the Powder River Basin, (2) a run-of-mine Pittsburgh #8 coal from the Appalachian Basin, (3) a washed commercial version of a Pittsburgh #8 coal, and (4) a physically beneficiated Pittsburgh #8 product produced by Southern Company. In addition, a bituminous coal obtained from the utility National Power in Great Britain is being tested at PSI PowerServe. This coal has been studied extensively as part of a comprehensive program involving several groups and combustion and deposition testing at bench-, pilot-, and full-scale facilities. This integrated program is led by the utility PowerGen.

3.1 Silverdale Coal

Ultimate, proximate, and ash analyses of the Silverdale coal were provided by Imperial College. Ultimate and proximate analyses are reported in Table 3-1 and the ash chemical composition analysis is provided in Table 3-2. The mineralogy of this coal is being determined by computer-controlled scanning electron microscopy (CCSEM) at Imperial College; data will be reported as soon as they are available.

Table 3.1. Ultimate and Proximate Analysis of Silverdale Bituminous Coal

Proximate (wt%) (as determined)	
Moisture	1.9
Volatile matter	32.9
Fixed carbon	49.0
Ash	16.2
Ultimate (wt%) (dry basis)	
C	67.8
H	4.7
N	4.6
O (difference)	6.3
S	3.4
Ash	16.2
HHV, Btu/lb (daf)	14,740

Because of the large quantity of Silverdale coal tested in the PowerGen program, ash and water content of the specific sample received by PSI were analyzed and compared with the "bulk" coal data provided by Imperial College. Comparisons were also made for the other four program coals. In each case, duplicate analyses were performed. Water content was determined by placing each sample in a ceramic boat, placing the boat in a drying oven, heating the sample to 120°C, holding it at temperature for 120 min, and measuring the weight change. Ash content was then determined by placing the dried sample in a tube furnace and

Table 3.2. Ash Chemical Analysis -- Silverdale Bituminous Coal (wt% of ash)*

SiO ₂	44.5
Al ₂ O ₃	24.5
Fe ₂ O ₃	22.0
CaO	2.4
MgO	1.0
Na ₂ O	0.6
K ₂ O	2.0
TiO ₂	1.0
P ₂ O ₅	0.2
So ₃	1.7
Other	0.2
*Data provided by Imperial College.	

heating it under flowing air to a temperature of 500°C , holding it there for approximately 30 min for devolatilization to be completed, and then heating it to 900°C to complete combustion. The sample was held at temperature for approximately 20 min before it was cooled to room temperature. The weight loss was then determined and used to calculate ash content. Results of these measurements for all five coals are presented in Table 3-3. In all cases, values obtained at PSI for the specific PSI PowerServe sample showed good agreement with data by the supplier (Silverdale coal) or the analytical laboratory (other coals; see Quarterly Report No. 3).

Table 3.3. PSI Measurements of Coal H₂O and Ash Content

	PSI H ₂ O	Reported H ₂ O	PSI Ash	Reported Ash
Pittsburgh #8 Run of Mine	1.2	1.02	27.5	27.44
Pittsburgh #8 Washed	0.8	1.4	7.5	7.48
Pittsburgh #8 Cleaned	2.0	2.0	5.1	5.21
Black Thunder	23.6	24.3	5.0	4.49
Silverdale	2.1	1.9	16.3	16.5

3.2 Repeat CCSEM Analysis of Run-of-Mine Pittsburgh #8

In Quarterly Report No. 3, three mineral size distributions were presented for the run-of-mine Pittsburgh #8 coal. Data reported by the University of Kentucky were in good agreement with data reported by Microbeam Technologies Inc. (MTI) using included/excluded mineral CCSEM analysis. A size distribution reported by MTI using standard CCSEM analysis was indicative of considerably smaller minerals, however. To resolve this

discrepancy, MTI re-analyzed the sample using standard CCSEM techniques along with ZAF correction of the composition data. As seen in Figure 3-1, the most recent MTI data fall between the two prior MTI analyses, but are close to the U. Kentucky data. In Table 3-4, mineral composition analyses for the latest MTI measurement are compared with prior MTI and U. Kentucky data. Quartz was less frequently detected and "unknown" phases more frequently detected than in prior runs (complete results reported in the appendix). It is clearly impossible to determine which one analysis is "correct" for this program. While averaging could be used to obtain "best" values for the data, the differences in facility and techniques used make this an unattractive option. It is therefore recommended that the University of Kentucky analysis be used for data interpretation in this program so that all coals can be compared on a consistent basis.

Figure 3-1. Mineral size distribution for run-of-mine Pittsburgh #8 by CCSEM.

Table 3.4. Comparison of (Kaiser) Pittsburgh #8 CCSEM Mineral Data -- UK and MTI (results expressed in wt%)

Mineral	UK	MTI (Inc/exc Analysis)	MTI (Std Analysis)	MTI (Repeat)
Quartz	21.7	16.3	18.7	8.7
Kaolinite	6.4	12.0	11.0	7.8
Montmorillonite	0.2	3.9	4.8	4.2
K-Al silicate*	22.0	27.4	25.3	32.0
Pyrite	11.9	11.7	8.3	7.6
Misc. silicates	22.7	10.0	11.0	13.4
(Kaol + Mis. sil.)	29.1	22.0	22.0	21.2
*"Illite", with more restrictive chemical definition, in UK categorization.				

3.3 CCSEM Mineral Distributions for U.S. Coals

CCSEM mineral distributions for the four U.S. coals were plotted on ternary diagrams to provide an indication of the spread in mineral composition for each coal. Each ternary diagram shows three elements: Al, Si, and either K or Ca. Compositions detected by CCSEM are indicated by a point within the ternary region of the diagram; the volume of particles with the indicated composition is indicated by the height of the associated peak. Only those particles containing at least 80 atom percent of the three indicated elements (on an oxygen-free basis) are shown. University of Kentucky CCSEM data were used in all cases.

In Figure 3-2, K-Al-Si ternary diagrams for the four coals are presented. Comparison of Figure 3-2(a), the run-of-mine Pittsburgh #8 coal, Figure 3-2(b), the washed Pittsburgh #8 coal, and Figure 3-2(c), the beneficiated Pittsburgh #8 coal, suggests that the K-Al-Si composition range becomes narrower as the coal is more deeply cleaned. The fraction of K-Al-Si particles that are non-potassium containing aluminosilicates also increases with increasing degree of coal cleaning. Caution should be exercised in interpreting these results - the SCS beneficiated coal, for example, was not derived from the washed commercial Pittsburgh #8 -- the differences may be a result of increasing degree of cleaning. Note, by way of comparison, the data presented for Black Thunder sub-bituminous coal in Figure 3-2(d). The narrow spread in compositions reflects the low potassium content of this coal.

Ternary diagrams for Ca-Al-Si, presented in Figures 3-3(a) through 3-3(d), show a similar trend. Figure 3-3(d), representing the Black Thunder coal, is markedly different from the bituminous coals. This is an expected consequence of the relatively high calcium content of this coal's ash. Again, Figures 3-3(a) through 3-3(c) are suggestive of a narrowing in composition range with increasing degree of coal cleaning.

(a) Run-of-mine Pittsburgh #8

(b) Washed Pittsburgh #8

Figure 3-2. K-Al-Si ternary diagrams for four program coals.

(c) Beneficiated Pittsburgh #8

(d) Black Thunder

Figure 3-2. K-Al-Si ternary diagrams for four program coals (cont.)

(a) Run-of-mine Pittsburgh #8

(b) Washed Pittsburgh #8

Figure 3-3. Ca-Al-Si ternary diagram for four program coals.

(c) Beneficiated Pittsburgh #8

(d) Black Thunder

Figure 3-3. Ca-Al-Si ternary diagram for four program coals (cont.).

SECTION 4

TASK 5.1 - ADVANCED TECHNIQUES FOR COAL AND ASH CHARACTERIZATION (University of Kentucky)

4. ADVANCED TECHNIQUES FOR COAL AND ASH CHARACTERIZATION

Ash samples generated by PSI PowerServe in their laboratory combustion furnace were analyzed for forms of iron by Mössbauer spectroscopy during the past quarter. The samples were generated by burning the four U.S. coals under conditions of differing oxygen concentration and residence time with the objective of measuring the transformations of crystalline and glassy iron phases.

In Table 4-1, data for ash generated during combustion of the washed Pittsburgh #8 bituminous coal are presented. For these experiments, all conducted under conditions of significant excess oxygen, iron present as Fe (+2) glass rapidly oxidized to Fe (+3) glass, with continuing oxidation to crystalline oxide (magnetite) also noted. Hematite, the fully oxidized form of crystalline iron, appears in increasing amounts with increasing residence time.

Table 4.1. Mössbauer Data for Washed Pittsburgh #8 Coal. PSI PowerServe combustion samples. 1500°C furnace set point, 15% O₂, 4 SCFM gas flow rate. SR=15.6.

MK#	CFFLS	Res Time (s)	Phases Present	IS	QS	HO	% Fe
1740	1155	0.25	Fe ⁺³ /Glass	0.33	1.15		
			Fe ⁺² /Glass	1.00	1.90		14
			Magnetite	0.32	0.02	495	12
			Magnetite	0.66	0.00	458	38
			Magnetite	0.67	0.00	416	21
			FeS	0.79	0.00	305	7
							8
1734	1156	0.40	Fe ⁺³ /Glass	0.42	0.88		12
			Hematite	0.38	-0.08	512	47
			Magnetite	0.31	0.00	491	23
			Magnetite	0.68	0.00	455	18
1737	1157	0.55	Fe ⁺³ /Glass	0.36	0.88		11
			Hematite	0.38	-0.08	515	40
			Magnetite	0.31	0.00	490	27
			Magnetite	0.65	0.00	456	23
1739	1158	0.72	Fe ⁺³ /Glass	0.42	0.96		9
			Hematite	0.40	-0.08	517	65
			Magnetite	0.37	0.00	492	9
			Magnetite	0.61	0.00	449	12

In Table 4-2, data collected at longer residence times and at a slightly lower wall temperature using the washed Pittsburgh #8 coal are presented. Wall temperature was decreased 100°C. In these experiments, oxygen partial pressure decreased during combustion, in contrast to the experiments reported in Table 4-1. Again, conversion of Fe (+2) in glass to

Fe (+3) in glass to crystalline oxides was observed with increasing residence time. In Table 4-3, the effects of changing combustion stoichiometry at fixed residence time for this same coal are shown. Fe(+2) glass was the dominant form observed under conditions of SR = 0.6. Table 4-4 presents similar data for the run-of-mine Pittsburgh #8 coal, with similar trends observed.

Table 4.2. Washed Pittsburgh #8 coal, 1400°C furnace set point, 15% O₂, 1 SCFM gas flow rate. SR = 3.9.

MK#	CFFLS	Res Time (s)	Phases Present	IS	QS	HO	% Fe
1727	1159	1.0	Fe ⁺³ /Glass	0.36	1.12		17
			Fe ⁺² /Glass	1.00	2.01		11
			Hematite + Magnetite	0.39	0.05	501	39
			Magnetite	0.67	0.00	462	20
			Magnetite	0.57	0.00	415	12
1728	1160	1.6	Fe ⁺³ /Glass	0.27	1.28		16
			Fe ⁺² /Glass	0.98	1.82		7
			Magnetite	0.33	0.00	493	49
			Magnetite	0.65	0.00	455	28
1729	1161	2.2	Fe ⁺³ /Glass	0.29	1.18		20
			Fe ⁺² /Glass	0.99	1.93		9
			Hematite + Magnetite	0.36	-0.03	498	51
			Magnetite	0.62	0.00	456	14
			Magnetite	0.65	0.00	425	6
1730	1162	2.9	Fe ⁺³ /Glass	0.37	1.07		18
			Hematite	0.43	-0.05	522	59
			Hematite	0.43	-0.04	501	13
			Magnetite	0.52	0.00	460	10

Data for ash generated during combustion of the beneficiated Pittsburgh #8 coal (SCS product) demonstrate a much higher percentage of iron in the glass relative to the other two Pittsburgh #8 coals. These data are shown in Table 4-5.

Data for ash generated during combustion of the Black Thunder sub-bituminous coal are presented in Table 4-6. Two points are worth noting. First, the data suggest that crystalline iron oxide may be incorporated into glassy phases to a greater extent at higher stoichiometric ratios. This is the only coal for which this phenomenon was observed. Second, increasing formation of (+3) iron at the expense of (+2) iron is observed at high stoichiometric ratios, consistent with results for other coals. The low concentration of iron in the Black Thunder coal leads to weak Mössbauer signals; however, additional experimentation and analysis will be conducted to address this.

Table 4.3. Washed Pittsburgh #8 coal, 1500°C furnace set point, 2.6 s residence time

MK#	CFFLS	Res Time (s)	Phases Present	IS	QS	HO	% Fe
1751	1163	1.2	Fe ⁺² /Wüstite (?)	0.88	0.95		24
			Fe ⁺² /Glass	1.03	2.12		25
			Fe ⁺³ /Glass	0.29	0.75		9
			Magnetite	0.33	0.00	491	21
			Magnetite	0.67	0.00	454	15
			Fe _{1-x} S	0.73	0.00	306	6
1756	1164	0.9	Fe ⁺² /Glass (?)	1.23	1.61		22
			Fe ⁺³ /Glass (?)	0.66	1.27		39
			Magnetite	0.28	0.00	491	12
			Magnetite	0.72	0.00	455	19
			Fe _{1-x} S	0.79	0.00	302	9
1752	1165	0.6	Fe ⁺² /Glass	0.97	1.35		55
			Fe ⁺³ /Glass	0.32	0.63		5
			Magnetite	0.26	0.00	484	11
			Fe _{1-x} S	0.72	0.00	306	29

Table 4.4. Run-of-Mine Pittsburgh #8 coal, 1500°C furnace set point, 2.6 s residence time

MK#	CFFLS	Res Time (s)	Phases Present	IS	QS	HO	% Fe
1754	1166	1.2	Fe ⁺² /Glass	1.03	2.02		64
			Fe ⁺³ /Glass (?)	0.50	1.03		18
			Magnetite	0.36	0.00	488	11
			Magnetite	0.68	0.00	449	7
1755	1167	0.9	Fe ⁺² /Glass	1.20	2.21		28
			Fe ⁺² /Glass	1.06	1.58		23
			Fe ⁺³ /Glass (?)	0.59	1.25		19
			Magnetite	0.51	0.00	459	23
			Fe _{1-x} S	0.71	0.00	305	8
1762	1168	0.6	Fe ⁺² /Glass	1.14	1.93		57
			Fe ⁺³ /Glass (?)	0.65	1.66		25
			Fe _{1-x} S	0.77	-0.08	307	17

Table 4.5. Pittsburgh #8 (SCS Beneficiated) Coal, 1500°C furnace set point, 2.6 s residence time

MK#	CFFLS	Res Time (s)	Phases Present	IS	QS	HO	% Fe
1759	1169	1.2	Fe ⁺² /Glass	1.03	1.96		64
			Fe ⁺³ /Glass	0.37	1.01		18
			Magnetite	0.28	0.00	488	11
			Magnetite	0.75	0.00	449	7
1764	1170	0.9	Fe ⁺² /Glass	1.15	1.95		44
			Fe ⁺² /Glass (?)	0.65	1.98		18
			Fe ⁺³ /Glass (?)	0.47	0.75		20
			Magnetite	0.59	0.00	463	8
			Fe _{1-x} S	0.50	0.00	285	10
1765	1171	0.6	Fe ⁺² /Glass	1.02	1.90		88
			Fe _{1-x} S	0.75	-0.05	305	9
			Fe _{1-x} S	0.51	0.35	267	3

Table 4.6. Black Thunder, 1500°C furnace set point, 2.6 s residence time

MK#	CFFLS	Res Time (s)	Phases Present	IS	QS	HO	% Fe
1772	1172	1.2	Fe ⁺² /Glass (?)	0.48	2.22		4
			Fe ⁺³ /Glass	0.31	1.26		96
1778	1173	0.9	Fe ⁺² /Glass (?)	0.89	1.23		45
			Fe ⁺³ /Glass (?)	0.24	1.28		55
1766	1174	0.6	Fe ⁺² /Glass	0.73	2.32		24
			Fe ⁺³ /Glass	0.48	0.96		54
			Wüstite (?)	1.01	0.81		22

SECTION 5

TASK 2 - FUNDAMENTAL COMBUSTION STUDIES UNDER REDUCING CONDITIONS (MIT)

5. FUNDAMENTAL COMBUSTION STUDIES UNDER REDUCING CONDITIONS

5.1 Introduction

The purpose of the task is to conduct fundamental experiments to follow the transformations of mineral matter under reducing conditions. The emphasis in the work will be on the transformation of iron and alkali metals which are known to be major actors in fouling and slagging. The results obtained during the past quarter are summarized below.

5.2 Experiment

The size distribution of the burnt particles have been obtained by using an Anderson cascade impactor. As studied by Helble (1987) and Kang (1991), the size distribution generated by combustion ash is typically log-normal. In our initial work we obtained the size distribution of ash generated by combustion of beneficiated Pittsburgh #8 coal as shown in Table 5.1.

Table 5.1. Test Conditions -- Collection Efficiency Measurement

Operational condition: $T = 1650 \text{ K}$, total flow rate = 30 l/min
Test sample: Al_2O_3 power $\leq 200 \text{ }\mu\text{m}$
Sample captured = 2.554g
Sample fed = 2.1522g
Recovery rate = $2.1522/2.554 = 84.6\%$

5.2.1 Recovery Rate Test

To make sure our experimental data are meaningful, we first evaluated the collection efficiency of samples. In the last report, we had reported a collection efficiency of 88% at room temperature. The following results (Table 5.2) were obtained at combustion conditions:

Table 5.2. Compositions of Coal

Moisture	2.00%
Volatile matter	36.3%
Fixed carbon	56.42%
Ash	5.21%

In addition to using Al_2O_3 as a test sample, we also used the ash in the coal to test the mass balance, since the total weight of ash does not change appreciably under ordinary combustion conditions. The coal used was a cleaned Pittsburgh #8 bituminous. Its composition is given in Table 5.2.

The PSI data are reported for a "utility grind" sample; in our experiments the 63/75 μm size cut was used. Using the ASTM procedure, we obtained an ash content of 4.61% for this size fraction of the beneficiated Pittsburgh #8 coal (Table 5.3).

Table 5.3. Conditions for Mass Balance Measurements with Coal Ash

Operational condition: $P = 1650 \text{ K}$, O_2 flow rate = 30 l/min
 Sample: $0.063 \text{ mm} \leq d_p \leq 0.075 \text{ mm}$
 Coal fed = 0.6888g
 Ash captured = 0.02799g
 Collection efficiency = $0.02799 / (0.6888 * 4.61\%) = 88.1\%$

This is repeatable. In the following calculation, we therefore use 88% as the collection efficiency.

5.2.2 Some Experimental Results on Ash Particle and Conversion

A. Experimental Condition 1

Main gas: 6 l/min; O_2 : 60%; N_2 : 40%
 Furnace temperature: 1650 K
 Length of reaction zone: 9.5 in.
 Coal feed rate: 0.0765 g/min
 Total coal fed: 0.7903g

Particle size distribution is reflected in Table 5.4.

B. Experimental Condition 2

Main gas: 6 l/min; O_2 : 10%; N_2 : 90%
 Furnace temperature: 1650 K
 Length of reaction zones: 9.5 in.
 Coal feed rate: 0.0765 g/min
 Total coal fed: 0.665g
 Total sample obtained: 0.24663g.

Particle size distribution is reflected in Table 5.5. The carbon content of the ash was clearly greater for the latter (10% O_2) case.

Table 5.4. Particle Size Distribution 1

Stage	Particle Size (μm)	Weight ($\times 10^{-5}\text{g}$)	%
Preseparator	>10	5277	50.5
1	9-10	2439	23.4
2	5.8-9	977	9.4
3	4.7-5.8	345	3.3
4	3.3-4.7	361	3.5
5	2.1-3.3	329	3.2
6	1.1-2.1	106	1.0
7	0.65-1.1	22	0.2
Final	0.43-0.65	55	0.5
Filter holder	<0.43	535	5.1

Table 5.5. Particle Size Distribution 2

Stage	Particle Size (μm)	Weight ($\times 10^{-5}\text{g}$)	%
Preseparator	>10	18290	74.2
1	9-10	2376	9.6
2	5.8-9	577	2.3
3	4.7-5.8	231	0.9
4	3.3-4.7	272	1.1
5	2.1-3.3	266	1.1
6	1.1-2.1	640	2.6
7	0.65-1.1	793	3.2
Final	0.43-0.65	746	3.0
Filter holder	<0.43	470	1.9

5.3 Discussions

The fate of iron in oxidizing atmosphere has been studied by many researchers. It is generally considered (Huffman et al., 1989) that the iron will undergo the following reactions:

Srinivasachar and Boni (1989) put forward a kinetic model for describing the transformation of excluded pyrite particles in the combustion environment. For the reducing atmosphere, Srinivasachar, Helble, and Boni (1990) pointed out that high locally reducing conditions, for example with staged or low air combustion, may worsen slagging with high iron coals. So the fate of iron is strongly dependent on the local oxidizing condition. Bodsworth and Bell (1972) listed some additional reducing reactions in their book:

To know what reaction takes place on the particle surface, we should distinguish the atmosphere surrounding the mineral particles in the coal during combustion. Therefore, the local concentrations of the species, especially CO and O₂, should be identified.

It is notable that the main combustion product of coal char under normal combustion environment is CO. Recently, Zeng and Fu (1993) presented an expression to calculate the ratio of CO/CO₂ on the carbon surface during combustion

$$\text{CO}/\text{CO}_2 = 600(\rho_s, Y_{\text{O}_2, \text{s}})^{-0.24} \exp(-8000/T_p)\tag{5-3}$$

where ρ_s is the density of the gas at surface in kg/m³ and $Y_{\text{O}_2, \text{s}}$ is the oxygen mole fraction on the surface. During combustion, the diameter of the particle decreases with time, the oxygen concentration on the surface increases, and the concentration of CO decreases whereas [CO₂] increases, which maintains the particle temperature approximately constant. The calculated changes of [CO] and [CO₂] can be shown in Figure 5.1.

If we assume that Fe₃O₄ and Fe₂O₃ are the main oxidation products of Fe, the only reducing reaction will be

Since in the absence of glass-phase iron, $[\text{Fe}]_{\text{total}} = [\text{Fe in Fe}_3\text{O}_4] + [\text{Fe in Fe}_2\text{O}_3]$, the concentrations of Fe₃O₄ and Fe₂O₃ are expected to show trends such as depicted Figure 5.2.

From the analysis above, we may know that [Fe₃O₄] and [Fe₂O₃] depend on the particle size, the ambient oxygen concentration, the ambient temperature as well as the properties of the coal (its composition and reactivity). For a shrinking char particle oxidation

Figure 5-1. $Y_{O,s}$ and CO/CO_2 as a function of dp .

Figure 5-2. $[Fe_3O_4]$ and $[Fe_2O_3]$ as a function of time.

model with a constant density (representative of a lignite char), the fraction char conversion = $1 - (d/d_0)^3$. For combustion at constant diameter and decreasing density (representative of a bituminous coal char), the diameter is independent of conversion. In this case, $[\text{Fe}_3\text{O}_4]$ and $[\text{Fe}_2\text{O}_3]$ may not be dependent on char conversion.

The above describes the ratio of $[\text{Fe}_2\text{O}_3]/[\text{Fe}_3\text{O}_4]$ in the products, assuming that all of the Fe_3O_4 has complete access to CO. In reality, mineral size effects will prevent most of the hematite from being reduced to Fe_3O_4 . In addition, the unreacted FeS_2 and the intermediate FeS and FeO will be present in the partially reacted chars. The forms of iron in the size segregated chars and ash will be determined by Mössbauer spectroscopy at the University of Kentucky.

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SECTION 6

TASK 2 - FUNDAMENTAL STUDY OF ASH FORMATION AND DEPOSIT INITIATION UNDER REDUCING CONDITIONS (PSI PowerServe)

6. FUNDAMENTAL STUDY OF ASH FORMATION AND DEPOSIT INITIATION UNDER REDUCING CONDITIONS

During the fourth quarter of this program, additional combustion experiments were conducted using the in-situ XAFS test furnace. These experiments, conducted jointly by PSI PowerServe and the University of Kentucky, focused on iron transformations. Also during the previous quarter, baseline combustion experiments to assess the importance of stoichiometric ratio and ash carbon content on ash particle stickiness were conducted at PSI PowerServe (PSI). These efforts are described in the following sections.

6.1 *In-situ XAFS Experiments*

6.1.1 *Preliminary Testing*

In early March a joint PSI-University of Kentucky team performed a preliminary test of the in-situ XAFS combustor. The goals of this test were:

- to train new operators on the system
- to replace the furnace retort and perform scheduled maintenance
- to ensure that the combustor was in working order prior to the on-line experiments
- to test a new material for use as deposition probes
- to assess the success of prior feeder modifications designed to minimize the effect of feeder fluctuations on the ash stream.

During these preliminary experiments, performed in an off-line building at Brookhaven National Laboratory, the washed Pittsburgh #8 was burned in air (1 SCFM), with a furnace setpoint of 1200°C. One of the difficulties encountered in previous in-situ XAFS experiments was fluctuations in the ash stream, caused by fluctuations in the coal feed. These fluctuations increased the background noise in the XAFS spectra to unacceptable levels. In order to alleviate this problem, a smaller auger was installed in the feeder, and a series of mixing chambers was installed immediately after the feeder. These chambers were designed to act as coal-air recirculating zones to minimize the effect of the periodic feed fluctuations caused by the rotation of the auger. However, when the system was tested, these chambers seemed to enhance, rather than minimize, the fluctuations. Reasons for this are unclear but may involve coal deposition in the chambers. The mixing chambers were, therefore, removed from the system.

Another modification to the experimental approach used previously involved the deposition probes used to collect deposit samples for in-situ analysis. These probes were

fairly large compared to the volume of the 6-way cross -- resulting in severe deformations in the flow pattern in the cross. In addition, very little deposit formed on the boron nitride disks used as collection substrates. Therefore, a new type of deposition probe was tested. This probe consisted of a 3/8-in. alumina rod with one end cut at an angle of 45 deg. The probe was installed with an "o"-ring to allow the rod to be positioned in the flow. After positioning the probe in the center of the 6-way cross, coal was fed to determine whether a deposit formed on the probe. Initially very little deposit was formed, possibly caused by several combustor system malfunctions, discussed later. However, when the system was functioning properly at the end of the test, a gray, powdery deposit was formed on the probe, suggesting that the rods would be suitable for use as deposition substrates.

During these "shake-down" experiments with the in-situ XAFS combustion system, plugging of the coal-air transport line in the diffuser was observed. This line, consisting of a 1/4-in. OD copper tube, became completely clogged with coal during operation, requiring the removal of the diffuser section from the top of the reactor. Once the diffuser had cooled, a thin metal wire was used to clean out the line. The diffuser was then re-installed and testing continued.

One other significant problem was encountered during the shake-down tests. The primary air heating tape shorted out -- burning a hole through the primary air transport line. After the primary air heating tape and the primary air transport line were replaced, testing continued.

Once these problems were corrected, the trial operation proceeded smoothly. The coal-ash stream fluctuations were decreased by the addition of the smaller auger, and deposits formed on the deposition probe. However, unlike during the initial experiments with this system, significant char combustion occurred in the 6-way cross -- as evidenced by a flame seen through viewports in the cross. This incomplete burnout was attributed to a low preheater temperature (caused by a malfunction in the building's electric system -- not in the combustor system itself), a low furnace setpoint, and a high coal feedrate. These conditions were to be corrected for the on-line experiments.

6.1.2 On-line In-situ XAFS Experiments

During the period between the preliminary testing and the on-line experiments, an oxygen meter was purchased by Bernie Manowitz at Brookhaven National Laboratory for use in the in-situ combustion experiments. In addition, in order to minimize the incomplete burnout noted in the preliminary test, the primary coal to be used in the on-line experiments (washed Pittsburgh #8) was size classified, and the <75- μ m size cut sent to Brookhaven. A suction pyrometer was also assembled for use in determining the gas temperature at the 6-way cross.

Approximately three weeks after the preliminary testing, the PSI-University of Kentucky team began the on-line XAFS experiments. The furnace was assembled in the hutch without incident. Initially the furnace could not be pressurized -- indicating a

significant leak in the system. After some modifications, without success, the furnace was heated to 1200°C. The leak was eventually sealed by pulling a strong vacuum on the system.

After the system was sealed and heated to 1300°C, a malfunction occurred in the preheater tape controller, causing the tape to overheat and short out. The replacement tapes were controlled by using two variacs. After all of the modifications were complete, the system was operated on coal to determine its stability and to test the detector manufactured at University of Kentucky. During the testing of the detector, the coal line again became clogged. The clogged tip caused the outlet of the feeder to clog. This plug caused the screw to pack coal into the tip -- causing the teflon block sealing the feeder to move away from the feeder. When the TV camera-monitor system used to monitor the 6-way cross suggested that no coal was being fed into the combustor, a visual check of the hutch revealed coal spilling from the feeder. The emergency shut-down procedure was then initiated. The operators then reported the spill to the light source operator and began cleaning the hutch.

In order to prevent any further spills into the hutch, as mandated by a meeting with the NSLS safety officers, the entire feeder assembly was encapsulated with two plastic bags (one inside the other). The bags would prevent coal from entering the hutch if a similar leak occurred. However, to prevent this type of leak, the coal feed line was reconfigured as shown in Figures 6-1 and 6-2. The transport air was moved so that the air entered the "T" fitting at the tip of the screw from the bottom. The coal being extruded from the tip of the screw was entrained immediately, as compared to the previous design. In addition, a "T" fitting was placed in the primary air line so that the coal was mixed with the primary air *before* entering the combustor. This configuration gave the added advantage of being easily cleaned if plugging occurred.

C-6943

Figure 6-1. Pre-release coal feed configuration.

C-6944

Figure 6-2. Post-release coal feed system.

While coal was being burned during repair of the detector, a flame was again observed in the 6-way cross. In order to maximize the residence time (and therefore the burnout), the gas feedrate was therefore decreased to 0.75 SCFM and 0.5 SCFM for the superstoichiometric and the substoichiometric conditions, respectively. Iron XAFS measurements were then performed under the conditions outlined in Table 6.1. For each condition the oxygen meter and the suction pyrometer were used, after the XAFS spectra were collected, to measure the conditions inside the 6-way cross. The spectra were collected using the alumina rods and alumina rods capped with boron nitride disks as deposition probes. Attempts were also made to perform calcium XAFS measurements with both the washed Pittsburgh #8 and the Black Thunder coals. These attempts were unsuccessful due to the weakness of the calcium signal. Analysis of the collected spectra are underway and should be complete in the next quarter.

Table 6.1. Oxygen Concentrations in In-situ XAFS Experiments

Stoichiometric Ratio	Oxygen Concentration (vol %)
2.45	21.0
0.9	9.0
0.7	8.4

Although several good (i.e., high signal to noise) spectra were collected, the spectra were for burning coal particles, *not* ash particles. A flame was visible in the 6-way cross -- indicating that coal particles were still burning as they passed the x-ray beam. In addition, ash samples taken from the ash trap after two experiments with stoichiometric ratios of 2.45 and 0.7 had carbon contents of 55 and 65%, respectively. The incomplete burnout may be due to the low primary air temperatures measured during the experiments.

The on-line experiments successfully collected iron XAFS spectra for several combustion conditions. The value of this data for understanding the transformation of iron under reducing conditions has yet to be determined. The on-line experiments also highlighted some areas where improvements could be made to increase the reliability of the system. These changes include modifications to the primary air line to minimize heat losses after the preheater, modifications to the detector, and modification of the deposition probe design. Many of these modifications will be implemented for future in-situ XAFS measurements.

6.2 Baseline Experiments

During the past quarter a number of experiments were performed to explore the effect of reducing conditions on ash particle stickiness. These experiments used the four U.S. coals and several different combustion conditions. The experimental conditions were:

- stoichiometric ratios of 0.6, 0.9, and 1.2.
- coal feedrate of 3.5 g/min
- furnace gas flowrate of 1 scfm
- furnace setpoint (wall temperature) of 1500°C. The correspondence between wall temperature and gas temperature was discussed in detail in Quarterly Report Number 3.

In these experiments, the stoichiometric ratio was varied by changing the oxygen feed into the furnace as shown in Table 6.2. At each condition, three deposition samples and two nitrogen quenched ash samples were collected. Both quench probe samples were analyzed for residual carbon and one sample of each set was sent to the University of Kentucky for CCSEM and Mössbauer analysis.

The effect of stoichiometric ratio on carbon burnout can be seen in Figures 6-3 through 6-6. As expected, carbon burnout increased with increasing stoichiometric ratio. The collection efficiency, Figures 6-7 through 6-10, remained constant or increased with stoichiometric ratio. There are several possible explanations for this behavior. For example, the large differences in oxygen concentration between each condition may have created a large difference in particle temperature. The presence of carbon at the lower stoichiometric ratios may also played a role in particle sticking under reducing conditions (see Subsection 6.3).

Coal	Stoichiometric Ratio	PO ₂ (atm)
Washed, Pittsburgh #8	1.2	27
	0.9	20
	0.8	18
	0.7	16
	0.6	14
Run of mine Pittsburgh #8	1.2	20
	0.9	15
	0.6	10
Beneficiated Pittsburgh #8	1.2	28
	0.9	21
	0.6	14
Black Thunder	1.2	19
	0.9	14
	0.8	12
	0.7	11
	0.6	9

Figure 6-3. Effect of SR on carbon burnout -- washed Pittsburgh #8 (DoE).

An experiment was performed with the washed Pittsburgh #8 to explore the effect of burning char particle temperature on ash particle stickiness. The furnace setpoint for this experiment was decreased to 1400°C to match particle temperatures in previous sub-stoichiometric combustion experiments. All of the other experimental variables were those used in the earlier experiment at stoichiometric ratio of 1.2. As can be seen from the data in

Figure 6-4. Effect of SR on carbon burnout -- Pittsburgh #8 (Kaiser-Parent).

Figure 6-5. Effect of SR on carbon burnout -- Pittsburgh #8 (Kaiser-cleaned).

Table 6.3, the collection efficiency did not change appreciably between the two experiments. Therefore, the increase in collection efficiency with stoichiometric ratio was due to other factors, including the presence of carbon at the lower stoichiometric ratios.

In order to explore the effect of carbon on ash stickiness, additional experiments were performed using the Black Thunder sub-bituminous and washed Pittsburgh #8 bituminous coals. These experiments used stoichiometric ratios of 0.7 and 0.8, with all other conditions being those used in the earlier experiments. The results from these experiments were similar

Figure 6-6. Effect of SR on carbon burnout -- Black Thunder.

Figure 6-7. Effect of SR on collection efficiency -- washed Pittsburgh #8 (DoE).

to those from the earlier experiments and are included in the previously presented plots for these coals. The effect of carbon on ash stickiness is discussed later (Subsection 6.3)

6.3 Effect of Reducing Conditions on Ash Stickiness - Short Residence Time Experiments

In order to gain better understanding of the factors that affect ash stickiness under reducing conditions, a number of experiments have been performed to assess the effect of carbon and unoxidized iron species on ash stickiness. Some of these experiments, described

Figure 6-8. Effect of SR on collection efficiency -- Pittsburgh #8 (Kaiser-Parent).

Figure 6-9. Effect of SR on collection efficiency -- Pittsburgh #8 (Kaiser-cleaned).

in detail in Quarterly Report #3, provided information on ash stickiness at short residence times when carbon and unoxidized iron compounds were present. Additional experiments, described in Subsection 6.2, directly measured the effect of reducing conditions on collection efficiency. This data was used to determine the role of carbon in ash stickiness.

Figure 6-10. Effect of SR on collection efficiency -- Black Thunder.

Table 6.3. Collection Efficiencies for Stoichiometric Ratio 1.2 Experiments

1400°C		1500°C	
1 m/s	5 m/s	1 m/s	5 m/s
30.4	50.5	16.2	30.0
26.5	40.3	29.3	43.1
26.0	47.4	24.3	41.7

6.3.1 The Effect of Iron on Ash Stickiness

As discussed in Quarterly Report No. 3, ash samples from the short residence time experiments were sent to the University of Kentucky for Mössbauer analysis. Preliminary Mössbauer data are shown in Table 6.4. No clear trend of iron oxidation with residence time was apparent. In fact, the presence of pyrrhotite in only the first sample (lowest residence time) supports the conclusion that char burn out was complete by 0.55 s (Helble et al, 1994). Therefore, it is not possible from this data to assess the effect of un-oxidized iron species on ash stickiness.

The information in Table 6.4, however, raises an interesting point about the oxidation rate of iron in glass. Immediately after the char is completely combusted, one would expect the Fe (+2) state in the glass to be dominant, or at least be present. However, the data in Table 6.4 suggest that this is not the case. One possible explanation is that the Fe (2+) in the glass oxidizes to Fe (3+) very quickly at high oxygen concentrations. For the first four residence times in Table 6.4, the oxygen concentration (15%) was relatively unaffected by

Table 6.4. Mössbauer Results from Short Residence Time Experiments

Residence Time (s)	Iron as Oxide (wt%)		Iron in Glass (wt%)	
	Fe ₃ O ₄	Fe ₂ O ₃	Fe ²⁺	Fe ³⁺
0.25*	66		12	14
0.40	41	47		12
0.55	50	40		11
0.72	26	64		10
0.99	30	41**	10	19
1.60	77		7	16
2.21	23	51**	9	20
2.87	11	71**		18
*Contained 8% FeS.				
**Includes magnetite.				

coal burnout, due to the high stoichiometric ratio. For the final four residence times, however, the stoichiometric ratio was lower, and the oxygen concentration was probably much lower. For the lower stoichiometric ratio case, the data suggest that oxidation was much slower. As the iron oxidation state in glass is suspected to play an important role on ash stickiness, additional work is needed to quantify this conclusion. Note that the Mössbauer analysis presented in Table 6.4 should only be used as a *qualitative* guide to understanding the rate of iron oxidation in glass.

Many of the difficulties in quantitatively interpreting Mössbauer data of glassy ash phases arise from the presence of other iron states in the ash, such as iron oxide. These oxide states have absorption peaks in the same region as the glasses. Therefore, when analyzing the spectra it is extremely difficult to appropriately fit the peaks in this region. Future work on the oxidation of iron in glass during combustion should either use coals where most of the iron is in the glassy phase or the oxide states should be separated as much as possible from the ash sample prior to the Mössbauer analysis if a quantitative result is desired.

6.3.2 The Effect of Carbon on Ash Stickiness

One of the effects of burning a coal under reducing stoichiometries is an increase in the carbon content of ash approaching heat exchange surfaces. Although the role carbon plays in determining ash stickiness under reducing conditions is unclear, it may serve to decrease the effective stickiness of the ash by physically preventing sticky ash particles from coming in contact with the heat exchange surfaces. In the past quarter, data from several experiments were used to determine the effect of ash carbon content on ash particle stickiness.

Data from the short residence time experiments and the baseline experiments with the washed Pittsburgh #8 coal are presented in Figure 6-11. In these experiments the collection efficiency and carbon content samples were collected independently. In order to illustrate

Figure 6-11. Collection efficiency versus carbon content -- washed Pittsburgh #8 (DoE).

the widest variability in collection efficiency for each condition, the data extremes for collection efficiency are plotted. As suggested in Quarterly No. 3 (Helble et al., 1994) the data suggest that there is a critical carbon content, below which carbon content has little or no effect on ash stickiness. Above this critical value, however, the ash stickiness (collection efficiency) decreases with increasing carbon content. For the washed Pittsburgh #8 coal, this critical value is approximately 60 to 70% carbon in the ash. Another coal that shows the same trend is the beneficiated Pittsburgh #8, as shown in Figure 6-12. For this coal the critical value is approximately 50%. The other study coals, however, did not exhibit this trend. For the run-of-mine Pittsburgh #8, Figure 6-13, and the Black Thunder sub-bituminous coal, Figure 6-14, there is no apparent effect of carbon content. For these coals, there are other factors that must be considered including rapid carbon conversion and the presence of extraneous ash.

In order to test our understanding of the role of carbon in ash stickiness, a simple model was created. If the carbon simply "gets in the way" of molten ash particles when the char contacts heat exchange surfaces, then there should be some critical point (as suggested by the data) when there is sufficient ash on the char surface for a particle to stick. After this critical point has been reached, the ash stickiness is only slightly dependent on carbon content. If this analysis is correct, then the effective ash stickiness should depend on the amount of ash exposed and the stickiness of the ash. Therefore, a preliminary model can be written:

$$\eta_{\text{effective}} = \eta_{\text{ash}} \cdot X_c \quad (6-1)$$

where $\eta_{\text{effective}}$ is the effective collection efficiency, η_{ash} is the ash collection efficiency (given by the maximum collection efficiency at the lowest carbon content), and X_c is the fraction of

Figure 6-12. Collection efficiency versus carbon content -- Pittsburgh #8 (Kaiser-cleaned).

Figure 6-13. Collection efficiency versus carbon content -- Pittsburgh #8 (Kaiser-Parent).

the char burned away (calculated from the proximate analysis and the carbon content in the ash).

The values for η_{ash} are given in Table 6-5. The model curves are shown in Figures 6-11 through 6-14. This simple model fits the data reasonably well for all coals except for the high ash run-of-mine Pittsburgh #8 coal. The discrepancy for this coal may be due to the simplicity of the model. This model does not consider the presence of extraneous

Figure 6-14. Collection efficiency versus carbon content -- Black Thunder.

Table 6.5. Ash Collection Efficiencies Used in Model

Coal	1 m/s (%)	5 m/s (%)
Pittsburgh #8 (run-of-mine)	40	63
Pittsburgh #8 (beneficiated)	24	40
Black Thunder	28	84
	Residence Time Experiments (%)	Baseline Experiments (%)
Washed Pittsburgh #8	75	50

minerals and therefore may underpredict the stickiness in some cases. Further modifications on this preliminary model may help increase the quality of fit for the other coals as well.

6.3.3 Planned Experiments

In order to gain more information on the effect of carbon and unoxidized iron species on ash stickiness, additional experiments are planned. These experiments will utilize the run-of-mine Pittsburgh #8 and a lower oxygen concentration (5%). By decreasing the oxygen concentration more data should be available on ash stickiness while significant carbon and unoxidized iron species are present. These experiments will be completed in the next quarter.

References

Helble, J.J. et al., "Fundamental Study of Ash Formation and Deposition: Effect of Reducing Stoichiometry". Quarterly Report No. 3, U.S. DoE Contract No. DE-AC22-93PC92190, Pittsburgh Energy Technology Center, Pittsburgh, PA (1994).

SECTION 7

TASK 4 - ENGINEERING MODEL FOR ASH FORMATION (PSI PowerServe)

7. ENGINEERING MODEL FOR ASH FORMATION

Early in this program several modifications were made to the engineering model for ash formation (EMAF). These modifications, discussed in detail in Quarterly Report No. 2 (Helble et al., 1993), were designed to increase the model's ability to simulate char combustion and mineral matter transformations. Specifically, the modifications allow the user to better control the char morphology by providing swelling parameters for conditions of "cenosphere" versus "no cenosphere" formation. Further, an option was included to allow fragmentation of cenospheres. Finally, switches were added to allow the user to specify the behavior of each mineral type (coalescing or not coalescence).

In order to evaluate the performance of the modified EMAF, several simulations were performed to predict the ash composition and particle size distributions (psd) for specific coals. These predictions were then compared to ash data from droptube experiments or field measurements for these coals. The coals included four bituminous coals, including two non-U.S. coals, a sub-bituminous coal, and a lignite. The results of these simulations are described in this section.

The mineral composition and size distributions, from CCSEM, used as model inputs for each coal were based on more detailed distributions presented elsewhere (Boni et al., 1990). In order to simplify the modelling process, only the major minerals were used as inputs. However, in many cases more minerals were included in these simulations than in previous EMAF simulations (Helble et al., 1993). As the original mineral size distributions (Boni et al., 1990) did not include a category for the unidentified, or mixed species, the size distributions for this category were estimated from the overall mineral size distribution and the distribution of all other species. Other important inputs, such as ASTM ash analysis, were used as originally presented.

For each of the simulations a char behavior pattern was assumed, based on the coal type (see Table 7.1). For example, based on the current knowledge of char formation mechanisms for American coals, the lignite and the sub-bituminous coals were assumed to burn without forming cenospheres (swelling parameters set to 1, no fragmentation allowed). The U.S. bituminous coals were assumed to form cenospheres during devolatilization. Field data on ash particle size and composition distributions for two non-U.S. coals were provided to PSI by the Aerosol Technology Group of VTT Technical Research Center of Finland. As no information regarding the behavior of the two non-U.S. coals was provided to PSI, two calculations were performed with each coal -- first assuming cenosphere formation and later assuming no cenosphere formation. The results for each simulation are discussed in Subsection 7.1. A summary of the results and a discussion of additional testing is provided in Subsection 7.2.

Table 7.1. Assumed Burnout Mechanism for Study Coals

Coal	Mechanism
Beulah lignite	No cenosphere formation
Eagle Butte sub-bituminous	No cenosphere formation
Kentucky 11 bituminous	Cenosphere formation
Upper Freeport bituminous	Cenosphere formation
Polish bituminous	No cenosphere formation Cenosphere formation
South African bituminous	No cenosphere formation Cenosphere formation

7.1 EMAF Predictions

7.1.1 Beulah Lignite Coal

In previous model evaluations (Helble et al., 1993), EMAF was used to simulate the behavior of primarily bituminous coals during combustion, with only one lignite tested. In order to test the applicability of the model for a wider range of coals, simulations were performed for a North Dakota lignite (Beulah). The mineral composition and size distributions for this coal can be seen in Tables 7.2 and 7.3. Kaolinite and pyrite represent 33.0% and 28.6% of the mineral mass, respectively. The unidentified, or mixed, species represent 14.3% (silicates) and 11.0% (other minor minerals). Most of the silicate species were very finely divided, while pyrite consisted of fairly large particles.

Table 7.2. Mineral Species Composition: Beulah Lignite

Mineral Species	Wt%	Elemental Composition (mole%)										
		Na	Mg	Al	Si	S	Cl	P	K	Ca	Ti	Fe
Quartz	13.2				97	1				1	1	
Kaolinite	33.0			42	52	2	1		1	1	1	1
Misc. silicates	14.3			30	57	3	1		2	3	2	2
Pyrite	28.6		1		1	66					2	31
Misc. mixed	11.0	2	4	12	15	24	4	2	3	20	15	6

For these simulations the coal was assumed to devolatilize without forming cenospheres. Figure 7.1 shows a comparison between the ash particle size distribution (psd) from PSI droptube experiments and the predicted ash psd for two simulations. In the full coalescence case all of the minerals are assumed to coalesce (1 ash particle produced per coal

Table 7.3. Mineral Size Distribution (μm) for Beulah Lignite

Mineral	<2.5 (wt%)	2.5-5 (wt%)	5-10 (wt%)	10-20 (wt%)	20-40 (wt%)	>40 (wt%)
Quartz	11	11	17	23	19	18
Kaolinite	42	7	9	13	12	17
Mix. silicates	73	6	7	7	7	0
Pyrite	1	1	3	12	26	56
Misc. Mixed*	16	13	8	11	12	40
Total	27	7	8	13	16	30

*Estimated from other minerals and total mineral distribution.

Figure 7-1. Ash psd: model versus data -- Beulah lignite - no cenospheres.

particle or excluded mineral). In the partial coalescence case quartz and kaolinite do not melt or coalesce. For the full coalescence simulation all of the resulting ash particles were greater than $10\ \mu\text{m}$. The partial coalescence simulation resulted in a much finer ash distribution due to the formation of one ash particle for each quartz and kaolinite particle. The measured ash psd was bounded by the two simulations. This suggests that full coalescence does not take place, perhaps due to minerals not melting. Char fragmentation is another, although less likely (Helble et al., 1993), possibility.

Figure 7.2 presents a comparison between the predicted and measured ash compositions. Each category represents the area percent (from CCSEM) of all particles that contain the elements specified (on a oxygen and carbon free basis). For example, the Si category represents the area percent of all particles that contain primarily silicon (probably quartz). As seen in Figure 7.2, the EMAF full coalescence predictions agree reasonably well with the measurements for this category. Due to the assumption that quartz does not coalesce

Figure 7-2. Ash composition: model versus data -- Beulah lignite - no cenospheres.

in the partial coalescence simulation, the amount of ash in the Si category is overpredicted in this case. For the Ca and Ca-Si-Al categories the model predicts values much lower than measured. The Ca-Si-Na category is bounded by the two model predictions.

Some of the differences between the predicted and measured ash composition can be attributed, in part, to the CCSEM analysis of the ash. Because CCSEM is primarily a *surface* analysis technique, rather than a bulk technique, compositions reported by CCSEM are strongly affected by species present on the surface, but in lower concentrations in the bulk (surface enriched). The EMAF, however, predicts the *bulk* particle compositions. Therefore, direct comparison of the two results may be misleading for those coals with significant surface enrichment. For example, the simulations discussed above predicted a much lower calcium concentration in the ash (the Ca category) than was reported by CCSEM. This may be due to the high fraction of organically bound calcium - leading to significant surface enrichment of this species. Therefore, in this case, the model predictions may represent a more realistic measure of the bulk ash composition than do CCSEM surface measurements. Sectioned CCSEM - analysis of the particle cross-sections - could be used to provide a better comparison with the bulk ash composition provided by EMAF.

7.1.2 Eagle Butte -- Sub-bituminous Coal

Another test of the model's flexibility was the simulations with the Eagle Butte sub-bituminous coal. The mineralogy for this coal is dominated by quartz (see Tables 7.4 and 7.5). This mineral represents 41.7% of all minerals. Silicate species (including quartz) represent approximately 70% of the mineral matter. Unidentified and mixed species represent 29% of the minerals. These minerals were fairly evenly distributed throughout the measured size ranges (Table 7.4).

Table 7.4. Mineral Species Composition: Eagle Butte Sub-bituminous

Mineral Species	Wt%	Elemental Composition (mole%)										
		Na	Mg	Al	Si	S	Cl	P	K	Ca	Ti	Fe
Quartz	41.7			1	96				1	1	1	1
Kaolinite	13.5	1		41	52	1	1		1	2	2	1
Illite	2.1			28	53	1	2		10	3	2	2
Misc. silicates	13.5	1	2	20	50	2	2		3	6	2	4
Pyrite	4.2			1		60				2		36
Fe-rich (siderite)	4.2			1	3	2		2	1	4	2	85
Ca-rich (calcite)	3.1	1		1	3	4	1	1	3	84	1	5
Misc. mixed	15.6	1	2	22	15	8	4		4	28	8	4

Table 7.5. Mineral Size Distribution for Eagle Butte Sub-bituminous

Mineral	<2.5 μm (wt%)	2.5-5 μm (wt%)	5-10 μm (wt%)	10-20 μm (wt%)	20-40 μm (wt%)	>40 μm (wt%)
Quartz	21	10	20	17	20	12
Kaolinite	9	10	31	17	22	11
Mix. silicates	37	16	18	8	5	16
Pyrite	9	7	22	30	28	3
Misc. Mixed*	26	10	18	12	11	22
Total	100	23	21	15	16	15

*Estimated from other minerals and total mineral distribution, siderite, calcite, and montmorillite assumed to have same distribution.

The simulations for this coal also were based on the assumption that no char cenospheres form during devolatilization as shown in earlier work (Helble et al., 1993). The predicted and measured ash psd can be seen in Figure 7-3. As can be seen from this figure, the measured ash psd is again bounded by the two simulations. These simulations again represent coalescence of all minerals and coalescence of selected minerals, as in the previous simulation. However, for these simulations it was assumed that siderite, calcite, and kaolinite did not coalesce (calcite and siderite were not present in the previous coal). The quartz in this coal contained significant impurities, lowering the melting point. Therefore the quartz was allowed to coalesce for this coal but not for the previous coal. Again the full coalescence simulation results in a coarser distribution than was reported by CCSEM. The partial coalescence case resulted in a finer distribution but contained more particles in the larger size ranges than was measured.

A comparison of the predicted and measured ash composition is shown in Figure 7-4. The EMAF overpredicts the amount of ash in the Si and Si-Al-Ca categories, while

Figure 7-3. Ash psd: model versus data -- Eagle Butte - no cenospheres.

Figure 7-4. Ash composition: model versus data -- Eagle Butte - no cenospheres.

underpredicting the Ca and Ca-Al-Si categories, for both simulations. These discrepancies are probably due to the surface bias of the CCSEM as discussed above.

7.1.3 Kentucky #11 Bituminous Coal

As part of an evaluation of the initial version of EMAF (Helble et al., 1992) simulations were performed using this coal. Therefore, the Kentucky #11 and the Upper Freeport coal were also included in this evaluation. Pyrite represents a large fraction of the mineral matter in the Kentucky #11 (Table 7.6). The pyrite is evenly distributed in the

Table 7.6. Mineral Species Composition: Kentucky #11 Bituminous

Mineral Species	Wt%	Elemental Composition (mole%)										
		Na	Mg	Al	Si	S	Cl	P	K	Ca	Ti	Fe
Quartz	20.0			3	94				1		1	
Kaolinite	9.0			40	51	3			2	2	2	2
Illite	17.0			28	54	3			10	1	2	4
Misc. silicates	25.0			21	61	2			11	2	2	4
Pyrite	26.0			2	3	63			1		1	33
Fe-rich (siderite)												
Ca-rich (calcite)												
Misc. mixed	3.0			11	30	11	4	3	6	14	17	6

individual size ranges (Table 7.7), but there is a large fraction in the larger (>20 μ m) size ranges. Illite and the miscellaneous silicate categories represent a significant fraction of the silicate species.

Table 7.7. Mineral Size Distribution for Kentucky #11 Bituminous

Mineral	<2.5 μ m (wt%)	2.5-5 μ m (wt%)	5-10 μ m (wt%)	10-20 μ m (wt%)	20-40 μ m (wt%)	>40 μ m (wt%)
Quartz	19	25	23	16	12	5
Kaolinite	33	16	28	12	6	4
Illite	34	24	21	8	9	4
Mix. silicates	26	14	20	15	14	11
Pyrite	10	9	14	14	21	33
Misc. Mixed*	35	0	0	8	23	0
Total	24	15	18	13	15	16

*Estimated from other minerals and total mineral distribution.

The EMAF simulations assumed that all coal particles greater than 10 μ m formed cenospheres during devolatilization, as shown in earlier work with a similar coal (Helble et al., 1993). In the simulations with the unmodified version of EMAF, the model overpredicted the amount of fine ash and overpredicted the amount of very large particles. In the simulations discussed here, Figure 7-5, this pattern was repeated but to a lesser degree.

The ash composition predictions, Figure 7-6, were also similar to those of the earlier simulations. The model overpredicted the interaction between iron and illite, overpredicting the Si-Al-Fe category and underpredicting the Si-Al-K category. The Si and Si-Al categories are in reasonable agreement.

It is somewhat unusual to have the ash composition comparisons suggest that the model overpredicts the amount of ash coalescence, but the model also overpredicts the

Figure 7-5. Ash psd: model versus data -- Kentucky #11 - cenospheres.

Figure 7-6. Ash composition: model versus data -- Kentucky #11 - cenospheres.

amount of ash in the small sizes. This combination suggests that random placement of the small minerals may be inaccurate, or the coal psd may have been incorrectly measured (Helble et al., 1992).

7.1.4 Upper Freeport -- Bituminous Coal

The Upper Freeport coal was also included in this study to compare the effects of the previously described modifications to EMAF. The mineral matter composition and psd for this coal can be seen in Tables 7.8 and 7.9. Similar to the previous coal, Si-Al-K species

Table 7.8. Mineral Species Composition: Upper Freeport Bituminous

Mineral Species	Wt%	Elemental Composition (mole%)										
		Na	Mg	Al	Si	S	Cl	P	K	Ca	Ti	Fe
Quartz	10.5			2	93				1	1	1	1
Kaolinite	7.4	1	1	38	49	2	3		2	2	1	1
Illite	36.8	1	1	28	51	1	2		12	2	2	3
Misc. silicates	20.0	1	1	20	57	2	1		7	1	2	10
Pyrite	18.9		1	2	4	59				1	1	33
Misc. mixed	6.3	1	3	13	30	12	8	2	9	7	10	10

Table 7.9. Mineral Size Distribution for Upper Freeport

Mineral	<2.5 μm (wt%)	2.5-5 μm (wt%)	5-10 μm (wt%)	10-20 μm (wt%)	20-40 μm (wt%)	>40 μm (wt%)
Quartz	8	14	26	20	26	6
Kaolinite	15	9	15	25	19	16
Illite	10	10	13	11	12	44
Mix. silicates	12	16	15	21	12	23
Pyrite	4	2	13	13	14	54
Misc. Mixed*	6	10	16	11	11	46
Total	9	10	15	15	14	36

*Estimated from other minerals and total mineral distribution.

(illite and miscellaneous silicate) comprise a significant fraction of the mineral matter. Other major minerals include pyrite, quartz, and kaolinite. Unidentified, mixed, species comprise 6% of the minerals. In general the minerals in this coal are evenly distributed throughout the size ranges, although pyrite, illite, and miscellaneous mixed occur primarily in the largest size range (>40 μm).

The Upper Freeport was also simulated assuming all coal particles greater than 10 μm form cenospheres during devolatilization. Figure 7-7 shows a comparison between the model predictions and the measured ash psd. In the previous simulations the unmodified EMAF predicted the <10- μm psd reasonably well. However, above this size the model underpredicted the intermediate size range. In the simulation with the modified EMAF, the model almost exactly predicted the ash psd. Most of the ash composition categories (Figure 7-8) also agree with the measurements for this coal. Only the Si-Al and Si-Al-Fe are underpredicted by the model.

Figure 7-7. Ash psd: model versus data -- Upper Freeport -- cenospheres.

Figure 7-8. Ash composition: model versus data -- Upper Freeport -- cenospheres.

7.1.5 Polish Bituminous Coal

In order to further test EMAF for non-American coals, simulations were made for a Polish bituminous coal. The mineral composition and size distribution for this coal can be seen in Tables 7.10 and 7.11. Major silicate minerals include quartz, illite, and mixtures of other silicates (miscellaneous silicate). Carbonates, including calcite, represent approximately 9% of the mineral matter. Other species, including unidentified phases, comprise 12% of the minerals.

Table 7.10. Mineral Species Composition: Polish Bituminous

Mineral Species	Wt%	Elemental Composition (mole%)										
		Na	Mg	Al	Si	S	Cl	P	K	Ca	Ti	Fe
Quartz	10.0				99				1			
Illite	32.0			26	56	2			12	1	1	2
Misc. silicates	27.0			20	59	2			11		2	4
Pyrite	7.0			1		65						34
Fe-rich (siderite)	3.0			2	2					2		94
Ca-rich (calcite)	2.0		1							96		3
Mixed carbonates	7.0		1		1	1		1		79		17
Misc. mixed	12.0			20	34	11	1	6	7	19	4	8

Table 7.11. Mineral Size Distribution for Polish Bituminous

Mineral	<2.5 μm (wt%)	2.5-5 μm (wt%)	5-10 μm (wt%)	10-20 μm (wt%)	20-40 μm (wt%)	>40 μm (wt%)
Quartz	12	25	16	17	6	24
Illite	19	26	19	24	6	6
Mix. silicates	24	24	24	13	7	9
Pyrite	16	47	6	8	1	14
Siderite	17	25	7	11	18	22
Calcite	15	52	4	4	11	13
Mixed carbonates	12	8	17	40	9	14
Misc. Mixed*	15	39	6	7	12	15
Total						

*Estimated from other minerals and total mineral distribution.

As previously discussed, no information was given to PSI regarding the behavior of this coal during devolatilization. Therefore, simulations were performed assuming cenospheres formed, and assuming no cenospheres formed. In the initial simulations (Figures 7-9 and 7-10), it was assumed that the coal did not swell during devolatilization. The mineral coalescence was divided into three different categories: full coalescence (all minerals coalesce), partial coalescence (selected minerals do not coalesce), and 1-ash per mineral (no minerals coalesce). The minerals not allowed to coalesce under the partial coalescence category, quartz and mixed carbonates, were selected based on the mineral composition and their known behavior in combustion systems. For example, pure quartz has a very high melting point and therefore would not likely form viscous melts to coalesce with other minerals. Illite, with a lower melting point, would be more likely to melt and coalesce.

Figure 7-9. Ash psd: model versus field data -- Polish bituminous -- no cenospheres.

Figure 7-10. Ash composition: model versus field data -- Polish bituminous -- no cenospheres.

As seen in Figure 7-9, the EMAF predictions for full coalescence and 1-ash per mineral bound the psd from the first electrostatic precipitator (ESP1, assumed to contain most of the ash mass). The partial coalescence prediction agreed fairly well with the measured ash psd. The predicted ash composition for partial coalescence, Figure 7-10, also agreed fairly well with VTT's measurements.

A second set of simulations were performed assuming the Polish bituminous coal reacted similarly to typical American bituminous coals. For this set of simulations, the coal

was assumed to swell and form cenospheres during devolatilization. Only the full coalescence and partial coalescence categories described above were included.

Predictions from the second set of simulations can be seen in Figures 7-11 and 7-12. The agreement between predicted and measured ash composition and psd is better than the previous case. The pure calcium fraction is again under-predicted in all model simulations. The opposite is true for the Si-Al-Ca category. This discrepancy is likely due to calcium enrichment on the surface of larger particles.

Figure 7-11. Ash psd: model versus field data -- Polish bituminous -- cenospheres.

Figure 7-12. Ash composition: model versus field data -- Polish bituminous -- cenospheres.

7.1.6 South African Bituminous Coal

The mineral size and composition information for the South African bituminous coal can be seen in Tables 7.12 and 7.13. This coal contained a large amount of kaolinite, representing almost all of the silicates. Other important minerals included quartz, illite, calcite, and pyrite. Approximately 7.4% of the minerals consisted of minor minerals.

Table 7.12. Mineral Species Composition: South African Bituminous

Mineral Species	Wt%	Elemental Composition (mole%)											
		Na	Mg	Al	Si	S	Cl	P	K	Ca	Ti	Fe	Ba
Quartz	7.3			1	93	1					4	1	1
Kaolinite	61.5			43	51	1	1		1	1	1	1	
Illite	3.2	1	1	35	48	2	1	1	8	1	1	1	1
Misc. silicates	6.7			32	53	2	1	1	2	4	2	4	
Pyrite	3.3			1	1	69					1	28	
Ca-rich (calcite)	7.4		9	1	2	4	1	1	1	79	1	1	1
Misc. mixed	7.4		4	21	27	5	2	5	2	19	4	7	4

Table 7.13. Mineral Size Distribution (μm) for South African Bituminous

Mineral	<2.5 μm (wt%)	2.5-5 μm (wt%)	5-10 μm (wt%)	10-20 μm (wt%)	20-40 μm (wt%)	>40 μm (wt%)
Quartz	18	35	14	14	6	13
Kaolinite	17	49	17	13	4	0
Illite	30	60	9	1	0	0
Mix. silicates	37	16	18	8	5	16
Pyrite	15	38	19	17	6	5
Calcite	15	30	16	16	11	12
Misc. Mixed*	35	44	7	10	4	0
Total						

*Estimated from other minerals and total mineral distribution.

The initial simulations were similar to those for the Polish bituminous coal. For the partial coalescence category, kaolinite and calcite were not allowed to coalesce. In this coal, the quartz contained significant amounts of impurities (Table 7.12) causing the mineral to melt at a much lower temperature. Therefore, quartz was allowed to coalesce for this coal, unlike the simulations with the Polish coal.

The ash psd predictions can be seen in Figure 7-13. The EMAF predicted distributions agreed reasonably well with the measured (from the first ESP) distribution.

Figure 7-13. Ash psd: model versus field data -- South African bituminous -- no cenospheres.

Again, the measured psd was bounded by the two model extremes. The partial coalescence best agreed with the data. For the ash composition predictions (Figure 7-14), the ash was dominated by the Si-Al category, arising from the extremely high kaolinite content. The partial coalescence case best predicted the amount measured in this category, and in the Si category.

Figure 7-14. Ash composition: model versus field data -- South African bituminous -- no cenospheres.

Figures 7-15 and 7-16 show the results of the second set of simulations, assuming cenosphere formation during devolatilization. The predicted ash psd agreed reasonably well with the field data, as did the composition predictions. As mentioned previously, the over-prediction of the Si-Al-Ca phase is likely due to calcium surface enrichment. In general, the agreement between prediction and data was better assuming cenosphere formation, than for the previous case (no cenosphere formation).

Figure 7-15. Ash psd: model versus field data -- South African bituminous -- cenospheres.

Figure 7-16. Ash composition: model versus field data -- South African bituminous -- cenospheres.

7.2 Summary of EMAF Simulations

As can be seen in the preceding discussion, the EMAF is reasonably successful in predicting the ash composition and psd for a wide range of coals. In some cases the discrepancies between the predicted and measured ash composition is due to the surface bias of the CCSEM. However, other evidence presented here and in previous EMAF evaluations (Helble et al., 1993) suggests that additional modifications may be required to better simulate the initial mineral distribution in the smaller size ranges.

In the next quarter additional simulations will be performed to verify the model predictions for additional coals. These coals will include an Illinois #6, the San Miguel lignite.

7.3 Submicron Aerosol Formation Model for EMAF

One of the goals of this work is to incorporate an aerosol formation submodel into the engineering model for ash formation (EMAF). The first step toward this goal, development of a simple model describing submicron ash formation, was completed in the last quarter. Much of the development of this model was completed under separate DoE funding as part of the program "Advanced Analytical Methods for Selection of Coal and Coal Blends," contract number DE-FG02-92ER81376. Modifications to the model to make it suitable for incorporation into EMAF have been conducted under this program. A description of the complete sub-model, including discussion of development work that occurred under the other DoE contract, is included here for completeness.

As part of this submodel development, the question was asked -- what does the submicron ash look like? VTT has observed two modes, ultrafine and intermediate. The ultrafine mode has been observed by other people making measurements of fly ash from coal-fired power plants (Schmidt et al., 1976; McElroy et al., 1982). Schmidt et al. used an EAA and they observed a peak at about 0.12μ and a broad peak from 0.2 to 0.5μ . McElroy et al. report EAA data from 0.01 to 0.3μ and low pressure impactor data from 0.3μ and up. Therefore the model needs to address both the formation of ultrafine ash and intermediate ash.

7.3.1 Ultrafine Ash Mode

The ultrafine mode can be ascribed to a vaporization-condensation mechanism. Taking into account all the observations mentioned above, the ultrafine mode has a peak (mass distribution) of 0.07 to 0.15μ . The variation in the diameter is mostly due to the combustion conditions; coal type is a second order effect. This can be seen in the data of McElroy et al. (1982) Six power plants of different designs were sampled. All but one were burning western sub-bituminous coals (see Table 7.14). Using data on NO emissions versus submicron mass loading, the effect of combustion conditions can be seen clearly (Figures 7-17 and 7-18).

Table 7.14. Summary of Data of McElroy et al.

Boiler	Coal Ash Content (wt% dry)	Total Mass Loading (g/m ³)	% Mass with D < 2 μm)	% Mass in Submicron Mode	Submicron Peak Diameter (μm)
360-MW, front wall fired, sub-bituminous coal	11	10.5	7	0.3	0.1
540-MW, tangential fired, Eastern bituminous coal	20	9.5	4	0.2	0.08
530-MW, opposed wall fired, sub-bituminous coal	12	6.4	4	1.3	0.14
113-MW, roof fired, sub-bituminous coal	9	3.4	8	2.2	0.14
360-MW, tangential fired, sub-bituminous coal	10	2.3	20	0.9	0.095
25-MW, front wall fired, sub-bituminous coal	4	1.7	8	0.5	0.075

Data are given on the mass loading of submicron aerosol as a function of NO content in the exhaust gas (Figure 7-17). Since NO is related to the peak combustion temperature, Figure 7-17 shows that the combustion conditions have a strong effect on the amount of mass in the ultrafine mode. The type of coal and furnace design do not seem to have a strong influence on the amount of ash in the ultrafine mode. Although, it should be noted that while this data set represents most types of boilers (except cyclone-fired), five out of six of the coals are Western sub-bituminous coals. The single Eastern coal fits the same trend, however. Figure 7-18 shows slightly better correlation ($r^2 = 0.57$) between NO and the percentage of ash in the ultrafine mode.

It should be noted that Schmidt et al. (1976) saw an increase in the amount of submicron aerosol when one burner was taken out of service (a simulated low NO_x condition). Microscopic analysis of the fly ash showed much more carbon in the fine aerosol with a burner out of service.

Figure 7-17. Mass loading in submicron mode (data of McElroy et al.).

Figure 7-18. Mass loading in submicron mode (data of McElroy et al.).

Thus, we can use a characteristic temperature in the furnace to predict the mass of ash which vaporizes to form the ultrafine aerosol mode. We should be able to develop one correlation for all furnace types as a preliminary prediction of vaporization. However, the work by Quann (1982) and others at MIT has shown that different coals show different amounts of ash vaporized when burned under the same combustion conditions. This will probably be a second order effect except for low rank coals containing a lot of sodium; for lignites, Quann and Sarofim (1982) saw 3 to 9% of the ash appear in the submicron mode and attributed this to the high sodium content of these coals.

What about the composition of the ultrafine mode? The most complete dataset is found in Quann and Sarofim (1982). They studied eight coals, two lignites, two sub-bituminous coals, and four bituminous coals. Most were burned at 1750 K in 20% O₂ which corresponds to a particle temperature of 2000 to 2100 K. The amount of material in the submicron ash (<0.5 µm final filter sample) was 0.9 to 1.7 % of the ash for the bituminous coals, 1 to 3% of the ash for the sub-bituminous coals, and 3 to 9% of the ash for the lignites. The very high vaporization rates for the lignites and one of the sub-bituminous coals seems to be due to large amounts of sodium in the coal. Certainly, the bituminous coals are pretty much the same in terms of the amount of ash vaporized. We probably should treat vaporization differently for coals of different ranks.

Based on the data at 1750 K/20% O₂, we can make some generalizations about coals of different rank.

Bituminous coals. The submicron mode is primarily a silicate with very little aluminum. From 0.5 to 1.5% of SiO₂ vaporizes, but only 0.1 to 0.15% of the Al₂O₃ vaporizes. The SiO₂ content of the submicron aerosol is 20 to 40%. It contains less than 2% Al₂O₃. The other constituents of the submicron mode are FeO (2 to 8% vaporized), MgO (1 to 4% vaporized), K₂O (2 to 12% vaporized), and Na₂O (25 to 40% vaporized).

Sub-bituminous coals. The submicron mode consists primarily of MgO and Na₂O with minor (<10 wt%) amounts of SiO₂, FeO, and CaO. Mg and Na are organically bound in these coals and are fairly volatile. Thus it is not surprising that they make up most of the submicron mode.

Lignite. The composition of the submicron mode is similar to that for the sub-bituminous coals, mostly Na₂O and MgO with some CaO and FeO. More iron seems to vaporize in these lignites, however. From 6 to 14% of the iron ends up in the submicron mode. The form of iron may be different in these lignites than in the sub-bituminous coals.

Vaporization of individual oxides was modeled by Quann (1982). Vaporization was assumed to proceed via formation of a reduced species, for example,

And the partial pressure of SiO is equal to

$$P_{\text{SiO}} = (a_{\text{SiO}_2} K_{\text{eq}} P_{\text{CO}})^{1/2} \quad (7-2)$$

where a_{SiO_2} is the activity coefficient and K_{eq} is the equilibrium constant.

For elements that are found in discrete mineral inclusions, internal diffusion resistance dominates the vaporization process and the ratio of the fraction vaporized to the burnout time is given by

$$\frac{f_v}{t_b} = \frac{9M_i c D_e x_i^{\text{eq}}}{\sqrt{3\Theta} \rho_i r_i r_o} \quad (7-3)$$

where the subscript I denotes the mineral inclusion and the subscript i denotes properties of the metal oxide species. The initial char particle diameter is r_o . This assumes a Thiele modulus of about 10. The approximation has removed the influence of char pore structure.

For atomically dispersed elements such as Ca and Mg in low rank coals, vaporization is controlled by external diffusion and

$$\frac{f_v}{t_b} = \frac{3\alpha c D_o M_i x_i^{\text{eq}}}{\Theta \rho_i r_o^2} \quad (7-4)$$

where α takes into account Stefan flow effects resulting from diffusion-controlled combustion.

As long as we can calculate the equilibrium vapor pressure of the species, we can estimate the vaporization rates. The species of interest are SiO_2 , CaO , MgO , FeO , Na_2O , and K_2O .

The simple equilibria between CO and CO_2 can be used (see Eq. (7-1)) for each metal species of interest, assuming that oxygen diffusing to the char particle surface is completely consumed and that CO is the only product of combustion. In this case, the bulk oxygen concentration, $P_{\text{O}_2,b}$, will determine the concentration of CO at the surface

$$P_{\text{CO}_2} = 2P_{\text{O}_2,b} / (1 + P_{\text{O}_2,b}) \quad (7-5)$$

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

Instead of calculating f_v/t_B from first principles, we will use the reported value at a reference temperature from the data of Quann (1982). The equations are

$$f_v/t_B = (f_v/t_B)_r (x_i/x_{ir}) (r_{or}/r_o) \quad (7-6)$$

for mineral particles and

$$f_v/t_B = (f_v/t_B)_r (x_i/x_{ir}) (r_{or}/r_o)^2 \quad (7-7)$$

for organically-bound elements. The subscript r denotes the reference condition. Quann's data were generated with a gas temperature of 1750 K and various oxygen partial pressures. The reference condition will be at an oxygen partial pressure (bulk) of 0.2. Two types of coal will be used, Illinois #6 bituminous coal and Montana Savage lignite. The activity of the various oxides in the ash will change depending on the composition of the ash. The activity coefficient is contained in the above equations, so it is best to use bituminous coal reference conditions when calculating vaporization from bituminous coals and low rank reference condition for low rank coals. Table 7.15 gives the reference conditions for both coals. The values of f_v/t_B were calculated by two different methods. For Si, Fe, Ca, and Mg data on the amount of each element vaporized (in $\mu\text{g/g}$ coal burned) and on the burnout times was used to calculate the quantity. For Al, Na, and K the amount of element vaporized was calculated from the composition of the bulk ash and submicron fume.

Table 7.15. Reference Conditions for Vaporization Calculations

Coal Rank	Illinois #6 Bituminous	Montana Savage Lignite
r_o (μm)	26.5	30.5
T_p (K)	2186	2000
f_v/t_B (s^{-1}) Total ash	0.6	1.65
Si	0.4	0.3
Al	0.04	0.05
Fe	0.5	4.0
Ca	0.04	0.58
Mg	0.74	10.51
Na	12.8	21.33
K	4.0	4.82

The equilibrium constants used were curvefits from JANAF data over a temperature range of 1500 to 2500 K as shown in Table 7.16.

Table 7.16. Equilibrium Constants for Vaporization of Metals

$\ln(K) = a + 10^4 b/T$	a	b
$\text{SiO}_{2(l)} + \text{CO} \rightleftharpoons \text{SiO} + \text{CO}_2$	18.6621	-5.9507
$\text{Al}_2\text{O}_{3(l)} + \text{CO} \rightleftharpoons 2\text{AlO} + \text{CO}_2$	38.2805	-16.7937
$\text{FeO}_{(l)} + \text{CO} \rightleftharpoons \text{Fe} + \text{CO}_2$	11.0258	-4.42495
$\text{CaO}_{(l)} + \text{CO} \rightleftharpoons \text{Ca} + \text{CO}_2$	10.1895	-5.1918
$\text{MgO}_{(l)} + \text{CO} \rightleftharpoons \text{Mg} + \text{CO}_2$	11.8032	-4.5773
$\text{Na}_2\text{O}_{(l)} + \text{CO} \rightleftharpoons 2\text{Na} + \text{CO}_2$	17.7349	-2.8271
$\text{K}_2\text{O}_{(l)} + \text{CO} \rightleftharpoons 2\text{K} + \text{CO}_2$	19.1685	-2.1940

To test the calculation of f_v/t_b , calculated values at other temperatures were compared with data reported by Quann (based on $\mu\text{g/g}$ coal burned). The calculated values for individual elements were normalized to the amount of *inherent* mineral matter in the coal to be consistent with Quann's calculation of the fraction vaporized. In the low rank coal, Na, Mg, and Ca were not normalized because these elements are organically bound. Tables 7.17 and 7.18 compare the calculated to the reported numbers.

Table 7.17. Calculation of f_v/f_b for Illinois #6 (44% inherent mineral matter)

T_p (K)	2457	2439
	f_v/t_b (s^{-1}) calculated (reported)	
Total ash	3.5 (3.5)	8.1 (14.0)
Si	4.0 (4.4)	10.6 (22.7)
Al	9.0	108.9
Fe	3.3 (4.7)	6.8 (8.7)
Ca	0.3 (0.17)	0.8 (2.7)
Mg	5.2 (3.6)	11.4 (11.4)
Na	82.9	141.3
K	22.2	34.6
NOTE: Al not used to calculated total ash vaporized.		

Table 7.18. Calculation of f_v/f_B for Montana Lignite (73% inherent mineral matter)

T_p (K)	2190	2364
	f_v/t_B (s^{-1})	calculated (reported)
Total ash	10.1 (0.26)	25.0 (17.0)
Si	1.8 (3.3)	5.7 (8.0)
Al	5.0	96.5
Fe	17.0 (13.7)	39.8 (17.9)
Ca	3.0 (8.2)	8.3 (27.5)
Mg	48.0 (42.2)	118.6 (77.8)
Na	94.1	173.5
K	18.6	30.7
NOTE: Al not used to calculated total ash vaporized.		

There is generally agreement within about 50% for Si, Fe, Ca, and Mg. The total amount of ash vaporized is predicted well, with an average error of about 20%. The calculated amount of aluminum vaporized is very high and there are no data available to check these numbers. Since aluminum does not vaporize extensively, it is reasonable to omit aluminum from the calculation of the total ash vaporized (as has been done here). Relatively large amounts of sodium and potassium are predicted to vaporized; alkali vaporization will be discussed below.

Silicates interact with sodium during combustion and this can effect the amount of sodium that vaporizes and ultimately condenses in the submicron fume. In an earlier DoE-funded mineral matter transformation study, a correlation was made between the amount of acid soluble sodium in the coal divided by the amount of silica in the ash and the fraction of sodium found in the submicron ash as shown in Figure 7-19. (Gallagher, 1992). These data were taken in the University of Arizona furnace on the a number of coals (including the Loy Yang Australian coal) at stoichiometric ratios of 1.2 to 1.3. The relationship between the fraction of sodium vaporized (f_{Na}) and the ratio of acid soluble Na to SiO_2 (x) was determined to be

$$f_{Na} = \begin{cases} 0.01, & x < 0.05 \\ 0.347427 + 0.4013384x + 0.111283x^2, & x \geq 0.05 \end{cases} \quad (7-8)$$

The amount of potassium appearing in the submicron ash was not correlated with the parameter x (as defined above). However, the amount of potassium vaporized was correlated with the amount of sodium vaporized ash shown in Figure 7-20. This relationship is given by

Figure 7-19. Fraction of Na vaporized for several coals (Gallagher, 1992).

Figure 7-20. Correlation of Na and K vaporized (Gallagher, 1992).

$$f_k = 0.007706 + 0.615746f_{Na} \quad (7-9)$$

These correlations should give results which agree with the calculations using Quann's data as a reference. At first glance, the amount of alkali species vaporized reflected in Quann's data seems high relative to Gallagher's data. It should be noted that the bulk oxygen concentrations, particle diameters and gas temperatures are very different between the two experiments. Also, Quann used a narrow range of coal particles while Gallagher burned a utility grind with a volume median diameter of about 25 μm . We can try, however, to compare the two data sets by choosing appropriate particle temperatures and bulk oxygen concentrations.

Two coals were chosen for the comparison, Illinois #6 and Beulah (North Dakota) lignite because they were burned in both investigations. The ratios of the acid soluble sodium to total silica for these two coals are 0.05 and 0.35, respectively. The results of the comparison are summarized in Table 7.19. The particle temperature was assumed to be 1700 K, based on the range of calculated particle temperatures in Bool's (1993) thesis. These particle temperatures indicate a bulk oxygen concentration of approximately 0.05, based on correlations between particle temperature and bulk oxygen concentration. The char burnout time is calculated from the relationship

$$d_p^2/t_B = 0.0138 \ln[1 + X_{O_2}^b] \quad (7-10)$$

For a particle diameter of 25 μm and a bulk oxygen concentration of 0.05, the char burnout time is calculated to be 9.3 ms.

Table 7.19. Comparison of Sodium and Potassium Vaporization Calculated by Two Methods

Coal	% Na Vaporized		% K Vaporized	
	Quann Data	Gallagher Data	Quann Data	Gallagher Data
Illinois #6	2.1	1.5	1.0	1.9
Beulah lignite	18.1	18.7	5.4	12.3

The equations developed by Quann can be used to calculate the fraction of sodium and potassium vaporized at conditions other than the reference conditions. The reference value of f_v/t_B for these two elements should be calculated from the correlations determined from the work of Gallagher.

The following quantities will be needed as input to calculate the fractional vaporization rates and composition of the ultrafine mode:

- burnout time (calculated from temperature, radius, and oxygen concentration)

- particle temperature (calculated from gas temperature and oxygen concentration)
- equilibrium constants for vapor pressures (as fn. of T_p)
- initial char particle radius
- bulk oxygen concentration (calculated from volatile content)
- coal rank.

The self-preserving aerosol model can be used to calculate the size distribution (Flagan and Friedlander, 1978). Initially, let us neglect scavenging of small particles by large (supermicron particles). The total volume of aerosol is constant and equal to the amount of material vaporized:

$$V = f_v M_{\text{ash}} \quad (7-11)$$

where M_{ash} is the ash loading in g/m^3 . The initial number of particles is therefore

$$N(0) = \frac{6V}{\pi D_0^3} \quad (7-12)$$

where D_0 is the initial particle diameter which can be calculated from nucleation theory. The initial diameter can be estimated to be one or two molecules since the saturation ratio is generally large. The rate of decay of the number distribution is given by

$$\frac{dN}{dt} = -\frac{1}{2} \left[\frac{3}{4\pi} \right]^{1/6} \left[\frac{6kT}{\rho_p} \right]^{1/2} \left[\frac{p}{RT} \right] I_1 V^{1/6} N^{11/6} \quad (7-13)$$

The size distribution is calculated from $N(t)$ and V as

$$n = \left[\frac{N^2}{V} \right] \Psi(\eta) \quad (7-14)$$

where $\eta = vN/V$. The function $\Psi(\eta)$ is tabulated by Friedlander (1977).

To make the calculation, we will assume that nucleation and coagulation happen on much faster time scales than those on which the gas temperature is changing. That is, we will impose a temperature-temperature history on the gas. For example, Flagan and Friedlander used the following temperature history to simulate the boiler: $T = 1800 \text{ K}$ for 0.5 s , $T = 1800 \text{ to } 1400 \text{ K}$ (FEGT) over 1 s , and $T = 1400 \text{ K to } 425 \text{ K}$ over 2 s .

The quantities needed to calculate the aerosol size distribution are:

- burnout time (calculated from temperature, radius, and oxygen concentration)
- gas temperature and residence time profile in the furnace (including FEGT)
- gas temperature at inlet to ESP
- fraction of ash mass vaporized
- total mass loading of ash.

7.3.2 Intermediate Mode

Unfortunately, CCSEM analysis does not provide information on particles less than approximately 1 μm . From measurements made by a European group, VTT, (Joutensaari et al., 1993), we believe that this mode does exist. The aerosol appears to consist of dense spheres which would suggest that the intermediate mode is not the product of a vaporization-condensation process. Instead, this mode may result from fine minerals in the coal. These have been observed via TEM (Hurley and Shobert, 1992) in sub-bituminous coals.

The approach taken here is somewhat simplified but does produce results that appear realistic. However, some refinement will be needed. The size distribution of minerals from eleven coals of various rank were examined. When the mineral distribution is calculated (examples in Figures 7-21 through 7-23), the largest number of minerals is found in the smallest size bin of approximately 1 to 2.5 μm .]

Figure 7-21. Illinois #6 minerals.

Figure 7-22. Eagle Butte minerals.

Figure 7-23. Beulah minerals.

The number of submicron minerals is approximated by assuming that the number distribution (on a log D_p basis) is symmetric about the 1 to 2.5 μm size range. The sizes chosen for the bins are 0.156 to 0.313, 0.313 to 0.625, and 0.625 to 1.25 μm . If the number distribution denoted by $n(D_p)$ is the number of minerals between D_p and $D_p + dD_p$ then my assumption is equivalent to

$$\begin{aligned} n(0.625) &= n(1.25) \\ n(0.313) &= n(2.5) \\ n(0.156) &= n(5) \end{aligned} \quad (7-15)$$

The calculation will be performed for each mineral class and then summed over all mineral classes. The mass distribution, $n_m(D_p)$ is then calculated for each mineral class of the submicron mode as

$$n_m(D_p) = \rho(\pi/6) D_p^3 n(D_p) \quad (7-16)$$

The entire mass distribution is then renormalized. The only point of comparison available is the Polish coal for which VTT measured the ash size distribution (Joutensaari et al, 1993). The result of the calculation is given in Table 7.20.

Once the amount of submicron minerals has been predicted, how do you transform that into ash? Based on VTT's observation of the intermediate mode, we assume that some of the ultrafine minerals are released from the char during devolatilization and char combustion. These minerals melt but do not otherwise interact.

If we assume that *all* the submicron minerals are released during combustion, we can calculate the mass distribution in Figure 7-24. (The total ash mass loading at 7% excess O_2 was calculated to be 10.2 g/Nm^3 ; VTT reports 6 g/Nm^3 .) The calculated submicron mass distribution is the right order of magnitude as compared to VTT's measured size distribution. Note that if all submicron minerals are released, the calculated ash psd contains 2.6% of the ash mass less than 1.25 μm and VTT reported 1.9% mass less than 1 μm .

This agreement between the amount of submicron ash calculated here and that reported by VTT is deceptive, for two reasons. First, it is probably not realistic to assume that all the submicron minerals are released during combustion; some will probably coalesce with larger minerals in the char particle. Second, the evidence from American coals suggests that vaporization contributes a substantial fraction of the submicron aerosol. In laboratory tests (Quann and Sarofim, 1982) and field tests (McElroy et al., 1982) the mass in the submicron aerosol has been shown to be a function of combustion conditions which has always been interpreted to mean that the submicron aerosol is the product of a vaporization-condensation mechanism.

Table 7.20. Mineral Mass Distribution for Polish Coal (submicron calculated)

Mineral (wt%)	0.16- 0.31 μm	0.31- 0.63 μm	0.63- 1.25 μm	1.25 2.5 μm	2.5- 5 μm	5-10 μm	10-20 μm	20-40 μm	40-80 μm	>80 μm	Total
Quartz	0	0.005	0.139	1.1	2.3	1.5	1.6	0.6	0.6	1.7	9.4
Illite	0.0002	0.016	0.731	5.8	8.0	5.8	7.4	1.8	1.8	0	31.5
Misc. sil	0.0002	0.012	0.784	6.3	6.3	6.3	3.4	1.8	2.1	0.3	27.2
Carbonates	0	0.001	0.101	0.8	0.54	1.1	2.7	0.6	0.5	0.5	6.9
Others	0.0001	0.012	0.778	6.2	6.0	4.5	4.2	1.9	0.8	0.5	25.0
Total	0.0006	0.045	2.53	20.3	23.1	19.3	19.3	6.8	5.8	2.9	100.

Figure 7-24. Calculated and measured submicron psd.

In VTT's experience with the Polish coal, the ultrafine (vaporization-condensation) mode does not contribute any significant amount of mass. However, many researchers assume that most of the mass in the submicron mode is a product of vaporization. Therefore we suggest that submicron coal minerals may contribute to the submicron ash *in addition to vaporized material*. In other words, the fine minerals represent the lower limit on the mass of submicron aerosol, in the limit of low temperatures and little vaporization.

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APPENDIX

Coal Mineral CCSEM Data
Run-of-Mine Pittsburgh #8
Additional Analysis 0 MTI

SUMMARY OF CCSEM RESULTS: PROG VERSION 3BF 7/21/90
SAMPLE DESCRIPTION ---> MTI 93-101 ABB-CE, Pitts #8 Rerun
SUBMITTER ---> PSI
RUN DATE AND TIME ---> 5 9 1994 13: 5

PERCENT EPOXY USED = 55.4
TOTAL MINERAL AREA ANALYZED AT HIGH MAG = 3910.1
NORMALIZED AREA ANALYZED AT HIGH MAG = 3066453.0
MINERAL AREA ANALYZED INTERMEDIATE MAG = 50358.5
NORMALIZED AREA ANALYZED INTERMEDIATE MAG = 2775261.0
TOTAL MINERAL AREA ANALYZED AT LOW MAG = 1014647.0
NUMBER OF FRAMES AT HIGH MAG = 12
NUMBER OF FRAMES AT INTERMEDIATE MAG = 16
NUMBER OF FRAMES AT LOW MAG = 38
TOTAL MINERAL AREA ON A COAL BASIS = 16.217
TOTAL MINERAL WGHT % ON A COAL BASIS = 27.609
TOTAL NUMBER OF POINTS ANALYZED = 2958
NUMBER OF POINTS UNDER THRESHOLD = 9

WEIGHT PERCENT ON A MINERAL BASIS

	1.0 TO 2.2	2.2 TO 4.6	4.6 TO 10.0	10.0 TO 22.0	22.0 TO 46.0	46.0 TO 100.0	TOTALS
QUARTZ	1.1	2.4	2.3	1.3	.9	.7	8.7
IRON OXIDE	.0	.0	.1	.0	.1	.2	.5
PERICLASE	.0	.0	.0	.0	.0	.0	.0
RUTILE	.0	.1	.1	.0	.0	.0	.3
ALUMINA	.0	.0	.0	.0	.0	.0	.0
CALCITE	.1	.3	.2	.1	.4	.5	1.6
DOLOMITE	.1	.8	.4	.5	.2	.0	2.0
ANKERITE	.0	.0	.0	.0	.0	.0	.0
KAOLINITE	1.2	1.5	3.3	1.0	.6	.2	7.8
MONTMORILLONITE	.6	1.2	1.1	.6	.5	.2	4.2
K AL-SILICATE	3.5	10.5	7.8	6.6	2.7	.8	32.0
*FE AL-SILICATE	.5	1.4	.4	.3	.1	.1	2.8
*CA AL-SILICATE	.1	.0	.1	.0	.1	.0	.3
*NA AL-SILICATE	.0	.0	.0	.0	.0	.0	.0
*ALUMINOSILICATE	.1	.1	.2	.2	.2	.2	1.0
* MIXED AL-SILICA	.7	1.1	.4	.6	.1	.0	2.8
* FE SILICATE	.0	.0	.0	.0	.0	.0	.0
* CA SILICATE	.0	.1	.0	.0	.1	.2	.4
CA ALUMINATE	.0	.0	.0	.0	.0	.0	.0
PYRITE	.8	.7	1.6	1.4	2.0	1.1	7.6
PYRRHOTITE	.0	.2	.0	.0	.0	.0	.2
OXIDIZED PYRRHO	.1	.0	.0	.1	.1	.0	.3
GYPSUM	.0	.0	.3	.2	.3	.3	1.2
BARITE	.0	.0	.0	.0	.0	.0	.0
APATITE	.0	.0	.0	.0	.0	.0	.1
CA AL-P	.0	.0	.0	.0	.0	.0	.0
KCL	.0	.0	.0	.0	.0	.0	.0
GYPSUM/BARITE	.0	.0	.0	.0	.0	.0	.0
* GYPSUM/AL-SILIC	.9	.9	.5	.2	.0	.0	2.4
* SI-RICH	.3	.8	.9	.7	.6	.1	3.4
CA-RICH	.1	.2	.0	.1	.1	.0	.5
* CA-SI RICH	.0	.0	.1	.0	.1	.2	.5
UNKNOWN	5.6	5.9	3.7	2.8	1.1	.7	19.8
TOTALS	15.7	28.1	23.6	16.7	10.4	5.5	100.0
10/7	20.0	41.2	21.9	15.4	1.0	2.5	
12/10	11.6	22.1	26.0	19.5	12.7	7.8	

NORMALIZED AREA IN EACH SIZE RANGE

	1.0 TO 2.2	2.2 TO 4.6	4.6 TO 10.0	10.0 TO 22.0	22.0 TO 46.0	46.0 TO 100.0	TOTAL
QUARTZ	76964.5	169503.7	164582.5	96341.3	66427.0	50224.5	624043
IRON OXIDE	.0	.0	5221.1	.0	4720.9	6523.0	16465
PERICLASE	.0	.0	.0	.0	.0	.0	
RUTILE	1544.9	3881.9	4099.1	.0	908.4	.0	10434
ALUMINA	.0	.0	.0	.0	.0	.0	
CALCITE	6258.2	19096.0	15994.6	4843.6	24494.0	34859.0	105545
DOLOMITE	8791.2	50096.7	25249.8	35953.3	9959.1	2317.3	132367
ANKERITE	.0	.0	.0	.0	.0	.0	
KAOLINITE	88508.3	108953.2	233385.3	73385.7	40902.5	13456.2	558591
MONTMORILLONITE	45893.2	90853.2	80086.0	47155.5	36705.3	17439.0	318132
K AL-SILICATE	251746.0	765072.3	567741.6	482886.2	199773.0	59542.3	32326761
FE AL-SILICATE	32733.8	93354.9	26170.7	20521.9	8880.3	5189.8	186851
CA AL-SILICATE	9379.4	.0	10533.2	.0	4962.7	.0	24875
NA AL-SILICATE	.0	.0	.0	.0	.0	.0	
ALUMINOSILICATE	5034.8	9818.6	16991.0	13877.3	14133.3	11342.8	71197
MIXED AL-SILICA	47524.4	75192.1	27472.9	45319.2	7202.3	.0	202710
FE SILICATE	1192.0	.0	.0	.0	.0	.0	1192
CA SILICATE	.0	7222.8	.0	.0	3947.1	13159.6	24329
CA ALUMINATE	.0	.0	.0	.0	.0	.0	
PYRITE	28577.4	27095.2	61810.9	52948.7	75210.6	40103.5	285740
PYRRHOTITE	1490.0	6822.8	.0	.0	916.8	.0	9229
OXIDIZED PYRRHO	1944.9	.0	.0	4924.1	2176.4	.0	9049
GYP SUM	1780.2	.0	23871.5	13862.4	25667.4	24166.0	89347
BARITE	.0	.0	.0	.0	.0	.0	
APATITE	.0	.0	2338.9	.0	1255.4	.0	3590
CA AL-P	.0	.0	.0	.0	.0	.0	
KCL	.0	.0	.0	.0	.0	.0	
GYP SUM/BARITE	.0	.0	.0	.0	.0	.0	
GYP SUM/AL-SILIC	62424.8	64103.0	34534.7	11070.5	3326.7	.0	175451
SI-RICH	20907.6	59138.9	62002.7	46445.7	44387.0	7135.0	240018
CA-RICH	6767.9	12571.2	2419.3	4506.9	6388.5	3484.4	36139
CA-SI RICH	.0	.0	3641.7	.0	4239.4	12589.8	20470
UNKNOWN	388782.5	415430.7	259128.8	193942.3	80526.6	46004.1	1383817
TOTALS	1088246.0	1978207.0	1627276.0	1147985.0	667110.8	347536.3	685636

AREA PERCENT MINERAL BASIS

	1.0 TO 2.2	2.2 TO 4.6	4.6 TO 10.0	10.0 TO 22.0	22.0 TO 46.0	46.0 TO 100.0	TOTALS
QUARTZ	1.1	2.5	2.4	1.4	1.0	.7	9.1
IRON OXIDE	.0	.0	.1	.0	.1	.1	.2
PERICLASE	.0	.0	.0	.0	.0	.0	.0
RUTILE	.0	.1	.1	.0	.0	.0	.2
ALUMINA	.0	.0	.0	.0	.0	.0	.0
CALCITE	.1	.3	.2	.1	.4	.5	1.5
DOLOMITE	.1	.7	.4	.5	.1	.0	1.9
ANKERITE	.0	.0	.0	.0	.0	.0	.0
KAOLINITE	1.3	1.6	3.4	1.1	.6	.2	8.1
MONTMORILLONITE	.7	1.3	1.2	.7	.5	.3	4.6
K AL-SILICATE	3.7	11.2	8.3	7.0	2.9	.9	33.9
FE AL-SILICATE	.5	1.4	.4	.3	.1	.1	2.7
CA AL-SILICATE	.1	.0	.2	.0	.1	.0	.4
NA AL-SILICATE	.0	.0	.0	.0	.0	.0	.0
ALUMINOSILICATE	.1	.1	.2	.2	.2	.2	1.0
MIXED AL-SILICA	.7	1.1	.4	.7	.1	.0	3.0
FE SILICATE	.0	.0	.0	.0	.0	.0	.0
CA SILICATE	.0	.1	.0	.0	.1	.2	.4
CA ALUMINATE	.0	.0	.0	.0	.0	.0	.0
PYRITE	.4	.4	.9	.8	1.1	.6	4.2
PYRRHOTITE	.0	.1	.0	.0	.0	.0	.1
OXIDIZED PYRRHO	.0	.0	.0	.1	.0	.0	.1
GYPSUM	.0	.0	.3	.2	.4	.4	1.3
BARITE	.0	.0	.0	.0	.0	.0	.0
APATITE	.0	.0	.0	.0	.0	.0	.1
CA AL-P	.0	.0	.0	.0	.0	.0	.0
KCL	.0	.0	.0	.0	.0	.0	.0
GYPSUM/BARITE	.0	.0	.0	.0	.0	.0	.0
GYPSUM/AL-SILIC	.9	.9	.5	.2	.0	.0	2.6
SI-RICH	.3	.9	.9	.7	.6	.1	3.5
CA-RICH	.1	.2	.0	.1	.1	.1	.5
CA-SI RICH	.0	.0	.1	.0	.1	.2	.3
UNKNOWN	5.7	6.1	3.8	2.8	1.2	.7	20.2
TOTALS	15.9	28.9	23.7	16.7	9.7	5.1	100.0

WEIGHT PERCENT MINERAL BASIS

	1.0	2.2	4.6	10.0	22.0	46.0	TOTAL
	TO	TO	TO	TO	TO	TO	
	2.2	4.6	10.0	22.0	46.0	100.0	
QUARTZ	1.1	2.4	2.3	1.3	.9	.7	
IRON OXIDE	.0	.0	.1	.0	.1	.2	
PERICLASE	.0	.0	.0	.0	.0	.0	
RUTILE	.0	.1	.1	.0	.0	.0	
ALUMINA	.0	.0	.0	.0	.0	.0	
CALCITE	.1	.3	.2	.1	.4	.5	
DOLOMITE	.1	.8	.4	.5	.2	.0	
ANKERITE	.0	.0	.0	.0	.0	.0	
KAOLINITE	1.2	1.5	3.3	1.0	.6	.2	
MONTMORILLONITE	.6	1.2	1.1	.6	.5	.2	
K AL-SILICATE	3.5	10.5	7.8	6.6	2.7	.8	32
FE AL-SILICATE	.5	1.4	.4	.3	.1	.1	
CA AL-SILICATE	.1	.0	.1	.0	.1	.0	
NA AL-SILICATE	.0	.0	.0	.0	.0	.0	
ALUMINOSILICATE	.1	.1	.2	.2	.2	.2	
MIXED AL-SILICA	.7	1.1	.4	.6	.1	.0	
FE SILICATE	.0	.0	.0	.0	.0	.0	
CA SILICATE	.0	.1	.0	.0	.1	.2	
CA ALUMINATE	.0	.0	.0	.0	.0	.0	
PYRITE	.8	.7	1.6	1.4	2.0	1.1	
PYRRHOTITE	.0	.2	.0	.0	.0	.0	
OXIDIZED PYRRHO	.1	.0	.0	.1	.1	.0	
GYPSUM	.0	.0	.3	.2	.3	.3	
BARITE	.0	.0	.0	.0	.0	.0	
APATITE	.0	.0	.0	.0	.0	.0	
CA AL-P	.0	.0	.0	.0	.0	.0	
KCL	.0	.0	.0	.0	.0	.0	
GYPSUM/BARITE	.0	.0	.0	.0	.0	.0	
GYPSUM/AL-SILIC	.9	.9	.5	.2	.0	.0	
SI-RICH	.3	.8	.9	.7	.6	.1	
CA-RICH	.1	.2	.0	.1	.1	.0	
CA-SI RICH	.0	.0	.1	.0	.1	.2	
UNKNOWN	5.6	5.9	3.7	2.8	1.1	.7	1
TOTALS	15.7	28.1	23.6	16.7	10.4	5.5	10

DATE

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